

Eleventh Annual Conference on Mass Spectrometry and Allied Topics

**May 19-24, 1963
San Francisco, California**

**Arranged by the Officers of
ASTM Committee E-14**

Eleventh Annual Conference on Mass Spectrometry and Allied Topics

**May 19-24, 1963
San Francisco, California**

**Arranged by the Officers of
ASTM Committee E-14**

PREFACE

This volume is a collection of papers presented at the Eleventh Annual Conference on Mass Spectrometry and Allied Topics*, held in San Francisco, California, May 19-24, 1963.

It is intended that this volume be distributed only to registrants of the Eleventh Annual Conference, and therefore, should not be considered as a publication. A particular acknowledgement is due to Dr. A. B. King for handling the details of program arrangement and for assembling and editing this volume.

N. D. Coggeshall, Program Chairman

* Arranged by the officers of the ASTM Committee E-14.

R. E. Fox, Chairman
N. D. Coggeshall, Vice-Chairman
A. G. Sharkey, Jr., Vice-Chairman
H. E. Lumpkin, Secretary
S. Meyerson, Member-at-Large
A. L. Wahrhaftig, Member-at-Large

TABLE OF CONTENTS

ELEVENTH ANNUAL CONFERENCE ON MASS SPECTROMETRY AND ALLIED TOPICS

San Francisco, California, May, 1963

Page
No.

THEORETICAL PROBLEMS RELATED TO MASS SPECTROMETRY

1.* Anisotropy in Angular Distribution of Molecular Dissociation Products, Gordon H. Dunn, National Bureau of Standards, Boulder, Colorado	1
2.* A Review of the Theory of Charge Transfer in Gases, Donald Rapp, Lockheed Missiles and Space Company, Palo Alto, California	2
3.* Some Aspects of Unimolecular Reactions, B. S. Rabinovitch, University of Washington, Seattle, Washington	16
4.* Kinetic Energy of Fragments of Unimolecular Decomposition, W. A. Chupka, Argonne National Laboratory, Argonne, Illinois	17

BASIC STUDIES I

5. Relation between Ionization Potential and Electro-negativity in Isoelectronic Free Radicals, I. P. Fisher and F. P. Lossing National Research Council Ottawa, Canada	18
6. Ionization of Polyatomic Molecules, T. E. Sharp, H. M. Rosenstock, and R. Zwanzig, National Bureau of Standards, Washington, D. C.	19
7. Higher Ionization Potentials in Alcohols and Water Measured by Electron Impact, Haken Sjogren and Einar Lindholm, Royal Institute of Technology, Stockholm, Sweden	26
8. Ionization Potential of Benzene, I. P. Fisher and F. P. Lossing, National Research Council, Ottawa, Canada	29
9. Ionization Cross Sections, R. E. Glick and J. A. Llewellyn, Florida State University, Tallahassee, Florida	30
10. Scattering of Low-Energy Electrons on Molecules, H. Ehrhardt and U. Erbse, University of Freiburg, West Germany	38

* Invited Paper

TABLE OF CONTENTS - Continued

	Page No.
BASIC STUDIES I - Continued	
11. A Proposed Analysis of the Charge State of Recoil Atoms Produced by High Energy Electron Impact, Gerald P. Calame and Frederick A. White, Rensselaer Polytechnic Institute	43
12. Initial Preparation and Metastable Transitions in Mass Spectra, H. M. Rosenstock, V. H. Dibeler and F. N. Harilee, National Bureau of Standards, Washington, D. C.	44
13. Metastable Intensities in Hydrocarbon Mass Spectra, John C. Schug, Gulf Research & Development Company Pittsburgh, Pennsylvania	50
14. A Metastable State of the Doubly Charged Carbon Dioxide Ion Amos S. Newton and A. F. Sciamanna, Lawrence Radiation Laboratory, University of California, Berkeley 4, California	58
15. Ionization Potential Study of High Molecular Weight Compounds, M. R. Stevens, Rocketdyne, Canoga Park, California	64
CERTAIN PHENOMENA IN COLLISION MASS SPECTROMETRY	
16.* Cross Sections of Ion-Permanent Dipole Reactions by Mass Spectrometry, Thomas F. Moran and William H. Hamill, Notre Dame University, Notre Dame, Indiana	65
17.* Charge Exchange Reactions, Wade L. Fite, General Dynamics/General Atomic, San Diego, California	70
18.* Long Lived Excited Ions in Collision Mass Spectrometry, J. William McGowan, Universite Laval, Quebec, Canada	82
19.* Dissociation Reactions, E. Lindholm, Royal Institute of Technology, Stockholm, Sweden	96
BASIC STUDIES II	
20. A Mass Spectrometric Study of Homonuclear and Heteronuclear Rare Gas Molecule Ions, M. S. B. Munson, J. L. Franklin, and F. H. Field, Humble Oil & Refining Company Baytown, Texas	101
* Invited Paper	

TABLE OF CONTENTS - Continued

	Page No.
BASIC STUDIES II - Continued	
21. Mass Spectrometric Observation of Electron and Proton Transfer Reactions between Positive Ions and Neutral Molecules, Part II, A. Henglein and G. A. Muccini, Mellon Institute, Pittsburgh, Pennsylvania and Hahn-Meitner Institut für Kernforschung, Berlin-Wannsee, Germany	102
22. Some Recent Experimental Mass Spectrometer Studies in the Chemistry Department of Brookhaven National Laboratory, L. Friedman, Brookhaven National Laboratory, Upton, L. I., New York	112
23. A Study of Selected Ions in the Mass Spectra of Benzenethiol and Deuterated Benzenethiol, D. G. Earnshaw, G. L. Cook, and G. U. Dinneen, Laramie Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Laramie, Wyoming	113
24. Organic Ions in the Gas Phase. Phenylated Cyclopropane Ion in the Decomposition of 3-Phenylpentane, Seymour Meyerson, American Oil Company, Whiting, Indiana; Harold Hart, Michigan State University, East Lansing, Michigan	119
25. Ionization and Dissociation Probabilities on the Three Nitrogen Molecules Involving the Mass 14 and 15 Isotopes, (Withdrawn) Donald P. Easter and Amos J. Coleman U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia	124
26. Metastable Transitions in Small Molecules, V. H. Dibeler and H. M. Rosenstock, National Bureau of Standards, Washington, D. C.	125
27. Studies in the Mass Spectra of Short Chain Esters, D. R. Black, W. H. McFadden and J. W. Corse, Western Regional Research Laboratory, Albany, California	135
28. Mass Spectra of Diaryl Sulfones, Seymour Meyerson, American Oil Company; and Harald Drews and Ellis K. Fields, Amoco Chemicals Corporation, Whiting, Indiana	140
29. Studies on the Stereochemistry of Organic Molecules by Mass Spectrometry I. The Erythro- and Threo-3-Phenyl-2-Butyl System (Withdrawn) P. E. Butler, Esso Research and Engineering Company, Linden, New Jersey; and C. H. DePuy, Iowa State University, Ames, Iowa	141

TABLE OF CONTENTS - Continued

	Page No.
INSTRUMENTATION I	
30. Continuous Ion Source for a Bendix Time of Flight Mass Spectrometer, Martin H. Studier, Argonne National Laboratory, Argonne, Illinois	142
31. A Simple Display System for Recording Rapid Changes in Mass Spectra, Kenneth A. Lincoln, U. S. Naval Radiological Defense Laboratory, San Francisco, California	149
32. A New Digitizer for Mass Spectra, R. F. Klaver and R. M. Teeter, California Research Corporation, Richmond, California	153
33. Development of a Solid State Digitizer for Mass Spectrometers, Edward M. Thomason, Monsanto Chemical Company, Texas City, Texas	157
34. The Model 17-Series Bendix Time-of-Flight Mass Spectrometer, G. J. O'Halloran and W. R. Wyess, The Bendix Corporation, Southfield (Detroit), Michigan	162
35. Performance of an Analytical Mass Spectrometer, C. M. Judson, R. F. Howard, and C. R. McKinney, Consolidated Electrodynamics Corporation, Pasadena, California	169
36. A New Type of Positive Ion Detector for the Simultaneous Measurement of Two Ion Beams, N. R. Daly, United Kingdom Atomic Energy Authority, Aldermaston, England	174
37. Ion-Counting for Rapid Measurements with Time-of-Flight Mass Spectrometers, D. R. McAdams, L. Lane, and J. G. Lemley, Esso Research Laboratories, Humble Oil & Refining Company, Baton Rouge, Louisiana	175
38. A New Continuous Quantitative Gas Analysis Method, W. J. Grubbs, G. H. Snider, F. I. Scott, E. I. Doucette Associates, Inc. Chatham, New Jersey; and J. Bloom, Air Force Cambridge Research Laboratories, Bedford, Massachusetts	185
39. Source and Multiplier Modifications of a Time-of-Flight Mass Spectrometer to Increase Sensitivity, W. K. Rohwedder, E. Selke, and E. D. Bitner, Northern Regional Research Laboratory, Peoria, Illinois	193

TABLE OF CONTENTS - Continued

	Page No.
APPLICATIONS OF HIGH RESOLUTION MASS SPECTROMETRY	
40.* Remarks on High Resolution Mass Spectroscopy, Clifford E. Berry, Consolidated Electrodynamics Corporation, Pasadena, California	199
41.* Instrumentation and Techniques of High Resolution Mass Spectroscopy, Heinrich Hintenberger, Max-Planck-Institut fur Chemie, Mainz, Germany	203
42.* Vacuum Spark Mass Spectroscopy of Solids, A. J. Ahearn, Bell Telephone Laboratories Inc. Murray Hill, New Jersey	223
43.* The Use of High-Resolution Mass Spectrography in the Determination of the Structure of Organic Molecules, K. Biemann, Massachusetts Institute of Technology, Cambridge, Massachusetts	235
ANALYTICAL TECHNIQUES	
44. Mass Spectrometry of Oximes H. R. Harless, Union Carbide Chemicals Company, South Charleston, West Virginia	241
45. The Mass Spectra of Dipeptides, Gregor A. Junk and Harry J. Svec, Iowa State University, Ames, Iowa	249
46. Mass Spectrometric Studies of Noble Gas Compounds, Martin H. Studier and Eric N. Sloth, Argonne National Laboratory, Argonne, Illinois	254
47. Low Voltage Sensitivities of Aromatic Hydrocarbons, H. E. Lumpkin and Thomas Aczel, Humble Oil & Refining Company, Baytown, Texas	261
48. A Study of the Ions Present in Active Nitrogen Using A Quadrupole Mass Spectrometer, G. Neil Spokes and Bert E. Evans, Stanford Research Institute, Menlo Park, California	270
49. Molecular Beam Studies of Thermal and Photolytic Degradation Products of Isotopically Labeled Metastable Inorganic Compounds, (Withdrawn) Amos J. Coleman and Donald P. Easter, U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia	276
* Invited Paper	

TABLE OF CONTENTS - Continued

ANALYTICAL TECHNIQUES - Continued

Page
No.

50. Comparison of Mass Spectrometric and Gas Chromatographic Analyses of High-Boiling Oils from Coal,
A. G. Sharkey, Jr., J. L. Shultz, and R. A. Freidel,
Bureau of Mines,
Pittsburgh, Pennsylvania 277

SOLID SOURCE INSTRUMENTATION

51. Mass Spectrometer System for Beam-Surface Interaction Studies,
David Lichtman,
Honeywell Research Center,
Hopkins, Minnesota 284
52. A Mass Spectrometer for the Study of Sputtering,
A. J. Smith, D. J. Marshall, L. A. Cambey and E. J. Michael,
Nuclide Corporation,
State College, Pennsylvania 290
53. Ion Source for Solid Materials,
Helmut J. Liebl and Richard F. K. Herzog,
Geophysics Corporation of America,
Bedford, Massachusetts 297
54. Some Preliminary Data on the Detection of Ions Sputtered from Glass Surfaces,
John T. Kerr,
Corning Glass Works,
Corning, New York 302
55. Analytical Applications of a Mass Spectrometer Equipped with Field Emission Ion Source,
H. D. Beckey,
Institut für Physikalische Chemie der Universität,
Bonn, Germany and
G. Wagner*,
Gaswarne-Institut,
Essen, Germany,
*Present address: Atlas Mess- und Analysetechnik GmbH,
Bremen, Germany 307
56. Performance of a High Resolution Mass Spectrometer,
C. M. Judson, C. G. Blanchard, and D. J. Comaford,
Consolidated Electrodynamics Corporation,
Pasadena, California 315
57. Spark Source Mass Spectroscopy for Microanalysis of Solids,
W. M. Hickam and G. G. Sweeney,
Westinghouse Research Laboratories,
Pittsburgh 35, Pennsylvania 319

MASS SPECTRAL STUDIES OF HIGH TEMPERATURE INORGANIC PROCESSES

- 58.* Composition of Sulfur Vapor,
J. Berkowitz, J. R. Marquart, and W. A. Chupka,
Argonne National Laboratory,
Argonne, Illinois 323

* Invited Paper

TABLE OF CONTENTS - Continued

MASS SPECTRAL STUDIES OF HIGH TEMPERATURE INORGANIC PROCESSES (Continued)		Page No.
59.*	Some New Experiments in High Temperature Mass Spectrometry, A. Buchler, A. D. Little, Inc. Cambridge, Massachusetts	324
60A*	The Dissociation and Polymerization Energies of Group IV- Group VI Molecules (*). J. Drowart and R. Colin, Universite Libre de Bruxelles, Brussels, Belgium	325
60B*	Thermochemical Study of the Homonuclear Diatomic Molecules and of Some Gaseous Oxides of Scandium Yttrium and Lanthanum and of The Molecule ScC_2^* . J. Drowart, G. Verhaegen and S. Smoes, Universite Libre de Bruxelles, Brussels, Belgium	329
61.*	Mass Spectrometric Studies of New High Molecular Weight Boron Sulfides, Frank T. Greene and Paul W. Gilles, University of Kansas, Lawrence, Kansas	336
62.*	Mass Spectrometric Study of Reaction of Water Vapor with Beryllium Oxide, Lowell P. Theard and Donald L. Hildenbrand, Aeroneutronic Division, Ford Motor Company, Newport Beach, California	337
63.*	Mass Spectrometric Studies of Inorganic Fluorides, G. D. Blue, T. C. Ehlert, J. W. Green, and J. L. Margrave, University of Wisconsin, Madison, Wisconsin	344
INSTRUMENTATION II		
64.	A Study of Different Designs of Cold Electron Sources Capable of Mass Spectrometric Application, M. K. Testerman, R. W. Raible, G. W. Grimes, J. R. Williams, B. E. Gilliland, University of Arkansas, Graduate Institute of Technology, Little Rock, Arkansas	350
65.	The Coincidence Mass Spectrometer, M. L. Vestal, M. Krause, A. L. Wahrhaftig and W. H. Johnston, William H. Johnston Laboratories, Inc. Baltimore, Maryland.	358
66.	Inverted Magnetron Type Mass Spectrometer, Richard F. Herzog and Walter P. Poschenrieder, Geophysics Corporation of America, Bedford, Massachusetts	366
67.	The Influence of Ion Entrance Aperture Size and Excitation Frequency on the Performance of a Satellite Quadrupole Mass Filter, Wilson M. Brubaker and Johannes Tuul, Bell & Howell Research Center, Pasadena, California	371
* Invited Paper		

TABLE OF CONTENTS - Continued

	Page No.
INSTRUMENTATION II - Continued	
68. Ion Beam Profiles in Three Dimensional Magnetic Fields, A. C. Lilly, Jr. and T. J. Weismann, Gulf Research & Development Company, Pittsburgh, Pennsylvania	379
69. The Atlas Quadrupole Mass Spectrometer, C. Brunnee, L. Delgmann, K. Kronenberger, Atlas Mess -- und Analysentechnik GmbH., Bremen, Germany	388
70. An Ion Source Using a Parallel-Plate Electron-Energy Selector, Dwight A. Hutchison, Louis G. Pobo and William K. Brookshier, Argonne National Laboratory, Argonne, Illinois	398
71. Mass Discrimination in Electron Multiplier Ion Detectors, C. R. McKinney, Consolidated Electrodynamics Corporation; and D. Maynes, California Institute of Technology, Pasadena, California	403
72. Tandem Magnetic Analyzer Mass Spectrometer Systems, E. J. Michael and D. J. Marshall, Nuclide Analysis Associates, State College, Pennsylvania	408
73. A Method for the Determination of Ion Source Pressures in Mass Spectrometers Operated at Very High Pressures, F. H. Field and M. S. B. Munson, Humble Oil & Refining Company, Baytown, Texas	414
SOLID SOURCE STUDIES I	
74. The Determination of Fluorine in ZrO_2 Corrosion Films by Spark Source Mass Spectrography, H. D. Cook, Bettis Atomic Power Laboratory, Pittsburgh, Pennsylvania	420
75. Analysis of Insulating Powders by Spark Source Mass Spectrometry, R. Brown and W. A. Wolstenholme, Associated Electrical Industries Ltd., Manchester, England	421
76. Construction Details of and First Results Obtained with a New Commercial Mattauch-Type Mass Spectrograph, K. E. Habfast, Atlas Mess -- und Analysentechnik GmbH., Bremen, Germany	430
77. A New Double Focusing Mass Spectrometer for Organic Analysis, M. Barber, R. D. Craig, R. M. Elliott and B. N. Green, Associated Electrical Industries Limited, Manchester, England	431

TABLE OF CONTENTS - Continued
SOLID SOURCE STUDIES I - Continued

	Page No.
78. Elemental Associations Observed in the Radio Frequency Spark Source, F. Neil Hodgson, Monsanto Research Corporation, Dayton, Ohio; Michael Desjardins, University of Cincinnati, Cincinnati, Ohio; and William L. Baun, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio	444
79. Use of Spark Source Mass Spectrograph as a Milliprobe Analyzer, Robert A. Wallace and John Roboz, General Telephone & Electronics Laboratories, Inc., Bayside, New York	451
80. A Method for Studying the Chemisorption and Exchange of Gases on Surfaces, Y. L. Sandler and W. M. Hickam, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania	457
81. Evaluation of Accuracy of Surface Ionization Mass Spectrometer Data, H. O. Finley, M. R. Clickner, E. E. Leuang, Jr. Atomic Energy Commission, New Brunswick Laboratory, New Brunswick, New Jersey	461
82. Mass Spectrometric Study of Sodium and Rubidium Diffusion in Tungsten, H. M. Love and J. J. White, Department of Physics, Queen's University, Kingston, Ontario, Canada	469
83. Precision, Accuracy, and Sensitivity in Spark Mass Spectrometry, C. M. Judson and C. W. Hull, Consolidated Electrodynamics Corporation, Pasadena, California	470
84. Analytical Techniques, Arthur J. Socha and Robert K. Willardson, Bell & Howell Research Center, Pasadena, California	474
INSTRUMENTATION AND ANALYTICAL TECHNIQUES	
85. Miniaturized Bendix Time-of-Flight Mass Spectrometers, J. F. Betts and G. J. O'Halloran, The Bendix Corporation, Southfield (Detroit), Michigan	483
86. An Improved Oscillographic Camera Technique for Time-Resolved Mass Spectrometer Data Recording, Richard T. Meyer, Sandia Corporation, Albuquerque, New Mexico	489

TABLE OF CONTENTS - Continued

INSTRUMENTATION AND ANALYTICAL TECHNIQUES - Continued		Page No.
87. Plasma Analysis with the Bendix Time-of-Flight Mass Spectrometer, G. J. O'Halloran and R. A. Fluegge, The Bendix Corporation, Southfield (Detroit), Michigan		496
88. Conversion and Evaluation of Diffusion to Ionic Pumping in Isotope Ratio Mass Spectrometer, (Withdrawn) W. S. Updegrave, Sinclair Research, Tulsa, Oklahoma		505
89. A Direct Determination of the ^3H - ^3He Mass Difference, P. E. Moreland, Jr., and K. T. Bainbridge, Harvard University, Cambridge, Massachusetts		506
90. The Determination of the Absolute Value of the Deuterium Content of Hydrogen and Water by Mass Spectrometry, R. Botter, Centre D'Etudes Nucleaires de Saclay, Saclay, France		511
91. The Products of Flash Pyrolysis of Phenol-Formaldehyde by Time-of- Flight Mass Spectroscopy, Henry L. Friedman, General Electric Company, King-of-Prussia, Pennsylvania		518
92. Identification of Decomposition Products of Polytetrafluoroethylene ("Teflon"-1 and "Teflon"-6) and Polyfluoroethylene propylene, ("Teflon"-100), Richard E. Kupel, Melvin Nolar, Robert G. Keenan, Mark Hite, and Lester D. Scheel, U. S. Department of Health, Education and Welfare, Public Health Service, Cincinnati, Ohio		525
93. Mass Spectral Studies of Kinetics Behind Shock Waves. The Thermal Decomposition of Hydrazine, R. W. Diesen, The Dow Chemical Company, Midland, Michigan		531
94. Determination of Hydrocarbon Types in Kerosene Range Distillates by Mass Spectrometry, L. R. Snyder, H. E. Howard and W. C. Ferguson, Union Oil Company of California, Brea, California		532
95. Analysis of Paraffin Wax in the C_{16} - C_{36} Range by Mass Spectrometry, F. J. Galbraith, V. A. Cirillo, Atlantic Refining Company, Philadelphia, Pennsylvania		533
SOLID SOURCE STUDIES II		
96. Isotopic Mass Spectrometry of the Elements, E. J. Spitzer and J. R. Sites, Oak Ridge National Laboratory, Oak Ridge, Tennessee		541

TABLE OF CONTENTS - Continued

SOLID SOURCE STUDIES II - Continued		Page No.
97.	Isotopic Analyses with a Spark Source Mass Spectrograph, F. D. Leipziger, Sperry Rand Research Center, Sudbury, Massachusetts	545
98.	Analytical Studies with Spark Source Mass Spectorgraph (Withdrawn) John Roboz, General Telephone & Electronics Laboratories, Inc., Bayside, New York	549
99.	Mass Spectrometric Analysis of B ¹⁰ in Boron Materials, H. O. Finley, A. R. Eberle and C. J. Rodden, Atomic Energy Commission, New Brunswick Laboratory, New Brunswick, New Jersey	550
100.	Solid Combustion Products Analysis by Spark Source Mass Spectrograph, A. V. Jensen, B. B. Goshgarian, N. E. Dane, Edwards Air Force Base, Edwards, California	555
101.	New Studies on the Diffusion of Hydrogen Through Hot Palladium, T. W. Martin and R. E. Rummel, Vanderbilt University, Nashville 5, Tennessee	566
102.	The Diffusion of Hydrogen in Natural and Synthetic Fused Quartz, R. W. Lee, General Motors Corporation, Warren, Michigan	567
103.	Determination of Gas Content of Metals with Spark Source Mass Spectrograph, John Roboz, General Telephone & Electronics Laboratories, Inc., Bayside, New York	572
104.	A Mass Scale Based on CH ₂ = 14.0000 for High Resolution Mass Spectrometry of Organic Compounds, E. Kendrick, Esso Research & Engineering Company, Linden, New Jersey	578
105.	Photographic Indexing Technique for Evaluating Emulsion Uniformity of Spectrographic Plates, J. M. McCrea, United States Steel Corporation, Monroeville, Pennsylvania	588
106.	The Energy Distribution of Ions Formed in the RF Spark Source, J. Rogers Woolston and Richard E. Honig, RCA Laboratories, Princeton, New Jersey	597
BIBLIOGRAPHY OF PUBLISHED AND UNPUBLISHED PAPERS ON MASS SPECTROMETRY FOR 1962		605
Subcommittee II Fundamental Aspects		606
Subcommittee III High Molecular Weights and Techniques		645
Subcommittee V Instrumentation and Techniques		650

ANISOTROPY IN ANGULAR DISTRIBUTION OF MOLECULAR DISSOCIATION PRODUCTS

Gordon H. Dunn
National Bureau of Standards
Boulder, Colorado

ABSTRACT

Anisotropies in the angular distributions of molecular dissociation products were known to some workers as early as 1935, but these anisotropies have been largely ignored by investigators dealing with dissociative collisions.

Selection rules based on general symmetry arguments have been derived¹ for dissociative collisions of electrons with diatomic molecules which indicate the qualitative nature of the anisotropies expected when a symmetry axis can be defined for the system of colliding particles. These selection rules and the choice of a symmetry axis appropriate to a given kind of dissociative collision are discussed.

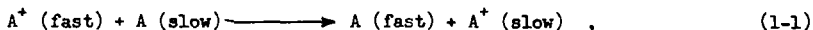
The effect of anisotropic distributions of products on the correct measurement of cross sections, energy distributions, and relative abundances will be pointed out. Recent experimental data on the dissociative ionization of H_2 by electrons will be presented to further illustrate the nature and degree of such effects.

1. G. H. Dunn, Phys. Rev. Letters 8, 526, (1962).

Donald Rapp
Lockheed Missiles and Space Co.
Palo Alto, California

1. Introduction:

When relatively fast ions are passed through a thermal gas, interchange of charge can occur by several different processes. Most of the theoretical and experimental work has been done on the 10-01 process in which a singly charged ion exchanges an electron with a neutral target. We can separate this into two sub-categories, symmetric resonant:



and asymmetric:



This review will attempt to describe the theory of these processes in the simplest terms possible, the emphasis being on clarity rather than rigor. Neither is the intent to be complete, for space limitations do not permit very extensive examination of every method. No attempt has been made to include references.

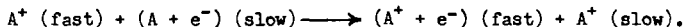
2. Regimes of Ion Velocity:

At low collision velocities the lower phase shifts in a scattered wave calculation for inelastic scattering with interchange of an electron must be evaluated. Typically, at velocities greater than $\sim 10^5$ cm/sec, one finds that many hundreds of phase shifts are required to evaluate the cross section. This is the condition sufficient for application of semi-classical procedures in determination of the phase shifts. The result is equivalent to an impact parameter method in which one uses the classical collision trajectory to describe relative motion of the nuclei, and time-dependent wave mechanics to determine transition probabilities for the electron to jump from one nucleus to the other during the passage of the ion near the target molecule. At velocities greater than 10^8 cm/sec, one cannot use the simple procedure valid for lower velocities because the ion velocity is comparable to the classical electron orbital velocity in the target molecule. A more specific treatment to include this condition leads to the result that the cross section falls off more rapidly with increasing ion velocity above 10^6 cm/sec than the elementary theory would predict. Most of the work described in this review will deal with the intermediate velocity regime between 10^5 and 10^8 cm/sec.

3. Symmetric Resonant Charge Transfer Between Atoms:

In dealing with symmetric charge transfer in the intermediate velocity regime, there are a number of approaches that can be taken. We shall illustrate the perturbed stationary state (PSS) approach and the linear combination of atomic orbitals method (LCAO) in an impact parameter calculation. We shall then demonstrate the equivalence of the scattered wave and impact parameter methods in the LCAO approximation. Finally, we shall illustrate the calculation for velocities in excess of 10^8 cm/sec in the LCAO approximation.

In general the calculations are strictly applicable only to the simple process $p + H \longrightarrow H + p$, in which p denotes proton. For larger atoms one must use a single valence electron in a one-electron orbital, picturing the process as:



According to this approximation, all charge transfer processes for ions in their parent gases behave like the process protons in a hydrogen atom gas, except for a scale factor relating to the different atomic size. The effective atomic size depends inversely on the ionization potential at large distances, so that the symmetric resonant charge transfer cross section depends inversely on the ionization potential. This conclusion has been verified experimentally in a large number of instances.

4. Impact Parameter Treatment of Charge Transfer:

One considers ions A^+ moving past an atom A in rectilinear trajectories with various distances of closest approach, b , for a given velocity v . The velocity is considered to be high enough that one may neglect variation in v and curvature in the path during the collision. For any but the very smallest impact parameters this is a good approximation. One then calculates the probability, $P(b,v)$, that the single valence electron on A will jump to A^+ during the interaction, on a single trajectory. The contribution that any impact parameter makes to the total cross section is proportional to the function $P(b,v)$ and to the cross-sectional area of an annular ring $2\pi b db$. The total cross section is therefore given by

$$\sigma(v) = \int_0^{\infty} P(b,v) 2\pi b db . \quad (4-1)$$

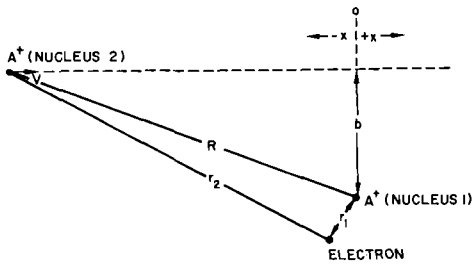


Figure 1 - Collision Coordinates. Nucleus 2 moves at velocity v past nucleus 1, to which the electron is initially attached.

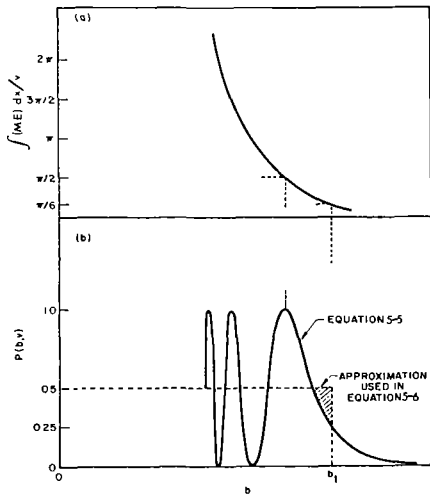


Figure 2 = (a) Variation of the integral from Eq. 5-5 with impact parameter, (b) Dependence of charge exchange probability on impact parameter as given in Eq. 5-5, and the approximation of Eq. 5-6.

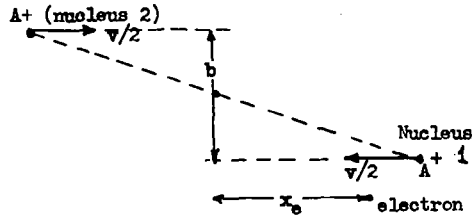


Figure 6- Coordinates for calculation of charge transfer at high velocities. The center of mass is fixed at the midpoint of the two nuclei, which approach each other, each with velocity $v/2$. The electron thereby possesses a velocity of $v/2$ with respect to the center of mass.

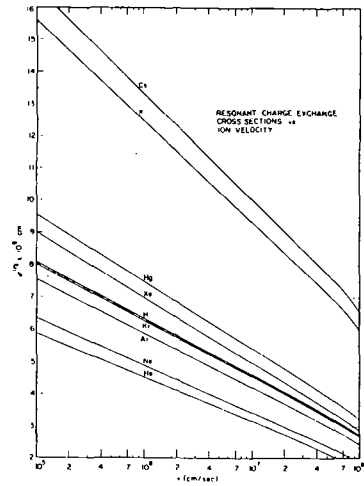


Figure 3 - Calculated symmetric resonant charge transfer cross sections for various atoms as a function of ion velocity. These results are based on a linear combination of semi-empirical orbitals, and are roughly commensurate with experiment.

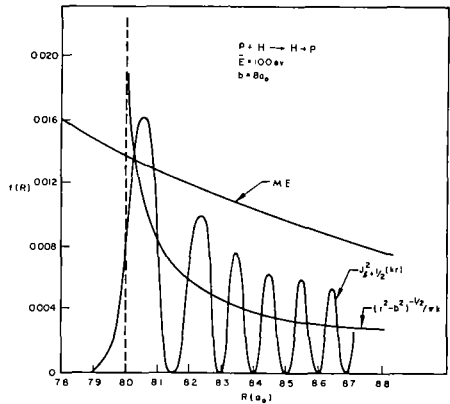


Figure 4 - Comparison of scattered wave and impact parameter calculations. In the scattered wave treatment one must integrate the Bessel function over the term ME from 0 to ∞ . In the impact parameter treatment one must multiply the monotonically decreasing curve over ME. At moderate velocities, this latter curve approximates the average of the Bessel function, and the two results should be nearly identical.

An illustration of the model chosen to represent the collision is shown in Fig. 1. The electron is initially located on nucleus 1 which is stationary. The ion (nucleus 2) moves in a straight line with constant velocity v , from $x = -\infty$ to $x = +\infty$. The classical trajectory is simply $x = vt$.

5. The LCAO Impact Parameter Method:

At any instant in time during the collision, one may consider the electron to exist in the field of two stationary A^+ ions. The nuclei move slowly enough that this adiabatic picture is a good approximation. The wave function for the electron in the combined field of the two nuclei is determined by the wave equation:

$$H_{e1} \Psi = [(-\hbar^2/2m) \nabla^2 + V_1(r_1) + V_2(r_2)] \Psi = \hbar i \dot{\Psi} \quad (5-1)$$

in which Ψ is the total wave function for the electron in space and time, and V_j is the binding potential to nucleus j . At infinite separation of the nuclei where the overlap of the atomic orbitals is zero, there are two degenerate solutions to this equation, namely the atomic orbitals $\phi_j(r_j) \exp(-i\omega t)$ centered on nucleus j ($j = 1, 2$). The frequency ω is determined by $\omega = I/\hbar$, where I is the ionization potential of the atom A . For large impact parameters one may write the total wave function as a linear combination of these orbitals, corresponding to location of the electron on one or the other nuclei:

$$\Psi = c_1(t) \phi_1(r_1) e^{-i\omega t} + c_2(t) \phi_2(r_2) e^{-i\omega t}, \quad (5-2)$$

and the probability of finding the electron on nucleus j at time t is $|c_j(t)|^2$. Equation 5-1 determines how the system changes with time during the collision. Upon inserting Eq. 5-2 into Eq. 5-1, this time dependence of Ψ becomes couched in terms of the time dependence of c_1 and c_2 , which ultimately locate the electron with respect to the nuclei.

The initial condition is $|c_1(-\infty)|^2 = 1$, and $c_2(-\infty) = 0$. The charge exchange probability for a particular collision trajectory is then given by $P(b, v) = |c_2(+\infty)|^2$. When Eq. 5-2 is inserted in Eq. 5-1, a differential equation in c_1 and c_2 as functions of time is obtained. Multiplying alternatively by ϕ_1^* and ϕ_2^* , and integrating over all space in the coordinates of the electron, two coupled equations are obtained which can be rearranged into the form:

$$\begin{aligned} i\dot{c}_1 &= (M.E.) c_2 \\ i\dot{c}_2 &= (M.E.) c_1 \end{aligned} \quad (5-3)$$

In these expressions, (M.E.) represents a grouping of matrix elements,

$$(M.E.) = \{ (V_2)_{21} - F(V_2)_{11} \} / \{ (1 - F^2) \hbar \},$$

in which $(V_j)_{jk}$ is the potential energy V_j integrated over all space between the functions ϕ_j^* and ϕ_k , and F is the overlap $\phi_1^* \phi_2$ integrated over all space. It can be shown that for large impact parameters the main part of (M.E.) is simply $(V_2)_{21}$. This term is the potential attracting the electron to nucleus 2, integrated between the orbitals on nuclei 1 and 2. This is just what one would expect from a calculation of this sort, the perturbation integrated between the initial and final states. The peculiar form of direct coupling in these equations is due to the fact that both nuclei attract the electron equally, and once the electron has jumped to nucleus 2 it is attracted back toward nucleus 1 by the very same type of perturbation. It is therefore understandable that the solutions of these equations are:

$$\begin{aligned} |c_2(t)|^2 &= \sin^2 \int_{-\infty}^t (M.E.) dt' \\ |c_1(t)|^2 &= \cos^2 \int_{-\infty}^t (M.E.) dt' \end{aligned} \quad (5-4)$$

in which there is a flow of probability back and forth from nucleus to nucleus. The charge transfer probability for a fixed impact parameter can be evaluated by replacing dt by dx/v , and integrating the time to $+\infty$:

$$P(b, v) = \sin^2 \int_{-\infty}^{+\infty} (M.E.) dx/v \quad (5-5)$$

A plot of $\int (M.E.) dx/v$ vs. b is given in Fig. 2, along with a plot of $P(b, v)$. At large impact parameters the total interaction is weak and there is only a small value for the integral and for the probability. As the impact parameter is reduced, the integral increases till it reaches $\pi/2$, at which point the probability is unity. At smaller impact parameters the integral increases continuously, whereas $P(b, v)$ oscillates, reaching maxima and minima at successive multiples of $\pi/2$ for the integral. These correspond to successive jumps of the electron back and forth between the nuclei. Because of the factor v in

the denominator of Eq. 5-5, the entire function $P(b, v)$ becomes elongated to larger b at lower velocities, resulting in a cross section which increases monotonically as the velocity is reduced. In actual practice one usually replaces this oscillating curve by its average, $\frac{1}{2}$, from $b = 0$ to b_1 , in which b_1 is determined as the point where $P(b_1, v) \approx \frac{1}{4}$. Then making use of Eq. 4-1,

$$\sigma = \frac{1}{2} \pi b_1^2. \quad (5-6)$$

If this entire calculation procedure is followed using semi-empirical orbitals: $\phi_j \sim \exp [-(I/13.6)^{\frac{1}{2}} r/a_0]$, in which I is in eV, the total cross sections shown in Fig. 3 result. For any process the cross section falls off slowly with increasing velocity, roughly such that $\sigma^{\frac{1}{2}}$ is a straight line when plotted vs. $\log v$. The absolute cross sections increase with decreasing ionization potential. These results may be shown to be commensurate with experiment.

6. The Perturbed Stationary States Approach In the Impact Parameter Method:

Consider a general quantum mechanical system having two degenerate states (when unperturbed) ϕ_1 and ϕ_2 with energies I . If a constant perturbation is now introduced, it will split the energy levels of the perturbed stationary states, which will be $(\phi_1 + \phi_2)$ with energy E_s , and $(\phi_1 - \phi_2)$ with energy E_a . Let the system be initially in unperturbed state ϕ_1 , and let the perturbation be applied from time 0 to τ . For $t < 0$, the time dependent wave function of the system is $\phi_1 \exp [-i(I)t/\hbar]$, whereas for $0 \leq t \leq \tau$, the total wave function must be some linear combination of the perturbed stationary states. This is due to the fact that the general solution of a wave equation is a superposition of all the particular solutions. Therefore, when the perturbation is on, the total wave function is

$$\bar{\Psi}(t) = a_s (\phi_1 + \phi_2) \exp (-iE_s t/\hbar) + a_a (\phi_1 - \phi_2) \exp (-iE_a t/\hbar) \quad (6-1)$$

in which the a 's are coefficients to be determined. But in order to make the unperturbed and perturbed wave functions identical at $t = 0$, one must choose $a_s = a_a = \frac{1}{2}$. The perturbed stationary states are independent of one another, and oscillate in time with different frequencies. At the end of the time period τ , the total wave function is

$$\bar{\Psi}(\tau) = \frac{1}{2} (\phi_1 + \phi_2) \exp (iE_s \tau/\hbar) + \frac{1}{2} (\phi_1 - \phi_2) \exp (-iE_a \tau/\hbar). \quad (6-2)$$

The two stationary states are now out of phase. Mathematical rearrangement of this expression leads to the result:

$$\begin{aligned} \bar{\Psi}(\tau) = & \phi_1 \exp [-i(E_a + E_s)\tau/2\hbar] \cos [(E_a - E_s)\tau/2\hbar] \\ & - i\phi_2 \exp [-i(E_a + E_s)\tau/2\hbar] \sin [(E_a - E_s)\tau/2\hbar]. \end{aligned} \quad (6-3)$$

After the perturbation is ended, the system must become a superposition of the unperturbed stationary states, so that

$$\bar{\Psi}(t) = b_1 \phi_1 \exp (-iIt/\hbar) + b_2 \phi_2 \exp (-iIt/\hbar) \quad (6-4)$$

for $t \geq \tau$, and the b 's are as yet undetermined coefficients.

Since expressions 6-3 and 6-4 for the wave function must be identical at $t = \tau$, the coefficients b_1 and b_2 may be determined easily:

$$\begin{aligned} b_1 &= e^{i\theta} \cos [(E_a - E_s)\tau/2\hbar] \\ b_2 &= i e^{i\theta} \sin [(E_a - E_s)\tau/2\hbar], \end{aligned} \quad (6-5)$$

in which θ is an unimportant phase factor: $\theta = (2I - E_a - E_s)\tau/2\hbar$. Since the absolute squares of the coefficients b_1 and b_2 determine the probability of finding the system in states ϕ_1 and ϕ_2 respectively, we find that the probability of a transition from state ϕ_1 to state ϕ_2 due to the perturbation is

$$P_{1 \rightarrow 2} = |b_2|^2 = \sin^2 [(E_a - E_s)\tau/2\hbar]. \quad (6-6)$$

The equations used in this calculation are exactly analogous to the equations involved in the classical problem of an oscillating pendulum which becomes weakly coupled to an identical (but initially stationary) pendulum. The expressions for the displacement of the two pendula are the same as for the two unperturbed stationary state wave functions in the above calculation and the quantities $E_a/\hbar$ and $E_s/\hbar$ represent the frequencies of the normal modes of the perturbed system. One finds a characteristic flow of displacement back and forth between the pendula determined by the same equations that cause probability to flow back and forth between the quantum mechanical systems.

A slightly more elaborate treatment shows that when the perturbation is not constant in time, Eq. 4-11 must be replaced by

$$P_{1 \rightarrow 2} = \sin^2 \int_{-\infty}^{+\infty} (E_a - E_s) dt / 2\hbar. \quad (6-7)$$

The application to symmetric resonant charge transfer is immediate. The two degenerate unperturbed stationary states are the atomic orbitals at infinite separation of the ion and atom. As the ion moves past the atom on the rectilinear trajectory shown in Fig. 1, the energies of the perturbed stationary states change in time, but the constitution of these states remain constant (i.e. $(\phi_1 \pm \phi_2)$). Therefore Eq. (6-7) applies directly with dt replaced by dx/v . It is the splitting of the perturbed stationary states which determines the probability of charge transfer in symmetric resonance:

$$P(b, v) = \sin^2 \int_{-\infty}^{+\infty} (E_a - E_s) dx / 2\hbar v. \quad (6-8)$$

We may now enquire into the relationship between Eqs. 6-8 and 5-5. Eq. 6-8 is the more rigorous because it expresses the wave function during the collision in terms of the molecular states that exist transiently. In fact, a more elaborate calculation in terms of the actual molecular wave functions (not merely the approximations $(\phi_1 \pm \phi_2)$) would yield the same result as given in 6-8 except that the accurate values for $(E_a - E_s)$ should be used. Since Eq. 5-5 is based on a linear combination of atomic orbitals, it is not surprising that (M.E.) turns out to be just exactly the LCAO approximation to the splitting $(E_a - E_s)/2\hbar$ of the molecular states. In the actual calculation of symmetric resonant charge exchange cross sections, one need never deal with wave functions at all if the energies E_a and E_s are known from other considerations. For the simple process $H^+ + H$ or $H + H^+$, the energy splitting $(E_a - E_s)$ is known very accurately, and an accurate calculation can be made from Eq. 6-8. For larger atoms, the splittings are not well established and one must rely on rough approximations such as the use of semi-empirical orbitals.

7. The Scattered Wave LCAO Calculation and its Relationship to the LCAO Impact

Parameter Calculation:

In this calculation, one again deals with a stationary target atom, but the incident ion beam is represented by a plane wave $\exp(ikx)$, in which $k = Mv/\hbar$ for the incident ion. The wave functions for an electron centered on nuclei 1 and 2 are, as before, ϕ_1 and ϕ_2 , respectively. The nuclear wave functions are denoted as ψ_1 with the electron on nucleus 1, and ψ_2 after charge transfer with the electron on nucleus 2. The asymptotic forms of these functions for large internuclear distances are:

$$\begin{aligned} \psi_1 &\sim e^{ikx} + f_e(\theta) e^{ikR}/R \\ \psi_2 &\sim f_1(\theta) e^{ikR}/R \end{aligned} \quad (7-1)$$

The function corresponding to the electron on nucleus 1 corresponds to an incident wave and a scattered wave, whereas the function corresponding to the electron on nucleus 2 corresponds only to an outgoing scattered wave. The cross section for charge exchange is

$$\sigma = 2\pi \int_0^\pi |f_1(\theta)|^2 \sin \theta d\theta \quad (7-2)$$

and the cross section for elastic scattering is a similar expression with f_1 replaced by f_e .

In the LCAO approximation the electron is in one atomic orbital or the other. Each electronic wave function is associated with a particular wave function, and since either is a legitimate solution of the Schrodinger equation, the total wave function must be taken as

$$\Psi = \phi_1 \psi_1 + \phi_2 \psi_2. \quad (7-3)$$

If this wave function is inserted in the wave equation:

$$H_{\text{tot}} \Psi = (\hbar^2 k^2 / 2M) \Psi, \quad (7-4)$$

in which H_{tot} is the total Hamiltonian for the electron and the two nuclei:

$$H_{\text{tot}} = H(\text{Eq. 4-1}) - (\hbar^2 / 2m) \nabla_e^2 + V_{12}(R), \quad (7-5)$$

one obtains a differential equation in the various wave functions. If this equation is multiplied alternately by ϕ_1 and ϕ_2 and integrated over all space in the electronic coordinates, a set of two coupled equations in the nuclear wave functions is obtained. These equations are:

$$\{ \nabla^2 + k^2 + (2M/\hbar^2) [(V_2)_{21} \pm (V_2)_{11}] / (1 \pm F) \} (\psi_1 \pm \psi_2) = 0. \quad (7-6)$$

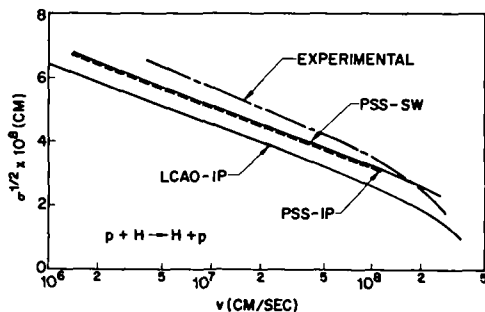


Figure 5- Theoretical calculations of cross sections for symmetric resonant charge transfer between protons and H atoms based upon the methods of Sec.5(LCAO-IP), Sec.6(PSS-IP), and Sec. 7 (PSS-SW), along with the experimental data.

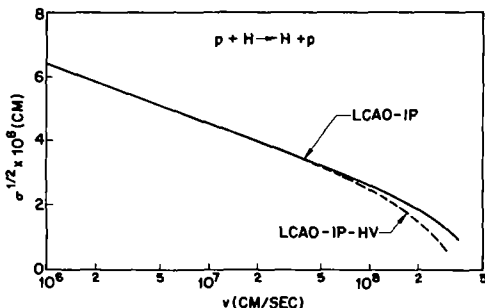


Figure 6a- Theoretical calculations of cross sections for charge transfer between protons and H atoms at high velocities, using the method of Sec. 5 (LCAO-IP) and the more rigorous method of Sec.6 (LCAO-IP-HV).

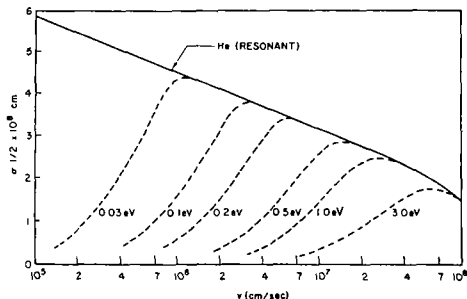


Figure 7a- Cross sections for a family of non resonant charge transfer processes in which the average ionization potential is that of He and the E's are as shown in the figure. All the curves go to the symmetric charge transfer cross section for He⁺ with He at high velocities.

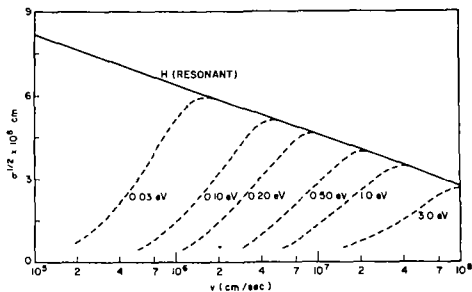


Figure 7b- Same as 7a, except for average ionization potential for that of H.

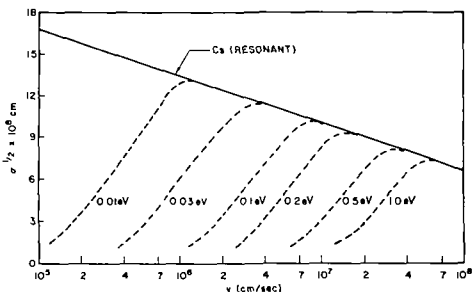


Figure 7c- Same as 7a, except that the average ionization potential is that of Cs.

When these equations are solved subject to the asymptotic forms given in Eq. 7-1, one obtains expressions in terms of phase shifts in the same manner as for simple elastic scattering from a fixed center of force. Expressions for $f_1 \pm f_0$ are obtained, and by subtraction,

$$f_1(\theta) = (4ik)^{-1} \sum_{\ell=0}^{\infty} (2\ell+1) (e^{2i\eta_{\ell}} - e^{2i\delta_{\ell}}) P_{\ell}(\cos \theta), \quad (7-7)$$

where η_{ℓ} and δ_{ℓ} are phase shifts associated with the asymptotic forms of $\{\psi_1 + \psi_2\}$ and $\{\psi_1 - \psi_2\}$, respectively. From Eq. 7-2, one may then show that

$$\sigma = (\pi/k^2) \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2(\delta_{\ell} - \eta_{\ell}). \quad (7-8)$$

This expression is directly analogous to Eq. 4-1 of the impact parameter method. Each value of the azimuthal quantum number ℓ corresponds to a particular angular momentum, according to the relationship $p^2 = \hbar^2 \ell(\ell+1)$. At high angular momenta (large classical impact parameters) ℓ is large compared to unity and one can treat p and ℓ as continuous variables. Therefore on differentiation, $p \, dp = \hbar^2 (2\ell+1) \Delta \ell$. But in this classical limit, the angular momentum is also given by $p = \hbar k b$, where b is the impact parameter. Therefore

$$2 \pi b \, db = p \, dp / \hbar^2 k^2 \approx (\pi/k^2) (2\ell+1) \Delta \ell. \quad (7-9)$$

If the right side of Eq. 7-7 is multiplied by $\Delta \ell$, which is unity, the sum over ℓ may be replaced by an integration over b for large ℓ . One therefore obtains

$$\sigma = \int_0^{\infty} \sin^2(\delta_{\ell} - \eta_{\ell}) 2 \pi b \, db \quad (7-10)$$

In order to compare the impact parameter treatment with Eq. 7-10 from the scattered wave treatment, we must use Jeffreys' approximation for the phase shifts corresponding to large values of ℓ . The result is

$$\delta_{\ell} - \eta_{\ell} = (\pi M/\hbar) \int_0^{\infty} (M.E.) [J_{\ell + \frac{1}{2}}(kR)]^2 R \, dR. \quad (7-11)$$

Combining this with Eq. 7-10, we obtain

$$\sigma = \int_0^{\infty} \sin^2 \left\{ (\pi M/\hbar) \int_0^{\infty} (M.E.) [J_{\ell + \frac{1}{2}}(kR)]^2 R \, dR \right\} 2 \pi b \, db. \quad (7-12)$$

This expression is the classical limit of the wave mechanical treatment and is directly comparable with that obtained from the impact parameter treatment, namely the result of combining Eq. 4-1 and 5-5:

$$\sigma = \int_0^{\infty} \sin^2 \left\{ \int_0^{\infty} (M.E.) \, dx/v \right\} 2 \pi b \, db \quad (7-13)$$

From a consideration of the Pythagorean relation between x , R , and b in Fig. 1, it can be shown that Eq. 7-11 becomes:

$$\sigma = \int_0^{\infty} \sin^2 \left\{ \int_0^{\infty} (M.E.) R \, dR / v(R^2 - b^2)^{\frac{1}{2}} \right\} 2 \pi b \, db. \quad (7-14)$$

We see by comparison of the arguments of the sine functions in Eqs. 7-12 and 7-14, that the impact parameter result involves integration of the function $[k(R^2 - b^2)]^{-1}$ over $(M.E.) R dR$, whereas the scattered wave result involves integration of $\pi [J_{\ell + \frac{1}{2}}(kR)]^2$ over the same integrand. Figure 4 shows that the impact parameter function is an approximation to the average of the scattered wave oscillating Bessel function. Therefore, at large ion velocities where the Bessel function oscillates many times in the important region of R , the impact parameter and scattered wave cross sections should be nearly identical. A more elaborate calculation shows that the P.S.S. scattered wave calculation has a similar relationship to the P.S.S. impact parameter calculation. Figure 5 shows calculations of the resonant charge exchange cross section for protons incident on ground state H-atoms, based on 1) a P.S.S. impact parameter calculation using the accurate energy splitting known for H_n^+ , 2) a P.S.S. scattered wave calculation using the accurate energy splitting, 3) an LCAO impact parameter treatment.

8. Symmetric Resonant Charge Exchange at High Velocities:

At high velocities, where the ion velocity becomes comparable to the classical orbital velocity of the electron on the atom, the simple picture of the collision given in Fig. 1 with the target atom at rest is not a good approximation. A more proper treatment is shown in Fig. 6. The center of mass of the system is fixed at "O", and the two nuclei approach each other on parallel lines with equal and opposite velocities $v/2$, in which v is the laboratory ion velocity relative to a stationary target. Now the proper form of the asymptotic atomic orbitals at infinite nuclear separation must include a term to express the fact the electron is hurtling toward the center of mass with velocity $v/2$.

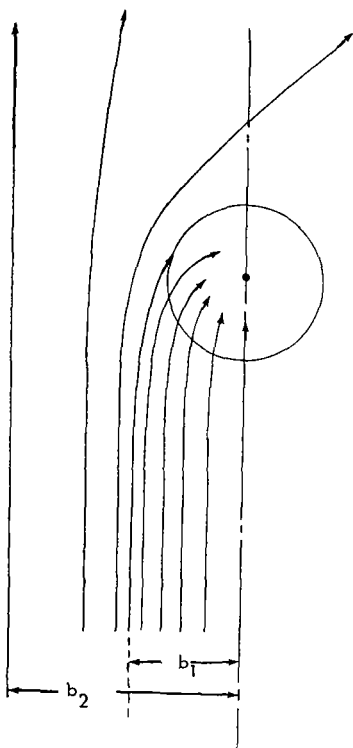


Figure 8 - Classical collision trajectories for ions incident on a fixed neutral scattering center at constant velocity as a function of impact parameter. All collisions with impact parameter less than b_1 result in direct impact with the scattering center. At high velocities charge transfer takes place out to large impact parameters like b_2 and one can neglect curvature in the inner trajectories. At low velocities, the impact cross section increases more rapidly till charge exchange occurs only out to trajectories like b_1 . In this case the cross section for charge transfer is determined by the capture cross section.

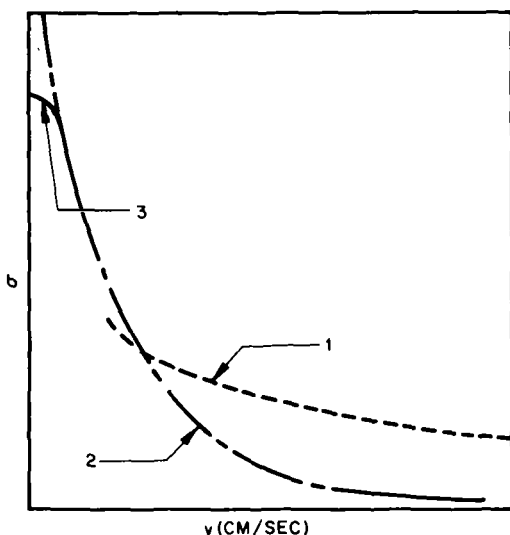


Figure 9 - Cross sections calculated for symmetric charge transfer. Curve 1 is the usual impact parameter result valid at moderate velocities. Curve 2 is calculated from Eq.

10-1 and is the capture cross section divided by 2. When curve 1 exceeds curve 2, one can neglect curvature of the inner trajectories. Curve 3 represents what happens to the cross section at very low velocities where the semi-classical method becomes a poor approximation. The lower phase shifts of a quantum mechanical calculation determine the cross section is finite, not infinite as the semi-classical method would predict.

Thus the atomic orbital located on nucleus 1 has the form

$$\phi_1(r_1) e^{-i\omega t} \exp[-i(m_e v/2\hbar)x],$$

where x is the distance from the electron to the center of mass, projected on the ion trajectory. The atomic orbital centered on nucleus 2 has a similar imaginary exponential, but of opposite sign. Unfortunately, the wave function as written above does not quite satisfy the Schrodinger equation, and a phase factor $\exp[-i(m_e v^2/8\hbar)t]$ must be inserted to eliminate a term resulting from differentiation of the plane wave term. Thus the proper atomic orbitals to be used are

$$\tilde{\phi}_1 = \phi_1(r_1) e^{-i\omega t} \exp[-i(m_e v/2\hbar)x] \exp[-i(m_e v^2/8\hbar)t] \quad (8-1)$$

$$\tilde{\phi}_2 = \phi_2(r_2) e^{-i\omega t} \exp[+i(m_e v/2\hbar)x] \exp[+i(m_e v^2/8\hbar)t].$$

Now the total wave function is taken as a linear combination of such orbitals,

$$\Psi = c_1(t) \tilde{\phi}_1(r_1, t) + c_2(t) \tilde{\phi}_2(r_2, t) \quad (8-2)$$

just as was done in the simpler approach given in Eq. 5-2.

Now the calculation proceeds in exactly the same way, except that the integrals involving different atomic orbitals (namely $(V_2)_{21}$ and F) contain a factor $\exp[-i(m_e v/\hbar)x]$ that does not occur in the simpler treatment. This factor results from the imaginary exponential terms in $\tilde{\phi}_1^* \tilde{\phi}_2$ and $\tilde{\phi}_2^* \tilde{\phi}_1$. Thus, for example,

$$F = \int_0^\infty \phi_1(r_1) \phi_2(r_2) \exp[-i(m_e v/\hbar)x] dx \quad (8-3)$$

In the coordinate system shown in Fig. 6, we note that most of the overlap $\phi_1 \phi_2$ occurs in the vicinity of $x \approx 0$. Thus the integrand in 8-3 has a range in x of perhaps a_0 . For low velocities, such that $(m_e v/\hbar)a_0 \ll 1$, the imaginary exponent is essentially zero, and the imaginary exponential term may be replaced by unity. One then retrieves the result of the simpler calculation given in Par. 5. At velocities above $\hbar/a_0 m_e = 2 \times 10^8$ cm/sec, one may expect increasingly greater errors in the result from Par. 5 as the velocity is increased. Below 2×10^8 cm/sec, the difference between the two calculations should rapidly decrease. Since the integrals are reduced by the imaginary exponential terms, the calculated cross section at high velocities falls below the calculation from Par. 5 based on the crude collision model. A comparison of the calculations from Fig. 5 with that based on the method described in this section (namely the LCAO impact parameter method including the effect of fast motion of the ion) for the simple process $H^+ + H \rightarrow H + H^+$ in Fig. 6a.

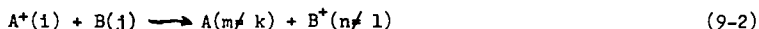
9. Asymmetric Charge Exchange:

The theory of asymmetric charge transfer has not been developed as completely as in symmetric charge transfer. However, semi-quantitative prediction of cross sections is possible, and qualitative understanding of the general trends in velocity dependence of the cross sections is not difficult. A good deal of theoretical progress on this problem will probably be made in the next few years.

We shall first contrast the electronic states involved in symmetric and asymmetric charge transfer. Whereas in symmetric transfer no change in electronic state is required (the molecular states do not interchange, but oscillate at different frequencies, leaving the electron on the other nucleus,) asymmetric transfer requires an electronic transition to a different potential curve. The initial and final states of asymmetric transfer ($A^+ + B$, and $A + B^+$) are asymptotic forms of two separate electronic states of AB^+ . The problem is to calculate the probability of jumping from one curve to the other during a collision. In collisions with relatively large impact parameters, one may assume that angular momentum and spin are conserved in such a process. Thus only transitions between states of AB^+ having identical symmetry are considered. In considering the process



in which the letters in parentheses indicate a particular electronic state, one need only include those states having the same symmetry. For a particular set of reactants $\{A^+(i) + B(j)\}$, one may further assume that there is only one set of products $\{A(k) + B^+(l)\}$ that lies close enough in energy that it has to be included. Processes of the type



are therefore neglected, and one has a two-state approximation. There are many systems for which several states of the products lie sufficiently close together in energy that the inclusion of more than one product state is essential. This has not yet been carried out in detail.

When $A^+(i)$ and $B(j)$ collide, several transient states of AB^+ may be formed. The probability that any state will be formed is proportional to its statistical weight. Only those states with identical symmetry with $\{A(k) + B^+(l)\}$ can produce charge transfer according to the assumptions of the previous paragraph. Therefore charge transfer is only possible in a certain fraction of the collisions, f , and the calculated cross section must be multiplied by this factor before comparison with experiment. An example is the process



There are two states of HeH which go asymptotically to $\{\text{He}^+({}^2S) + \text{H}({}^2S)\}$, having symmetries ${}^3\Sigma$ and ${}^1\Sigma$. Only a single state of HeH , ${}^1\Sigma$, goes to $\{\text{He}({}^1S) + \text{H}^+\}$. In the forward reaction, $\frac{1}{4}$ of the collisions produce ${}^1\Sigma$ states that can produce charge transfer, whereas $3/4$ produce ${}^3\Sigma$ states that cannot. Therefore f for the forward reaction is $\frac{1}{4}$. In the backward reaction, $f = 1$ because the ${}^1\Sigma$ state can produce charge transfer. The ratio of cross sections for forward and backward reactions should therefore be $\frac{1}{4}$.

We shall now illustrate the calculation for large impact parameters. The assumptions necessary to carry out the calculation are not very good at small impact parameters. One may hope that the larger impact parameters dominate in determining the magnitude of the cross section in the integral of Eq. 4-1. At large impact parameters the molecular wave functions for $(A^+ + B)$ and $(A + B^+)$ resemble the atomic orbitals ϕ_B and ϕ_A , respectively. Furthermore, the energies of the electronic states are close to the atomic energies, and we may write the total wave function analogously to Eq. 5-2 as:

$$\Psi = c_A(t) \phi_A(r_A) e^{-i\omega_A t} + c_B(t) \phi_B(r_B) e^{-i\omega_B t} \quad (9-4)$$

where ϕ_j is again the atomic orbital for the electron on nucleus j , $\omega_j = I_j/\hbar$, and I_j is the ionization potential of atom j ($j = A, B$). The time dependent wave equation is the same as Eq. 5-1, except that the subscripts 1 and 2 should be replaced by A and B. The procedure is then the same as in the symmetric case. The wave function in Eq. 9-4 is inserted in the time dependent wave equation, and the result is a differential equation in c_A and c_B as before. Now the equation is multiplied alternately by ϕ_A and ϕ_B , and integrated over all space to obtain two coupled equations in the c 's. Upon rearrangement, one obtains the equations

$$\begin{aligned} i \dot{c}_A &= (M.E.)_1 \exp(i\Omega t) c_B \\ i \dot{c}_B &= (M.E.)_2 \exp(-i\Omega t) c_A \end{aligned} \quad (9-5)$$

with

$$\Omega t = (\omega_A - \omega_B) t + \int_{-\infty}^t (\eta_1 - \eta_2) dt',$$

and the other terms are groupings of matrix elements.

For processes of type 1-2, it is possible to show that at large impact parameters it is a reasonable approximation to set $(M.E.)_1 \approx (M.E.)_2 = "M.E."$ and $\Omega \approx \omega_A - \omega_B = " \omega "$.

We may then qualitatively analyze the behavior of the solutions to these modified equations:

$$\begin{aligned} i dc_B/dx &= [(M.E.)/v] e^{i\omega x/v} c_A \\ i dc_A/dx &= [(M.E.)/v] e^{-i\omega x/v} c_B \end{aligned} \quad (9-6)$$

The term $(M.E.)/v$ depends on x as a "bell shaped" function, rising to a maximum at $x = 0$, and decreasing to zero at $\pm \infty$. It is qualitatively similar to the corresponding term in Eq. 5-3, having a "width" in x , a , of several a_0 . At very high velocities, such that $\omega a/v \ll 1$, the imaginary exponentials in 9-6 do not oscillate over the range of x that $(M.E.)$ is finite, and may be replaced by unity. Equations 9-6 then become identical with Eqs. 5-3, and the cross section for asymmetric charge transfer depends on ion velocity in the same way as symmetric resonant charge transfer. At very low velocities, such that $\omega a/v \gg 1$, the imaginary exponentials oscillate wildly over the interaction region, reducing the transition probabilities to small values. This follows from the perturbation solution

$$|c_B(\infty)|^2 \approx \left| \frac{1}{v} \int_{-\infty}^{\infty} [(M.E.)/v] \cos(\omega x/v) dx \right|^2 \quad (9-7)$$

valid at large impact parameters. At low velocities the cosine term reduces the integral more than the $(1/v)$ term acting in the opposite direction, and $\delta(v)$ falls off as v is

decreased. At some intermediate velocity such that $\omega a/v \approx 1$, there is one oscillation over the interaction region, and this balances the pre-exponential $(1/v)$ factor, giving rise to a maximum cross section. This condition for the ion velocity for maximum σ , known as the "adiabatic criterion," may be written as

$$\frac{a}{4\pi v} \frac{|\Delta E|}{\hbar} = \frac{(2\pi a) \Delta E}{\hbar v} \approx 1. \quad (9-8)$$

with $\Delta E = I_A - I_B$. Since a is of the order of $1 \text{ \AA}$, it is not surprising that empirically the best value of $(2\pi a)$ is $7 \text{ \AA}$.

When Eqs. 9-6 are solved, one obtains results in terms of the "average" ionization potential of the two atoms, and the ΔE for the process. A family of curves may then be drawn for a constant average ionization potential (the dependence on this parameter is not critical) and varying ΔE . All the curves will tend at high velocities toward the symmetric cross section for the appropriate ionization potential, as given in Fig. 3. At lower velocities, the curves will reach maxima at velocities determined by Eq. 9-8, and then decrease rapidly toward zero. Examples for average ionization potentials equivalent to He, H, and Cs are shown in Fig. 7.

The effect of the considerations presented in Sec. 8 on asymmetric charge transfer at high velocities has not been investigated adequately. As an educated guess, it is probably similar in its resultant effect of decreasing the charge transfer cross section below that calculated from the model of Fig. 1.

10. Symmetric Charge Transfer at Low Velocities:

At "very low" velocities one may still use the general formulation given in Eqs. 7-1 through 7-8, but the high-velocity approximation for the phase shifts that would make the result equivalent to an impact parameter treatment is no longer valid. One must instead solve Eqs. 7-6 for the phase shifts η_l and δ_l , inserting them directly in 7-8 for the cross section. In the limit of zero velocity, only the $l=0$ and $l=1$ phase shifts contribute. Since Eqs. 7-6 are like ordinary Schrodinger equations with potentials composed of matrix elements, one concludes that the cross section must go to a finite (though large) limit at zero velocity. No calculations of such zero-velocity cross sections for charge exchange have been made yet.

Starting from a velocity high enough that the rectilinear trajectory impact parameter method is a good approximation, let us consider what happens when we reduce the velocity. At any velocity, the classical trajectories for ions impinging on a stationary target atom as a function of impact parameter as shown in Fig. 8. At relatively high velocities, charge transfer can occur out to large impact parameters for which the trajectories are essentially straight lines. Neglect of the curvature of inner impact parameters leads to essentially no errors in σ . As the velocity is reduced, charge transfer can occur at slightly larger impact parameters, but the curvature of the trajectories persists out to much larger impact parameters. A "low" velocity region is reached where the curved trajectories in the attractive potential at large impact parameters draw in ions from large impact parameters to close enough proximity so as to increase the cross section beyond that calculated from the simple impact parameter treatment. The velocities are still great enough to justify use of the classical trajectories. In this "low" velocity region, the cross section is probably mainly dependent on how many ions and atoms are brought into proximity by the long range R^{-4} attractive potential, and not by the detailed wave mechanics of electron transfer. The cross section for such "capture" collisions is well known to be

$$\sigma_c = \frac{2\pi e}{v} \sqrt{\frac{\alpha}{\mu}} \quad (10-1)$$

in which α is the polarizability of the neutral, μ is the reduced mass, and e is the electronic charge. Since the probability of charge transfer in such a collision is probably $\sim \frac{1}{2}$, one might guess the cross section for charge exchange to be $\sigma = \frac{1}{2} \sigma_c$ at "low" velocities. As the velocity is reduced further, the lower phase shifts become dominant in the scattered wave treatment, and the use of classical trajectories becomes a very poor approximation. One then gets to a region of "very low" velocity in which the cross section heads toward a finite intercept at zero velocity, despite the fact that a semiclassical calculation would (incorrectly) give $\sigma \rightarrow \infty$ as $v \rightarrow 0$.

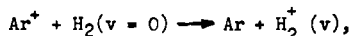
The cross section for symmetric resonant charge transfer is therefore expected to have the form shown in Fig. 9. At moderate velocities the cross section is determined by the rectilinear trajectory calculation described earlier. At about 10^3 cm/sec , a transition to the "low" velocity region occurs, so that below this velocity, σ is determined by Eq. 10-1. As the velocity approached zero, the cross section heads toward a finite intercept. The velocity at which σ begins to fall off below Eq. 10-1 is that for which the angular momentum $\hbar kb$ becomes comparable to unity, or about 10^4 cm/sec .

In practical applications such as mass spectrometry, shock tube, or ionospheric work, one may be interested in cross sections at thermal energies (0.03 to 0.2 eV). Although, to be sure, these are low velocities compared to typical ion accelerating fields, they are not necessarily "low" quantum mechanically. Charge transfer in the upper atmosphere often falls in the impact parameter velocity region, not the low velocity region.

11. Molecular Charge Transfer:

For collision velocities below 10^6 cm/sec, one may separate the electronic and nuclear motion in accord with the Born-Oppenheimer principle. An impact parameter treatment similar to that given in Sec. 4 then becomes possible, except that the appropriate orbitals have the form $\phi_{el}(r_e) \phi_{nuc}(r_n)$, where r_e is the position vector of a single valence electron with respect to the molecular ion and r_n is the position vector locating the relative positions of the nuclei in the molecular ion. If these orbitals are used in a calculation similar to that of Sec. 5, one obtains a result which is similar to that for charge exchange between atoms, except that an additional factor appears in "(M.E.)". This factor results from integration of the nuclear wave functions of the molecular ion and the molecule over the internuclear distance of the molecule, is the square of the familiar "overlap" integral. It is due to the fact that charge transfer occurs very rapidly compared to motion of the nuclei, so that when a molecule loses an electron (or a molecular ion gains an electron) it does so before the nuclei can move appreciably. In symmetric resonant charge transfer between N_2^+ and N_2 , the vibrational overlap for ground states happens to be nearly unity so there should be little effect. However, for H_2^+ and H_2 , the vibrational overlap (squared) between ground states is more like ~ 0.1 so that the cross section should be considerably smaller. In fact, experimentally, this happens to be true. An interesting test of this theory could be made by accurately studying symmetric resonant charge transfer between H_2^+ and H_2 , and D_2^+ and D_2 . Since the vibrational overlap (squared) in $D_2 - D_2^+$ is ~ 0.04 , the cross section should be considerably smaller for D_2 than for H_2 at the same velocities.

In asymmetric charge transfer, excitation to an excited final state may produce a closer resonance than ground state reaction, and may therefore be favored over the ground state reaction. For



E has the values 0.35 ev, 0.07, -0.20, -0.47, for $v = 0, 1, 2, 2$, respectively. Therefore, charge transfer to the $v = 1$ state of H_2^+ , which is most nearly resonant, is probably dominant. The vibrational overlap (squared) to this state is about 0.31.

For more complicated molecules, such as in charge exchange between Xe^+ and C_2H_4 , excited vibrational levels are so closely spaced that an effective near resonance is almost always possible. Such processes display high cross sections even at low collision velocities.

12. Charge Transfer in Non- 1001 Collisions:

When a charge transfer process occurs, it is denoted (ijk) in accord with the charge states of the reactants and products:



So far we have considered only 1001 charge transfer. We only have space to very briefly comment on non 1001 charge transfer.

First consider 2002 charge transfer. The total wave function may be written as in Eq. 5-2, except that two orbitals on each nucleus must be included. Thus each term $\phi_i(r_i)$ must be replaced by $\phi_{i1}(r_{i1}) \phi_{i2}(r_{i2})$, where a, b denote the two electrons. Then upon going through the same procedure, this time integrating over the coordinates of both electrons, one ends up with Eqs. 5-3 with M.E. replaced a slightly different grouping of matrix elements. The final result is that the cross section behaves just like that for a 1001 process in its velocity dependence, but with lower absolute value. Similar results are to be expected for any nonc process.

Symmetric resonant charge transfer between negative ions and neutrals such as $-1, 00, -1$ are very similar in theoretical treatment and cross section behavior to 1001 charge transfer.

An interesting case is 2011 charge transfer. Here there is no possibility of a symmetric process. However, one can have an "accidental" asymmetric resonance, such as



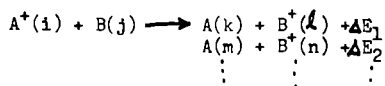
in which $\Delta E = 0.0$ ev. The question now arises as to what the velocity dependence of the cross section for this process is. One may use the approach of Sec. 7, except that in Eq. 9-5, more careful analysis of the term Ω is required. It turns out that it is no longer permissible to set $\Omega \approx \omega$, because the integrals involved in $(\eta_1 - \eta_2)$ are such as to make this term large for process 12-2, whereas it is small for process 1-2. Furthermore, since $\omega = 0$ in this particular case, we have $\Omega t = \int (\eta_1 - \eta_2) dt$, and Ω is appreciable. But this acts just like an effective non resonance in a 1001 process. Thus one expects a cross section for a resonant 2011 process to behave like that for a non resonant 1001 process. This has recently been experimentally verified.

For general ijk processes, it has been found that Eq. 9-8 is a rough estimate of the velocity at which a maximum cross section is reached. Little theoretical work has been done on this class of processes.

13. Participation of Excited States in Charge Transfer:

In many experimental studies of charge transfer, the primary ion beam is produced by very energetic electrons, and therefore contains many excited states of the primary ion. Each excited state has a different charge transfer cross section, and it appears that the main cause of disparity of results between different investigators for the same process is the different distribution of initial excited states in each experiment.

Even in an experiment in which the primary ion beam contains only a single state, there is the possibility of several excited states being produced in the products:



This means that the two state approximation made by neglecting processes 9-2, may not in fact, be a very good approximation. The theoretical treatment indicated to include excited states is a multi-state treatment, in which Eq. 9-4 is replaced by:

$$\Psi = \sum_j C_{Aj}(t) \phi_{Aj}(r_A) e^{-i\omega_{Aj}t} + \sum_n C_{Bn}(t) \phi_{Bn}(r_B) e^{-i\omega_{Bn}t}$$

Now if the system is initially in state $\phi_{B0}(r_B)$, the probability of charge transfer to state $\phi_{Aj}(r_A)$ is $|C_{Aj}(\infty)|^2$. The perturbation matrix is now larger than 2×2 but the rest of the calculation is analogous.

14. Contrast Between Charge Transfer and Ion-Atom Interchange:

We shall discuss this question in terms of an example of H^+_2 reacting with H_2 . The charge exchange process is



whereas the ion-atom interchange process is



The cross section for process 14-1 follows the usual velocity dependence for charge exchange processes outlined in Figs. 3 and 9. Above 10^3 cm/sec, σ for 14-1 falls off slowly with velocity, roughly as $\sigma^{\frac{1}{2}} = a - b \ln v$. As such, the "rate constant" $k = \sigma v$ for this process is far from constant, and increases sharply with increasing v . Below about 10^3 cm/sec, curve 2 of Fig. 9 begins to dominate, and the "rate constant" does in fact remain constant since $\sigma \sim v^{-1}$ in this region.

The ion atom interchange process 14-2, on the other hand has $\sigma \sim v^{-1}$ for all moderate velocities (there is some unconfirmed evidence this may not quite be right,) and the "rate constant" is in fact a constant. The cross section for such a process falls off rapidly compared to charge transfer. For example, whereas σ_1 for 14-1 and σ_2 for 14-2 are roughly equal ($\sim 50A^2$) at $\sim 10^3$ cm/sec, σ_2 falls off to less than $1A^2$ at 10^1 cm/sec, whereas σ_1 remains at $20A^2$.

To say that a process is charge transfer, and report a "rate constant" with no velocity range given, is not a very useful result because the rate "constant" depends strongly on velocity.

15. Some Representative References:

Although the intent is not to supply a complete list of references on charge transfer, it seems desirable to present a few selected references for each topic so that a reader can more quickly obtain additional information if desired.

- | | |
|---------------|--|
| Secs. 4 and 5 | 1 - E.F. Gurnee and J.L. Magee, J.Chem. Phys. <u>26</u> , 1237 (1957).
2 - D. Rapp and W.E. Francis, J. Chem. Phys. <u>37</u> , 2631 (1962). |
| Sec. 6 | 3 - T.J.M. Boyd and A. Dalgarno, Proc. Phys. Soc. <u>A72</u> , 694 (1958).
4 - D. Rapp and I.B. Ortenburger, J. Chem. Phys. <u>33</u> , 1230 (1960).
5 - D.R. Bates, H.S.W. Massey, and A.L. Stewart, Proc. Roy. Soc. (London) <u>A216</u> , 437 (1953). |
| Sec. 7 | Ref. 1
Ref. 5
6 - A. Dalgarno and H.N. Yadav, Proc. Phys. Soc. <u>A66</u> , 173 (1953). |
| Sec. 8 | 7 - R. McCarroll, Proc. Roy. Soc. <u>A264</u> , 547 (1961). |

Sec. 9 Ref. 2

S

Sec. 10 Ref. 2

Sec. 11 Ref. 1

Sec. 12 8 - D.R. Bates and N. Lynn, Proc. Roy. Soc. (London) A253, 141 (1959).

SOME ASPECTS OF UNIMOLECULAR REACTIONS

B. S. Rabinovitch
University of Washington
Seattle, Washington

No Manuscript or Abstract Available

KINETIC ENERGY OF FRAGMENTS OF
UNIMOLECULAR DECOMPOSITION

W. A. Chupka
Argonne National Laboratory
Argonne, Illinois

No Manuscript or Abstract Available

RELATION BETWEEN IONIZATION POTENTIAL AND ELECTRONEGATIVITY IN
ISOELECTRONIC FREE RADICALS

I. P. Fisher and F. P. Lossing
Division of Pure Chemistry
National Research Council
Ottawa, Canada

ABSTRACT

The molecular ionization potentials along the isoelectronic series CH_4 , NH_3 , H_2O and HF show wide variations which are apparently controlled by factors other than the nuclear charge of the central atom. The ionization potentials of the free radicals along the isoelectronic series CH_3 , NH_2 and OH , on the other hand, give a relation between ionization potential and Pauling electronegativity which is linear to within the experimental error ($\approx 0.1\text{v}$). (The F-atom does not conform to this relation.) It would appear that the energies of the non-bonding electrons in these free radicals are, in fact, largely controlled by the nuclear charge of the central atom. Data are now available for one other isoelectronic series of radicals: benzyl, anilino, and phenoxyl. For this series the ionization potential is again linearly dependent on the electronegativity of the side group atom, but the slope of the line is less than one-half as great. This can be understood in terms of the delocalization of charge over the C-atoms in the ring, which thereby decreases the effect of the electronegativity of the central atom in the side-group. One other isoelectronic series, for which only two members are known, $\text{CH}_2 = \text{CH} - \text{CH}_2\text{CH}_2$ and $\text{CH}_2 = \text{CH} - \text{CH}_2\text{O}$, gives a dependence nearly the same as that of the cyclic radicals. If this relation is valid, some conclusions can be drawn regarding the ionization potentials of free radicals belonging to other isoelectronic series, in which the data is incomplete or of doubtful validity.

Ionization of Polyatomic Molecules

T. E. Sharp*, H. M. Rosenstock and R. W. Zwanzig

Physical Chemistry Division
National Bureau of Standards
Washington, D. C.

This paper sketches the derivation of Franck-Condon factors for polyatomic molecules. Specific application is made to the case of linear symmetric triatomic molecules having linear symmetric ions. The results are discussed in connection with shapes of ionization efficiency curves, accessibility of ion vibrational ground states (0-0 transitions), detailed and total vibrational energy distributions, and interpretation of dissociation processes.

The molecular model adopted for the calculation is a set of harmonic oscillators. It is well known that for accurate computation of relative vibrational transition probabilities for diatomic molecules, anharmonicity has to be considered 1/. This additional complexity is omitted from the derivation but is discussed qualitatively. Further, the effects of rotation are neglected.

Method. The central problem is the calculation of harmonic oscillator overlap integrals in n dimensions where the initial and final states have different bond lengths and force constants. The method of calculation is similar to that for the diatomic harmonic oscillator case, and only the latter will be sketched out. The additional features involved in the polyatomic case are indicated.

The simplest diatomic case is that of a transition from the vibrational ground state of a molecule to the n -th vibrational level of the ion. In general, both the force constant and equilibrium internuclear distance change is going from the molecule to the ion. The method used is the method of generating functions 2,3/. One has to calculate the vibrational overlap integral

$$I(0, n) = \int_{-\infty}^{\infty} \psi_0'(q') \psi_n(q) dq \quad (1)$$

where $\psi_0'(q') = (v'/\pi)^{1/4} \exp(-\frac{1}{2} v' q'^2)$ = molecule vibrational wave function

$$\psi_n(q) = (v/\pi)^{1/4} (2^n n!)^{-1/2} \exp(-\frac{1}{2} v q^2) H_n(v^{1/2} q)$$

= ion vibrational wave function

with $v = (4\pi^2/h) \nu$ = the "reduced" frequency

$$q = \left(\frac{m_X m_Y}{m_X + m_Y} \right)^{1/2} (R - R_{eq})$$

= the mass-weighted displacement from the equilibrium internuclear separation,

H_n = the n -th Hermite polynomial, and the prime (') indicates the corresponding quantities for the molecule.

The generating function for Hermite polynomials is

$$\exp[-t^2 + 2(v^{1/2} q) t] = \sum_{n=0}^{\infty} H_n(v^{1/2} q) t^n / n! \quad (2)$$

i.e., the n -th Hermite polynomial is the coefficient of $\frac{t^n}{n!}$ in the

series expansion of the exponential on the left hand side of the equation. Using this generating function one can directly obtain an expression in which the desired integral is a similar coefficient in a series expansion. On multiplying the integral by t^n and summing one obtains

$$\sum_{n=0}^{\infty} \left(\frac{2^n}{n!} \right)^{1/2} I(0, n) t^n = \left(\frac{v v'}{\pi^2} \right)^{1/4} \int_{-\infty}^{\infty} \exp[-\frac{1}{2} (v q'^2 + v q^2)] \left[\sum_{n=0}^{\infty} H_n(v^{1/2} q) t^n / n! \right] dq$$

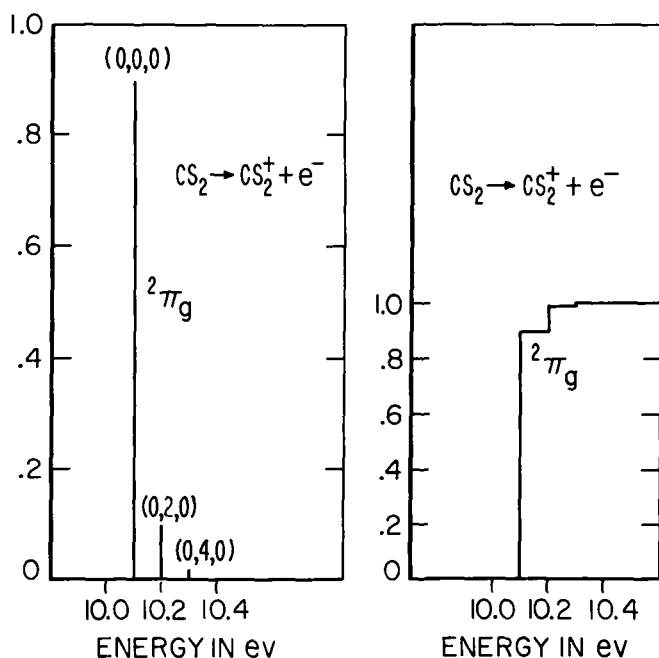


Fig. 1. Transition from the ground state of carbon disulfide molecule to vibrational levels of the ion ground electronic state. (a) Transition probabilities (b) Photoionization threshold behavior.

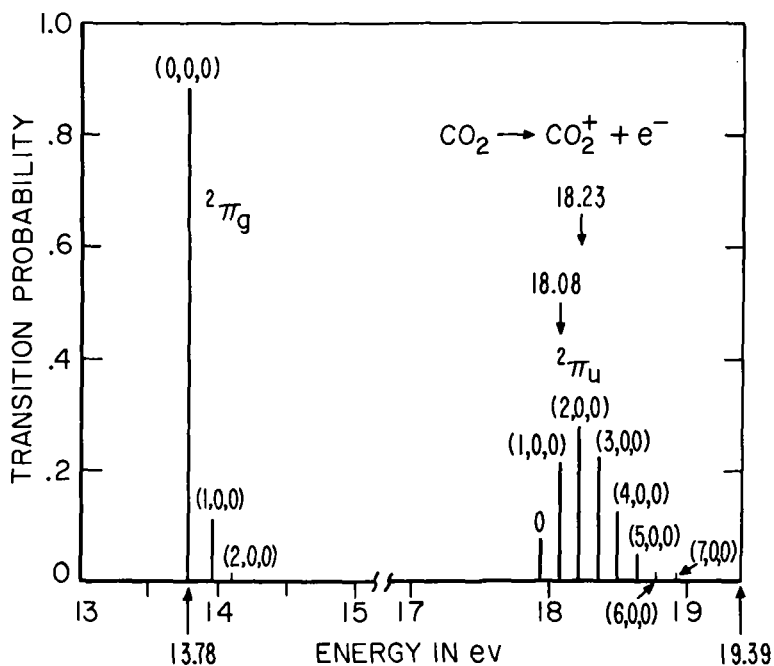


Fig. 2. Transition probabilities from the ground state of carbon dioxide to vibrational levels of the ion ground and excited electronic states.

and now using the above generating function on the right hand side, there results

$$\sum_{n=0}^{\infty} \left(\frac{2^n}{n!} \right)^{1/2} I(0,n) t^n = \left(\frac{r r'}{\pi^2} \right)^{1/4} \exp(-t^2) \int_{-\infty}^{\infty} \exp \left[-\frac{1}{2} (r' q'^2 + r q^2) + 2 r^{1/2} q t \right] dq \quad (4)$$

The displacement coordinate q' can be expressed in terms of the coordinate q by

$$q' = a q + b \quad (5)$$

where $a = 1$ and $b = r a q - r' e q$

On substituting this into the preceding expression, completing the square in the exponential, and regrouping the terms, one obtains

$$\sum_{n=0}^{\infty} \left(\frac{2^n}{n!} \right)^{1/2} I(0,n) t^n = \left(\frac{r r'}{\pi^2} \right)^{1/4} \exp \left[-\frac{1}{2} r' t^2 - \frac{2 r^{1/2} r' t}{r+r'} + \left(\frac{2 r}{r+r'} - 1 \right) t^2 \right] \times \int_{-\infty}^{\infty} \exp \left[-\frac{1}{2} (r+r') (q-\alpha)^2 \right] dq \quad (6)$$

where α is a function of r, r', t and b , but not of q . The integral is readily evaluated as $[2\pi/(r+r')]^{1/2}$, and the result is

$$\sum_{n=0}^{\infty} \left(\frac{2^n}{n!} \right)^{1/2} I(0,n) t^n = I(0,0) \exp(c t^2 + \alpha t) \quad (7)$$

where $I(0,0) = [4 r r' / (r+r')^2]^{1/4} \exp(-\frac{1}{2} r' t^2)$
 $c = \frac{2 r}{r+r'} - 1$ $\alpha = -\frac{2 r^{1/2} r' t}{r+r'}$

The individual integrals are now readily obtained by expanding the right hand exponential and collecting coefficients of the desired power of t . For example, one finds readily that

$$\left(\frac{2^{1/2}}{1!} \right)^{1/2} I(0,2) t^2 = I(0,0) (c + \alpha^2/2) t^2$$

This completes the basic method.³

The following modifications are important: To find $I(m,n)$, the overlap integral from the m -th vibrational level of the diatomic molecule to the n -th level of the ion, repeat the basic method inserting the proper wave function in equation (2), multiplying through by $(2^m/m!)^{1/2} u^m$, and summing over the dummy variable u from zero to infinity. The remaining steps are analogous to those above.

In the polyatomic case, the mass-weighted coordinates q are replaced by column vectors of normal mode coordinates Q , the reduced frequencies ν are replaced by the diagonal matrix Γ , and the wave function contains a product of Hermite polynomials, one for each vibrational normal mode. A product of dummy variables (one per Hermite polynomial) and a multiple sum is required in the analogy to equation (3). The generating function relation (2) holds for each Hermite polynomial-dummy variable pair. The a and b of equation (5) become transformation matrices A and B

$$Q' = A Q + B$$

where $A = (L')^{-1} L$

and $B = (L')^{-1} (S_{eq} - S'_{eq})$

where the S 's are internal coordinates⁵

and $S = L Q$

The final results are too voluminous to be listed here, and they will be published elsewhere.

Linear Symmetric Triatomic Molecule

For the case of a linear symmetric triatomic molecule Y-X-Y undergoing transition to a linear symmetric ion, the expansion simplifies to a product of one dimensional integrals, and the following

results are obtained.

$$\text{Let } N_i = \nu_i / \nu_i',$$

the ratio of the vibrational frequency in the ion to that in the molecule

$$i = \begin{cases} 1 & \text{(symmetric stretch)} \\ 2 & \text{(doubly degenerate bend)} \\ 3 & \text{(antisymmetric stretch)} \end{cases}$$

$$R = r_{eq}/r'_{eq} \text{ the ratio of the equilibrium Y-Y bond lengths in the ion and the molecule}$$

then

$$C_{11} = (N_1 - 1) / (N_1 + 1)$$

$$C_{22} = (R^2 N_2 - 1) / (R^2 N_2 + 1)$$

$$C_{33} = (N_3 - 1) / (N_3 + 1)$$

$$d_1 = -0.487 \text{ amu}^{-1/2} \text{ cm}^{1/2} \text{ \AA}^{-1} (m_Y \nu_i)^{1/2} (\nu_{eq} - \nu'_{eq}) / (1 + N_i)$$

$$\text{and } I(0,0) = 4R(N_1 N_2^2 N_3)^{1/4} [(1+N_1)(1+R^2 N_2)^2 (1+N_3)]^{-1/2} \exp[-\frac{1}{8} d_1^2 (1+N_1)]$$

From symmetry arguments 6 it is easily shown that the probability of excitation from the ground state of the molecule to the combination (1,m,n)-th state of the ion is equal to the product of probabilities of excitation to the overtone states, i.e.

$$p(1,m,n) = p(1,0,0) \cdot p(0,m,0) \cdot p(0,0,n)$$

Table I
Franck-Condon Factors for Excitation
from Ground State of Molecule Y-X-Y

Quanta in mode			Transition probability/[I(0,0)] ²
$\frac{1}{0}$	$\frac{2}{0}$	$\frac{3}{0}$	1
1	0	0	$d_1^2/2$
2	0	0	$(C_{11} + d_1^2/2)^2/2$
3	0	0	$3(d_1^2 C_{11} + d_1^2 C_{11} + d_1^3/6)^2/4$
4	0	0	$3(C_{11}^2 + d_1^2 C_{11}^2 + d_1^4/12)^2/8$
5	0	0	$15(d_1^2 C_{11}^2 + d_1^3 C_{11}/3 + d_1^5/60)^2/16$
...	...	...	...
0	odd	0	0
0	2	0	C_{22}^2
0	4	0	C_{22}^4
0	6	0	C_{22}^6
...	...	...	...
0	0	odd	0
0	0	2	$C_{33}^2/2$
0	0	4	$3C_{33}^4/8$
...	...	...	...

Application to CS₂ and CO₂

Spectroscopic data on polyatomic ions is exceedingly scarce. As far as we know, spectra have been analyzed only for CS₂⁺ 7, CO₂⁺ 8, N₂O⁺ 9 and diacetylene ion 10. Calculations are reported here for CS₂⁺ and CO₂⁺. The spectroscopic constants used are given in table 2. The calculated relative transition probabilities are shown in figs. 1 and 2. In the notation (1,j,k), i refers to the symmetric stretching, j to the degenerate bending, and k to the antisymmetric stretching vibrations. In the CO₂⁺ diagram, fig. 2, the total transition probabilities to the two electronic states have been arbitrarily taken as equal.

Table 2

Molecule and Ion Constants

Carbon Disulfide

State	Energy	Bond Length	Vibrational Frequencies		
			Symmetric Stretch	Bend (2)	Asymmetric Stretch
$2\Pi_g$ (ion)	10.80 e.v.	1.5542A	617 cm^{-1} .0765 e.v.	409.5 cm^{-1} .0508 e.v.	1477(?) cm^{-1} .1831 e.v.
$1\Sigma_g^+$	0	1.5545A	656 cm^{-1}	801.9 cm^{-1}	1523 cm^{-1}

Carbon Dioxide

$2\Pi_u$ (ion)	18.08 e.v.	1.229A	1131 cm^{-1} .1402 e.v.	560 cm^{-1} .0694 e.v.	1895 cm^{-1} .2349 e.v.
$2\Pi_g$ (ion)	13.78 e.v.	1.177A	1280 cm^{-1} .1587 e.v.	632 cm^{-1} .0784 e.v.	2305 cm^{-1} .2858 e.v.
$1\Sigma_g^+$	0	1.163A	1361 cm^{-1}	673 cm^{-1}	2379 cm^{-1}

Discussion

a. Input and distribution of energy, and fragmentation.

The results show that in the vertical transitions to the CS_2^+ ground state, only the bending vibration can be excited; whereas in the CO_2^+ ground state, only the symmetric stretching vibration can be excited. Further, in these cases, only the low levels are involved, and the (0,0,0) level is most strongly excited. Within the validity of the harmonic oscillator approximation (see below) this leads to the clear conclusion that no ion fragmentation is possible by direct vertical transition to the ion ground electronic states. In the transition to the excited CO_2^+ state the symmetric stretching frequency is again the only one excited, but this time to a considerable extent.

The calculations permit an estimate to be made of the relative importance of changes in frequencies and bond length in shifting transition to higher vibrational levels. A change of a factor of two in the bending frequency in going from CS_2 to CS_2^+ , leaves the (0,0,0) transition as the predominant one, and causes a shift of only 10% intensity to the first excited bending level. However a change of .066A in bond length from CO_2 to CO_2^+ ($2\Pi_u$) causes the maximum absorption to shift to the third excited symmetric stretching vibration. Even the change of .014A in going to the ground electronic CO_2^+ state causes a 12% shift away from the (0,0,0) transition. Small changes in bond length are thus far more important than much larger changes in frequencies.

b. Ionization threshold behavior.

The assumption is made that the step function behavior for the photoionization threshold is valid over the entire energy range considered here. Idealized photoionization curves based on the calculated transition probabilities are shown in fig. 1 and 3. In the case of CO_2 it is arbitrarily assumed that the photoionization cross sections to the two electronic states are equal. It is seen that the ground state transition has a distinct step function behavior. The transition to the excited state of CO_2^+ , however, is a staircase function extending over more than one electron volt, in spite of the accessibility of the ground vibrational level of that state.

The vertical arrows in fig. 3 indicate the electronic states found by Tanaka, Jursa, and Leblanc.^{11/} The high probability of transition to excited symmetric stretching levels, and the energy spacing support to the conjecture that the values (18.08 and 18.23 ev) observed by Tanaka, et al correspond to two vibrational levels of this electronic state,^{12/} rather than to different electronic states.

c. Anharmonicity.

Even the early calculations of vibrational intensities of diatomic band spectra indicated clearly that the harmonic oscillator approximation was inadequate, especially for transitions involving large changes in quantum number. The calculated degree of excitation in the CO_2^+ (${}^2\Pi_u$) case is so high that the effects of anharmonicity become significant.

On the other hand, the harmonic oscillator approximation is quite good for low lying vibrational levels. Consequently the conclusions concerning the impossibility of dissociation by direct vertical transition to the CO_2^+ and CS_2^+ electronic ground state remain valid.

d. Limitations.

The method presented for calculating Franck-Condon factors depends upon several assumptions. Rotations have been neglected. In practice, the rotations may be expected to smear out the sharp vibrational transitions calculated here. It has also been assumed that the normal modes of the initial state are expressible as a linear combination of normal modes of the final state. This assumption breaks down, for example, in the case of a linear molecule having a bent ion. The transformation of a bending vibration into a rotation of the molecule requires consideration of the angular momentum coupling problem, a task which has been deliberately avoided here. Finally, the Fermi resonance of the symmetric stretching mode and the even overtones of the bending mode in CO_2^+ has been ignored in this simple treatment.

Conclusions

1. A method has been developed for calculating, to the harmonic oscillator approximation, Franck-Condon factors for polyatomic molecules (except for linear-to-bent transitions).

2. Explicit results have been presented for the case of linear symmetric triatomic molecules having linear symmetric ions.

3. Numerical calculations have been carried out with CO_2 and CS_2 for transitions from the ground state of the molecule to the ground state of the ion and also to an excited state of CO_2^+ . In all cases transitions to the ground vibrational level of the various states are accessible.

4. In transitions to the excited CO_2^+ , there is considerable excitation of the symmetric stretching vibration.

5. The calculations show that, in making high vibrational levels accessible, small changes in bond length are far more significant than even large changes in force constants.

*National Academy of Sciences--National Research Council
Postdoctoral Resident Research Associate.

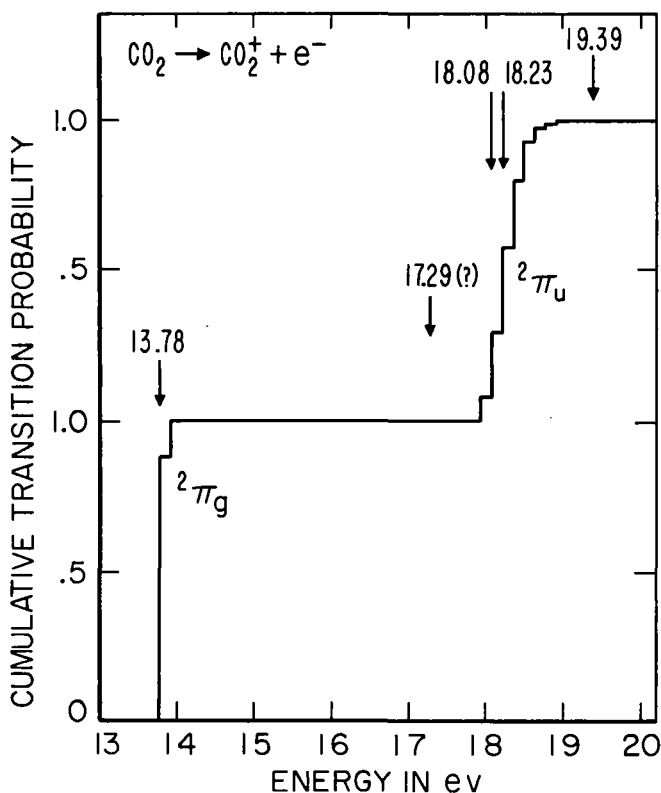


Fig. 3. Photoionization efficiency curve for carbon dioxide. Each transition arbitrarily set equal to unity.

Bibliography

1. Nicholls, R. W. and A. L. Stewart in D. R. Bates, *ATOMIC AND MOLECULAR PROCESSES*, Academic Press, New York, (1962) p. 60.
2. Hutchisson, E., *Phys. Rev.* **36**, 410 (1930)
3. Schroedinger, E., *Ann. d. Phys.* **80**, 486 (1926).
4. Rainville, E., *SPECIAL FUNCTIONS*, Mamillan, New York (1960) Ch. 11.
5. Wilson, E. B., Jr., J. C. Decius, and P. C. Cross, *MOLECULAR VIBRATIONS*, McGraw-Hill, New York, (1955).
6. Herzberg, G. and E. Teller, *Z. Physik. Chem.* **B21**, 410 (1933).
7. Callomon, J. H., *Proc. Roy. Soc. (London)*, **A244**, 220 (1958).
8. Bueso-Sanllehi, F., *Phys. Rev.* **60**, 556 (1941); S. Mrozowski, *Phys. Rev.* **60**, 730 (1941); **62**, 270 (1942); **72**, 682, 691 (1947).
9. Callomon, J. H., *Proc. Chem. Soc.*, 313 (1959).
10. Callomon, J. H., *Can. J. Phys.* **34**, 1046 (1956).
11. Tanaka, Y., R. S. Jursa, and F. J. LeBlanc, *J. Chem. Phys.* **28**, 350 (1958).
12. Collin, J., *J. chim. phys.* **57**, 424 (1960).

HIGHER IONIZATION POTENTIALS IN ALCOHOLS AND WATER MEASURED BY ELECTRON IMPACT.

Håkan Sjögren and Einar Lindholm

Physics Department, Royal Institute of Technology,
Stockholm 70, Sweden

It has been shown using ion impact experiments or quasi-equilibrium mass spectral theory that in the lower alcohols the parent ion dissociates completely when the supplied energy is more than about 1 eV above the ionization energy. It is then evident that if a mass spectrometer is used to observe breaks in the ionization efficiency curve of the parent ion above this dissociation limit the interpretation of such breaks will be difficult.

Ion currents resulting from collisions of quasi-monochromatic electrons from a Fox electron gun with molecules of water, methanol and ethanol have therefore been studied without mass spectrometric analysis. The curve of ion current vs. electron energy can be approximated as straight lines with distinct knees. These are interpreted as higher ionization potentials of the molecules.

The full paper has been printed in Physics Letters 4, 85 (1963).

Collision between Ar^+ and C_3H_8

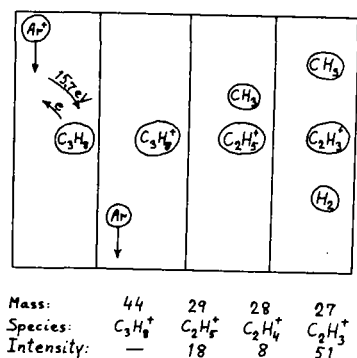


Fig. 1.

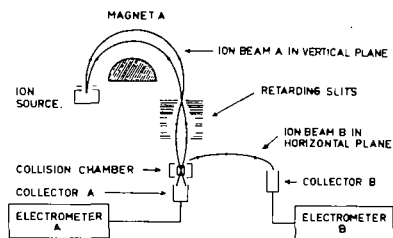
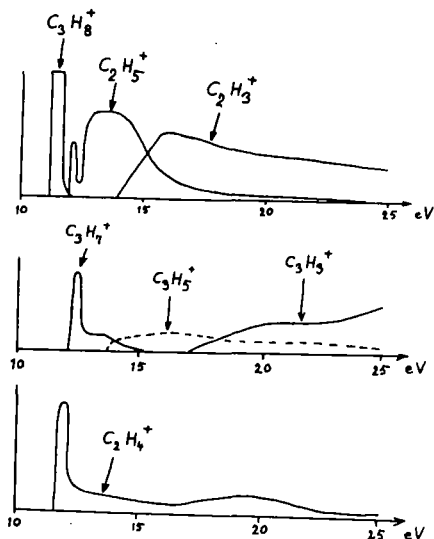


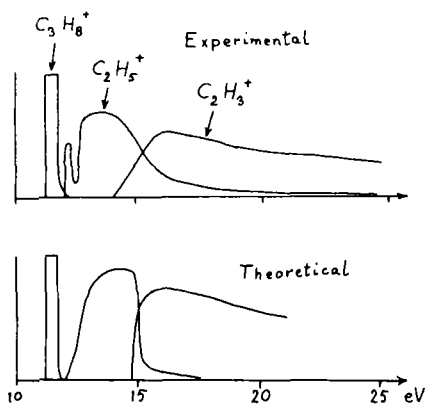
Fig. 2.



Breakdown graph for propane.

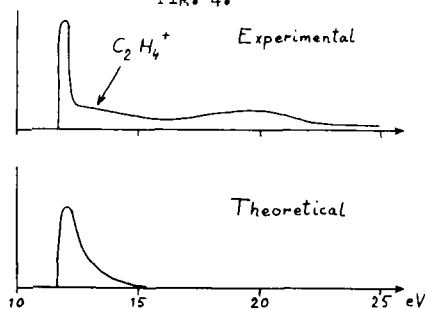
(Pettersson and Lindholm, Arkiv Fysik 24, 49 (1963))

Fig. 3.



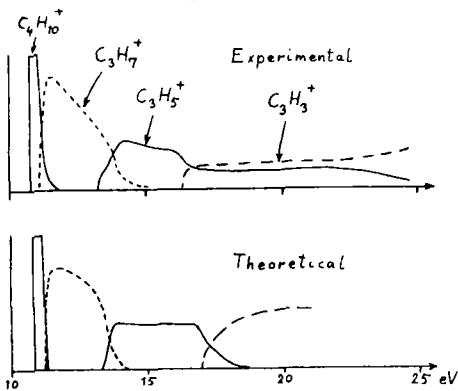
Comparison with theoretical breakdown graph for propane (Vestal, Wahrhaftig, and Johnston)

FIG. 4.



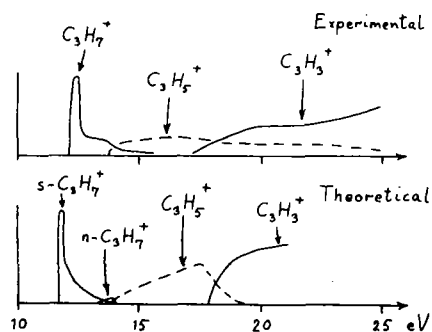
Comparison with theoretical breakdown graph for propane (Vestal, Wahrhaftig, and Johnston).

Fig. 6.



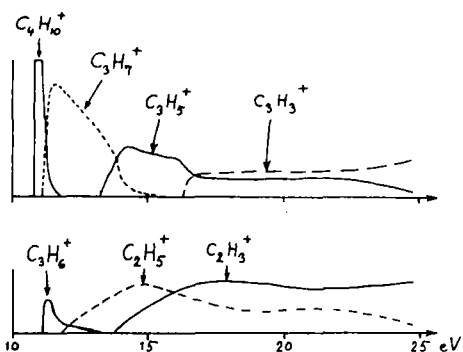
Breakdown graph for n-butane
Experimental by Chupka and Lindholm
Theoretical by Vestal, Wahrhaftig and Johnston.

Fig. 8.



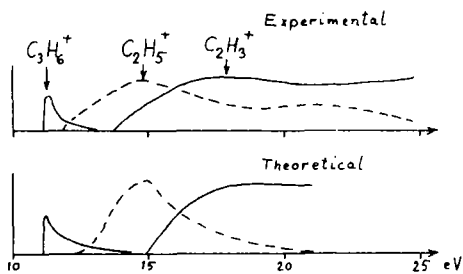
Comparison with theoretical breakdown graph for propane (Vestal, Wahrhaftig, and Johnston)

Fig. 5.



Breakdown graph for n-butane
(Chupka and Lindholm, in press)

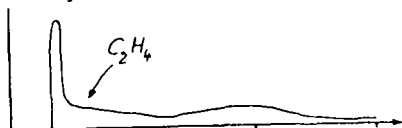
Fig. 7.



Breakdown graph for n-butane
Experimental by Chupka and Lindholm
Theoretical by Vestal, Wahrhaftig and Johnston.

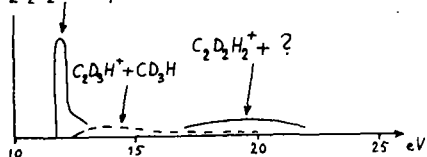
Fig. 9.

From C_3H_8 :



From $CD_3CH_2CD_3$:

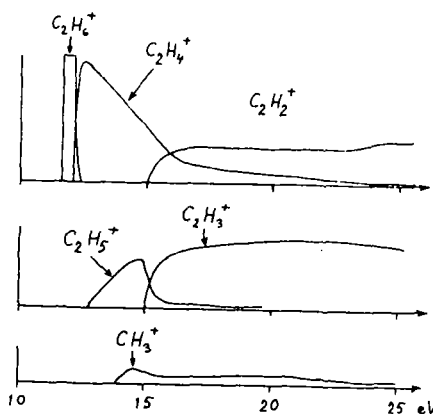
$C_2D_2H_2^+ + CD_4$



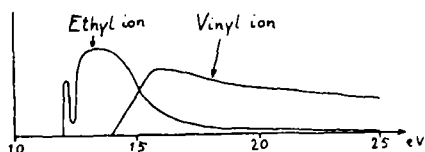
Formation of ethylene ions from propane and deuterated propane.

$CH_3CD_2CH_3$ gives similar results.

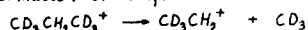
Fig. 10.



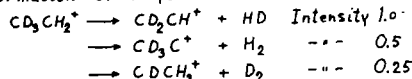
Breakdown graph for ethane
Fig. 13.



Formation of ethyl ion:



Formation of vinyl ion:



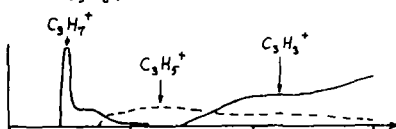
Explanation: a) randomization
b) isotope effect

At high energies: no isotope effect.

Fig. 11.

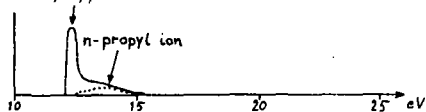
Formation of propyl ions:

From C_3H_8 :



From $CD_3CH_2CD_3$:

s-propyl ion



Hydride ion transfer gives mainly n-propyl ions

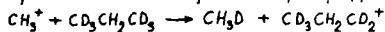


Fig. 12.

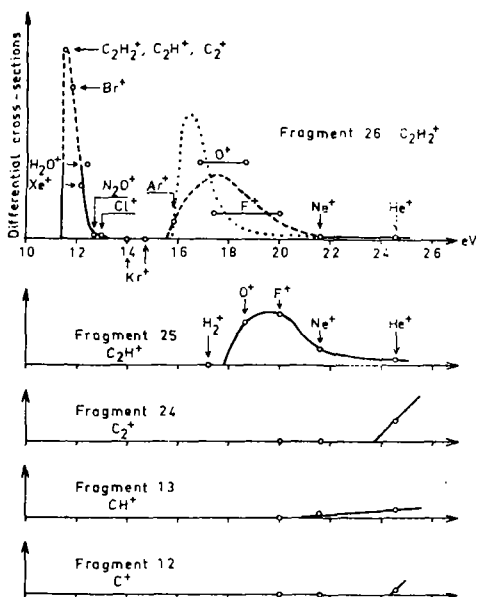


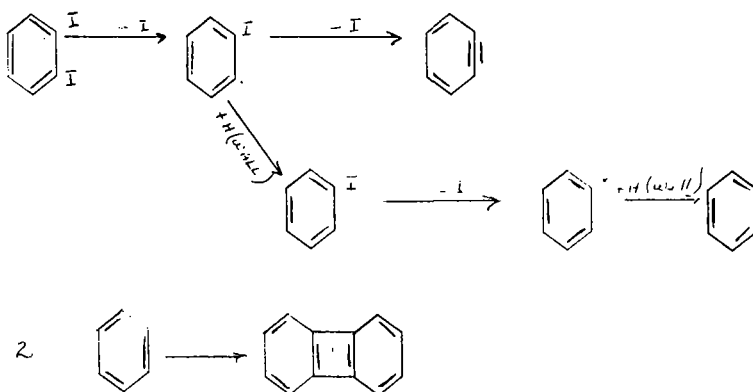
Fig. 14. Differential cross-sections for formation of charged fragments from acetylene as a function of energy.

IONIZATION POTENTIAL OF BENZYNE

I. P. Fisher and F. P. Lossing
Division of Pure Chemistry
National Research Council
Ottawa, Canada

ABSTRACT

The unusual chemical intermediate, benzyne (1,2-dehydrobenzene) is known from its extensive reactions in solution, and has recently been observed in the gas phase by flash spectroscopy (Berry et al). We have produced benzyne in a reactor coupled to a mass spectrometer, by the thermal decomposition of o-diiodobenzene at 950° at low pressure (10^{-3} mm). Other products observed are iodophenyl radicals, phenyl iodide, phenyl radicals, benzene, and a compound of parent mass 152, presumably biphenylene. The sequence of reactions is thought to be as follows:



Measurement of the ionization efficiency curves for benzyne and benzene in the presence of a Xenon standard leads to the vertical ionization potentials: benzyne 9.75 v, benzene 9.50 v.

The thermal decomposition of m- and p-diiodobenzene in the same apparatus leads also to the formation of a species of mass 76, but which has a much lower ionization potential, 9.46 v. This ionization potential can be shown to correspond to the linear C_6H_4 isomer, $HC \equiv C-CH=CH-C \equiv CH$. The absence of the dimeric product at mass 152 supports this conclusion.

IONIZATION CROSS SECTIONS*

R. E. Glick and J. A. Llewellyn
Chemistry Department
Florida State University

Electron impact induced ionization of nitrogen has been extensively studied: quantitative measurements of total ionization were made by Tate and Smith¹, and qualitative studies of ionization efficiencies for N_2^+ and N^+ have been made on at least six other occasions²⁻⁷. We have attempted to make a quantitative study of the ionization cross sections for N_2^+ and N^+ and on this occasion we would like to report results obtained over a small range of bombarding energy close to the ionization threshold.

The principal experimental difficulties associated with quantitative studies for individual ions involve (a) the energy distribution in the ionizing beam, (b) kinetic energy of the product species and (c) the collection geometry. Significant progress toward overcoming these difficulties has been made using a modified time-of-flight mass spectrometer as discussed previously⁸. Results obtained for individual ions were consistent with earlier total ionization measurements when summed over all species.

The kinetic energy and collection geometry are minimized by using the T.O.F. Spectrometer, where pulsed operation permits the use of high ion collecting fields, and grid ion optics rather than slits improve collection. Pulsed R.P.D. techniques⁹ give reasonable energy resolution for the bombarding electrons, but satisfactory operation along the lines indicated by Fox and co-workers⁹ was not readily achieved. Several possible gun configurations were evaluated (Figure 1) and beam analysis using a retarding potential indicated that the ideal clipping process usually described, giving the differential current sketched in Figure 2(i) was unattainable. The optimum effective differential current was that shown in Figure 2(ii). The gun configuration labeled (v) in Figure 1 was finally adopted, a "reverse McDowell and Frost" configuration with the variable retarding potential placed on the second slit. Retarding analysis of the

*Supported by A.E.C. Division of Biology and Medicine and the Florida State University Nuclear Program.

TABLE I

CRITICAL POTENTIALS N_2^+

	Fox ²	Frost ⁴	Clarke ¹⁰	Dorman ³	Kaneko ⁷	This Work	Spectroscopic
$X_2^2\epsilon$	15.60	15.63			15.63	15.6	15.576
Autoionization a	a	a	c	d	16.2	a	
$A_2^2\epsilon$	16.93	16.84			17.00	16.8	16.694
$B_2^2\epsilon$	18.84	18.76			18.94	18.8	18.746
$C_2^2\epsilon$	b	23.53			e	23.6	23.586

- a. Not observed
 b. Data do not extend to 24 volts.
 c. There is a hump in the ionization curve with a maximum at about 16 eV.
 d. First differential curve indicates ionization at about 16 eV.
 e. The ionization curve is linear from 19 to 25 eV.

TABLE II

RELATIVE SLOPES N_2^+

	Fox ²	Frost ⁴	Kaneko ⁷	This Work
$X_2^2\epsilon$	1	1	1	1
$A_2^2\epsilon$	0.2	6	0.5	2
$B_2^2\epsilon$	0.6	4	0.4	2.1
$C_2^2\epsilon$		36		0.83

TABLE III

CROSS SECTIONS^a N_2^+

Volts	16	17	18	19	20	21
$Q_{cm^2} \times 10^{-16}$	0.006	0.027	0.068	0.11	0.188	0.258
$Q_{ref(1)}$					0.20	
Volts	22	23	24	25	30	
$Q_{cm^2} \times 10^{-16}$	0.329	0.402	0.485	0.566	1.08	
$Q_{ref(1)}$				0.61	1.04 ^b	

- a. The vertical axes of Figures 3 and 4 should be multiplied by 2.53×10^{-2} to obtain Q in $cm^2 \times 10^{-16}$.
 b. Tate and Smith's value of 1.04 includes a contribution from N^+ which we estimate to be about $0.07 cm^2 \times 10^{-16}$ so that 1.08 should be compared with a value of about $0.97 cm^2 \times 10^{-16}$ derived from their data.

electron beams produced by this configuration showed a distribution of the differential current about 0.1 V wide with a low energy tail containing less than 5% of the differential current extending not more than 0.05 V below. Adjustment of the filament-slit distance proved to be critical and optimum operation was obtained when the retarding potentials (with $\Delta V \sim 0.1V$) were within 0.3 V of the filament potential. The experimental method compared differential ion currents for N_2^+ and N^+ with those for argon ions produced from mixtures of known composition. Using known cross sections for argon ionization, the values for the nitrogen ionization processes were calculated.

Figures 3, 4 and 5 illustrate our results and show good agreement with earlier qualitative studies^{2,4}. Because of the different instruments involved and the varying aims of the investigators, no quantitative agreement can be expected. A more detailed comparison of results is made in Tables I, II and III. Significantly, we find no evidence for autoionization N_2^+ production in agreement with the observations of Fox and Hickam², and Frost and McDowell⁴ but in disagreement with Dorman, Morrison and Nicholson³ and more recently, Kaneko⁷. Clarke¹⁰, using a 127° sector electron energy selector, finds a hump in the curve, but it is not known whether this can be attributed to inadequate energy resolution or to autoionization. We interpret our results in terms of the $X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$ states of N_2^+ and the two electron transition to the $C^2\Sigma_u$ state. The cross sections when summed are in reasonable agreement with total ionization cross sections¹.

Tables IV, V and VI summarize the N^+ measurements and contrast them with the results of other workers. The discontinuities in the cross section curve can be associated with the production of $N^+(^3P)$ and various states of the nitrogen atom 4S 2D 2P . Agreement with thermochemical and spectroscopic measurements indicates that product kinetic energies are virtually zero, for each process at threshold. The mechanism for production of N^+ at threshold energies is obscure. It has been observed that the $V = 3$ level of the $C^2\Sigma_u$ state of N_2^+ is relatively highly populated in a He- N_2 discharge. This has been attributed to an inverse predissociation of the C state from the

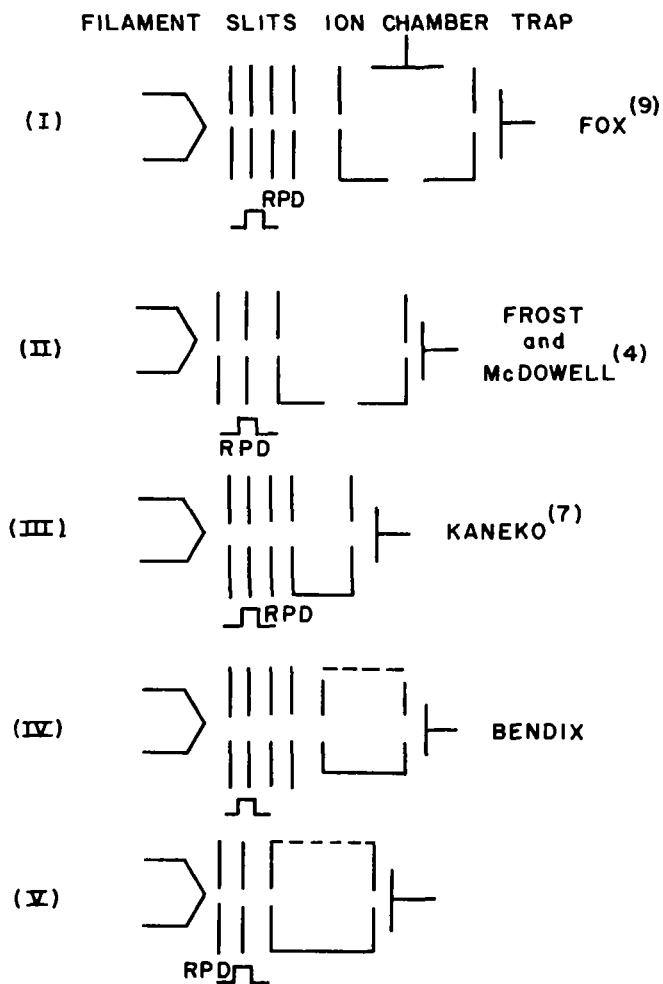


FIGURE 1

Gun configurations evaluated for R.P.D. operation.

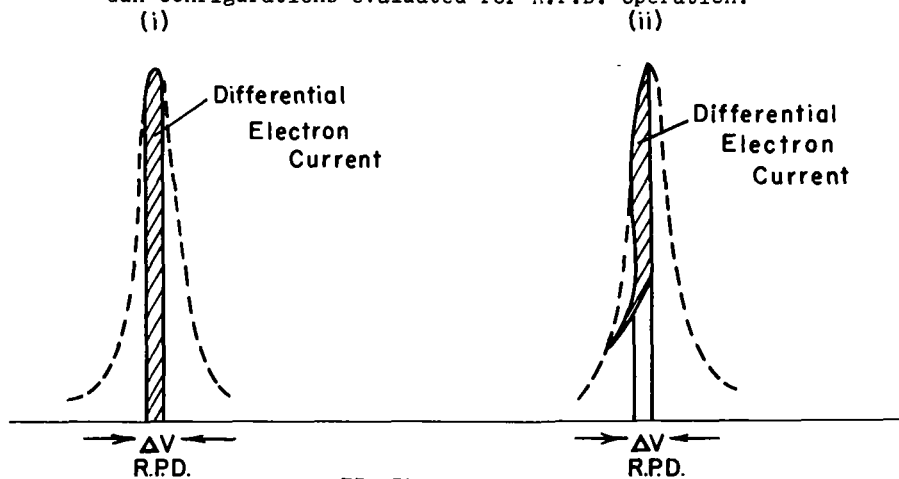


FIGURE 2

$N(^4S)$ $N^+(^3P)$ products of the $B^2\Sigma_u^+$ state which lie within 280 cm^{-1} of the $V = 3$ level of $C^2\Sigma_u^+$ ¹¹ and it has been suggested that the electron impact N^+ production process may be the reverse of this sequence¹², i.e.

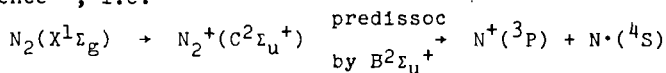
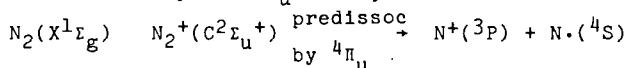


Figure 6 provides a convenient reference to the states¹⁶. Carroll has investigated the C state and considers that the predissociation, if it is present, is a feeble process and probably results from the action of the $^4\Pi_u$ state. Although the B and C states are known to have peculiarities in their potential energy curves, Field and Franklin¹³, on the basis of Morse curve calculations, suspect that a predissociation of the C state by the B state is unlikely. Two further processes appear possible:

- (a) A forbidden predissociation (as suggested by Carroll) of the C state by the $^4\Pi_u$ state, i.e.



- (b) A transition to the $^2\Pi_g$ at a point level with the dissociation asymptote of this state of $N_2^{+14,15}$.

The $^4\Pi_u$ state is predicted to be repulsive, but if (a) is adopted the total potential energy change on going from dissociated N^+ and $N\cdot$ to the internuclear distance extremum of the $V = 3$ of $C^2\Sigma_u^+$ is 280 cm^{-1} , so that product kinetic energy would be negligible. There is no evidence for N_2^+ production via the $^2\Pi_g$ state from our measurements, but this could arise from the shallow potential well ($D \sim 2.0\text{ eV}$ for $^2\Pi_g$) and the difference in internuclear distance between $N_2(X^1\Sigma_g^-)$ and $N_2^+(^2\Pi_g)$. The transition to $^2\Pi_g$ is a two electron transition but is no more unlikely on this basis than that to the $C^2\Sigma_u^+$ which takes place fairly readily, although less so than X, A or B N_2^+ production, and as an overall N^+ production method, the $^2\Pi_g$ route will probably be more efficient than $C^2\Sigma_u^+$ followed by a forbidden predissociation. That the onset of N^+ production is not steep and the slope is the least observed in the N_2 system, suggests that the process is not one of high probability.

Excited atom productions set in as two stronger processes at about 26.7 and 27.9 volts for $N(^2D)$ and $N(^2P)$ respectively.

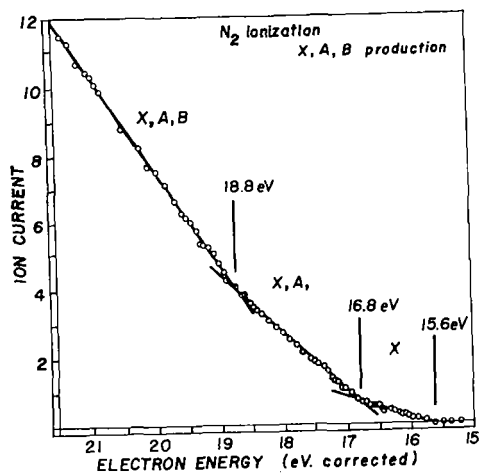


FIGURE 3

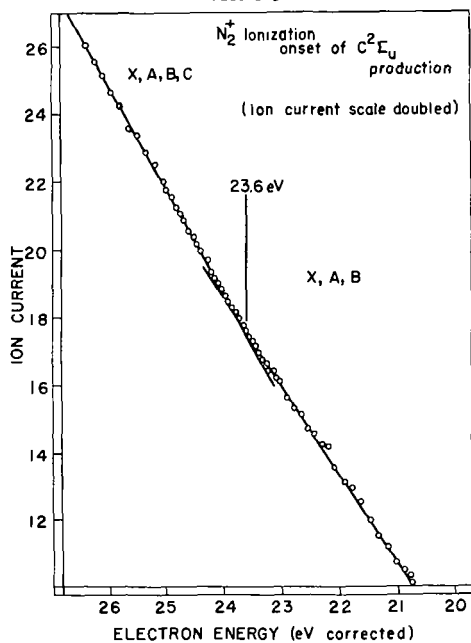


FIGURE 4

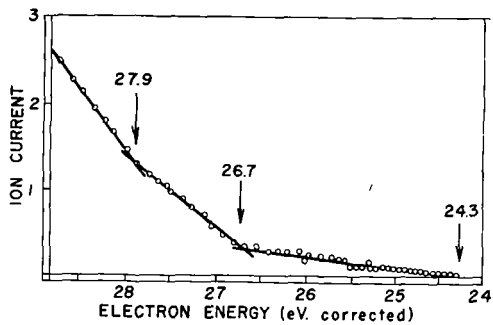


FIGURE 5

N^+ Production

Little can be said except to point out again that energy considerations preclude the presence of kinetic energy in the fragments so that repulsive states mentioned by Mulliken¹⁸ are probably not involved in these higher energy processes.

LIST OF REFERENCES

1. Tate and Smith, Phys. Rev. 39 (1932) 270.
2. Fox and Hickam, J. Chem. Phys. 22 (1954) 2059. N_2^+ .
3. Dorman, Morrison and Nicholson, J. Chem. Phys. 32 (1960) 378. N_2^+
4. Frost and McDowell, Proc. Roy. Soc. A236 (1957) 278, N^+ ; A232 (1955) 1347, N_2^+ .
5. Hagstrum, J. Chem. Phys. 23 (1955) 1178, N^+ .
6. Burns, J. Chem. Phys. 23 (1955) 1347, N^+ .
7. Kaneko, J. Phys. Soc. Japan 16 1587 (1961).
8. Glick and Llewellyn, 15th Annual Gaseous Electronics Meeting, Boulder, 1962.
9. Fox, Hickam, Kjeldaas and Grove, Rev. Sci. Instr. 26 1101 (1955).
10. Clarke, Can. J. Phys. 32 (1954) 764.
11. Douglas, Can. J. Phys. 30 (1952) 302.
12. McDowell "Conference on Applied Mass Spectrometry," Inst. of Petroleum, London, 1953.
13. Field and Franklin, Electron Impact Phenomena (A.P. 1957, N.Y.) pp. 65,66.
14. Tanaka, Can. J. Phys. 39 (1961) 1142.
15. Janin and D'Incan, Compt. Rend. 246 (1958) 3436.
16. Gilmore, private communication in Tanaka¹⁴.
17. Carroll, Can. J. Phys. 880 37 (1959).
18. Mulliken "The Threshold of Space" Ed. M. Zelikoff (Pergamon 1957) p. 169.

TABLE IV

CRITICAL POTENTIALS N^+

Clarke			Burns		
eV	N $\cdot$	N $^+$	eV	N $\cdot$	N $^+$
24.3	4S	3P	24.3	4S	3P
26.66	2D	3P	26.2	4S	1D
28.06	2P	3P	26.7	2D	3P
Frost			This Work		
eV	N $\cdot$	N $^+$	eV	N $\cdot$	N $^+$
24.32	4S	3P	24.3	4S	3P
26.66	2D	3P	26.7	2D	3P
27.93	2P	3P	27.9	2P	3P

TABLE V

 N^+ RELATIVE SLOPES (with respect to $N_2^+(X^2\Sigma)$)

4S	3P	0.16
2D	3P	0.92
2P	3P	0.53

TABLE VI

CROSS SECTIONS N^+ (The vertical axis of Figure 5 should be multiplied by 1.64×10^{-2} to obtain Q in 10^{-16} cm^2 .)

eV	25	26	27	28	29	30
Q $\text{cm}^2 \times 10^{-16}$	0.0016	0.0038	0.0090	0.024	0.048	0.072

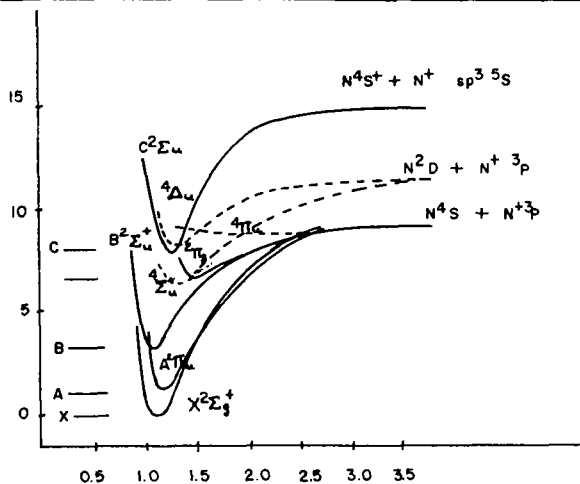


FIGURE 6

States of N_2^+

SCATTERING OF LOW ENERGY ELECTRONS ON MOLECULES

H. Ehrhardt and U. Erbse

Physikalisches Institut der Universität Freiburg, Germany

Introduction

In the last decade numerous experiments have been carried out, in order to check the assumptions and results of the Statistical Theory of Mass Spectra.¹ For these reasons in addition to examining mass spectra, the appearance-potential curves, their derivatives, and kinetic energy distributions of fragment ions were measured. Experiments on charge exchange, photoionization, and metastable ion decay have thrown considerable light on these problems. We have used an entirely different approach using electron scattering experiments which we feel should contribute additional insight into some of the problems associated with the mass spectra theory. In particular, our experiments were originally designed to obtain information on the energy transferred from the bombarding electrons to the target molecule and to investigate experimentally the assumption of a continuum of states as opposed to discrete energy states in polyatomic molecular ions.

Experimental

In this experiment an electron and a molecular beam are crossed at 90° , and the energy of the scattered and ejected electrons were measured as a function of the initial electron energy and the angle. A schematic diagram of the apparatus used is shown in Fig. 1. The electron gun is gold plated and bakable up to 250°C . It is pumped mainly from the rear through a metal screen on which a negative potential is applied so that no stray electrons can leave the gun. In this way, the electron background in the experimental chamber is reduced considerably. The electron beam is generally between 10^{-7} and 10^{-8} amps, the half width of the energy inhomogeneity is about 1 eV. The spherical metal screen adjacent to the vacuum chamber wall acts as the electron beam collector and in addition it removes background electrons. The remaining electron background accounts for about 1% of the scattering rate into the collector. However, in the forward direction, where primary beam electrons can enter the collector cone, it is impossible to make measurements at angles less than about 10° - 15° . The detector for the scattered electrons can be scanned through 145° with respect to the electron beam in a plane perpendicular to the molecular beam. The angular resolving power is about $\pm 2^\circ$. It contains a retarding field system in which the retarding screen has a mesh width of only 0.002" and 50% transmission. The energy resolution is in the order of 1%. The scattered electrons are counted with a conventional electronic arrangement having a resolving time of 4 μ sec. The molecular beam is formed by effusing from a tube and a greater part enters and is condensed on a liquid nitrogen trap (not shown in Fig. 1). The beam pressure at the reaction zone is about 10^{-4} mm Hg. Any stray magnetic fields in the interaction region is compensated by three pairs of Helmholtz coils mutually perpendicular to one another. The residual field is in the order of 5 milligauss.

Fig. 2 shows the intensity of the electron beam versus the angle from the scattering center when no molecular beam is flowing. It shows that with the use of the retarding technique we can only measure at angles higher than 10° , because the intensity of the beam has dropped from about 10^{-7} to 10^{-15} amps, which is of the same order of magnitude as the current expected from the scattering electrons.

The apparatus was tested with neon because the energy states were known and the angular distribution of the scattered electrons measured by Nicoll and Mohr² in some earlier experiments. The potentialities and limitations of the apparatus in its present stage can be realized by considering the results shown in Fig. 3. Plotted are the counts/sec of scattered electrons versus the retarding voltage and the derivative of this curve. Even in the presence of substantial elastic-scattered electrons, steps can clearly be seen due to the excitation of the 3p and 4p states of neon, but all closer lying states and the ionization limit are smeared out because of the spread in the energy of the primary electrons. Similar results were obtained at different primary energies and angles.

Experiments and Discussion

Extensive measurements with the lower paraffines have been carried out mainly with n-heptane in two types of experiments:

(1) The number of scattered electrons was measured versus retarding voltage at fixed scattering angles.

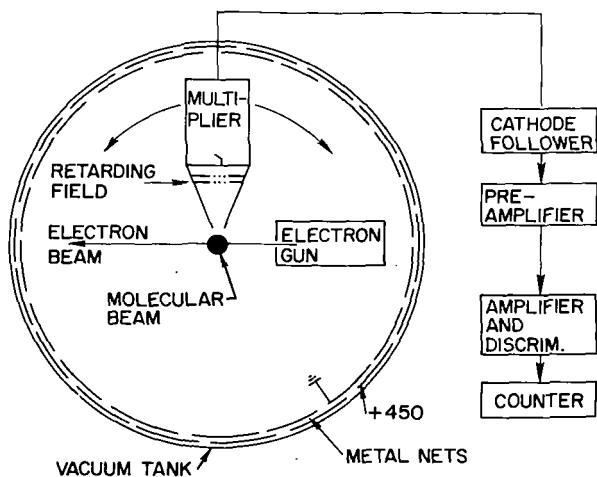


Fig. 1--Schematic diagram of electron scattering apparatus.

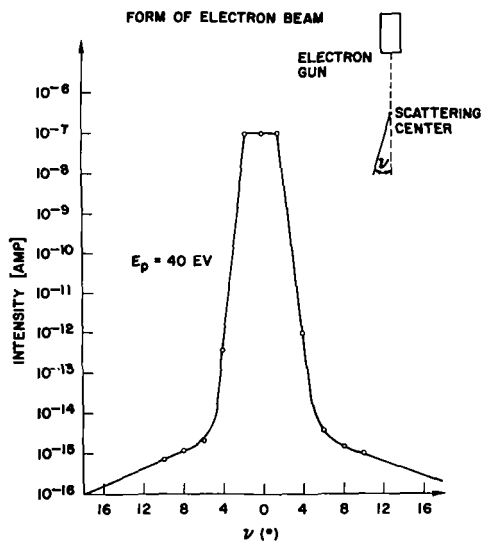


Fig. 2--Angular distribution of primary electron beam. The angle ν is taken with respect to the interaction zone as shown in the upper part of the figure.

(2) the number of scattered electrons was measured versus scattering angle at fixed retarding potentials.

The range of energies of the primary electrons used was between 25 and 200 ev.

Fig. 4 shows a typical example obtained with a crossed n-heptane and an electron beam of 30 ev energy. The electrons scattered into 90° are plotted versus the retarding potential V_{ret} . The scale U_E indicates the energy lost by the electrons in the collision. In addition to the elastically scattered electrons one can see there is an excitation of the n-heptane about 8 ev above the ground state. This is in good agreement with optical absorption measurements. Surprising is the small number of electrons scattered in this energy range compared to the number scattered above the ionization limit. This situation occurs for all measured angles and all beam energies employed. On the other hand, Beck and Osberghaus³, studying several different paraffins with 200 ev electrons, have measured the ratio of the number of processes resulting in ion formation to the number resulting in only neutral products and they obtained a ratio of 1.1 ± 0.2 . This means, that a relatively large number of the processes leading to only neutral products must result from excitations in which the bombarding electron loses more than the ionization energy. These collisions may be interpreted by assuming that in the interaction the colliding electron excites more than one valence electron of the molecule.

In Fig. 5 is presented a portion of a plot of counts/sec versus retarding potential in which a great deal of structure is observed. The curve is constructed from many sets of measurements; the error bars are drawn three times larger than the statistical error. This curve shows that above the ionization limit there are energy regions in which the transition probability is greater than in neighboring regions. This phenomenon is in contradiction to one of the assumptions of the mass spectral theory.¹ Although the effects are small, we feel they are real. Furthermore, we expect even more interesting details, if these measurements were repeated using a more monoenergetic electron beam.

With high energy (200 ev) primary electrons, the scattered and the ejected electrons (due to ionization of n-heptane molecules) are distinguishable, as is indicated in Fig. 6. This conclusion is further supported by the fact that angular dependence of the intensity of the ejected electrons is spherically symmetric, whereas the elastic and inelastic scattered electrons show the expected forward scattering (see Fig. 7). The separation of the ejected from the scattered electrons could not be observed in the case of n-heptane for bombarding electrons with less than 70 ev, nor in the case of neon, where we tried up to 500 ev.

Using high energy primary electrons and measuring at a rather large scattering angle, we observed that the electrons transfer a large amount of excitation energy to the molecule, in the average about 30 ev (see Fig. 6). Since the intensity for inelastic scattering is especially high in forward direction, and we have only measured down to about 15° , we are not able to say anything about the energy transfer in electron collisions on large molecules, integrated over all angles. However, a rough estimation of the number of high energetic processes (high means more than 30 ev) compared to all processes seems to be as high as 20%. The estimation was made using the measurements of the angular distributions of the scattered and ejected electrons (Fig. 7). Since the ejected electrons have a spherical distribution, extrapolation and, therefore, the integration from zero to 180° can be carried out. On the other hand, the extrapolation of the curve for the scattered electrons must be done so that the number of the scattered electrons over all angles is about twice the number of the ejected electrons, since the number of neutral and ion processes have been shown to be equal.² This, of course, holds only for high primary electron energies where the scattered and the ejected electrons can be separated.

REFERENCES

1. H. M. Rosenstock, A. L. Wahrhaftig, M. Wallenstein, and Henry Eyring, Proc. Nat. Acad. Sci. U.S. 38, 667 (1952).
2. F. H. Nicoll and C. B. O. Mohr, Proc. Roy. Soc. Lond. 142, 647 (1933).
3. D. Beck and O. Osberghaus, Z. Physik. 160, 406 (1960).

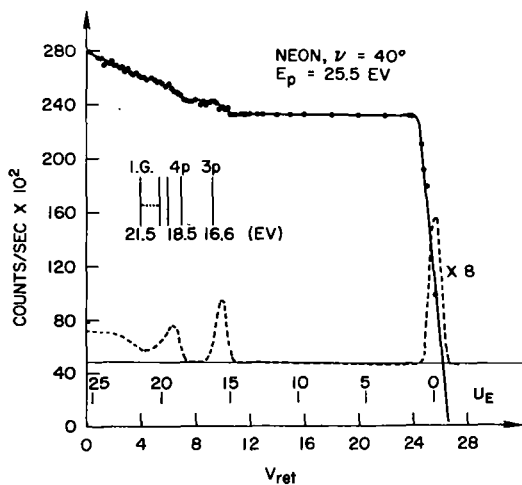


Fig. 3--Test measurement on neon. The solid line represents plot of intensity of scattered electrons versus retarding potential (V_{ret}). The dashed line indicates first derivative of solid curve and is proportional to probability of detecting an electron which has lost the energy U_E during the collisions.

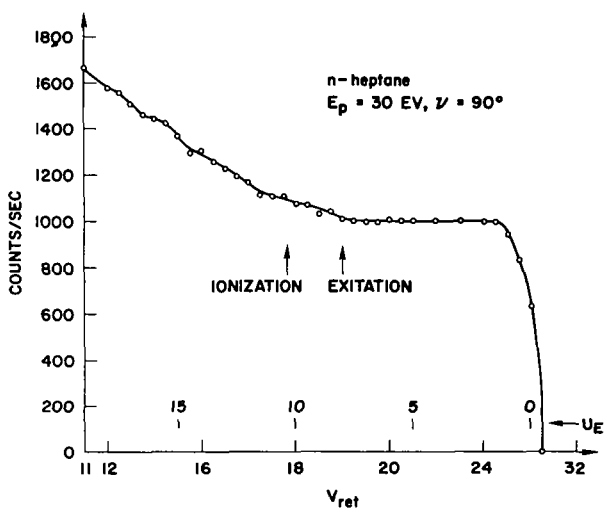


Fig. 4--Retarding potential (V_{ret}) plot of electrons scattered from n-heptane into 90° .

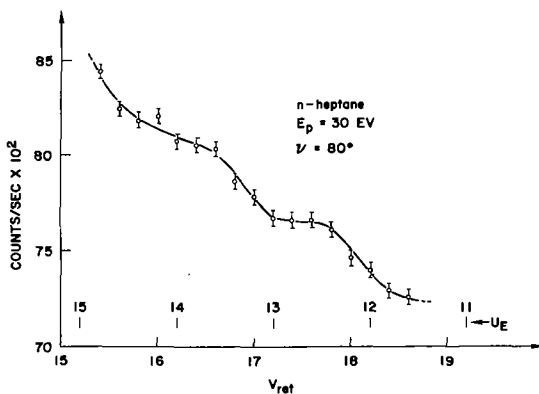


Fig. 5--Portion of a retarding potential plot showing structure in the curve.

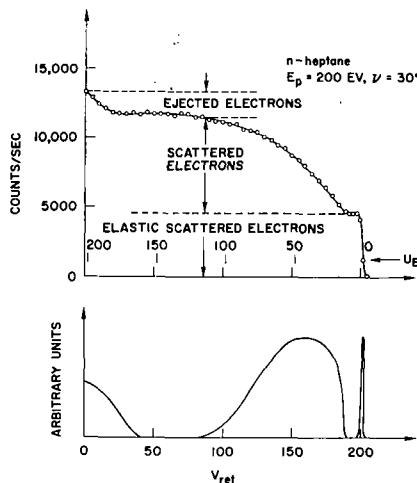


Fig. 6--Retarding potential plot which distinguishes scattered and ejected electrons using 200 ev bombarding electrons.

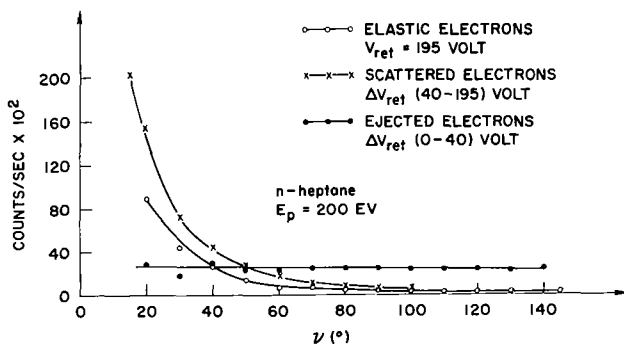


Fig. 7--Angular distributions of elastically, and inelastically scattered, and ejected electrons from n-heptane using 200 ev bombarding electrons.

A PROPOSED ANALYSIS OF THE CHARGE STATE OF RECOIL ATOMS
PRODUCED BY HIGH ENERGY ELECTRON IMPACT*

Gerald P. Calame and Frederick A. White
Department of Nuclear Engineering and Science
Rensselaer Polytechnic Institute

ABSTRACT

In support of a broad radiation damage program, an experiment has been suggested that may contribute to a more detailed understanding of radiation kinetics and the production of displaced atoms. The experiment is specifically concerned with the charge state of recoil atoms produced by direct electron impact. With the high current intensity 100 Mev RPI Linac, it appears possible to produce recoil atoms in a sufficient number to analyze them in a large radius of curvature, double-focusing system.

Short electron bursts (0.1 to 4.5 microseconds) will impinge on a thin target. Recoil atoms will first enter a large radius of curvature electrostatic lens, pass, through a magnetic momentum filter, and finally be detected by an electron multiplier suitably "gated" with respect to the Linear Accelerator so as to determine the ion transit time. The relatively long flight path of the ion (≈ 3 meters) will be sufficient so that single positive ions can be detected out of phase with the intense electron burst and its associated bremsstrahlung.

- * This work sponsored by the National Aeronautics and Space Administration.

Initial Preparation and Metastable Transitions in Mass Spectra

H. M. Rosenstock, V. H. Dibeler and F. N. Harllee
Physical Chemistry Division
National Bureau of Standards
Washington, D. C.

Abstract

Variation of initial preparation to search for non-equilibrium kinetic effects (Frey 1/) is discussed in connection with the kinetics of unimolecular ionic decomposition processes occurring in the mass spectrometer. A particular example, dependence of the rates of competing metastable transitions of hexyl ions on mode of preparation is studied in detail. The hexyl ions were prepared by electron impact ionization and decomposition of a variety of normal alkanes, n-hexyl bromide and di-n-hexyl ether. At low electron energies (30ev) the ratio of the competing metastable transitions is constant within experimental error. This supports the applicability of the quasi-equilibrium theory of mass spectra to such processes. At higher electron energies there is a slight dependence of the ratio on parent ion mass.

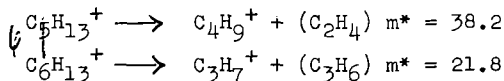
Introduction

Some years ago it was postulated that the ionic decomposition processes observed in the mass spectrometer could be described by unimolecular reaction kinetics. 1/ The development of this approach since that time has led to a (not unexpected) very close parallel to more well known branches of reaction kinetics in the formulation and resolution of experimental-theoretical discrepancies. The most noteworthy of these is the problem of accurate counting of reactant and activated complex states and its implications regarding the question of effective oscillators. Recent references to this problem are cited below 2-6/. It has been stated by several workers that the experimental facts can be accounted for with proper enumeration of the states. However, the molecular models on which the counting of states is performed are still oversimplified. This is particularly true in mass spectrometry. In view of this, it is desirable to carry out experiments which test the central assumption--applicability of equilibrium reaction kinetics--without floundering in a morass of assumed states and their accurate enumeration.

Frey 1/ pointed out explicitly several years ago that an immediate consequence of the assumption of equilibrium reaction kinetics is that the kinetic behavior of an excited molecule should depend only on its energy content and not on the details of the preparation leading to that energy. An example of this was given by Butler and Kistiakowsky 8/ who showed that the reaction of CH_3 radicals with propylene and with cyclopropane led to the same relative amounts of methyl cyclopropane and butenes as products.

This suggestion, studying the effects of varying initial preparation on the course of a reaction, is of course also applicable to mass spectrometric kinetics studies. In fact, a little reflection on this theme very quickly leads to a wide variety of such test experiments 2,9/. These include comparison of breakdown curves produced by vertical ionization with those produced by charge exchange, comparison of product distribution of ion-molecule reactions with decomposition of corresponding intermediate ions produced by electron impact, and the energy dependence of metastable transitions observed in photoionization experiments. Still another comparison, which may be performed on a single experimental apparatus, is the study of competing metastable transitions.

The mass spectra of a variety of hydrocarbons containing seven or more carbon atoms show two metastable transitions involving hexyl ions.



Appearance potential data indicate that the onset of the two transitions are within 0.2 - 0.3 ev of one another ^{10/}. This suggests that the reactions are in competition with one another. Since these reactions both occur as metastable transitions, they have comparable values for the unimolecular rate constants in the metastable range at the same excitation energy. If, now, the hexyl ions are prepared from different precursor ions it is probable that the detailed distribution of the excitation energy may differ, depending on the origin of the ion. Unless there is sufficient redistribution of this excitation energy, such a non-equilibrium effect might manifest itself as a difference in the relative importance of the two competing reactions in the metastable range. The API tabulation of mass spectra ^{11/} gives numerous data on the metastable transitions. These are given in table 1. The large scatter of values may be due to a variety of hexyl ion structures produced in the different compounds, to different methods of measuring relative abundances of metastable transitions and to variations of experimental apparatus and parameters. In particular, the normal alkane series show as large a variation among themselves as does the group as a whole.

Table 1
Ratio of Competing Hexyl Metastable
Transitions (^{38.2}/_{21.8}) ^{a/}

<u>API No.</u>	<u>Compound</u>	<u>Ratio</u>
15	2-methyl-hexane	0.3
18	2,2-dimethyl-pentane	0.3
20	2,4-dimethyl-pentane	0.5
21	3,3-dimethyl-pentane	0.3
22	2,2,3-trimethyl-butane	0.3
39	n-octane	0.4
41	3-methyl-heptane	0.5
43	3-ethyl-hexane	0.7
46	2,4-dimethyl-hexane	0.7
48	3,3-dimethyl-hexane	0.4
49	3,4-dimethyl-hexane	0.5
50	2-methyl-3-ethyl-pentane	0.4
51	3-methyl-3-ethyl-pentane	0.9
54	2,2,3-trimethyl-pentane	0.5
132	nonane	0.6
247	4-methyl-octane	0.9
249	2,4-dimethyl-3-ethyl-pentane	0.9
136	2,3,3-trimethyl-hexane	0.7
137	2,3,5-trimethyl-hexane	0.4
142	2,2,3,4-tetramethyl-pentane	0.7
144	2,3,3,4-tetramethyl-pentane	0.5
109	Decane	0.8
403	n-undecane	0.5
404	n-dodecane	0.3

^{a/}taken from reference 11.

It was decided to carry out a series of measurements which would minimize variations due to experimental conditions. A series of straight chain compounds was chosen.

Experimental

The hydrocarbons n-heptane through n-tetradecane, were NBS Standard samples. The n-hexyl bromide and the di-n-hexyl ether were Eastman Organic Chemicals. All materials were used without further purification. The Eastman compounds showed no significant impurities in their mass spectra.

The details of the experimental apparatus have been described elsewhere ^{12/}. Briefly, it consists of a 12-inch radius of curvature 60° sector field single focusing mass spectrometer. The mass spectrum could be scanned by varying either the magnetic field or the high voltage. The results reported here are for magnetic scanning. The vacuum in the analyzer tube was $1-2 \times 10^{-8}$ torr. base pressure and 5×10^{-8} torr. with sample present. At this pressure collision processes

make no contribution to the metastable transitions under investigation.

Mass spectra were obtained in the usual manner using electrons of nominally 70 ev energy, with an ion accelerating voltage of 4 KV. The relative abundance of the two metastable transitions was determined with electron energies of 30, 50 and 70 ev. The spectrum was scanned at least five times in the neighborhood of each peak at carefully regulated scanning speed. A typical recording is shown in fig. 1. The baseline of the peak was defined by drawing a line tangent to both wings of the peak. The contribution of a superposed integral mass peak was eliminated also by drawing a straight line tangent. This procedure is admittedly arbitrary but is simple and not subjective. As a result, the absolute values of the abundances of the two peaks have little significance. However, we are interested here only in finding out whether there are significant changes in the ratio of the two measured ion currents. For this purpose the procedure is quite adequate. The area of each peak was measured five times with a planimeter. A typical set of values of individual area measurements on all five scans of a given peak is shown in fig. 2 for the 38.2 peaks and in fig. 3 for the 21.8 peak of n-tetradecane. The data are plotted in the form of cumulative probabilities which, with the abscissa used here, gives a straight line if the values are normally distributed. It is apparent from these graphs that the probable error of the ratio of the metastable transitions is about five percent. Similar results were obtained for all the compounds studied, with errors ranging from four to seven percent. The factors contributing to this scatter include peak height scatter and precision of the peak area measurement with the planimeter.

Results and Discussion

The metastable ratios found for the various compounds at the three electron voltages are listed in Table 2. It is evident that the spread of values is considerably less than that found from the API tabulation. It is to be noted that the values of the ratios are quite different from those in the tabulation. This is due to the fact that magnetic scanning was used in this study, whereas the API values represent results obtained by varying the accelerating voltages. Some runs on the present apparatus with varying accelerating voltage gave ratio values which were reasonably close to those reported in the API tabulation. This merely points to the difficulty of establishing absolute values for these quantities. However, to a good approximation, these instrumental artifacts are of no consequence here. Coggeshall ^{13/} has discussed this problem in detail.

Table 2
Ratio of Competing Hexyl ion
metastable transitions (38.2)
21.8

Compound	30 v	50 v	70 v
n-Heptane	1.59	1.61	1.80
n-Octane	1.63	1.79	1.64
n-Nonane	1.61	1.57	1.69
n-Decane	1.44	1.63	1.62
n-Undecane	1.53	1.46	1.61
n-Dodecane	1.47	1.49	1.51
n-Tridecane	1.65	1.55	1.57
n-Tetradecane	1.54	1.42	1.44
n-Hexyl bromide	1.62	1.60	1.61
di-n-Hexyl ether	1.61	1.44	1.58

A statistical analysis of the data was carried out to establish whether there were any significant differences between the results at the different electron energies and whether there was any dependence on the molecular weight of the parent compound. The data were fitted to straight lines of the form

$$R = r_0 + b (M-154.3)$$

where R is the ratio and M is the molecular weight. The parameters and their probable errors (95% confidence interval) are given in Table 3. It is seen that the average ratios of the three groups of data do not differ significantly. However, only the 30 ev data is independent of the molecular weight. For those data one can

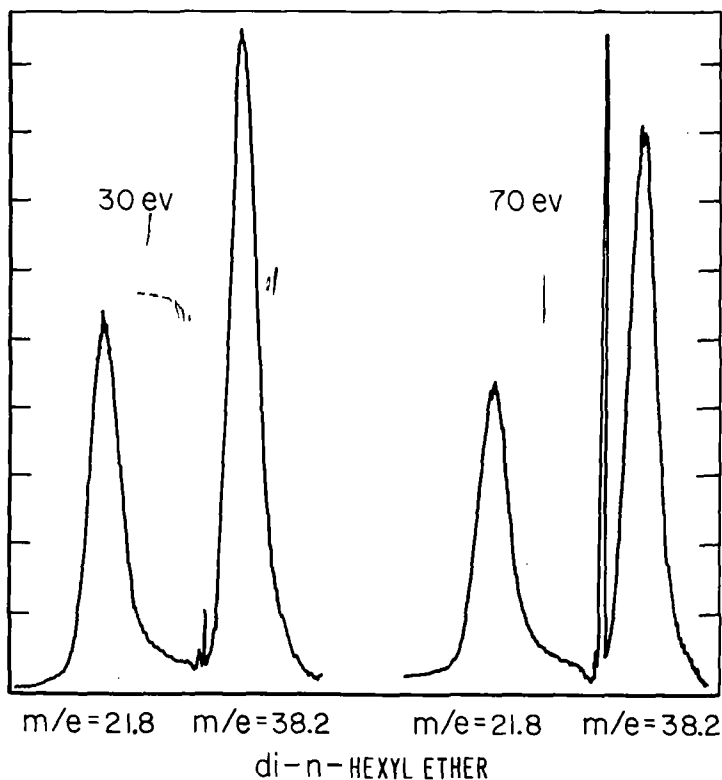


Fig. 1. Tracing of typical scan of the hexyl ion metastable transitions in the mass spectrum of di-n-hexyl ether.

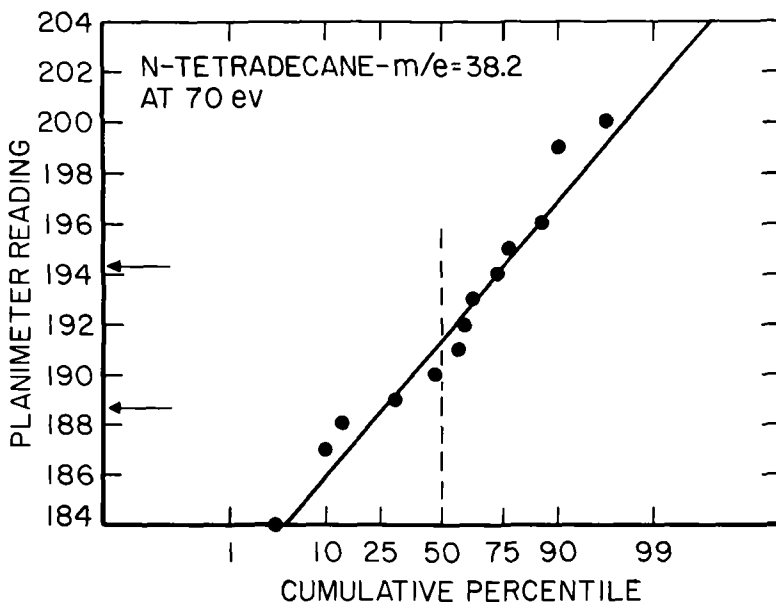


Fig. 2. Distribution of planimeter readings for the determination of the area of the mass 21.8 metastable transition of n-tetradecane.

state that the ratio is constant for these compounds with a probable error (95% confidence interval) of 3%. The data at higher electron energies show a significant decrease with increasing molecular weight. Further, the statistical analysis indicates that the scatter of values represents a population whose individual values are known with a standard error of 4.5%. This figure is in accord with the estimates of the reliability of the individual ratio values given earlier.

Table 3
Molecular Weight Dependence of
Metastable Ratio, R.

Electron energy	r_0 $\frac{a}{b}$	b
30 v	1.569 ± 0.062	-0.00018 ± 0.00177
50 v	1.556 ± 0.065	-0.00252 ± 0.00187
70 v	1.607 ± 0.037	-0.00260 ± 0.00118

$\frac{a}{b}$ Parameters of the equation $R = r_0 + b(M-154.3)$, obtained by least squares.

The constancy of the 30 ev ratios indicates that in the rate constant range of 10^5 - 10^6 sec⁻¹ there are no non-equilibrium effects due to variation in the mode of preparation of the hexyl ion. It is, of course, impossible to state whether this indicates a similarity of initial distribution in phase space of the hexyl ions immediately after formation by unimolecular decomposition of the various precursor ions or whether the similarity is achieved by rapid redistribution of the excitation energy after the decomposition process. There is also the possibility that the hexyl ions undergoing the metastable transitions may consist of several isomers with possibly different metastable ratios. All that can be concluded at present is that, whatever the isomer or isomers may be in this series of straight chain compounds there is no evidence of different behavior at low electron energies.

The summary of results reported in the API compilation, Table 1, suggest that even branched compounds may lead to hexyl ions of similar behavior. It would be of interest to study these with comparable precision. These results support the usefulness of the quasi-equilibrium kinetics description of ionic decomposition processes. The results at the higher electron energies, showing a small but significant decrease in the ratio with increasing molecular weight are unexplained. One possibility is that some of the hexyl ions contributing to the metastable transitions may be formed with kinetic energy, with resulting changes in the collection efficiencies for the different non-integral masses.

Acknowledgment-We would like to acknowledge numerous stimulating and helpful discussions with Dr. M. Krauss on the problems of initial preparations and non-equilibrium effects.

Bibliography

1. H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, Proc. Nat. Acad. Sci. 38, 667 (1952).
2. G. M. Wieder and R. A. Marcus, J. Chem. Phys. 37, 1835 (1962).
3. J. H. Current and B. S. Rabinovitch, J. Chem. Phys., 38, 783 (1963).
4. M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, J. Chem. Phys. 37, 1276 (1962).
5. H. M. Rosenstock and M. Krauss, in "Advances in Mass Spectrometry", Pergamon Press, Oxford (1962).
6. M. Wolfsberg, J. Chem. Phys. 36, 1072 (1962).
7. H. M. Frey, Trans. Faraday Soc. 56, 51 (1960).
8. J. N. Butler and G. B. Kistiakowsky, J. Am. Chem. Soc. 82, 759 (1960).
9. H. M. Rosenstock and M. Krauss, in "Mass Spectrometry of Organic Ions", F. W. McLafferty, ed., Academic Press, New York (1963).

(Concluded on next page)

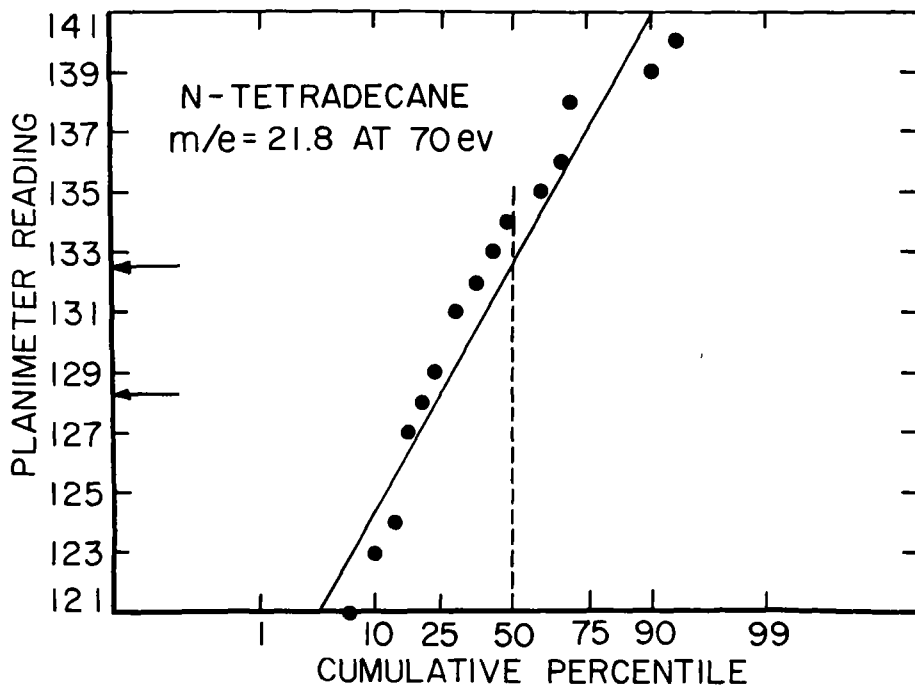


Fig. 3. Distribution of planimeter readings for the determination of the area of the mass 38.2 metastable transition of n-tetradecane.

Bibliography - Concluded

10. V. H. Dibeler, unpublished work.
11. American Petroleum Institute Research Project 44, "Catalog of Mass Spectra Data", Carnegie Institute of Technology, Pittsburgh, Pa.
12. V. H. Dibeler and H. M. Rosenstock, J. Chem. Phys. to be published.
13. N. D. Coggeshall, J. Chem. Phys. 37, 2167 (1962).

METASTABLE INTENSITIES IN HYDROCARBON MASS SPECTRA

John C. Schug
Gulf Research & Development Company
Pittsburgh, Pennsylvania

ABSTRACT

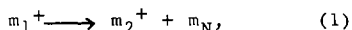
This paper discusses the possibilities of obtaining useful information from so-called "metastable-lifetime" measurements. An approximate method is described for computing the ratios of parent ion-to-metastable peak intensities via the statistical theory. The predictions of the statistical theory are compared with those of models employing a small number of discrete rate constants. It is shown that in certain instances it should be possible to determine which model is correct. Data for the 30.4 and 31.9 metastables of n-butane appear to substantiate the validity of the statistical theory.

I. INTRODUCTION

The true nature of the metastable peaks in hydrocarbon mass spectra is apparently still an open question. It has never been definitely established whether the metastable dissociations occur at a single rate, as indicated by the earliest research¹⁻³, at several different rates as assumed by Momigny⁴ and Coggeshall⁵, or at many different rates, as predicted by the statistical theory of mass spectra⁶. The present paper is concerned with the possibility of settling this important question.

Although it is possible in principle to determine which model is correct, we are unable to form a judgment from currently available data. When more and better data become available, the results presented in the remaining portion of this paper will enable one to determine the origin of metastable peaks.

We consider a typical fragmentation,



which gives a metastable peak at apparent mass

$$m^* = m_2^2 / m_1. \quad (2)$$

The internal energy, E , of the parent ion (m_1^+) is taken as the independent variable, and the appearance potential of this ion is taken as the origin of energies. The activation energy of reaction (1) is ϵ_1 , and its rate is $k = k(E)$. In the event that other reactions compete with (1), $K(E) = \sum k(E)$ gives the total rate for disappearance of the parent.

Other necessary definitions are: $I(m)$, the intensity of mass peak m ; $P(E)$, the normalized internal energy distribution of the parent ion; t_R , the residence time of the parent ion in the ionization and acceleration regions of the mass spectrometer; and t_M , the time spent by the ion in the analyzing region of a 180° instrument (or the field-free region of a sector instrument), during which its dissociation contributes to $I(m^*)$. In conventional systems, all residence times are in the microsecond range⁵.

It is convenient to consider the ratio $[I(m_1)/I(m^*)]$ because (a) this minimizes possible discrimination effects, and (b) in the discrete rate-constant model¹⁻⁵, the variation of the ratio's logarithm with t_R gives the rate constant directly. The general expression for this ratio is

$$I(m_1)/I(m^*) = [g + J(t_R + t_M)] / [J'(t_R) - J'(t_R + t_M)], \quad (3)$$

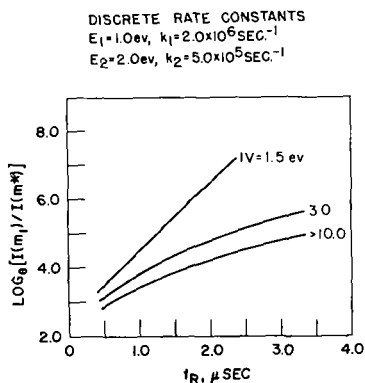


Fig. 1. Variation of $[I(t_R)/I(m^*)]$ with residence time and ionizing voltage predicted by a model with two discrete rate constants.

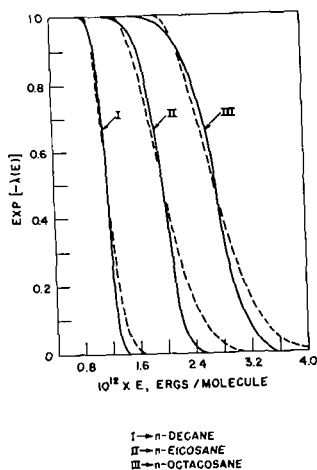


Fig. 2. Comparison of accurate functions $\exp \{-\lambda(E)\}$ with approximations of Eq. (14) for several molecules.

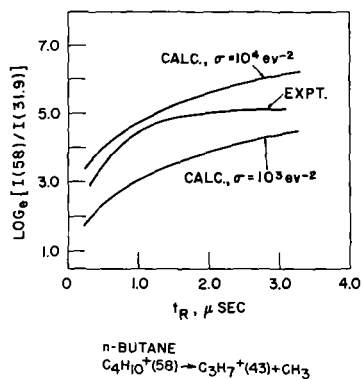


Fig. 3. Approximate dependence of $[I(t_R)/I(m^*)]$ upon residence time as predicted by the statistical theory for the 31.9 metastable of n-butane.

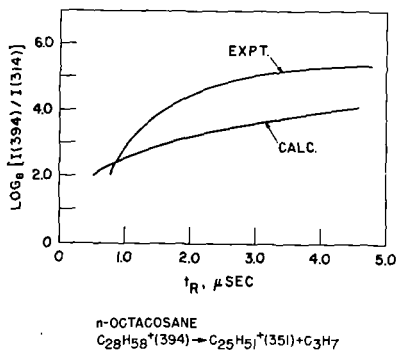


Fig. 4. Approximate dependence of $[I(t_R)/I(m^*)]$ upon residence time as predicted by the statistical theory for the 314. metastable of n-octacosane.

where

$$g = \int_0^{\epsilon_1} P(E) dE \quad (4)$$

$$J(T) = \int_{\epsilon_1}^{\infty} \exp[-TK(E)] P(E) dE \quad (5)$$

$$J'(T) = \int_{\epsilon_1}^{\infty} [k(E)/K(E)] \exp[-TK(E)] P(E) dE \quad (6)$$

For the most part, the calculations of the following sections neglect competitive reactions; in this case, $k(E) = K(E)$ and $J(T) = J'(T)$.

A useful alternative expression can be obtained by considering a distribution of rate constants, rather than of energies:

$$P(K) = P(E) (dE/dK) \quad (7)$$

In the absence of competing reactions, this leads to

$$I(m^*) = \int_0^{\bar{k}} \exp(-t_R k) [1 - \exp(-t_M k)] P(k) dk \quad (8a)$$

$$I(m_1) = g + \int_0^{\bar{k}} \exp[-(t_R + t_M)k] P(k) dk \quad (8b)$$

where $\bar{k}$ is the maximum possible dissociation rate.

II. DISCRETE RATE CONSTANTS

It is obvious from the results that have been published by Momigny⁴ and Coggeshall⁵ that the existent data on metastable intensities can be described in terms of a small number of discrete rate constants. With such a model data are interpreted via Eqs. (8) with

$$P(k) = \sum_i N_i \delta(k - k_i), \quad (9)$$

where N_i is the relative number of parent ions capable of dissociating at the rate k_i , and $\delta(k - k_i)$ is a Dirac delta function. One obtains

$$I(m^*) = \sum_i N_i [1 - \exp(-t_M k_i)] \exp(-t_R k_i), \quad (10a)$$

$$I(m_1) = g + \sum_i N_i \exp[-(t_R + t_M)k_i], \quad (10b)$$

where g is simply the total fraction of parent ions which are incapable of dissociating.

We have neglected possible discrimination effects and used Eq. (10a) to analyze Coggeshall's data (obtained with seventy-volt ionizing electrons)⁵ on the metastable peak at $m^* \approx 31.9$ of n-butane. With two discrete rate constants, a least-squares type analysis showed that the data could be reproduced almost exactly with $k_1 = 1.9 \times 10^6 \text{ sec}^{-1}$, $k_2 = 1.0 \times 10^5 \text{ sec}^{-1}$, and $N_1/N_2 = 4.24$. If the threshold law⁷ is assumed valid, each N_i is given by

$$N_i = (V - E_i) T(E_i), \quad (11)$$

n-BUTANE, VWJ MODEL
 $C_4H_{10}^+ \rightarrow C_3H_7^+ + CH_3$, $e = 0.93 \text{ eV}$

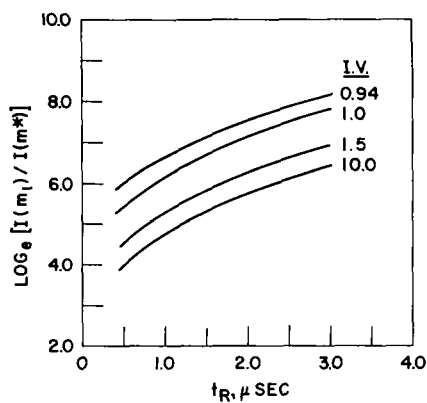


Fig. 5. Dependence of $\{I(m_1)/I(m^*)\}$ on residence time and ionizing voltage calculated by statistical theory for the model of Vestal, Wahrhaftig, and Johnston.

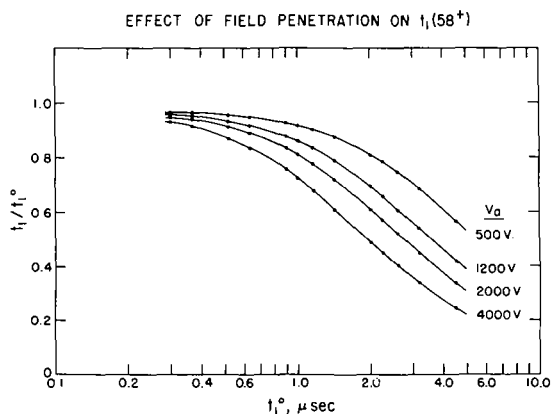


Fig. 6. Effect of field penetration on t_1 for a mass 58 ion.

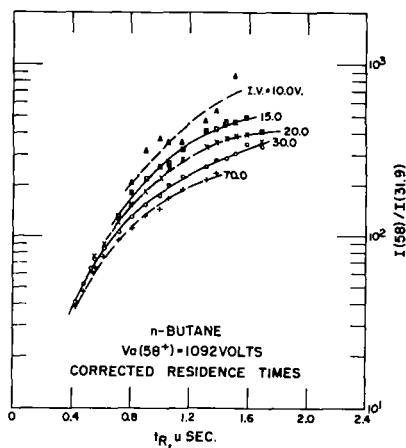


Fig. 7. Variation of the n-butane 31.9 metastable intensity observed with CEC 21-103 spectrometer.

where V is the ionizing voltage, and $T(E_i)$ is a transition probability to level E_i . The relative values of N_1 and N_2 obtained would indicate that there are two dissociative levels with very different energies. Further studies on this metastable (see section IV) show that this is not true, however. No doubt the data could still be rationalized in terms of this model with discrete energy levels and dissociation rate constants, but this will not be attempted at the present time.

In Fig. 1 is shown the dependence of the ratio $I(m_1)/I(m^*)$ upon the ionizing voltage that is predicted by this model. This graph was developed for the parameters $E_1 = 1.0$ ev, $k_1 = 2.0 \times 10^6$ sec $^{-1}$, $E_2 = 2.0$ ev, $k_2 = 5.0 \times 10^5$ sec $^{-1}$, $N_2/N_1 = (V-E_2)/(V-E_1)$ and $g/N_1 = 10$. The feature in Fig. 1 that characterizes this model is that, when V decreases below E_2 , a drastic change in slope should be observed. Such behavior has been reported by Momigny⁴ for a metastable dissociation of $C_6H_5CN^+$, and this at first glance appears to be a strong argument in favor of the model. However, it is felt that this work should be redone under better experimental conditions.

It should be noted that if k_1 and k_2 are reversed, the character of Fig. 1 becomes changed. In this case, when the ionizing voltage is dropped below the level E_2 , the slope change occurs in the low residence-time range; that is, the curve flattens out in the opposite direction from that depicted. Also, if $k_1 = k_2$, the curves become essentially straight lines, and are independent of the ionizing voltage.

III. THE STATISTICAL THEORY

It is presently impossible to obtain general analytic expressions based on the statistical theory, so we have employed a number of approximations to simplify the calculations. That the approximations are sufficiently accurate is indicated by two facts: (a) the calculated results are rather insensitive to the available parameters; and (b) numerical calculations for n -butane using the model and rate-constant expressions of Vestal, Wahrhaftig, and Johnston⁹ give results essentially indistinguishable from the approximate ones.

It is convenient to employ reduced dimensionless times and rate constants, defined by

$$\theta = T/(10^{-6} \text{ sec}), \quad (12)$$

$$\lambda(E) = k(E)/(10^6 \text{ sec}^{-1}). \quad (13)$$

After examining the dependence of the numerically determined⁸⁻¹⁰ function, $\exp[-\lambda(E)]$, upon the energy E , and the size of the parent ion, it was decided to employ the approximation,

$$\exp[-\lambda(E)] \cong 1, \quad \epsilon_1 < E < \bar{E} \quad (14a)$$

$$\cong \exp[-\sigma(E-\bar{E})^2], \quad E > \bar{E} \quad (14b)$$

where both σ and $\bar{E}$ are parameters which depend on the size of the parent ion. The nature of this approximation is shown in Fig. 2. The solid curves have been evaluated numerically for C-C bond dissociations in n -decane, n -eicosane, and n -octacosane ions for $\epsilon_1 = 0.8 \times 10^{-12}$ ergs, and employing the same frequency distributions described in an earlier study.¹¹ The dotted curves show the approximations (14) using the parameters $(\sigma, \bar{E}) = (9.46 \times 10^{24} \text{ ergs}^{-2}, 0.9 \times 10^{-12} \text{ ergs})$ for decane; $(1.59 \times 10^{24}, 1.3 \times 10^{-12})$ for eicosane; and $(1.08 \times 10^{24}, 1.9 \times 10^{-12})$ for octacosane. For smaller molecules than these, σ rapidly increases and $\bar{E}$ decreases;

e.g., for n-butane $\sigma \approx 10^{28}$ ergs $^{-2}$ and $\bar{E} = \epsilon_1$ seems appropriate. When $\bar{E} \neq \epsilon_1$, it is convenient to redefine the functions (4)-(6) by using $\bar{E}$ rather than ϵ_1 in the integral limits; this convention is employed below.

For an energy distribution there was chosen the function

$$P(E) = 2\gamma E \exp(-\gamma E^2). \quad (15)$$

With the additional definition

$$\varphi = \sigma \theta + \gamma \quad (16)$$

the integral (5) can be evaluated as

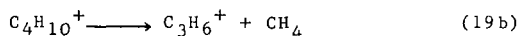
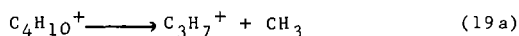
$$J(T) = (\gamma/\varphi) \exp\left[\gamma \bar{E}^2 (\gamma/\varphi - 1)\right] \times \left\{ \exp(-\gamma^2 \bar{E}^2 / \varphi) + \bar{E} (1 - \gamma/\varphi) \sqrt{\pi \varphi} \left[1 - 2 \operatorname{erf}(2\gamma \bar{E} / \sqrt{2\varphi})\right] \right\}, \quad (17)$$

which is not too cumbersome for hand calculation. For small molecules (e.g., butane), where σ is very large, Eq. (17) can be further simplified to

$$J(T) = (\gamma/\sigma\theta) \exp(-\gamma \bar{E}^2) \left[1 + (\sigma\sigma Q)^{1/2} \bar{E}\right] \quad (18)$$

Some results predicted with these approximations are compared with experimental data in Figs. 3 and 4, for C-C bond scission in n-butane and n-octacosane, respectively. The experimental data shown here were determined with 70 volt electrons using the procedure recently described by Coggeshall.⁵ The calculated curves were derived with the parameters $\epsilon_1 = 0.5$ ev, $\gamma = 0.5$ ev $^{-2}$, and the σ and $\bar{E}$ values mentioned above. Reasonable agreement is obtained between theory and experiment, although some discrepancy in the curvature of the plots is apparent.

As long as $P(E)$ is a reasonably smooth function, the ratio $I(m_1)/I(m^*)$ is apparently determined by two parameters: the activation energy; and the rate of change of $k(E)$ with E . Intensity calculations can, therefore, be used to advantage in testing these features of proposed fragmentation models. As an example of this, we have computed the metastable intensities for the processes



of n-butane using the model of Vestal, Wahrhaftig, and Johnston. The calculations were made numerically without using any of the approximations offered above. The resulting metastable intensities were orders of magnitude too small, but were brought into agreement with experiment⁵ by increasing the proposed⁹ activation energies from about 0.4 ev to about 0.93 ev. This result disagrees with appearance potentials and, therefore, indicates that some other changes are required in the model; these have not been investigated further.

We have utilized the above example of n-butane to illustrate in Fig. 5 the dependence of $I(m^*)$ upon the ionizing voltage that is predicted by the statistical theory. Once again, these calculations were performed numerically; the only change made in the model of Vestal et al.⁸ was in the activation energy

as noted in the previous paragraph. It is seen that (a) the curvature of these plots compares favorably with that in Fig. 3, and (b) as the ionizing voltage is changed the curves shift vertically but do not experience any change in shape.

IV. EXPERIMENT AND DISCUSSION

Comparison of Figs. 1 and 5 indicates that under favorable circumstances it is possible to differentiate between the models described in Sections II and III by making studies at different ionizing voltages and looking for changes in curve shapes.

Before doing experiments, it was decided to investigate the effect of field penetration on ion residence times in the various parts of the spectrometer. The approximation for field penetration described by Smythe¹¹ was employed (a detailed description will be given at a future time). Considering the ideal case of a particle traversing the central plane of a slit system, it was found that penetration of the acceleration field into the ionizing region has a profound effect on the time (t_1) required for an ion to reach the first slit. The estimated results are shown for an ion of mass 58 in Fig. 6, where t_1^0 is the ideal residence time (computed⁵ for no field penetration) and t_1 is the actual residence time. The time (t_2) required for an ion to travel from the first slit to the exit slit is almost independent of repeller voltage, and is only slightly affected by field penetration. This phenomenon further narrows the already small range⁵ of experimentally realizable residence times ($t_R = t_1 + t_2$), and makes the experiments less valuable. It should be noted that Fig. 6 shows the maximum effect of field penetration. Actually, there will always occur a distribution of residence times because ions are created at many different positions in space.

An experimental program is under way, and some typical results [for reaction (19a)] are shown in Fig. 7. These data were obtained on a CEC 21-103 instrument, with the procedure described by Coggeshall.⁵ Data for the 30.4 metastable of reaction (19b) show essentially identical behavior to those in Fig. 7.

Additional data are being obtained with the double-focussing mass spectrometer which was recently built by Weismann et al.¹² This instrument employs a grid instead of the usual first slit, and this should essentially eliminate the field penetration. In addition, the collection system incorporates an electron multiplier to increase the sensitivity. With this instrument, one can study much longer residence times than with the CEC 21-103. The data so far obtained for the 30.4 and 31.9 metastables of n-butane indicate that the curves of Fig. 7 flatten out and become almost constant at longer residence times; the curves for all ionizing voltages remain essentially parallel. Taken in conjunction with Fig. 7 and the discussion of previous sections, these data indicate that the statistical theory gives a valid description for these two reactions.

Numerous aspects of this problem require additional study for a complete understanding; and much more data are needed in order to determine if the conclusion reached is true in general.

ACKNOWLEDGMENTS

The author is extremely grateful to Dr. A. B. King, Dr. T. J. Weismann, and Mr. A. C. Lilly, Jr. for many fruitful discussions and for their aid and cooperation in obtaining the data.

REFERENCES

1. J. A. Hipple and E. U. Condon, Phys. Rev. **68**, 54 (1945).
2. J. A. Hipple, R. E. Fox, and E. U. Condon, Phys. Rev. **69**, 347 (1946).
3. J. A. Hipple, Phys. Rev. **71**, 594 (1947).
4. J. Momigny, Bull. Soc. Chim. Belg. **70**, 291 (1961). ✓
5. N. D. Coggeshall, J. Chem. Phys. **37**, 2167 (1962).
6. H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, Proc. Natl. Acad. Sci. U.S. **38**, 667 (1952).
7. S. Geltman, Phys. Rev. **102**, 171 (1956).
8. M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, Theoretical Studies in Basic Radiation Chemistry (Aeronautical Research Laboratories Report ARL 62-426, 1962).
9. M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, J. Chem. Phys. **37**, 1276 (1962).
10. J. C. Schug, J. Chem. Phys. **38**, 000 (1963).
11. W. R. Smythe, Static and Dynamic Electricity (McGraw-Hill Book Co., Inc., New York, 1950), p. 91.
12. A. C. Lilly, A. S. Kasmer and T. J. Weismann, paper presented at the Conference for Analytical Chemistry and Applied Spectroscopy (Pittsburgh, Pennsylvania, March, 1963).

A METASTABLE STATE OF THE DOUBLY CHARGED CARBON DIOXIDE ION

Amos S. Newton and A. F. Sciamaana

Lawrence Radiation Laboratory
University of California
Berkeley, California

ABSTRACT

A metastable state in CO_2^{++} dissociating into $\text{CO}^+ + \text{O}^+$ with a half-life of $2.3 \pm 0.2 \mu$ secs. has been observed. The corresponding metastable peaks are observed at $(M_1/q_1)^* = 35.6$ and $(M_2/q_2)^* = 11.6$ respectively. The widening of these peaks with accelerating voltage shows the repulsion energy to be 2.7 eV and the corresponding charge separation at fragmentation to be 5.3 Å. The appearance potential of CO_2^{++} was found to be 38.0 ± 0.2 eV, and this value is discussed in terms of the various repulsion energies and energy balances. It is concluded the data is consistent with an immediate fragmentation into CO^+ ($^2\Sigma$) and O^+ and the metastable fragmentation into CO^+ ($^2\Pi_1$) and O^+ . The fragmentation of CO_2^{++} enriched in ^{18}O has also been reinvestigated. It is shown that the unsymmetrical doubly charged molecule ion ($\text{C}^{16}\text{O}^{18}\text{O}^{++}$) has a lower yield than the corresponding symmetrical molecule ions containing ^{16}O and ^{18}O respectively.

INTRODUCTION

In 1952 it was reported that the doubly charged ion of CO_2 containing one ^{18}O atom was relatively less abundant than the doubly charged ion of normal CO_2 .⁽¹⁾ This difference was attributed to an increased fragmentation of the isotopically unsymmetrical molecule and it was suggested that the doubly substituted C^{16}O_2 should show the same fragmentation pattern as normal CO_2 . Recently higher concentrations of oxygen-18 have become available and the problem has been reinvestigated. In the course of the work it was found that a metastable state of CO_2^{++} exists and some studies have been made in regard to this metastable transition.

EXPERIMENTAL

The mass spectrometer used in this work was a Consolidated Electrodynamics Corporation Model 21-103A. The normal operation of the instrument is with an ionizing current at 37.5μ amps from a rhenium filament. Modifications described elsewhere were made for reducing the repeller voltages and anode voltage during appearance potential measurements.⁽²⁾

Isotopically enriched O_2 was prepared by the electrolysis of water enriched in ^{18}O . The resulting O_2 was purified by passing it through a liquid N_2 trap, condensing it in a liquid hydrogen trap with pumping to as low a pressure as possible. Only traces of N_2 were detectable as impurities in the O_2 . Carbon dioxide was prepared from this O_2 by exploding an exactly 2 to 1 molar ratio of O_2 and C_2N_2 in a quartz vessel. The yield of CO_2 was almost quantitative and trace impurities of CO , NO and NO_2 were removed by trap-to-trap distillation using -196°C and -140°C traps. The resulting enriched CO_2 had an ^{18}O content of 58.1% and was isotopically equilibrated.

EXPERIMENTAL RESULTS

In a CEC-103 type mass spectrometer in normal operation, ion repellers in the ion source are run at a constant fraction of the accelerating voltage in order to keep the ion collection efficiency constant. The actual ionizing voltage is, however, a function of repeller voltage and in an experimental determination of the effect of repeller voltage on the observed voltage shift of the Kr^{++} and Ne^+ appearance potentials, 45% of the average repeller voltage was found to be added to the nominal ionizing voltage. In addition, a shield voltage is normally used behind the filament and this is normally run at about 7.5% of the ionizing voltage. This difference in voltage between the shield and filament was found to be about 70% effective in adding to the electron energy. Therefore, a nominal ionizing voltage of 70 volts in a voltage scan from 4000 to 400 volts, the effective ionizing voltage varies from 96.5 to about 75 volts using an average repeller voltage of 1.3% of V_a and a shield setting of 7.4% V_i .

In Fig. 1, the calculated actual ionizing voltage at a nominal ionizing voltage of 70 volts is shown (solid curves A) while dotted curves B show the nominal ionizing voltage at each accelerating voltage necessary to keep the actual ionizing voltage at 80 volts. The importance of this change in actual ionizing voltage with accelerating voltage in voltage discrimination work is shown in Fig. 2 where the ionization efficiency curves of CO_2^{++} and Ar^{++} show different slopes in the region from 70 to 95 volts.

With a corrected actual ionizing voltage of 80 volts, the voltage discrimination curves of CO_2^{++} and Ar^+ are identical within reading error of 0.2% from 300 to 3800 volts showing there is no mass discrimination over this mass range between 300 and 3800 volts accelerating voltage. In Fig. 3 the voltage discrimination curves of CO_2^{++} and Ar^{++} show markedly different behavior, the Ar^{++} being almost flat while the CO_2^{++} rises by almost 20% between 300 and 3800 volts. Such behavior is characteristic of 1) an ion of high

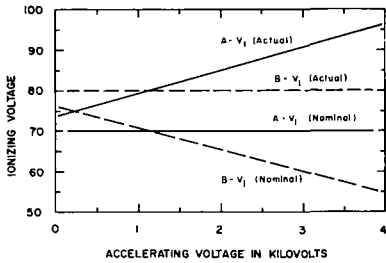


Fig. 1. Nominal vs actual ionizing voltage as a function of accelerating voltage under normal operating conditions
 A) Actual V_i for a nominal V_i of 70 V I.R. = 1.50% V_0
 B) Nominal V_i for an actual V_i of 80 V O.R. = 1.13% V_0
 Shield = 7.4% V_i

MU-30917

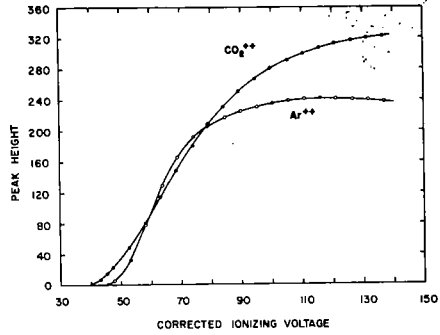


Fig. 2. Ionization efficiency curves for Ar^{++} and CO_2^{++} under normal operating conditions.

I.R. = 15.0 V Shield = 7.4% V_i
 O.R. = 11.3 V V_0 = 1000 V

MU-30918

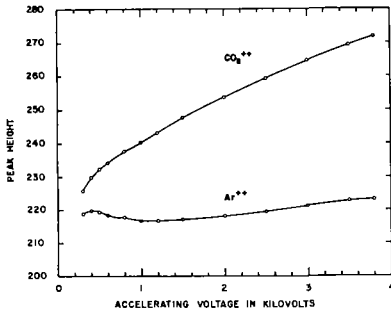


Fig. 3. Accelerating voltage discrimination curves for Ar^{++} and CO_2^{++} at V_i (actual) = 80 V.

MU-30919

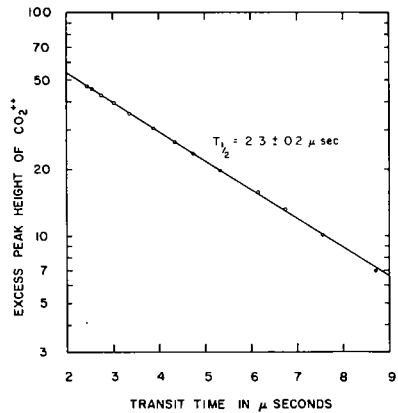


Fig. 4. Decay of $CO_2^{++}(m)$ in transit from formation in ion source to collector.

MU-30920

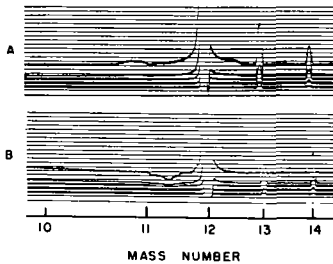


Fig. 5. Metastable peak from $CO_2^{++}(m)$ at $(M/q)^m = 11.6$. Scanned at $MV_0 = 38,000$, $400 \mu CO_2$, nominal $V_i = 70$ V.

A - metastable suppressor grounded
 B - metastable suppressor at 1.016 V_0

MU-30921

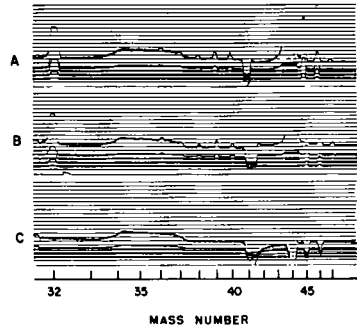


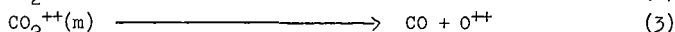
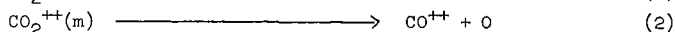
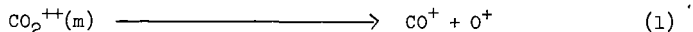
Fig. 6. Metastable peak from $CO_2^{++}(m)$ at $(M/q)^m = 35.6$. Scanned at $MV_0 = 121,600$, $400 \mu CO_2$, nominal $V_i = 70$ V. Galvanometers off at $M/q = 44$ in A and B.

A - metastable suppressor grounded
 B - metastable suppressor = 1.016 V_0
 C - metastable suppressor = 1.048 V_0

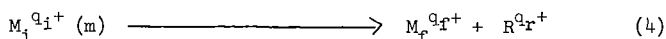
MU-30922

initial kinetic energy or 2) a metastable ion decaying in flight. Since there is no physical process by which a molecule ion of appreciable initial kinetic energy can be formed by electron irradiation with 80 volts electrons, it was concluded that process 2) was the cause and a metastable form of CO_2^{++} exists. Subtraction of the curves in Fig. 4 after normalization of the Ar^{++} peak heights by trial and error yield a straight line semi-log plot when the abscissa is converted to a time scale from time of formation to time of collection. Figure 4 shows a half-life of 2.3 ± 0.2 μsec for the metastable ion. This same value was obtained whether CO_2^{++} and Ar^{++} were run separately or together. The probable error, ± 0.2 μsec , placed on this value is an estimate of the maximum the curves can be shifted by ignoring the low voltage points and the possible error on the constancy of the actual ionizing voltage of 80 volts. In Fig. 4 all points were corrected for leak rate as each curve required about 15 minutes to run, the time being consumed in resetting the magnet and the nominal ionizing voltage for each point.

If CO_2^{++} exists in a metastable state, there are three possible ways it can decay.



According to the generalized metastable transition equation, the apparent M/q of the product ions from the transition:



$$(M/q)^* = (M_f/q_f)^2 \div M_1/q_1 \quad (5)$$

Calculations on reactions 1, 2, and 3 show that in 1) the metastable ions should appear at apparent masses of 35.6 for CO^+ and 11.6 for O^+ , reaction 2) the apparent mass of CO^{++} should be 8.9 and for reaction 3) the O^{++} should appear at mass 2.9. A search for these metastable peaks showed broad peaks at about mass 11.6 and mass 35.6 as shown in scans A of Figs. 5 and 6 respectively. No other metastable peaks were seen at 400 μ pressure and 37.5 μamps ionizing current.

The kinetic energy of these ions, i.e., the metastable suppressor voltage required for cutoff of the peaks is readily shown to be given by equation (6) if the approximately 3% potential well in the metastable suppressor field is ignored.

$$V_{\text{mss}} = V_{\text{acc}}(M/q)^* \div M_f/q_f = V_{\text{acc}} M_f/q_f \div M_1/q_1 \quad (6)$$

From this equation it is seen that the mass 11.6 peak should be cut off at 72% of the accelerating voltage while 127% of the accelerating voltage would be required to cut off the mass 35.6 peak. In Fig. 5 curve B at the normal metastable suppressor setting of 1.6% above the accelerating voltage mass 11.6 peak is eliminated. The dip at mass 11.3 in both A and B is caused by negative ions created by mass 12. In Fig. 6 curves B and C show that even at the maximum setting of the metastable suppressor, 4.8% above the accelerating voltage there is no effect on the mass 35.6 peak. Curve C shows every normal peak eliminated and, in fact, reversed, owing to negative ion creation when these normal ions are retarded back to the collector slit. The behavior with metastable suppressor of these two metastable peaks is confirming evidence of their creation from doubly charged ions by reaction (1) as a metastable peak can only have a higher kinetic energy than its parent ion when the fragment ion is of higher M/q than the parent ion.

Some Soviet work⁽³⁾ has reported a number of collision-induced transitions in CO_2 giving rise to peaks at masses 3.27, 5.14, 5.82, 9.14 mass units. Under our operating conditions we see none of these peaks. Table I shows the effect of pressure on the metastable peaks at masses 11.6 and 35.6 showing their peak height to be linear with pressure

Table I. Effect of Pressure on Metastable Peak Height

$P(\mu)$	PEAK HEIGHTS	
	$(M/q)^* = 11.6$	$(M/q)^* = 35.6$
100	0.2	0.5
200	0.5	1.1
400	1.0	2.2

hence from a bimolecular process. The width of the peaks is caused by charge repulsion of the fragments on separation. From the change in peak width with accelerating voltage, i.e., transit time, and assuming the maximum width to be due to those ions with kinetic energies perpendicular to the trajectory and decaying at the ion source accelerating slit, the kinetic energy of each of these ions has been calculated as shown in Table II. The

calculated energy for each ion result in good agreement of total kinetic energy and corresponds to a charge separation of 5.3 Å at separation. This appears to be a reasonable value if the charges at fragmentation are located on the oxygen atoms, it being only slightly over twice the normal distances between oxygen atoms in CO_2 .

Table II. Fragmentation Energy and Charge Separation in CO_2^{++} (m)

	MV	Peak width mass units	ΔW (m.u.)	Calculated K. E. eV
Mass 11.6	38000	1.8 ₆	1.6 ₄	1.7 ₂
	11310	3.5 ₀		
Mass 35.6	121600	4.1 ₀		
	38400	6.6 ₀	2.5 ₀	1.0
Observed Total K.E.				2.7 ₂ eV

Calculated Total K.E.

1) from O^+ ion = 2.70 eV

2) from CO^+ ion = 2.75 eV

Charge separation from K.E. of fragments = 5.3 Å

Appearance potential curves on CO_2^{++} have been run at various accelerating voltages, in each case comparing them to a Kr^{++} standard run at the same voltage to see if the formation of the metastable state could be detected in the A. P. curves. The curves appear identical and an appearance potential of 38.0 ± 0.2 volts compared to Kr^{++} at 38.56 volts found.⁽⁴⁾ One of these curves is shown in Fig. 7. The internal consistency was better than ± 0.1 volts. This compares with Dorman and Morrison's figure of 36.5 volts which appears to be low.⁽⁵⁾ The break about 6 volts above the appearance potential was also observed by Dorman and Morrison. It appears not to be connected with the formation of the metastable state but this conclusion is only tentative. The upward break in the Kr^{++} curve was also observed by Dorman and Morrison.⁽⁶⁾

Coming back to the original problem of the effect of isotopic substitution on the fragmentation probability of isotopically substituted CO_2^{++} , the results of determinations of the pattern factors of $\text{CO}_2^{++}/\text{CO}_2^+$ in the various isotopically substituted molecules at 1000, 2000, and 3000 volts accelerating volts are presented in Table III.

Table III. Ratios of $\text{CO}_2^{++}/\text{CO}_2^+$ for Various Isotopic Compositions at Various Ion Accelerating Voltages

Accelerating Voltage	PEAK PATTERN AT V_{acc}		
	1000	2000	3000
Peak Ratio			
22/44	1.41 ₅	1.63 ₇	1.82 ₁
23/46	1.34 ₇	1.55 ₈	1.73 ₁
24/48	1.41 ₁	1.63 ₉	1.82 ₁

In each case the pattern of 22 with respect to 44 is equal to that of 24 with respect to 48. In the unsymmetrical molecule, however, the pattern of 23 with respect to 46 is below the value for the symmetrical molecule by about 5%. The level of the pattern factor for CO_2^{++} with respect to CO_2^+ rises with accelerating voltage because the actual ionizing voltage increases (nominal $V_i = 70$ volts) with increase in repeller voltage as the accelerating voltage as shown in Figs. 1 and 2.

The ionization efficiency curves of all three isotopic species of CO_2^{++} extrapolate to the same value of the appearance potential (38.0 eV compared to Kr^{++} at 38.56 eV) and the curve for $M/q = 23$ shows no behavior suggesting its increased dissociation.

A study of the metastable behavior of CO_2^{++} of each isotopic composition show that

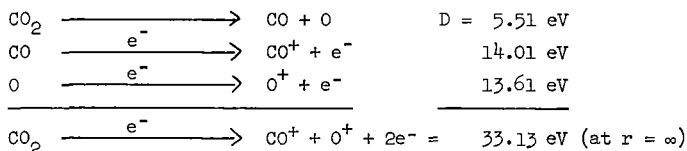
within experimental error, they all have the same half-life and initial yield (relative to the stable state of CO_2^{++}), values of 2.3, 2.5, and 2.4 μsec being observed for the half-life of masses 22, 23, and 24 respectively. Thus an increased rate of disassociation of the metastable state of CO_2^{++} in the isotopically unsymmetrical molecule $\text{C}^{16}\text{O}^{18}\text{O}$ cannot be invoked to explain the low yield of the unsymmetrical ion. The increased disassociation of this ion must be in that part of the ion which dissociates by a fast process ($t_{1/2} < 0.1 \mu\text{sec}$).

In Fig. 8 the ratios of peak heights of 23/22 and 24/22 have been plotted as a function of nominal ionizing voltage and it is seen that as the appearance potential of CO_2^{++} is approached, the ratio of 23/22 peak heights approaches that of 46/44, showing that at the appearance potential of CO_2^{++} , the molecules of all three isotopic compositions exhibit the same probability of formation as is assumed to be the case with the singly charged ions. As the data represent an extrapolation based on progressively smaller peaks, it is not possible to definitely decide whether the increased instability of the unsymmetrical molecule begins at the appearance potential or a few volts above it.

DISCUSSION

The occurrence of a metastable state of CO_2^{++} dissociating into two singly charged ions is the first such type of metastable dissociation observed. Meyerson and Vander Haar⁽⁷⁾ have reported metastable states of several doubly charged ions of aromatic compounds which dissociate into a doubly charged ion and a neutral molecule, but $\text{CO}_2^{++(m)}$ does not dissociate in this manner. The metastable peaks in CO_2 are diffuse owing to coulombic repulsion of the charged species which explains why they have not previously been recognized. The behavior of the $(M/q)^* = 35.6$ peak with voltage applied to the metastable suppressor demonstrates conclusively its origin from a doubly charged ion. This behavior further suggests that a general survey of the spectrum of any molecule at high metastable suppressor values will show the presence or absence of metastable peaks where M/q of the final ion is greater than M/q of the initial ion, i.e., a doubly charged ion breaking into heavier and lighter fragment ions. The metastable peak observed will, of course, be due to the heavier ion. This method is of limited utility at present owing to the reversal of all normal peaks and the occurrence of dips several mass units before high singly charged peaks which result from negative ions produced when these ion beams strike the collector slit. A modification of the metastable suppressor will be required before the method can be applied to complex molecules.

The observed appearance potential of CO_2^{++} (38.0 eV compared to 38.56 eV for Kr^{++} standard) can be reconciled with the measured repulsion energy of CO^+ and O^+ from the metastable state, only if the CO^+ from the metastable state is formed in an excited state, $2\Pi_1$ state, at 2.53 eV above the $2\Sigma^+$ state of CO^+ .⁽⁸⁾ Hall⁽⁹⁾ has observed a high kinetic energy O^+ ion of 3.5 eV kinetic energy in the mass spectrum of CO_2 and measured the appearance potential of this ion as 35 eV compared to his observed value of 36 eV for CO_2^{++} . If this O^+ is from the fragmentation of CO_2^{++} , and the appearance potential suggests this to be the case, then the repulsion energy of fragmentations is about 5.0 eV and the following energy balance can be set up.



If one adds to this the 5.0 eV repulsion energy calculated from Hall's observed O^+ energy, the result, 38.13 eV, balances our observed appearance potential quite well. The only way, however, the repulsion energy of the metastable state can be brought into agreement with the formulation is for the metastable state to dissociate into O^+ and the $2\Pi_1$ state of CO^+ , with the resultant total energy now being 38.3 eV. These numbers are certainly within experimental error of each other, and imply a fairly shallow well in the CO_2^{++} curve as well as an intersystem crossing between the states dissociating into O^+ and the $2\Sigma^+$ state of CO^+ and the state dissociating into O^+ and the $2\Pi_1$ state of CO^+ . We cannot, however, draw the actual potential energy surfaces for these two states from this meager data. The above correspondence of energies may be fortuitous and the actual situation more complicated than that suggested above. The above formulation of the double ionization process does not agree with that proposed by Dorman and Morrison⁽⁵⁾ who suggest the doubly charged ion of CO_2 is formed from the separated products $\text{C}^+ + \text{O}^+ + \text{O}$ rather than $\text{CO}^+ + \text{O}^+$.

We have not been able to isolate the high kinetic energy 3.5 eV O^+ ion observed by Hall. Rather the high kinetic energy O^+ ions we observe in CO_2 at low accelerating voltage and high metastable suppressor settings cover a broad band in which peaks at 1.7 volt and 3.5 volt could be overlapping without resolution. Further, there is no conclusive proof that the observed high kinetic energy O^+ ions are all formed from the doubly charged state, rather than almost wholly or at least partly from a high lying repulsive state of CO_2^+ .⁽²⁾

This work was performed under the auspices of the U.S. Atomic Energy Commission.

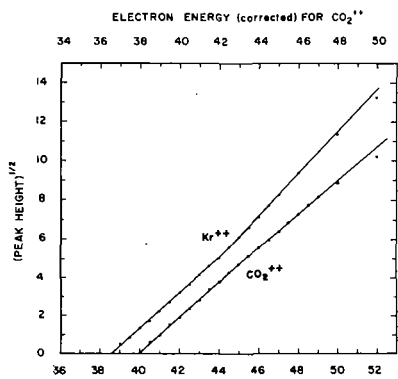


Fig. 7. Ionization efficiency curves for CO_2^{++} and Kr^{++} .
 $V_g = 1000$ V, Repellers ~ 1 V, Shield = 0

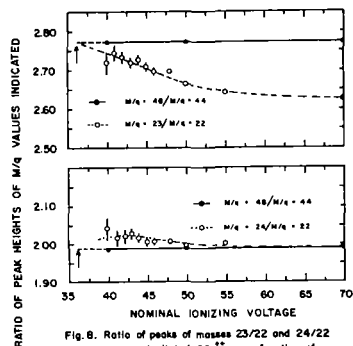


Fig. 8. Ratio of peaks of masses 23/22 and 24/22 in isotopically substituted CO_2^{++} as a function of nominal ionizing voltage.

Arrow points to CO_2^{++} A.P. on this voltage scale.

REFERENCES

1. Newton, A. S., J. Chem. Phys. 20, 1330 (1952).
2. Olmsted, J. III, K. Street, Jr. and A. S. Newton. Olmsted, J. III, UCRL Report 10687, Lawrence Radiation Laboratory, Berkeley, Calif., Feb 18, 1963. J. Chem. Phys., submitted for publication.
3. Kupriyanov, S. E., M. V. Tikhomirov, V. K. Potapao and P. Ya. Karpova, Zhur. Eksptl. i. Teoret. Fiz., 30, 569 (1956). Trans. Soviet Phys. J.E.T.P. 3, 459 (1956).
4. Field, F. H. and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, 1957. p.245.
5. Dorman, F. H. and J. D. Morrison, J. Chem. Phys. 35, 575 (1961).
6. Dorman, F. H. and J. D. Morrison, J. Chem. Phys. 34, 1407 (1961).
7. Meyerson, S. and R. W. Vander Haar, J. Chem. Phys. 37, 2458 (1962).
8. Herzberg, G., "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p.522.
9. Hall, R. M. S., Nature 187, 683 (1960).

IONIZATION POTENTIAL STUDY OF HIGH MOLECULAR WEIGHT COMPOUNDS

M. R. Stevens
Rocketdyne
Canoga Park, California

ABSTRACT

The ionization potentials of 10 solid compounds are presented. Compounds examined include seven polynuclear aromatic hydrocarbons, two substituted aromatics, and one metallo-organic material. All measurements were made with a modified Bendix Time-of-Flight Mass Spectrometer equipped with a Fox-type ion source and Knudsen-cell inlet system.

CROSS SECTIONS OF ION-PERMANENT DIPOLE REACTIONS BY MASS SPECTROMETRY

Thomas F. Moran and William H. Hamill

Department of Chemistry and Radiation Laboratory
University of Notre Dame, Notre Dame, Indiana

INTRODUCTION

The integrated cross section for collision of an ion with a polarizable molecule in the ion source of a mass spectrometer has been described by Gioumouis and Stevenson² in terms of point particles. A modification of this treatment allows for the physical size of the colliding species.³ Experimental results from this laboratory^{4,5,6} have been adequately explained in terms of this description, both for large and small molecules.

The present study examines the long range forces between an ion and a molecule possessing a permanent dipole making use of the previous results concerning the hard core cross section of the colliding species.

The potential V between an ion and polarizable molecule having a dipole moment μ which is oriented in the position of minimum energy is

$$V = e\mu/r^2 + e^2\alpha/2r^4 \quad (1)$$

where e is the electronic charge, α the polarizability and r the distance between the ion and molecule. The Lagrangian equations of motion for this system were solved by standard techniques⁷ and the approximation that the relative velocity of the colliding pair is given by the velocity of the ion, the collision cross section as a function of ion energy E is

$$\sigma(E) = \sigma_D E^{-1} + \sigma_L E^{-1/2} \quad (4)$$

where σ_D is $\pi e\mu(m_1 + m_2)/m_2$ and σ_L is $\pi \{2e^2\alpha(m_1 + m_2)/m_2\}^{1/2}$. μ is reduced mass. The integrated cross section Q is

$$Q = E_e^{-1} \int_{E_i}^{E_e} \sigma(E) dE \quad (5)$$

where E_e is the energy of the primary ions at the ion-exit slit and E_i is the initial energy of the ions. Designating the transmission coefficients for chemical reaction to be P_D for interactions corresponding to σ_D and P_K for knock-on encounters in the cross sectional area σ_K and taking

$$\sigma(E) = P_D(\sigma_D E^{-1} + \sigma_L E^{-1/2} - \sigma_K) + P_K \sigma_K \quad (6)$$

we obtain, from Eqs. (5) and (6) when $E_e \gg E_i$ and $E_t < E_e$ (see below) :

$$Q = E_e^{-1} P_D \sigma_D \ln E_e/E_i + 2 P_D \sigma_L E_e^{-1/2} + \sigma_K (P_K - P_D) \quad (7)$$

with the assumption that the dipole axis and the molecule are colinear. The latter assumption is required by the very large measured reaction cross sections.

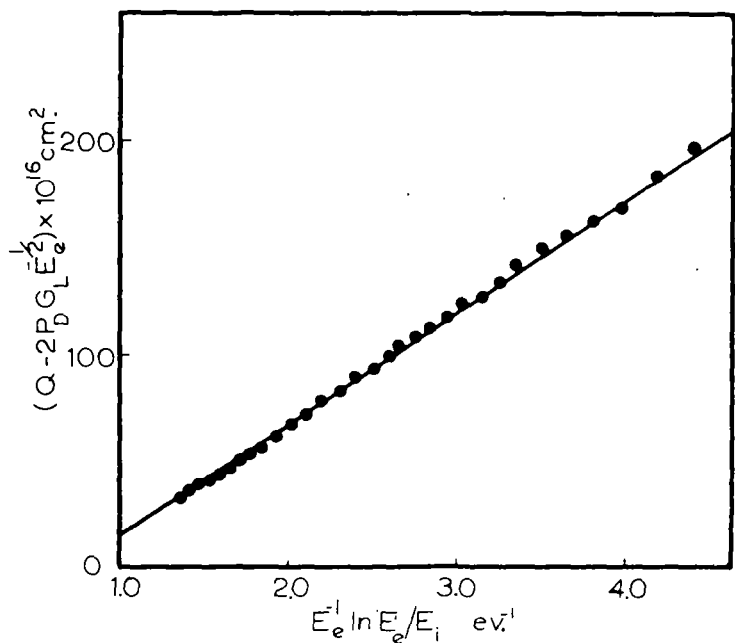


Fig. 1 $Q - 2P_D \sigma_L E_e^{-1/2}$ vs. $\ln E_e^{-1} \ln E_e / E_i$ for the reaction $\text{CH}_3\text{CN}^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{CH}_2\text{CN}$ at low ion velocity for $E_\phi > E_t$ (see Eq. 7).

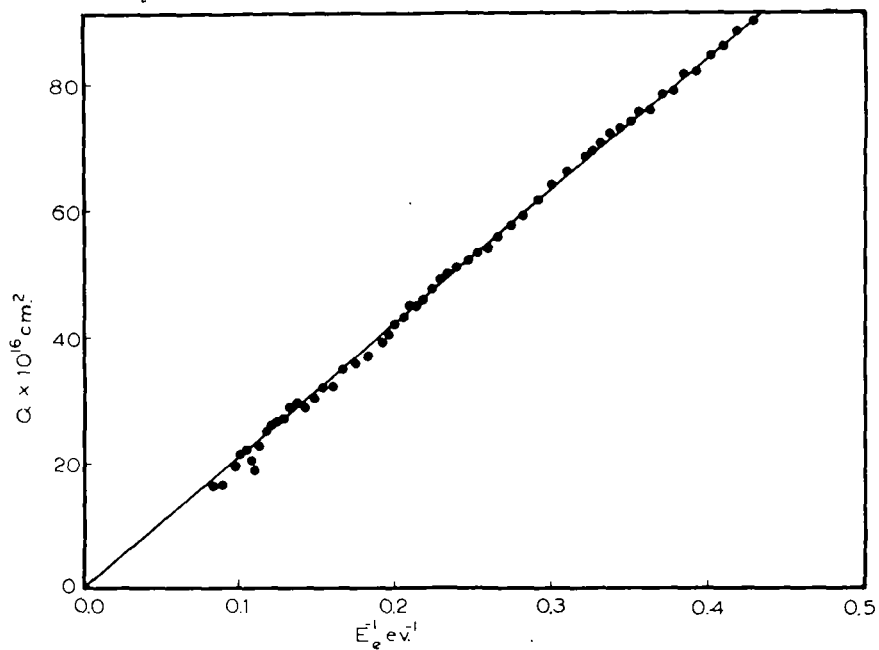


Fig. 2 Q vs. E_e^{-1} for the reaction $\text{CH}_3\text{CN}^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{CH}_2\text{CN}$ at high ion velocity for $E_\phi > E_t$ (see Eq. 8).

As the ion energy increases the energy-dependent cross section of Eq. (6) becomes smaller than and is eclipsed by, the hard molecular cross section σ_K arising from short range repulsive forces at a characteristic transitional energy E_t , viz

$$\sigma_K = \sigma_D E_t^{-1} + \sigma_L E_t^{-1/2} \quad (8)$$

At ion energy above E_t , the integral of Eq. (5) between limits E_i to E_t and E_t to E_e becomes

$$Q = E_e^{-1} \{ P_D \sigma_D (\ln E_t / E_i - 1) + P_D \sigma_L E_t^{1/2} \} + P_K \sigma_K \quad (9)$$

At the minimum of potential energy the dipole is aligned with the r vector, although libration through a small angle leads to essentially the same cross section. If all orientations of the dipole are taken to have equal probability at a distance where the cross section is determined by the ion-induced dipole forces, the cross section will be of the form $\sigma(E) = \sigma_L E^{1/2}$. However, the measured Q is an integrated cross section and there will be collisions at all ion energies to E_e . An expression for Q must take into account the possibility that at very low ion energies the molecule can assume the position of minimum energy and Eq. (7) applies.

As the ion-molecule relative velocity increases the phase angle will lag until, at some energy E_ϕ , the collision cross section no longer obeys Eq. (4) and becomes simply $\sigma(E) = \sigma_\phi E^{1/2}$. The transition is taken to be sharp, for simplicity. The integral of Eq. (5) from E_i to E_ϕ and E_ϕ to E_e , for ion exit energy settings above E_ϕ gives:

$$Q = E_e^{-1} (P_D \sigma_D \ln E_\phi / E_i) + 2 P_D \sigma_L E_e^{-1/2} + \sigma_K (P_K - P_D) \quad (10)$$

The transition at E_ϕ will be succeeded by another at E_t when $\sigma_K = \sigma_L E_t^{-1/2}$. That is for $E_e > E_t > E_\phi$ the integral of Eq. (5) from E_i to E_ϕ , E_ϕ to E_t and E_t to E_e becomes:

$$Q = E_e^{-1} (P_D \sigma_D \ln E_\phi / E_i + P_D \sigma_L E_t^{1/2}) + P_K \sigma_K \quad (11)$$

RESULTS AND DISCUSSION

Parent-daughter relationships in ion-molecule reactions are commonly assigned on the basis of appearance potential measurements. Since several primary ions may contribute⁹ when cross section measurements are made with 70 ev electrons the method can identify only the reacting ion of lowest appearance potential. The extent to which a molecular ion contributes to form a given secondary ion can be determined by comparing cross sections just above threshold and at 70 ev electron energy, except in the case of excited ion-molecule reactions as reported by Henglein¹⁰. In the present work it has been found that the most probable ionic reaction product in our ion-dipole systems is a protonated molecule and that both molecular and fragment primary ions may undergo this type of reaction. Thus, Q measured at 70 ev must be corrected by the factor $Q_{\text{threshold}}/Q_{70 \text{ ev}}$. The fragmentation pattern is one of the factors that determines the importance of contributions from ions other than the molecular ion. Since E_t and E_ϕ are affected by the mass of the primary ion, the energy dependence is quantitative only when all important contributing primary ions

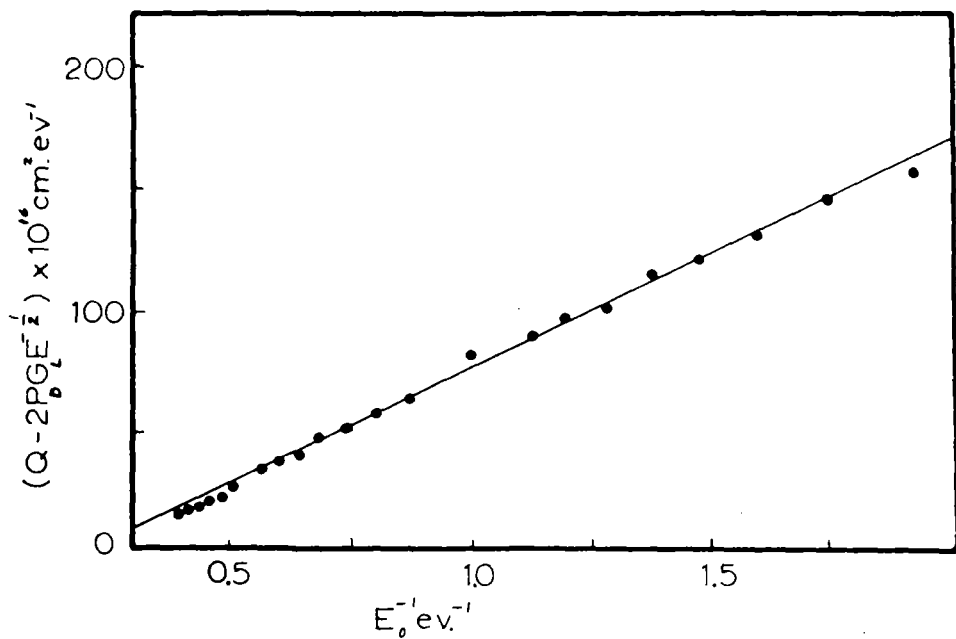


Fig. 3 $Q - 2P_{D^{\sigma}} L_e^{-1/2}$ vs. E_e^{-1} for the reaction $CD_4^+ + CH_3CH_2CN \rightarrow CH_3CH_2CND^+ + CD_3$ at intermediate ion velocity for $E_{\phi} < E_t$ (see Eq. 10).

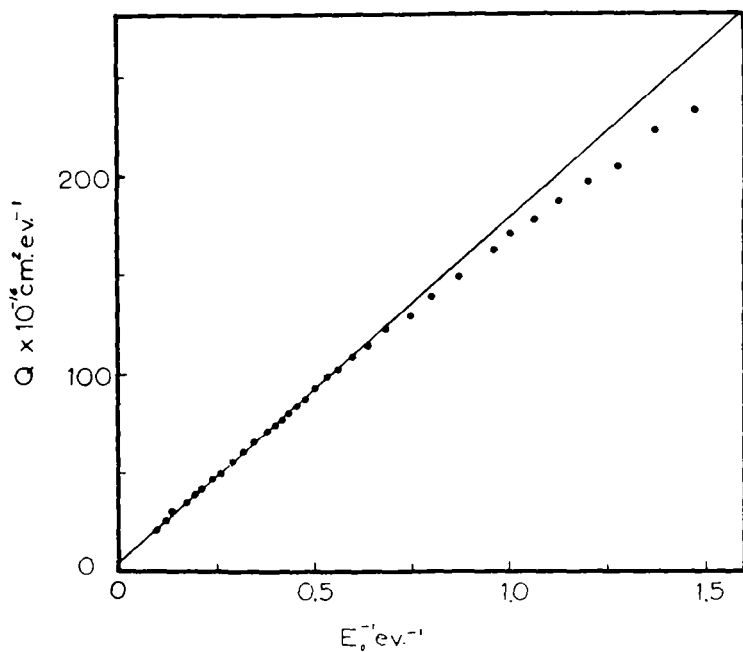


Fig. 4 Q vs. E_e^{-1} for the reaction $CD_4^+ + CH_3CH_2CN \rightarrow CH_3CH_2CND^+ + CD_3$ at high ion velocity for $E_{\phi} < E_t$ (see Eq. 11).

differ by no more than a few mass units.

When E_ϕ exceeds E_t Eq. (7) can be tested in the low energy range as in Fig. 1 by plotting $Q - 2P_D \sigma_D E_e^{-1/2}$ vs. $E_e^{-1} \ln E_e/E_i$ where E_i is determined by the temperature of the ion source, 250° . The slope is $P_D \sigma_D$ and the intercept $\sigma_K(P_K - P_D)$ according to Eq. (7). Theoretical values of σ_L and σ_D were used and trial values of P_D in $Q - 2P_D \sigma_L E_e^{-1/2}$ chosen until consistency with the required slope was achieved. The intercepts of the high and low energy regions according to Eqs. (7) and (9) are $P_K \sigma_K$ and $\sigma_K(P_K - P_D)$. σ_K can be determined from these intercepts knowing P_D from the low energy region and it is also given by Eq. (8). Above E_t , Q follows a linear E_e^{-1} dependence as in Fig. 2 and the slope is predictable using parameters established in the lower energy region.

When E_ϕ lies below E_t , Eqs (10) and (11) can be applied as in Figs. 3 and 4. When energies lower than E_ϕ are in an accessible range Eq. (7) is applicable and the data are handled in the manner of Fig. 1 where the slope is $P_D \sigma_D$. The intercepts of the high and low energy regions are $P_K \sigma_K$ and $\sigma_K(P_K - P_D)$. σ_K is determined from these intercepts knowing P_D from the low energy region and it is also given by $\sigma_K = \sigma_L E_t^{1/2}$. E_ϕ is the highest energy at which $Q - 2\sigma_L E_e^{-1/2}$ vs. E_e^{-1} deviates. E_ϕ can also be determined from the slope of $Q - 2\sigma_L E_e^{-1/2}$ vs. E_e^{-1} in the intermediate range which is $P_D \sigma_D \ln E_\phi/E_i$, knowing the value of $P_D \sigma_D$ from the low energy region. The various methods of determining the parameters agree. Above E_t , Q follows an E_e^{-1} dependence and the slope can be predicted using the parameters from the lower energy region.

REFERENCES

- 2 G. Gioumouis and D. P. Stevenson, J. Chem. Phys., 29, 294 (1958).
- 3 N. Boelrijk and W. H. Hamill, J. Am. Chem. Soc., 84, 730 (1962).
- 4 R. F. Pottie, A. J. Lorquet and W. H. Hamill, *ibid.*, 84, 529 (1962).
- 5 L. P. Theard and W. H. Hamill, *ibid.*, 84, 1134 (1962).
- 6 D. A. Kubose and W. H. Hamill, *ibid.*, 85, 125 (1963).
- 7 For example see Goldstein, Classical Mechanics, Addison-Wesley Press, Inc., Cambridge (1959).
- 9 H. VonKoch and E. Lindholm, Arkiv f. Fysik 19, 123 (1961)
- 10 A. Henglein, Z. Naturforschg., 17A, 37 (1962).

CHARGE EXCHANGE REACTIONS

Wade L. Fite
General Atomic Division of General Dynamics Corporation
John Jay Hopkins Laboratory for Pure and Applied Science
San Diego, California

ABSTRACT

This paper reviews the processes wherein the charges on two colliding particles are altered and on the experimental methods used to study these processes. In the high energy range, a comparison is made between the equilibrium beam method of determining neutralization and stripping cross sections and the slow ion detection methods used to study charge transfer. Thermal energy reactions which have been studied using afterglow mass spectrometers are reviewed and the results of various laboratories are compared. After summarizing outstanding problems pertaining to charge exchange reactions, some consideration is given to the effects of these reactions in other mass spectrometer applications.

I. INTRODUCTION

The term "charge exchange" is used somewhat ambiguously in the literature, ranging in meaning from any heavy particle collision process whereby the charge of one of the colliding particles is altered, down to the simple process known increasingly frequently in present-day literature as "charge transfer" or "electron transfer". In this review, major attention will be given to the charge transfer process which can be written down in terms of an ion, A^+ , colliding with a heavy neutral particle, B , by



where ΔE is the energy defect of the process (which in the simplest case is just the difference between the ionization potentials of A and B).

Viewing this process as a simple electronic transition, the general considerations of quasi-adiabatic theory of Massey¹ for inelastic heavy particle collisions obtain. In brief summary, these considerations hold that at low relative velocities between the colliding particles, the perturbation of the neutral particle by the passing ion changes sufficiently slowly that no electronic transition is excited. In consequence, at low relative velocities, the cross section is small. At the other extreme, that of high initial relative velocity, the time of interaction is sufficiently small that the transition does not occur readily. Intermediate to these extremes, the transition probability and the cross section reach a maximum value which occurs at a relative velocity, $v_{\max}$, given by

$$v_{\max} \approx \frac{a|\Delta E|}{h} \quad (2)$$

where h is Planck's constant and a is a length of atomic dimensions. For the case of charge transfer, Hasted² has found that $a \approx 8A$ seems to fairly well fit a large number of processes involving singly-charged ion processes.

More detailed theoretical treatment of charge transfer has been carried out by a number of authors, and reviews by Hasted² and Bates³ can be recommended as general background reading. In addition, the fact that a theoretical review is given at this meeting by Donald Rapp⁴ justifies directing our attention in this paper to the experimental aspects of charge transfer and other charge changing processes.

II. HIGH ENERGY CHARGE TRANSFER

The basic physical quantity of interest in charge transfer is the cross section as a function of energy. It is evident from Massey's formula (Eq. (2)) that for energy defects of a few ev, the ion energies at which maximum cross sections would be expected are of the order of kev, and most charge transfer measurements have been made with energies of this general magnitude. Customarily the ions have been made in an appropriate ion source, magnetically analyzed, accelerated and then permitted to pass through a gas target. In a simple charge transfer reaction such as (1), there are clearly three signals readily available for experimental use: (a) fast atom signals, (b) fast ion signals, and (c) slow ion signals; all three have been used in different experimental approaches. In most cases of interest, the charge transfer cross section is much larger than the cross section for scattering of the fast particle through an appreciable angle, so that to very good approximation, charge transfer leaves the trajectories of the two colliding heavy particles

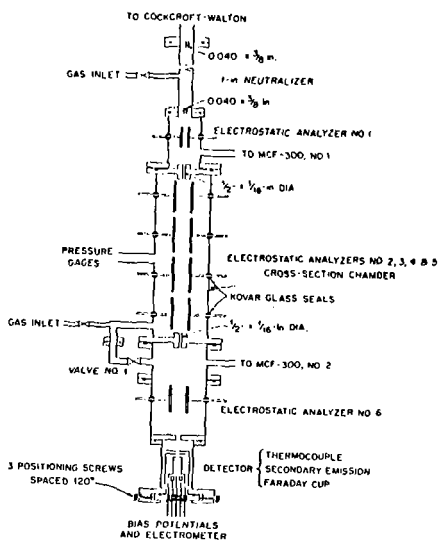


Fig. 1--Schematic diagram of the apparatus of Stier and Barnett⁶ for the measurement of electron capture and loss cross sections using fast particle detection.

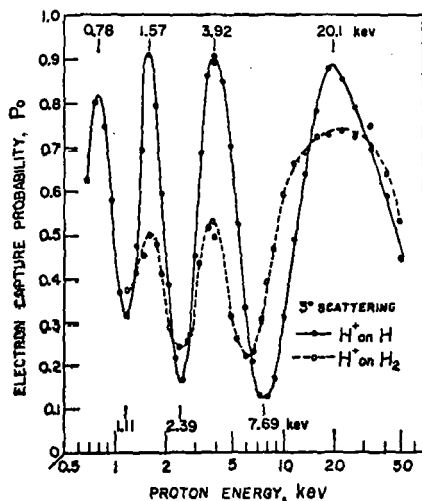


Fig. 3--Electron capture probability of protons in collision with hydrogen atoms, where the collisions are sufficiently "hard" to deflect the past particles through 3°. These data are from Lockwood and Everhart.⁷

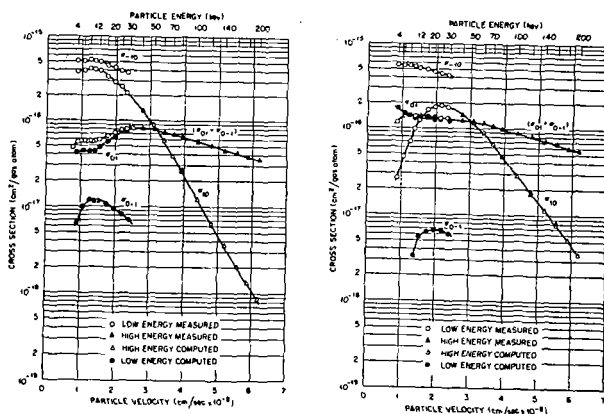


Fig. 2--Cross sections for electron capture by protons (σ_{10}), electron loss by fast hydrogen atoms (σ_{01}), electron capture by H atoms to form H⁺ ions (σ_{0-1}) and electron loss from H ($\sigma_{-1,0}$) in target gases of H₂ (left side) and He. In the H₂ data the given cross sections should be multiplied by 2 to obtain the cross section for a target H₂ molecule.

unaltered -- only the transfer of an electron from one particle to the other occurs.

A. Fast Particle Detection

One commonly used experimental method is based on an analysis made by Wien⁵ over half a century ago. It involves the use of thick gas targets and detection of fast particles. We consider here the simple case where a fast particle can be either neutral or singly ionized.

As an A^+ ion beam enters a gas of particles B at a number density n , electron capture occurs (cross section σ_{10}) and the beam becomes a mixture of fast ions and fast neutrals. The neutrals are subject to electron stripping (cross section σ_{01}), so that if we designate the fraction of fast particles which are ionized as F_1 and the fraction of fast neutrals as F_0 , then

$$dF_1/dx = n(\sigma_{01}F_0 - \sigma_{10}F_1) \quad (3)$$

and

$$F_1 + F_0 = 1. \quad (4)$$

If the target is sufficiently thick, dF_1/dx approaches zero and the beam achieves equilibrium fractions of the charge states. From Eqns. (3) and (4) it follows that the equilibrium fraction of the singly charged state is

$$F_{1\infty} = \frac{\sigma_{01}}{\sigma_{01} + \sigma_{10}} \quad (5a)$$

$$F_{0\infty} = \frac{\sigma_{10}}{\sigma_{01} + \sigma_{10}} \quad (5b)$$

and it can be shown that measurement of F_1 and F_0 as a function of the product nx yields the relationships

$$\sigma_{01} = \frac{F_{1\infty}}{nx} \log_e \frac{1 - F_{1\infty}}{F_1(nx) - F_{1\infty}} \quad (6a)$$

$$\sigma_{10} = \frac{F_{0\infty}}{nx} \log_e \frac{1 - F_{1\infty}}{F_1(nx) - F_{1\infty}} \quad (6b)$$

Similar relationships can be deduced by analogous arguments for cases where the charge states are more than two in number.

A typical piece of apparatus for measurement of "electron capture and loss cross sections" is shown in Fig. 1. This is one of several pieces of equipment used by Stier and Barnett.⁶ A beam of ions from an accelerator entered at the top of the apparatus. The beam could be neutralized by electron capture collisions, with the remaining charged species being swept out by Electrostatic Analyzer No. 1. The remaining fully neutral beam then entered the main collision chamber. The tube could be used (through use of Electrostatic Analyzer No. 6) to measure charge fractions in an equilibrated beam, but more often this apparatus was used to measure the attenuation of the fast neutral beam (with electrostatic analyzers in the main chamber being used to deviate any neutrals which became charged in collisions) to determine electron loss cross sections, σ_{01} and negative ion formation cross sections σ_{0-1} .

Figure 2 shows some of the results obtained by Stier and Barnett for the case of a fast beam of protons and hydrogen atoms interacting with H_2 (left hand graph) and He (right hand graph). Because the negative hydrogen ion H^- exists, the cross sections σ_{-10} and σ_{0-1} for stripping and forming H^- are shown in addition to the positive ion cross sections.

With regard to the positive ion charge transfer, two features are particularly appropriate to point out. The first is that the electron capture cross sections σ_{10} display peaks as suggested by the near-adiabatic theory arguments and at energies of the order of several kev. In addition, the velocity of the peak for $p + H_2$ is substantially lower than that for $p + He$, just as would be expected in view of the energy defects for the processes being about 2 and 11 ev, respectively, again in accordance with Eq. (2). The second point of interest is that the electron capture cross sections near the peak values are as large as or larger than the actual atomic sizes. Clearly the total cross section for electron capture derives its magnitude from electrons transferring from one atom to another when the atoms are substantially separated in distance. Equally obviously, there are many values of impact parameter between the colliding particles that

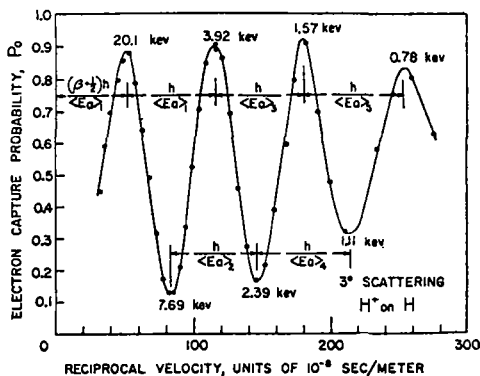


Fig. 4--The results of Fig. 3 replotted to show capture probability as a function of inverse relative velocity of the colliding particles. The regularity of the oscillatory pattern is to be noted.

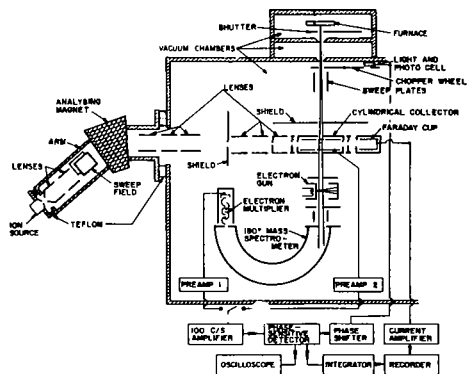


Fig. 5--Modulated crossed beam experiment of Fite et al.¹² for the measurement of the total charge transfer cross section in collisions of protons and hydrogen atoms.

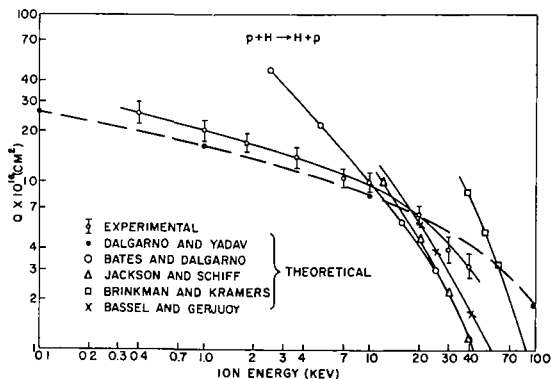


Fig. 6--Total cross section for charge transfer in proton-hydrogen atom collisions comparing experimental results¹² with several theoretical calculations. The calculation of H. G. Brinkman and H. A. Kramers (Proc. Acad. Sci. Amsterdam 33, 973, 1930) uses the simplest Born approximation. Modified Born calculations are shown in the curves of D. R. Bates and A. Dalgarno (Proc. Phys. Soc. Lond. A66, 972, 1953) and J. D. Jackson and H. Schiff (Phys. Rev. 89, 359, 1953). The calculation of R. H. Bassel and E. Gerjuoy (Phys. Rev. 117, 749, 1960) employs a distorted wave approximation. The perturbed stationary state calculations of A. Dalgarno and H. N. Yadav (Proc. Phys. Soc. Lond. A66, 173, 1953) differ substantially from the other approximations used and treat the entire collision in terms of an H_2^+ molecular ion model in which internuclear separation varies.

contribute to the total cross section.

In regard to impact parameter, it is particularly interesting to examine a different type of electron capture and loss experiment, with detection of the fast particles, which has been carried out in recent years by Everhart and his associates⁷ at the University of Connecticut. In these experiments a beam of ions is directed at a thin target of gas, and particle detection is made at a few degrees off the axis of the fast beam. From classical mechanics it is clear that a given small range of angle of detection must be associated with a very limited range of impact parameters. Further, it can be shown that the impact parameter must be much smaller than the atomic dimensions. Basically the collisions are those in which the nuclei interact to give the angular deflection, so that the ion passes through the target gas particle; and effectively only one impact parameter is under study at a time.

Everhart and his associates have concentrated their attention on the fractions of emerging fast particles which are in various charge states, and most interesting results, in this case for protons colliding with hydrogen atoms and molecules, are shown in Fig. 3. The oscillatory nature of the probability of neutralization as a function of initial ion energy gains more significance when a plot of the capture probability as a function of inverse velocity is plotted, as is done in Fig. 4. It is seen on this plot that the oscillations are quite regular.

Since the inverse velocity is a measure of the time of interaction of the two colliding particles, Fig. 4 shows that the electron, in the resonant case of $p + H$ collisions, actually oscillates between one proton and the other. Such behavior is predicted by quantum mechanical arguments presented by Firsov,⁸ Bates,⁹ and other theoreticians.¹⁰ Oscillatory behavior between particles where resonance is not obtained is also predicted and has been studied by the Connecticut group.

The oscillatory behavior is not generally seen in total charge transfer measurements, since a particular oscillatory pattern is associated with a given value of impact parameter, and all impact parameters contribute to the total cross section. The separate oscillatory patterns are thus averaged out.

B. Slow Particle Detection

Experiments which detect the production of slow ions in collisions between fast ions and slow neutrals have perhaps seen more usage for the study of charge transfer. Here there is some ambiguity between charge transfer and ion-impact ionization, both of which yield slow ions; however, the two processes can be separated by virtue of the fact that ionization also yields a slow electron. Hence, in measuring slow particles for studying charge transfer, both electrons and ions must be measured and both the ionization and the charge transfer cross sections are obtained.

The usual experimental arrangement involves taking an analyzed ion beam and passing it through a collision chamber containing a thin target of gas. Either all slow ions are measured (say to a pair of condenser plates such as were used as electrostatic analyzers in Stier and Barnett's apparatus), or mass spectrometric detection of the slow ions can be employed. An alternative method is to run the gas target as a beam and let the ion beam cross the neutral beam.

In either case, in the slow ion detection method where thin targets are used, the cross section is obtained from the formula

$$\frac{dI_B}{dx} = Q n_B I_A \quad (7)$$

where I_A is the primary current of A^+ ions, $\frac{dI_B}{dx}$ is the current of ions B^+ produced per unit path length of I_A through the gas of number density n_B , and Q is the total cross section for slow ion production (or charge transfer after correction has been made for ionization of B particles by the fast ion beam).

Figure 5 shows a block diagram of a crossed beam experiment for charge transfer measurement, this particular one being selected because it has been used to measure the total cross section for $p + H$ charge transfer,^{11,12} which was the case for which data from Everhart were presented to illustrate the oscillatory nature of charge transfer. This apparatus, which was used at General Atomic to study hydrogen atom charge transfer, takes a beam from a furnace source, modulates the beam mechanically, and then crosses it with the fast ion beam. Slow ions are collected either by a total ion collector or in the mass spectrometric detector shown. The modulation is interposed in order to distinguish charge transfer with beam particles as opposed to charge transfer with the background gas in the vacuum chamber. The beam signals are ac at the modulation frequency, and the background gas gives rise to dc signals which can be separated electronically.¹³

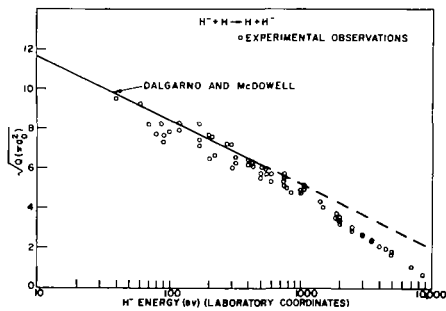


Fig. 7--Cross section for charge transfer between H and H atoms compared with the perturbed stationary state calculation of Dalgarno and McDowell¹⁵.

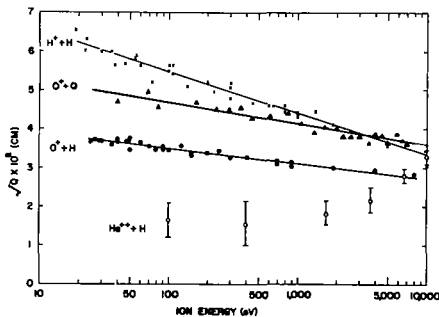


Fig. 8--Cross sections for the symmetrically resonant charge transfer collisions between H and H, and between O⁺ and O. The accidentally resonant process between O⁺ and H is seen to display the characteristic of resonant charge transfer over the energy range in this figure, but the process He⁺ + H -> He (n=2) + H⁺ does not. The data are from Ref. 15.

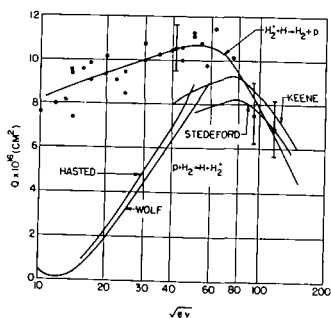


Fig. 9--Data¹¹ comparing the inverse charge transfer processes $H^+ + H_2 \rightleftharpoons H + H_2^+$.

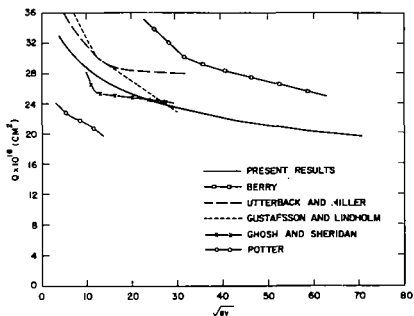


Fig. 10--Comparison of data for the charge transfer process between H⁺ and H₂. Curves shown are from R. F. Potter (J. Chem. Phys. 22, 974, 1954), S. H. Ghosh, and V. P. Sheridan (J. Chem. Phys. 27, 1436, 1957), E. Gustafsson and Y. Lindholm (Arkiv Fysik 18, 219, 1961), R. O. Utterback and G. H. Miller (Rev. Sci. Instr. 32, 1101, 1961), and R. W. Berry (Phys. Rev. 74, 848, 1948). The "present results" are those of R. F. Stebbings, B. R. Turner, and A. C. E. Smith (J. Chem. Phys. 38, 2277, 1963).

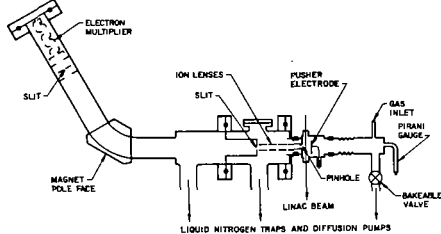


Fig. 11--Afterglow mass spectrometer used by Pite et al.²⁶ to study thermal-energy charge exchange and ion-atom interchange collisions.

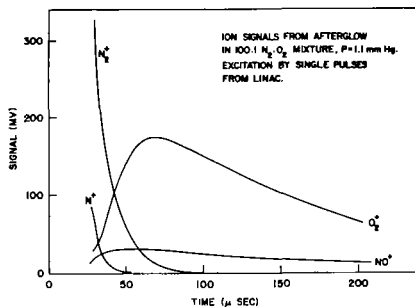


Fig. 12--Overlay of oscilloscope traces in an afterglow mass spectrometer experiment in a 100:1 H₂:O₂ gas mixture. Data are from Ref. 26.

Results for $p + H$ charge transfer are given in Fig. 6, and the experimental data are compared with several theoretical calculations for this process. Of particular interest is the absence of a peak in this cross section curve. This is expected, however, because of the fact that the process is fully resonant. Not only is there no energy defect, but the ions, both before and after, are identical -- they are single protons.

Figure 7 shows another total cross section curve, in this case for $H^- + H$ charge transfer, which is also a symmetric process. The purposes in showing this curve are two: first, to illustrate the fact that charge transfer occurs with negative as well as positive ions, and second to illustrate that resonant charge transfer has a cross section depending on energy as

$$\sigma^{1/2} = A - B \log E.$$

This energy dependence is quite predictable theoretically and the comparison of the prediction of Dalgarno and McDowell¹⁴ is seen to be quantitatively quite satisfactory.

These two cases represent an extremely simple situation where the process is fully resonant. We have seen in the data of Stier and Barnett the case of two non-resonant processes, $p + H_2$ and $p + He$. Yet, a third general case in charge transfer is that of "accidental resonance", by which it is meant that the energy defect is zero but the two ions are not chemically identical. Considerable interest accrues to these cases and in passing it is of interest to consider Fig. 8. This figure¹⁵ shows two resonant cases, $H^+ + H \rightarrow H + H^+$ and $O^+ + O \rightarrow O + O^+$, and two accidentally resonant cases, $O^+ + H \rightarrow O + H^+$ and $He^+ + H \rightarrow He^+(n=2) + H$. It is seen that over the energy range examined the $O^+ + H$ charge transfer appears to be resonant but that the $He^+ + H$ process does not, despite the fact that $He^+(n=2)$ and H have identical ionization potentials. The important point in connection with accidental resonance is that the effective energy defect is not necessarily the infinite separation energy defect; that the effective energy defect should be thought of as the difference in energy between the two quasi-molecular states at the internuclear separation at which the charge transfer actually occurs. Illustrating this point, as the He^{++} and H approach, forming a quasi $(He^{++}H)$ molecule, polarization of the H by the He^{++} makes a weakly attractive force between the two. As the two separate after the charge transfer, coulomb repulsion in the quasi (He^+H) molecule is operative. The potential energy which has to be added at the separation at which the electron transfer takes place can be thought of as the effective energy defect, which, in the case of $He^{++} + H$ charge transfer is of the order of 7 ev. By similar arguments, one would expect that at very low energies the $O^+ + H$ charge transfer might no longer appear resonant. The differences in the polarizabilities of the H and O atoms would introduce a small energy defect at separations at which the electron transfer could occur and at the lowest relative velocities there would be insufficient perturbation to excite the electronic transition over this small energy defect.

The cases which have received the major experimental attention are those involving no resonance whatever. Reviews such as are given in references 2, 16, 17, and 18 and a compilation of charge transfer cross section measurements assembled by O. Heinz and E. J. Reiner¹⁹ summarize excellently almost all of the results which were obtained up to about 1960. Generally speaking, the non-resonant charge transfer results are rather similar to those given in Fig. 2 and in Fig. 9 and extend to lower energies the results for $H^+ + H_2$ charge transfer.

Figure 9 is also presented here for a second reason -- to illustrate some of the remaining problems in higher energy charge transfer measurement. This figure treats the inverse processes, $p + H_2 \rightleftharpoons H + H_2^+$. One would expect on the basis of detailed balancing that these two processes would have similar cross section curves when plotted as a function of relative velocity. Although Fig. 9 is a plot on the basis of energy rather than velocity, it is clear that the data of Fite, Brackmann, and Snow¹¹ on $H_2^+ + H$ give much larger cross sections at lower energies than would be expected. Presumably the differences arise because of uncertainty of the actual states of both the reactants and the products. In the forward reaction, for example, the state of the H_2^+ is unknown, although at these low energies the H must almost certainly be in the groundstate. In the inverse reaction there is no assurance that the H_2^+ from the ion source used gave these ions in the same states as were produced in the forward reaction. Likewise there is no assurance that the resulting H_2 in the inverse reaction was in the groundstate, although the H_2 reactant in the forward reaction certainly was.

What is being said here basically is that if we are to retain our present conceptions of the charge transfer process, it is necessary to ascribe discrepancies such as are evident in Fig. 9 to uncertainty as to the internal energy states of the particles participating in the charge transfer collision.

Perhaps the point can be further illustrated by reference to Fig. 10, which compares the results of various laboratories on the charge transfer between N_2^+ ions and N_2 . While

the same overall features of the cross section curve are forthcoming from the various data, there are serious discrepancies in the results -- far greater than differences in carefulness would seem to warrant. It is fairly obvious to hypothesize that much of the difference between the results lies in the fact that the various laboratories used different sources of the N_2^+ ions and that the populations of the ion states differed from laboratory to laboratory. Some evidence is already being gathered in various laboratories to support this hypothesis. Utterback,²⁰ for example, has recently examined charge transfer of O_2^+ on N_2 using a controlled electron bombardment source for the O_2 and has found that the charge transfer cross section curve at low ion energies depends strongly on the electron energy used to produce the O_2^+ ions. Presumably such shifts in the charge transfer curve could arise only from differences in population of states of the O_2^+ ions produced by electrons of different energies. Similar experiments have been carried out in other laboratories, and indeed the discussion of J. W. McGowan²¹ at this meeting bears very strongly on this point. Clearly, further investigation of the effects of initial ion states in charge transfer collisions will constitute a major direction for research in heavy particle collisions in the immediate future.

In addition to concern with initial states of the reactants, another rather recent direction for charge transfer collision experimentation involves determination of the final states of products. In these researches, detection of excited products has been made spectroscopically for the most part. Kistemaker and his associates²² have used a grating spectrometer in conjunction with otherwise conventional apparatus to detect the states of both neutral and ionic products in heavy particle collisions, and similar experiments involving excitation of the Balmer series when using hydrogenic ions have been carried out at the University of Arkansas. Experiments by Dunn, Geballe, and Pretzer²³ have used iodine-vapor-filled photon counters²⁴ to detect Lyman- α production in collisions of protons with various gases, and experiments to study both charge transfer and excitation into both the 2S and 2P states in collisions of protons and atomic hydrogen are now under way using crossed beam techniques at General Atomic. Perhaps this last case will be of particular value in comparing experiment with the theory of charge transfer into excited states, for the $p + H$ collisions have received the most detailed theoretical treatment.

Unquestionably, in the area of high energy charge transfer, the role of internal energy in the reactants and the products is the major enigma at present.

III. LOW ENERGY CHARGE EXCHANGE

Experiments on charge changing collisions which employ ion beams begin to fail as the energy of the colliding particles is reduced, primarily because of space charge effects which limit ion currents and generate serious sensitivity and signal-to-noise problems. In combination with this fundamental problem, such practical problems as imperfections in ion-optical systems and the fairly broad energy spreads associated with most ion sources make the experimental approaches using ion beam techniques highly unattractive at energies less than a few ev.

In order to reach the thermal energy range, where heavy particle collision data are needed for several important applications, other experimental techniques must be employed. One of these, which has seen a great amount of service for several decades, involves the measurement of mobilities of positive ions in gases in drift tube experiments. Actually the measured mobility can be related only to a total collision cross section, it has long been known that the mobilities of ions in their parent gases are substantially lower than in other gases. This observation has been explained in terms of resonant charge transfer, for which the cross section is not only large but also always produces an ion starting from rest after the collision. For resonant and near resonant charge transfer, mobility measurement continues to offer an excellent experimental method.

An entirely different technique which has seen service in at least three laboratories^{25, 26, 27} involves the mass-spectrometric monitoring of afterglows. In this technique, a mixture of gases is placed in a confined volume and this mixture is then weakly ionized by a pulse of rf power or other means. After cessation of the pulse, the positive ions are fairly representative of the gases placed in the afterglow volume. As time elapses, however, the ions undergo collisions with the neutral gas molecules and both ion-atom interchange and charge exchange occur to effect a change in the relative populations of the ions. Placing a small aperture in the afterglow chamber allows the ions diffusing to the walls to be extracted, accelerated, and mass analyzed. The analyzed ion currents which are observed then indicate the different ion-neutral collision processes which are occurring in the afterglow, and the time histories of the detected ion currents give an index to the rates at which the processes proceed.

Figure 11 shows a diagram of such an experiment, this being one in use at General Atomic.²⁶ The apparatus is basically a bakeable, 60° magnetic sector mass spectrometer whose source is an afterglow chamber rather than a conventional electron bombardment source. Gas is introduced into the chamber at the right and it is excited either by a pulse of rf

power or by a pulse of electrons from the General Atomic Linear Electron Accelerator (40 mev). Ions then leave the afterglow chamber through the pinhole and are accelerated and focussed by the ion lenses. Not shown in the figure is a small electron gun placed just outside the afterglow chamber which can be used to electron-impact-ionize neutral gas escaping through the pinhole. By use of this gun, the partial pressures of gases in the afterglow chamber can be determined. The time constant of the electron multiplier used to detect the analyzed ions and its associated circuitry was made less than 1 microsecond so that quite rapid reactions can be followed with the instrument.

Figure 12 shows an overlap of oscilloscope traces observed with a 100:1 mixture of $N_2:O_2$ where the excitation was provided by a pulse of relativistic electrons from the linear accelerator. No other ions in significant quantities were observed. This figure would seem to indicate that the two major processes occurring in the afterglow are the ion-atom interchange process, $N^+ + O_2 \rightarrow NO^+ + O$, and the charge exchange process, $N_2^+ + O_2 \rightarrow N_2 + O_2^+$. Both processes appear to have very similar rates.

Before discussing further the experimental methods and results, it is appropriate to digress briefly to emphasize that in this section the words "charge exchange" rather than "charge transfer" are being used. It is to be noted that in the $N_2^+ + O_2$ process given above, the infinite separation energy defect for the groundstates is about 3 ev. Recalling that where there is an energy defect a sharp perturbation is required to effect an electronic transition, and that at thermal velocities the relative motions of the particles are insufficient to produce a sharp perturbation, it would seem that the $N_2^+ + O_2$ process yielding O_2^+ cannot be "charge transfer" in the sense of a collision-induced electronic transition if all particles are in or near their groundstates.

There is a certain appeal to considering the process yielding O_2^+ in the afterglow to be one of accidentally resonant charge transfer where the states of the resulting O_2^+ and N_2 are excited so as to make the effective energy defect be zero. While this interpretation would preserve the concept of the process still being one of "charge transfer", considerations of the type applied by Bates and Lynn²⁶ to the case of accidental resonance as opposed to true resonance in charge transfer between atoms would lead one to question this interpretation.

It would appear to this reviewer that perhaps the basic physics of thermal processes such as those that lead to O_2^+ production in collisions between N_2^+ and O_2 is not yet properly identified. It is in deference to this opinion that the whole question about the physics involved will be begged by continuing to use in this section the general term "charge exchange" rather than the more specific "charge transfer".

Returning to the matter of results from afterglow mass spectrometer experiments, there have been two methods used to obtain rate coefficients from ion history curves such as are shown in Fig. 12. In the first method, attention is directed toward the rate of decay of a single primary ion, after it has been determined that only one type of secondary ion appears to be associated with the loss of the primary ion (e.g., in the case of the charge exchange results of Fig. 12, it appears that O_2^+ only is generated by decaying N_2^+ , so attention would focus on the decay of N_2^+). After the plasma density has dropped to where electron-ion recombination can be neglected, the total decay of the primary ion arises both through collisions in the gas phase under study, with a reaction rate k , and through ambipolar diffusion to the walls of the entire plasma. Thus the overall exponential decay rate, Z , can be expressed as

$$Z = \frac{D_a}{\Lambda^2} + kp_2 \quad (8)$$

where D_a is the ambipolar diffusion coefficient of the primary ion, Λ is the diffusion length for the afterglow chamber (usually taken to be the fundamental mode when observations are limited to late times in the afterglow) and p_2 is the partial pressure of the neutral gas with which the primary ions interact to produce the secondary ions. If p_2 is very much smaller than the total gas pressure, then variations in p_2 should not affect the total pressure appreciably nor the ambipolar diffusion coefficient. Thus, by varying p_2 and observing Z , a linear plot should be obtained, the slope of which is the rate constant, with the intercept being the diffusion term.

The second method for handling data avoids the explicit consideration of ambipolar diffusion by studying the ratio of secondary to primary ion currents as a function of time. It can be shown²⁶ that the ratio, R , of number densities of secondary to primary ions at any point in the plasma is given by

$$\frac{\partial R}{\partial t} = \left[(\alpha_1 - \alpha_2) n_e + \left(D_2 \frac{\nabla^2 N_2}{N_2} - D_1 \frac{\nabla^2 N_1}{N_1} \right) \right] R + kp_2(1+R) \quad (9)$$

for a case where a single primary is producing a single secondary ion, where α_1 is the

electron-ion recombination coefficient, D_i is the ambipolar diffusion coefficient, and N_i is the ion density of the i -th species, and n_e is the electron density. Assuming that the measured ion currents are proportional to the ion densities in the vicinity of the aperture through which the ions leave the afterglow chamber, then the ratio of measured currents should obey the same expression. If the primary and secondary ions are similar in mass, charge, number of atoms, etc., it is reasonable to expect that the differences appearing in the first term in Eq. (9) would make the entire first term small. Even if it is not small, however, it becomes unimportant if one interests himself in small times where R is small and $\frac{dR}{dt} \sim kp_2$.

By using the second method of data analysis on the process in Fig. 12, the rates obtained by Fite et al.²⁶ are about $2 \times 10^{-10} \text{ cm}^3\text{sec}^{-1}$ for $N_2^+ + O_2$ charge exchange and about $5 \times 10^{-10} \text{ cm}^3\text{sec}^{-1}$ for $N^+ + O_2 \rightarrow NO^+ + O$.

To the present time, only one process has been examined by as many as three different groups of investigators using afterglow mass spectrometry. This process is $O^+ + O_2 \rightarrow O + O_2$. (Since none of the three groups used isotopic labeling, whether the process is charge exchange or ion-atom interchange is a moot question.)

Dickinson and Sayers²⁵ at Birmingham studied the decay of the O^+ ions in collisions with O_2 using an afterglow of a pulsed rf discharge in helium-oxygen mixtures and a rf mass spectrometer of the linear accelerator type. Langstroth and Hasted²⁷ at University College London did a similar experiment using similar equipment, although they excited the afterglow by a pulsed dc discharge. They too used the first method of data analysis. Both the first and second types of data analysis were applied to more recent experiments at General Atomic which used both He and Ne as buffer gases.

The rather poor state of reliability of afterglow mass spectrometry as a means to obtain thermal energy reaction coefficients is indicated by the results of the three laboratories. Dickinson and Sayers' value, $2.5 \times 10^{-11} \text{ cm}^3\text{sec}^{-1}$, is in marked conflict with Langstroth and Hasted's $1.2 \times 10^{-12} \text{ cm}^3\text{sec}^{-1}$. The General Atomic group's range of values presently lies between 4 and $8 \times 10^{-11} \text{ cm}^3\text{sec}^{-1}$, depending on experimental conditions.

The origin of these very large discrepancies in the rate constant for $O^+ + O_2 \rightarrow O + O_2^+$ is not clear. Since there were no obvious errors made in any of the investigations, it seems likely that the many unassessed complexities of the experimental technique itself are responsible in some way. Particularly suspect are such purely plasma phenomena as plasma potential variations and ion sheath formation and decay in the vicinity of the ion extraction aperture. Clearly, other experimental methods are urgently needed to study energy charge exchange processes -- methods which avoid the problems of extracting an ion from an afterglow.

Among the possible techniques to accomplish this are those of ion cyclotron resonance coupled with afterglows. Recent experiments of Wobschall, Graham, and Malone²⁹ have used ion cyclotron resonance in weakly ionized gases to determine collision frequencies from the absorption line shapes. While these experiments to date relate more closely to mobility measurements, they would seem to offer a particularly interesting possibility in regard to charge exchange collisions between non-identical species as well.

IV. CHARGE EXCHANGE AND MASS SPECTROMETRY

In light of the nature of this topical conference, it seems appropriate to conclude with some brief reference to the relations between charge exchange generally and mass spectrometry.

Clearly, the first relation is that the techniques of mass spectrometry have been widely employed in the experiments on charge transfer. Mass-spectrometric methods produce and analyze the fast beams in the higher energy experiments, and mass spectrometers are used to detect the slow ions produced in the heavy particle collision. It has been mass spectrometers which have been used to study ion decay in thermal plasmas up to the present. There is every indication that whatever form charge exchange research takes in the future, mass spectrometers of one form or another will be the major instrumental components.

Perhaps a little less obvious are the consequences of charge transfer research to more conventional mass spectrometry, however. It would seem clear that the analytical chemist should concern himself with charge transfer in the tube of his analyzer. Resonant charge transfer cross sections become large at typical mass spectrometer ion energies, and the danger of losing certain ions between the source and the detector is a very real one in some analytical mass spectrometers. Since the charge transfer cross section will depend strongly on the ion species in any given residual gas, the ion populations arriving at the detector may not be the same as those leaving the source, particularly if the vacuum in the analyzer is not the best.

Another consequence of charge transfer research of some potential interest for analytical mass spectrometry comes from the afterglow mass spectrometry experiments. In particular, the mass spectrum late in the afterglow is very rich in secondary ions as compared with primary ions. If the primary ion can exchange charge with an impurity to produce a secondary ion, then the long time that an afterglow is held permits a considerable amplification of secondary ion signal relative to the primary ion signals. As a case in point in helium of the "spectroscopically pure" classification; i.e., less than 50 ppm impurity both by manufacturer's claim and conventional mass analysis, it is found that after about 2 milliseconds in the afterglow, the major ion present is Ne^+ . Also in helium, unmeasurably small concentrations of CO are indicated in the afterglow spectrum by the appearance of C^+ , probably formed by dissociative charge exchange. Indeed it would appear that where a given charge exchange cross section is large for a primary ion and an impurity neutral, the time in the afterglow permits the ions to seek out the impurities and ionize a very high fraction of them. It seems probable that charge exchange can be used to provide ultra-sensitive detection of certain impurities in certain gases.

REFERENCES

1. H. S. W. Massey, Rep. Progr. Phys. 12, 249 (1949).
2. J. B. Hasted, "Inelastic Collisions between Atomic Systems", Advances in Electronics and Electron Physics, Vol. 13 (Academic Press, New York, 1960).
3. D. R. Bates, "Theoretical Treatment of Collisions between Atomic Systems", Chapter 14 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).
4. D. Rapp, Proceedings of this conference.
5. W. Wien, Ann. Physik 27, 1025 (1908).
6. P. M. Stier and C. F. Barnett, Phys. Rev. 103, 896 (1956).
7. G. J. Lockwood and E. Everhart, Phys. Rev. 125, 567 (1962); F. P. Ziemba, G. J. Lockwood, G. H. Morgan, and E. Everhart, Phys. Rev. 119, 1552 (1960).
8. O. B. Firsov, Zh. Eksper. i. Teor. Fiz. USSR, 21, 1001 (1951).
9. D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. A216, 437 (1953).
10. D. Rapp and R. E. Francis, J. Chem. Phys. 37, 2631 (1962).
11. W. L. Fite, R. T. Brackmann, and W. R. Snow, Phys. Rev. 112, 1161 (1958).
12. W. L. Fite, R. F. Stebbings, D. G. Hummer, and R. T. Brackmann, Phys. Rev. 119, 663 (1960).
13. W. L. Fite and R. T. Brackmann, Phys. Rev. 112, 1141 (1958).
14. A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. Lond. A69, 463 (1959).
15. W. L. Fite, A. C. H. Smith, and R. F. Stebbings, Proc. Roy. Soc. Lond. A268, 527 (1962).
16. H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Ch. VIII (Oxford University Press, 1962).
17. J. B. Hasted, "Charge Transfer and Collisional Detachment", Chapter 18 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).
18. S. K. Allison and M. Garcia-Munoz, "Electron Capture and Loss at High Energies", Chapter 19 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).
19. O. Heinz and E. J. Feinler, "Tabulation of Atomic and Molecular Charge-Transfer Cross Sections", Stanford Research Institute Report, Interim Technical Report No. 1, SRI Project No. SU-2853 (1961).
20. N. G. Utterback, private communication, 1962.
21. J. W. McGowan, Proceedings of this conference.
22. T. J. M. Sluyters, E. de Haas, and J. Kistemaker, Physics 25, 1376 (1959).
23. G. H. Dunn, R. Geballe, and D. Pretzer, Phys. Rev. 128, 2200 (1962).
24. W. L. Fite, R. T. Brackmann, and K. E. Hagen, Rev. Sci. Instr. 29, 125 (1958).
25. P. H. G. Dickinson and J. Sayers, Proc. Phys. Soc. Lond. 76, 137 (1960).
26. W. L. Fite, J. A. Rutherford, W. R. Snow, and V. A. J. van Lint, General Discussions of the Faraday Society 33, 264 (1962).

(Continued on next Page)

REFERENCES - Concluded

27. G. F. O. Langstroth and J. B. Hasted, General Discussions of the Faraday Society 33, 298 (1962).
28. D. R. Bates and N. Lynn, Proc. Roy. Soc. A253, 141 (1959).
29. D. Wobschall, J. R. Graham, Jr., and D. P. Malone, Paper No. F-6, 15th Annual Gaseous Electronics Conference, Boulder, Colorado, October, 1962.

J. William McGowan*

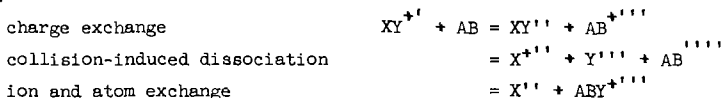
Department de Physique, Université Laval, Québec, Canada

Abstract

It is important not only to measure collision cross sections involving ground state ions (and neutrals), it is equally important, and often more so, to determine the role that excited species play in the collision. It is the purpose of this review paper to summarize what has been done thus far on excited ion-molecule collisions to; 1) identify the long lived excited ions present in the ion beam, 2) measure the concentrations of excited ions in the excited beam, and 3) measure the collision cross sections associated with these ions.

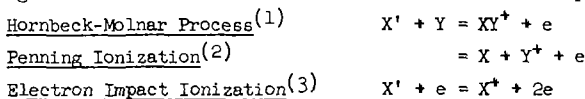
INTRODUCTION

In the following review, we will consider the effect of electronic and vibrational excitation upon some ion molecule reactions. We have chosen to consider the following reactions:



In all instances, the parent ion is excited and, in the general cases listed above, the product ion and neutrals may be either in the ground state or in any number of excited states. Exothermic, endothermic and energy resonant reactions will be considered.

Many collisions which involve excited molecules belong to the general topic of collision mass spectroscopy. Though we won't discuss them in detail we will list a few of them to give a reference which will lead to the bulk of the papers available today.



We have chosen to discuss the collisions of $XY^{+'}$ over others because these reactions have already been discussed at length by others who have spoken in these symposia. Drs. Rapp(4) and Fite(5) have reviewed the theoretical and experimental aspects of charge exchange. Prof. Lindholm(6) has discussed some particular cases of collision-induced dissociation while Dr. Dunn(7) discussed a related subject: "Anisotropy in the Angular Distribution of Dissociation Products". Prof. Hamill(8) has considered both the theoretical and experimental facets of ion and atom exchange reactions. For general reference to these subjects we may then turn to the referenced reports. We will limit our discussion to the role of excited states in ion-molecule reactions.

Before proceeding, we must determine which excited ions we are interested in. Definitely, we are interested in those excited states which are forbidden electric dipole radiation to their ground state.(9) They are designated metastable and have mean lifetimes which range from a millisecond to many seconds; which is much longer than the time necessary for us to conduct our experiments.

The second group of states which must be considered are those long-lived states(10) which are permitted dipole radiation but which have a mean life of a microsecond to many tens of microseconds. The reason for this comparatively long mean life can be seen in the equation for the probability of radiation from state m to state n, which is the reciprocal of the mean life for this transition. The relation is

$$A_{nm} = \frac{4}{3c^4} E_{nm}^3 |R_{nm}|^2 = \frac{1}{\tau} \quad (1)$$

* Presently at General Atomic Division of General Dynamics Corporation, John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California.

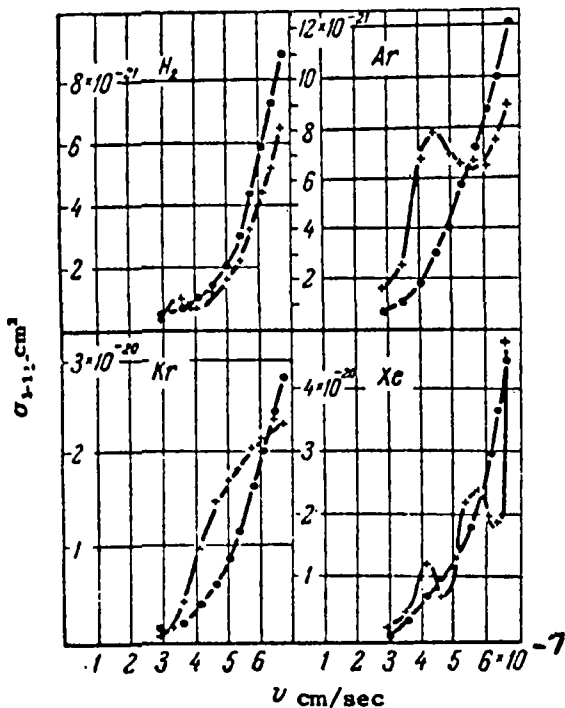


Fig. 1--A change in the double charge transfer cross section Na^+ going to Na^- resulting from a change in the parent ion source. The black dots correspond to data taken with a thermionic source while the crosses correspond to those taken with a discharge source.

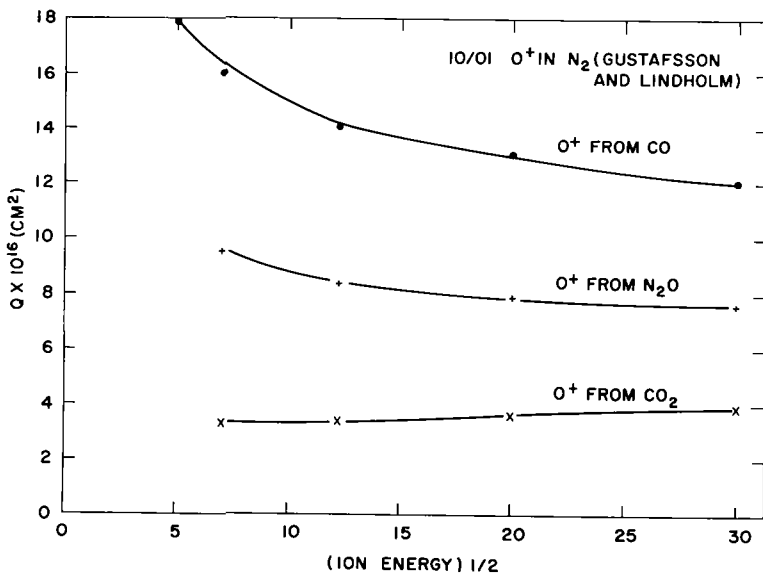


Fig. 2--A change in composition of the O^+ parent ion beam resulting from a change in source gas. This change is reflected by a dramatic shift in the total charge transfer cross section of O^+ in N_2 .

In it we see that the probability of radiation, A_{nm} , is dependent on the cube of the energy interval, E_{nm} . When the energy interval is small, the radiative mean life can be long. Similarly, from the equation we see for diatomic molecular ions that the probability is dependent upon the square of the Franck-Condon overlap integral which is contained in $|R_{nm}|^2$. When this overlap is small, i.e., when vertical transitions on the Franck-Condon picture cannot easily occur, then the probability of transition is small and the radiative mean life is correspondingly long.

The time between reactive collisions in most experiments at pressures below 0.1 mm Hg normally ranges from a fraction of a microsecond to ten microseconds. Clearly, many ions, which from selection rules are called radiative, must be included with metastable ions when we consider the action of excited ions in collision. For us then all of these ions will be treated as metastable.

Our caution in associating excited parent ions and product ions and neutrals with our ion-molecule reaction results, and now our final recognition of the role they play, parallels the method of understanding described by Lord Russell.⁽¹¹⁾ "My method invariably is to start with something vague and puzzling, something which seems indubitable but which I cannot express with any precision". He then goes on, "The process which results from prolonged attention is just like watching something approaching through a thick fog: at first it is only a vague darkness but, as it approaches, articulations appear and one discovers that it is a man or a woman, a horse or a cow or what not".

In Figs. 1, 2 and 3, we show examples of how metastables, the "vague darkness" of ion collisions, took different forms in different laboratories. In Fig. 1 we show an example from a Russian laboratory.⁽¹²⁾ In the figure are plotted cross sections for the transfer of two electrons to Na^+ ions. It is the cross section versus ion velocity which is recorded for four different gases. In each of the four cases, two different sources of ions were used; a thermionic source giving the structureless curves, and a discharge source, giving the curves with considerable structure.

In Fig. 2 we give a second example from Prof. Lindholm's laboratory. It is the asymmetric charge exchange of O^+ in N_2 .⁽¹³⁾ Here the mode of formation of the parent ion is kept constant but the gas from which the parent ion is derived is changed, giving rise to a very large change in the total cross section.

In Fig. 3 we give a third but somewhat different example taken from the work at l'Université Laval⁽¹⁴⁾ and from another of the Russian laboratories.⁽¹⁵⁾ In this case, the ion energy is kept constant while the cross section for the collision-induced dissociation of H_2^+ is measured as a function of the ionizing electron energy. As the electron energy is increased, there is a marked increase in the cross section which, after some structure, most probably approaches a pseudo-saturation like that shown in the Russian data.

In all three instances, there is apparently a change in the parent ion beam composition, which has a sizeable effect upon the value of the cross section. It seems clear then that, in all cases, we are not discussing the cross section with a ground electronic or vibrational state of the parent ion but rather we are confronted with a bulk cross section which is the sum of the cross sections for a number of states in the parent ion beam, times their respective relative populations in the ion beam.

TOTAL CROSS SECTIONS

Let us now ask what happens when we break the total ion-collision cross section curve into its component parts. Since Drs. Rapp and Fite have given us a thorough background, let us consider the general case of charge exchange,

$$X^{+} + Y = X'' + Y^{+} + \Delta E$$

Here the total cross section associated with all states of the parent ion beam can be written⁽¹⁶⁾

$$Q_T(X^+) = \sum_i Q_i \left(\frac{P_i}{\sum_j P_j} \right) \quad (2)$$

where the Q_i 's are the cross section each state of the parent while the term in brackets represents the relative population of each of these states in the ion beam. In this, the general case, it must be remembered that the Q_i 's are themselves composite cross sections; i.e.

$$Q_i = \sum_m \sum_n Q_{ijk} \quad (3)$$

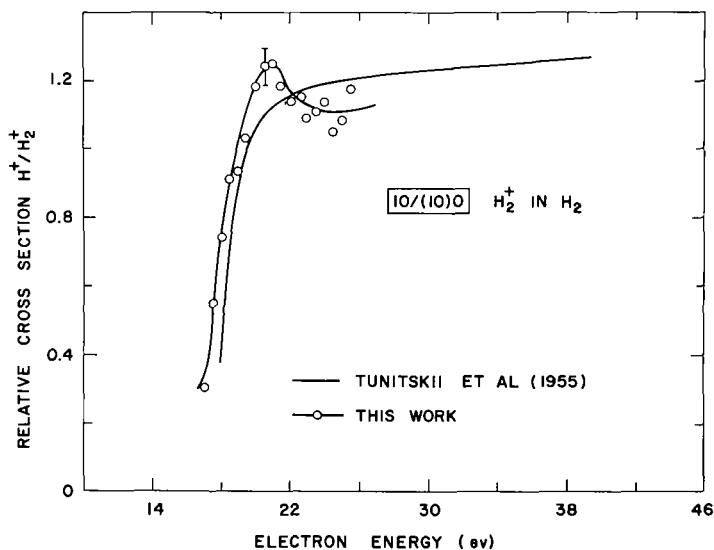


Fig. 3--Electron energy dependence of the cross section for the collision-induced dissociation of H_2^+ . The ion collision energy is fixed near 2.0 Kev.

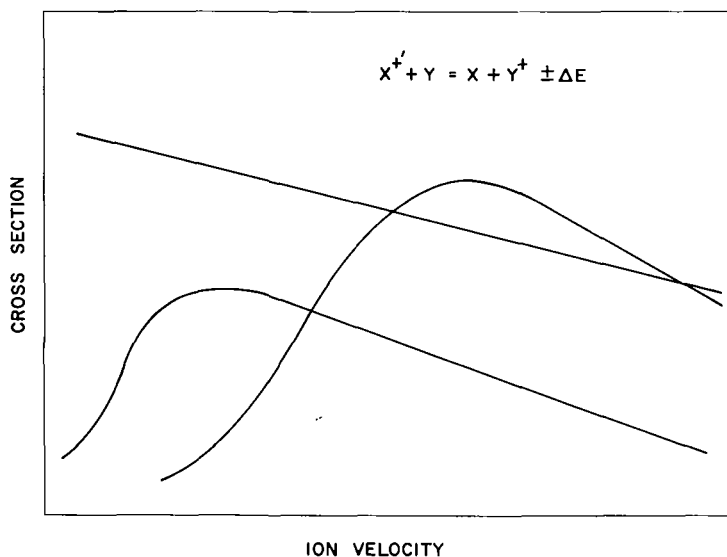
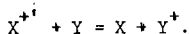


Fig. 4--Three values of charge exchange cross section associated with three different states of the parent ion. For this example, it is assumed that all products are formed in their ground state and that the ground state ions are resonant, those in the first excited state have a maximum collision cross section at low ion velocities, while those in the second excited state have their maximum charge exchange cross section at a higher velocity.

where the subscripts j and k are associated with the states of the product ion and neutral particle. As we have already shown in Fig. 3, the population of ion states in the ion beam is a definite function of the energy of the electrons which form the parent ion; i.e., $P_i = P_i(E_e)$.

Rather than discuss the general case of charge exchange, we will analyze a simpler case where the products are formed only in their ground state;



In Fig. 4, we show the cross sections associated with each of three states of the parent ion. The ground state ion in the charge exchange has a resonance form. The first excited state shows a maximum at low velocities while the second excited state has a maximum at a larger velocity.

Now in Fig. 5 we shall construct several total cross section curves that one might observe when different proportions of ions are present in the parent ion beam. When the ions of the parent beam are all in the ground electronic state, as would be the case when the ionizing electrons in the source have an energy below the appearance potential of the first excited state, the cross section is resonant (linear curve, Fig. 4). When the electron energy is increased so that the composition is (0.8, 0.2, 0) for the relative proportions of the ground, first and second excited state, we get a curve like the nearly resonant curve in Fig. 5. When the proportions are changed to (0.4, 0.4, 0.2), perhaps by increasing the electron energy, we see that the resonant form completely disappears and the structure which is associated with the first and second excited states begins to appear. Finally when the proportions reach (0.2, 0.2, 0.6), the structure which is associated with both excited states becomes pronounced.

It is from structure in the total cross section curves that Prof. Lindholm⁽¹³⁾ and Drs. Gilbody and Hasted⁽¹⁷⁾ argue for the existence of different excited states in their parent ion beams and for the formation of excited products.

From Fig. 5 we can see what would happen if the parent ion velocity were kept constant and the electron energy were allowed to vary. Clearly, at the point of cross over in Fig. 5, when the electron energy is increased, the cross section remains nearly unchanged. If we choose, instead, a velocity above the crossover point and measure the total cross section as a function of the electron energy, we find that the cross section first decreases a little and then increases as the proportion of the second excited state becomes predominant. At a velocity below the crossover, the cross section decreases as we increase the electron energy. The excited ions with lower cross section than the ground state ion essentially dilute the ion beam.

In Fig. 6 we have experimental evidence for the latter two cases.⁽¹⁸⁾ The asymmetric charge exchange of O^+ in O_2 and N^+ in N_2 show marked increases with electron energy as the proportion of excited ion states increases in the parent beams. The case of supposed resonance, N_2^+ in N_2 , shows a marked decrease as ions other than ground state ions are formed in the ion beam. This case has been verified experimentally by Dr. Utterback⁽¹⁹⁾ in recent work.

POPULATION AS FUNCTION OF ELECTRON ENERGY

We have already shown how the total cross section changes as the relative population of ground state and excited state ions changes. But even this measurement is a bulk measurement. Let us look more carefully at the ionization efficiency (IE) curve of the parent ion in order to determine something about the relative populations of states. In Fig. 7 (the upper curve) we have the IE curve for a parent ion. There are two states of the ion and our electron energy distribution is good enough so that we are able to make the separation. For simple ionization it is generally held that the probability function for a state remains a linear function of the electron energy E_e for some interval above the threshold of the next state. Some verification of this comes from the study of the H_2^+ formation where the various vibrational energy levels were identifiable.⁽²⁰⁾ Also, the work of Fox, et al and that of Foner and Nall⁽²²⁾ supply additional verification. However, there is still some uncertainty as to whether or not this linear extrapolation is always good and, if it is, over what energy interval it is applicable. If we assume that it is applicable, then at some energy E_e above the appearance potentials of the second threshold, Fig. 7, the relative proportions of each state is the slope of the curve above the threshold minus that below, times the energy interval from the threshold to E_e ; so that for the i th state,

$$P_i = (a_i - a_{i-1}) (E_e - AP_i). \quad (4)$$

If we take the parent ion of Fig. 7 into collision at some fixed ion energy, we can expect to have an "ionization efficiency" type curve for the products if we vary

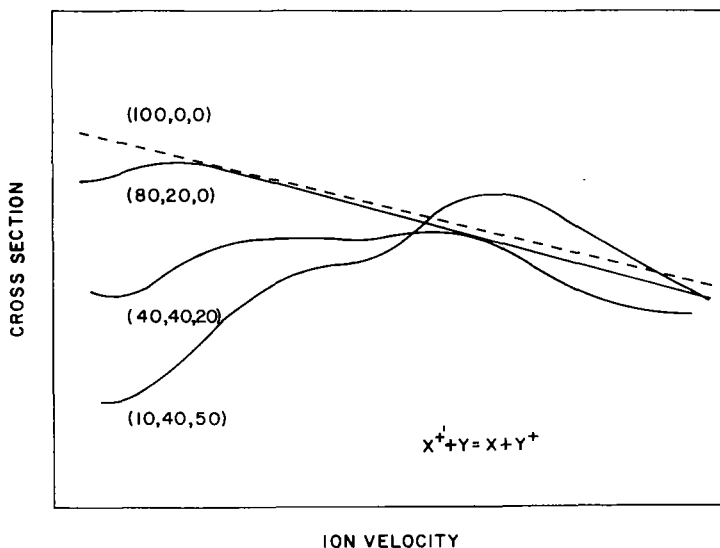


Fig. 5--
The total cross section curves when the curves of Fig. 4 are combined in different proportions. The proportions are given in the brackets.

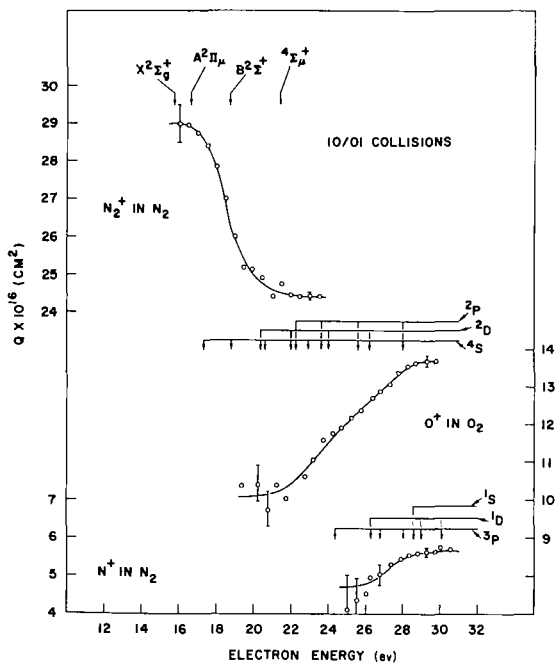


Fig. 6--Electron energy dependence of charge exchange cross section when the ion energy is fixed. The labelled arrows are associated with identified thresholds.

the ionizing energy (lower curve Fig. 7). This curve should reflect the states of the parent ion; but if the cross section for one state of the parent is markedly different from that of the other, the ratio of the differences of the slopes of the product beam to that of the parent will be different. It has been demonstrated⁽¹⁶⁾ that the cross section for each state of the parent ion can be written as

$$Q_1 = k (b_i - b_{i-1}) / (a_i - a_{i-1}). \quad (5)$$

Provided we know k , which includes the target density and dimension, we can obtain absolute values for the Q_1 's.

N_2^+ METASTABLES

Now let us see what the application of some of these methods to collision-induced dissociation tells about the excited ions in the N_2^+ ion beam. We will combine this with what has been learned from charge-exchange and ion-exchange reactions to make the picture more complete.

In Fig. 8, we show the results of the collision-induced dissociation of N_2^+ in N_2 for an ion energy of 1.6 KeV.⁽²³⁾ The total cross section curve shows simply that some non-ground-state ions, with a cross section greater than that of the ground state ions, are formed as the electron energy in the source is increased. The labeled arrows are spectroscopic thresholds either identified by others or, in the case of the $4\Sigma_u^+$ state of N_2^+ , predicted by Prof. Mulliken.⁽²⁴⁾

The relative cross section measurements are more informative. We see from the steps, the thresholds of change in cross section. These were measured in a manner similar to that described above (see Eq. 5).

In Fig. 9 we show the potential energy diagrams for the lower states of N_2 and N_2^+ as taken from the publication of Tanaka, et al.⁽²⁵⁾ (private communication with Dr. F. R. Gilmore). Comparing the thresholds of relative cross section shown in Fig. 8 with those of the diagram in Fig. 9, we see that the first contribution comes from the $A^2\Pi_u$ state of N_2^+ , which corroborates the identification of the A state as being the diluent of the parent ion beam in case of symmetrical charge exchange, as in Fig. 6. The $A^2\Pi_u$ state has also been identified by Gilbody and Hasted⁽¹⁷⁾ and by Gustaffson and Lindholm⁽¹³⁾ as contributing to their collisions. Although this state is permitted to radiate through its electric dipole, it represents a case where the energy interval between the radiating state and the ground state is small so that the mean life must be greater than several microseconds (refer Eq. 1).

As seen in Fig. 8, the next threshold is not associated with the ground vibrational state of the $B^2\Sigma_u^+$ electronic state of the N_2^+ ion but rather with some higher value. The threshold is at 19.6 eV ± 0.3 which corresponds to the $v=3$ level of this ion. From the potential diagram, and from spectroscopic studies,⁽²⁶⁾ we know there is a very strong interaction between the B and the A states at this point. It seems then, that the ions formed in the B state cross to the A state and enter into collision as ions in the A electronic state.⁽²³⁾

The next group of thresholds for collision-induced dissociation of N_2^+ appear below the predicted threshold for the metastable $4\Sigma_u^+$ state of the ion. The thresholds are⁽¹⁸⁾ 21.1, 21.5, 21.8 and 22.2 ± 0.3 eV. The thresholds for the formation of N_3^+ found in a number of laboratories agree with those found for collision induced dissociation indicating, without a doubt, that the same state or states of the parent ion are involved. Kaul and Fuchs⁽²⁷⁾ have set the N_3^+ threshold as 21.7 ± 0.5 eV. Early measurements of Cermak and Herman⁽²⁶⁾ identified this threshold with the $B^2\Sigma_u^+$ state of the N_2^+ ion but Prof. Hamill has informed me that they have since re-examined this case. The most recent study is that of Curran.⁽³⁰⁾ He used the RPD method to identify the thresholds. He finds multiple thresholds (see Fig. 10) which agree quite well with those identified through collision-induced dissociation. They are 21.04 ± 0.5 , 21.8 ± 0.1 , and 22.2 ± 0.2 eV with perhaps a fourth possible threshold at 21.5 eV.

From the weight of the combined evidence above, it seems reasonable to suggest that the position of the $4\Sigma_u^+$ state discussed by Prof. Mulliken⁽²⁴⁾ must be corrected. It would seem reasonable that it should be lowered by a large fraction of an eV and that the position of the potential minimum might be decreased by a small amount. It may well be that the position of a second metastable state, the $4\Pi_g$ not shown in the diagram of Fig. 9, may also have to be revised.

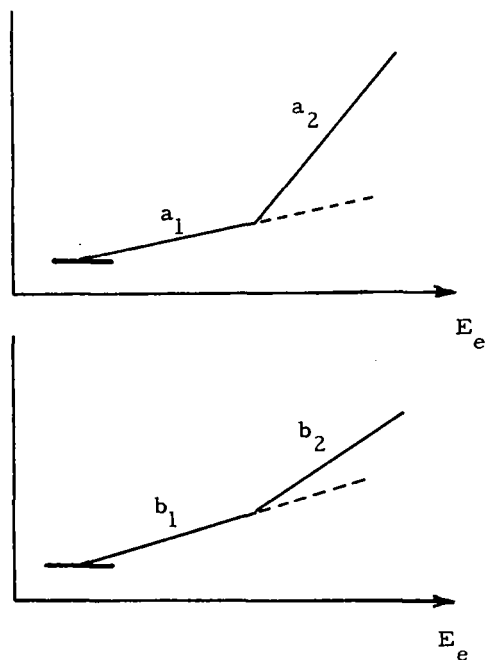


Fig. 7--An example of ionization efficiency curves near threshold of a parent ion in comparison with that of a product ion. The imaginary process in charge exchange and the parent ion beam is made up of ions in two states.

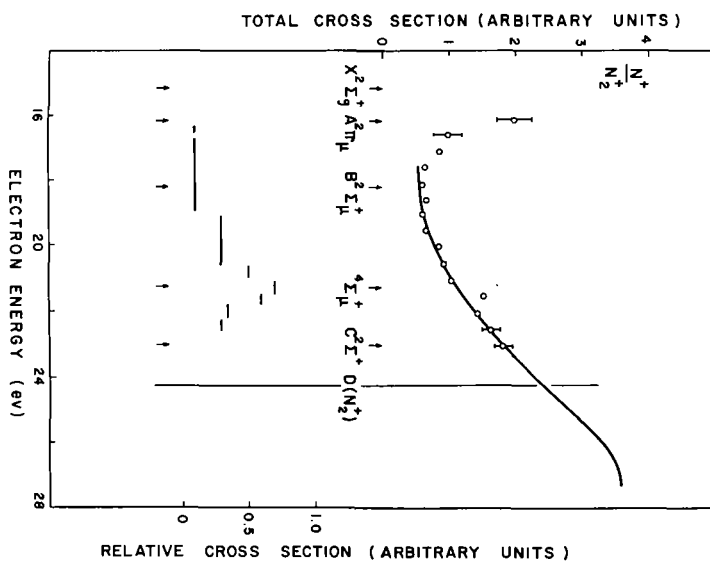


Fig. 8--Electron energy dependence of the total and relative cross sections for collision-induced dissociation of N_2^+ in collision with N_2 . Ion energy is kept constant at 1.6 Kev. The labelled arrows correspond to known or predicted structure. The beginning of each step in the relative cross section corresponds to a threshold of a new long lived ion state.

EXPERIMENTAL METHODS AND RESULTS

Finally we will discuss the experimental methods thus far applied to metastable ion molecule reactions. Associated with each method are a number of results. We shall list many of them, particularly those associated with atmospheric ions, but shall delete from the listing the numerous more complex reactions.

At thermal energies and just above them, ion-molecule reactions have been studied in the slightly modified source of the standard mass spectrometer.⁽⁸⁾ The energy range limits the study primarily to resonant and exothermic reactions. The number of such studies reflects the number of mass spectrometers in use today; however, only in a few laboratories have there been identifications of metastable ion collisions. Collisions in the mass spectrometer source are characterized by a control of gas pressures in the source and of the ionizing electron energy. By combining threshold measurements with mass spectral identification, the parent and product ions can be identified in most cases. There is limited control of the energy of the parent ion, and it would seem some confusion still exists regarding the exact laws governing ion and atom exchange reactions at low ion energies. (It follows naturally from this review to suggest that some of this confusion might result from uncertainties in the states of the particles involved.) The recent work by Curran,⁽³⁰⁾ wherein he uses near mono-energetic electron methods for ion and atom exchange reactions, is monumental. More recently, Weingartshover and Clarke⁽³¹⁾ and Hamill⁽³²⁾ have used similar methods. In Table I, we list some of the reactions recognized as involving long lived ions. With this listing we give the ion state and the reference.

TABLE I
EXCITED ION-MOLECULE REACTIONS STUDIED
IN THE MASS SPECTROMETER SOURCE

ION	PROBABLE EXCITED STATE	REACTION	REFERENCE
Ar ⁺	² P _{1/2}	Ar ⁺ + N ₂ = Ar + N ₂ ⁺	41
CS ₂ ⁺	² π _{3/2u}	CS ₂ ⁺ + CS ₂ = CS ₃ ⁺ + CS	30, 36, 37
H ₂ ⁺	¹ Σ _g ⁺ v>0	H ₂ ⁺ + He = HeH ⁺ + H	42
N ₂ ⁺	⁴ Σ _μ ⁺	N ₂ ⁺ + Ar = ArN ⁺ + N	6, 27
		N ₂ ⁺ + Kr = KrN ⁺ + N	6
H ₂ ⁺	¹ Σ _g all v	H ₂ ⁺ + H ₂ = H ₃ ⁺ + H	31
I ₂ ⁺		I ₂ ⁺ + H ₂ O = H ₂ OI ⁺ + I	38
Kr ⁺	² P _{1/2}	Kr ⁺ + CH ₄ = CH ₃ ⁺ + H + Kr	35
N ₂ ⁺	⁴ Σ _μ ⁺	N ₂ ⁺ + N ₂ = N ₃ ⁺ + N	6, 27, 28, 29, 30
N ₂ ⁺	X, v = 0, 1, 2	N ₂ ⁺ + Ar = N ₂ + Ar ⁺	41
O ₂ ⁺	² π _μ (⁴ Σ _g)	O ₂ ⁺ + O ₂ = O ₃ ⁺ + O	29, 34
O ₂ ⁺	⁴ π _μ	O ₂ ⁺ + D ₂ = O ₂ D ⁺ + D	40

More complex apparatus has been used to study ion-molecule reactions at higher ion energies. In many instances several mass spectrometers are used to separate the parent from the product ions.^(5,12,13) In some cases, this has been accomplished with one machine by using Aston banding^(15,16,48) to effect a separation. In still other cases, reactions are studied where there is not likely to be confusion between species, thus eliminating the necessity of one or more mass spectrometers (for example, see Refs. 5, 19). The higher ion energy experiments can be broken into three groups, all of which have as one variable the target gas pressure.

In the first group, the electron energy is kept constant (i.e. source conditions unchanged) but the ion energy is varied. From the structure in the total cross section curves similar to that already discussed (see Fig. 5), one can argue for the existence of excited parent and product ions and neutrals. This is characteristic of the work done in Prof. Lindholm's and Prof. Hasted's laboratories. Results of this type of experiment are listed in Table 2.

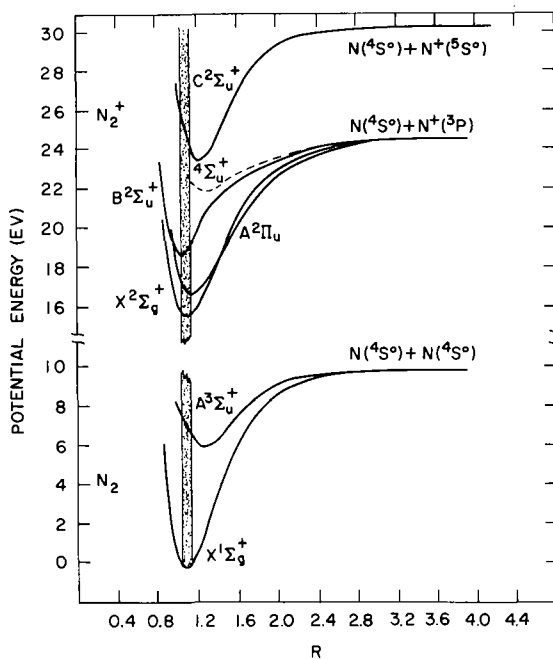


Fig. 9--The energy diagrams for some states of N_2 and N_2^+ .

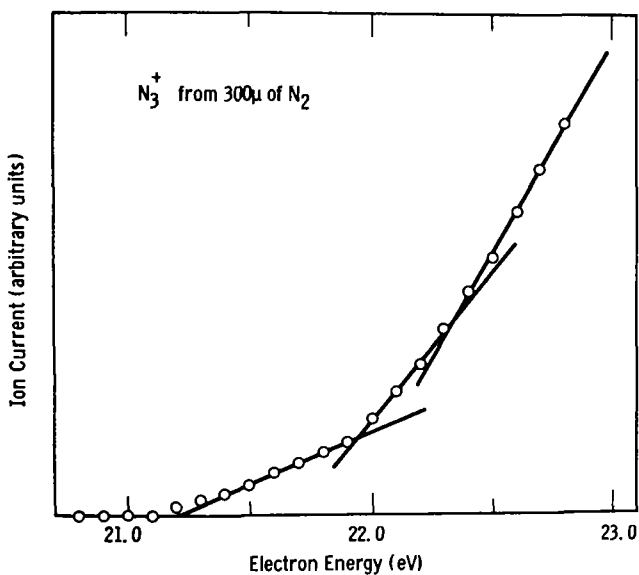


Fig. 10--The electron energy dependence of the formation of N_3^+ .

TABLE 2
EXCITED ION-MOLECULE REACTIONS AT HIGH ION ENERGIES -
SOURCE CONDITIONS FIXED AND THE ION ENERGY IS CHANGED

ION	PROBABLE EXCITED STATE	COLLISION	REFERENCE
C ⁺	⁴ P	From several reactions.	44, 17
H ₂ ⁺	¹ Σ _g ⁺ (range of v)	Several reactions.	13, 46
Kr ⁺	² P _{1/2}	Kr ⁺ + Kr = Kr + Kr ⁺	40
Li ⁺	³ S, ¹ S	Li ⁺ + Kr = Li ⁻ + Kr ⁺⁺	12
N ⁺	¹ D ¹ S	N ⁺ + Kr = N + Kr ⁺ From dissociative charge transfer	43, 17 17, 45
N ₂ ⁺	A ² π _μ	From several reactions	13, 43, 17
Na ⁺	³ S ₅ , ³ P ₂ , ³ S ₃ , ³ P ₀	Na ⁺ + Xe = Na ⁻ + Xe ⁺⁺	12
O ⁺	² P, ² D	From dissociative charge transfer	13, 12
O ⁺	² S	O ⁺ + Xe = O + Xe ⁺	45
Xe ⁺	² P _{1/2}	From dissociative charge transfer	45

In the second group of high energy experiments, the ion energy is kept constant while the source electron energy is varied. From a ratio of the ionization efficiency type curve for the product ion to that for the parent ion, we see clearly in Fig. 6, a marked change in the cross section due to an excited state in the parent beam. However, we have demonstrated that there was more to be derived from the ratio of the differences of slopes of these curves (see Fig. 7). Results of group two experiments are summarized in Table 3.

TABLE 3
EXCITED ION-MOLECULE REACTIONS AT HIGH ION ENERGIES -
ION ENERGY FIXED, ELECTRON ENERGY CHANGED

ION	PROBABLE EXCITED STATE	COLLISION	REFERENCE
Ar ⁺	near Ar ⁺⁺ threshold	Ar ⁺ + Ar = Ar ⁺⁺ + Ar + e	23, 47
	² P _{1/2}	Ar ⁺ + Ar = Ar + Ar ⁺	23
CO		CO ⁺ + CO = C ⁺ + O + CO	48
H ₂ ⁺	¹ Σ _g ⁺ (all v's)	H ₂ ⁺ + H ₂ = H ⁺ + H + H ₂	14, 15, 16
N ⁺	¹ D	N ⁺ + N ₂ = N + N ₂ ⁺	18
N ₂ ⁺	A ² π _μ B ² Σ _μ ⁺ → A ² π _μ	Several experiments. N ₂ ⁺ + N ₂ = N ⁺ + N + N ₂	18, 19 18
	⁴ Σ _μ ⁺	N ₂ ⁺ + N ₂ = N ⁺ + N + N ₂	18
O ⁺	² D	O ⁺ + O ₂ = O + O ₂ ⁺	18
O ₂ ⁺	b ⁴ Σ _g ⁺ → a ⁴ π _μ	O ₂ ⁺ + N ₂ = O ₂ + N ₂ ⁺	19
O ₂ ⁺	a ⁴ π _μ ; b ⁴ Σ _g ⁺	O ₂ ⁺ + O ₂ = O ⁺ + O + O ₂	18
	higher states	O ₂ ⁺ + O ₂ = O ⁺ + O ⁻ + O ₂ ⁺	18

Finally we might consider a third group of high energy experiments which, in reality, is a combination of the previous two. By varying both the energy of the bombarding ion and the energy of the ionizing electron which produces that ion, one can expect to trace out the cross sections associated with each of the excited states of the parent ion. The end result of such experiments is to derive curves similar to those in Fig. 4. Little work is complete but programs of this type are presently underway.^(19,49,50) At the same time, Dr. Hasted⁽³³⁾ has initiated work to produce ground state parent ions in an attempt to eliminate the confusion brought into cross section measurements by excited states.

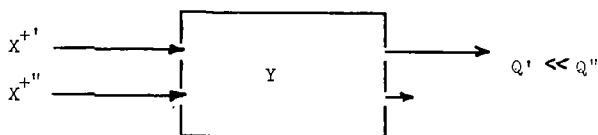
There is the possibility that still other methods will be applicable to the study of metastable ions in collisions. A group at Stanford Research Institute has begun to study the kinetic energy distribution of the charge transfer product ions as a function of their angular distribution. From this information and from the mechanics of the collision, they hope to be able to identify not only the state of the parent ion but also the states of the products. Also, the work underway in the FOM Laboratory for Mass Separation in Amsterdam, wherein the states of the charge transfer products are spectroscopically identified, no doubt will do much to further dissect the total cross section.

CONCLUSIONS

The work thus far done on excited ion-molecule reactions has pointed to the many states of the parent ion that are active in collision. Through some experiments we have obtained information about the concentrations of these ions in the beam, and through others we have been able to measure the absolute cross sections for the different states. Until recently, however, the most effort has been spent measuring bulk cross sections even though it is not certain that this information is what is needed. In many instances it definitely is not. It seems clear now that the lack of agreement between laboratories on values of some collision cross sections stems, at least in part, from differences in composition of parent ion beams.

How can we cope with this problem of excited states? In this review we have outlined some of the methods which have been applied and are being applied. (Similarly, methods are being developed for the study of neutrals as well.) But while we are in a speculative position we suggest that some of the following things might be done:

*We might develop a number of reactive sieves which would permit us to enrich our parent ion beam with one ion state or another by choosing a particular pre-collision (refer to the sketch).



*Perhaps, too, certain reactions which involve metastable states can be used to determine the metastable composition of the bombarding ion beam. For example, we can imagine that an absolute measurement of the measured reaction rate for the formation of N_3^+ might be used by others to determine the " Σ_u " content in the parent ion beam.

Since the study of excited states of ions and molecules is once again developing at a tremendous rate, this review cannot possibly be completely up to date. We trust, however, that by presenting the results of some laboratories and by describing the approaches used by them and by others, we have helped illuminate the "vague and puzzling" problem of ions in excited states entering into collision.

REFERENCES

1. Hornbeck, J. A. and Molnar, J. P., Phys. Rev., 84, 621 (1951); Munson, M. S. B., Field, F. H., Franklin, J. L., J. Chem Phys., 37, 1790 (1962).
2. Sholette, W. P. and Muschlite, Jr., E.E., J. Chem. Phys., 36, 3368 (1962); Ferguson, Eldon E., Phys. Rev., 128, 210 (1962).
3. Fite, W. L. and Brachman, R. T., 6th International Conference on Ionization Phenomenon, Paris 1963.
4. Rapp, Donald, "A Review of the Theory of Charge Exchange Between Gaseous Ion and Molecules", Proceedings of this conference.
5. Fite, W. L., "Charge Exchange Reactions", Proceedings of this conference.
6. von Koch, H. and Lindholm, E., "Dissociation Reactions of Hydrocarbons, Formed In Collisions with Positive Ions", Proceedings of this conference.
7. Dunn, Gordon, "Anisotropy in Angular Distribution of Molecular Dissociation Products" Proceedings of this conference.
8. Hamill, W. H., "Atom and Ion Exchange Reactions", Proceedings of this conference.
9. Garstang, R. H., Atomic and Molecular Processes (Academic Press, New York, 1962), Chapter 1.
10. Herzberg, G., Spectra of Diatomic Molecules (Van Nostrand Co., New York, 1950), p. 20; Nicholls, R. W., Atomic and Molecular Processes (Academic Press, New York, 1962), Chapter 2.
11. Lord Bertrand Russell, "My Philosophical Development", New York, 1959.
12. Fogel, Ya. M., Soviet Phys. Uspekhi, 3, 390 (1960).
13. Gustaffson, E. and Lindholm, E., Arkiv Fysik, 18, 219 (1960).
14. McGowan, J. Wm. and Kerwin, L., In preparation.
15. Tunitskii, N. N., et al, Dokl. Akad Nauk SSSR, 101, 1083 (1955).
16. McGowan, J. Wm. and Kerwin, L., Can. J. Phys., 41, 316 (1963).
17. Gilbody, H. B. and Hasted, J. B., Proc. Roy. Soc., A 238, 334 (1956).
18. McGowan, J. Wm. and Kerwin, L., Submitted to Journal of Geophysical Research.
19. Utterback, N., In preparation for publication and Proceedings 3rd Conference of Physics of Electrons and Atomic Collisions, London, North Holland, 1963.
20. Marmet, P. and Kerwin, L., Can. J. Phys., 38, 972 (1960).
21. Fox, R. E., Hickam, W. M. and Kjeldaa, Jr., T., Phys. Rev., 89, 555 (1953).
22. Foner, S. N. and Nall, B. N., Phys. Rev., 122, 512 (1961).
23. McGowan, J. Wm. and Kerwin, L., Proceedings 2nd Conference of Physics of Electrons and Atomic Collision, Boulder, 1961 (Bejamin, Inc.), p. 36.
24. Mulliken, R. S., The Threshold of Space (Pergamon Press, 1957), p. 169.
25. Tanaka, Y., Namioka, T., Jursa, A. S., Can J. Phys., 39, 1138 (1961).
26. Reference 10, p. 264, Private communication with Dr. F. R. Gilmore.
27. Kaul, W., and Fuchs, R., Z. Natur., 15a, 326 (1960).
28. Saporoschenko, M., Phys. Rev., 111, 1550 (1958).
29. Curran, R. K., Submitted for publication 1962.
30. Cermak, V. and Herman, Z., J. Chim. Phys., 55, 51 (1959).

31. Weingartshover, A. and Clarke, E. M., In preparation 127° Electrostatic Analyser Used For H_3^+ Formation.
32. Hamill, W. H., Group Using R.P.D. Method To Study Ion-Molecule Reactions.
33. Hasted, J. B., Adv. Electronics and Elect. Phys., 13, 1 (1960).
34. Herron, J. T. and Schiff, H. I., Can. J. Chem., 36, 1159 (1958).
35. Meisels, Hamill, Williams, J. Phys. Chem., 61, 1456 (1957); Meisels, G. G., J. Chem. Phys., 31, 284 (1959).
36. Collin, J., J. Chim. Phys., 57, 424 (1960).
37. Henglein, A., Z. Natur., 17a, 37 (1962).
38. Henglein, A. and Muccini, G. A., Z. Natur., 15a, 584 (1960).
39. Kubose, D. A. and Hamill, W. J., J. Am. Chem. Soc., 85, 125 (1963).
40. Karmohapatrd, S. B., J. Chem. Phys., 35, 1524 (1961).
41. Marmet, P. and Morrison, J. D., J. Chem. Phys., 36, 1238 (1962); McGowan, Marmet, Kerwin, Proceedings 3rd Conference of Physics of Electrons and Atomic Collisions, London, 1963, North Holland.
42. von Koch, H. and Friedman, L., J. Chem. Phys. 38, 115 (1963).
43. Hasted, J. B., Proc. Roy. Soc., A212, 235 (1952).
44. von Koch, H. and Lindholm, E., Arkiv. Phys., 19, 123 (1961).
45. Pettersson, E. and Lindholm, E., Arkiv. Phys. 24, 49 (1963).
46. McClure, G. W., Accepted for publication Phys. Rev.
47. McGowan, J. Wm. and Kerwin, L., Submitted Can. J. Phys.
48. Kuprianov, S. E., et al, Soviet Phys. JETP, 3, 459 (1956).
49. Papp, N. and Kerwin, L., Study of Collision Induced Dissociation; Hussien, McGowan, Kerwin, Study of Near Resonant Symmetric and Asymmetric Charge Exchange.

DISSOCIATION REACTIONS.

E. Lindholm

Royal Institute of Technology
Stockholm 70, Sweden

In this paper the results will be reported of some recent measurements on the dissociation of some hydrocarbon ions, obtained in collisions with positive ions. The hydrocarbons are propane, butane, deuterated propane, ethane and acetylene. All work has been performed in Stockholm.

Propane and butane.

Fig. 1 shows how the mass spectrum is obtained in a special case. Ar^+ ions are sent into the propane gas and charge exchange takes place. The Ar^+ is neutralized and gives off its ionization energy, 15.7 eV, to the propane. The propane ion that is formed is highly excited and dissociates as in an ordinary mass spectrometer.

Fig. 2 shows the apparatus [1]. The ions are produced in an ordinary mass spectrometer and are retarded before they enter the collision chamber. In the collision chamber their velocity can be varied from 900 eV down to 2 eV. In the collision chamber the pressure of the propane gas is 10^{-4} mm mercury. The fragments from the propane are then analyzed in another mass spectrometer, placed horizontally.

In the table below some mass spectra of propane are shown [2].

Ion	RE (eV)	Intensity for different masses						
		44	43	41	39	29	28	27
C^+	11.3 (and higher)	54	15	6	2	7	4	8
H^+	13.6	0	10	8	2	53	15	8
Ar^+	15.7	0	1	15	0	18	8	51
He^+	24.6	0	1	4	37	1	4	26
Species		C_3H_8^+	C_3H_7^+	C_3H_5^+	C_3H_3^+	C_2H_5^+	C_2H_4^+	C_2H_3^+

RE means the recombination energy of the incident ion. We have bombarded propane with 21 atomic and 23 molecular ions and have been able to plot the mass spectrum as a function of the recombination energy of the incident ion.

Fig. 3 shows the result for propane. C_3D_8 gives approximately the same breakdown graph.

The statistical theory of mass spectra has recently been improved and applied to propane by Vestal, Wahrhaftig and Johnston [3].

Fig. 4 shows a comparison between experiment and theory for some fragments from propane. The overall agreement is good, but in the ethyl ion curve there is a deep minimum. This is due to a high and narrow peak in Fig. 5.

Fig. 5 shows a comparison for some other fragments. Also here the general agreement is good. A small detail is that the propyl ion peak is displaced a little to the left in the lower diagram. The reason is that the theoreticians have used a lower AP than we have obtained, and this explains the minimum in the ethyl ion curve in the last slide.

Fig. 6 shows the comparison for the last fragment. The long tail in the experimental curve is due to two new processes that have not been considered by the theoreticians.

Fig. 7 shows the breakdown graph for butane [4]. Also for this molecule Vestal, Wahrhaftig and Johnston have performed calculations, and the agreement is rather satisfactory also in this case, as is evident from Fig. 8 and Fig. 9.

The results with propane and butane show that the improved statistical theory of mass spectra now is able to give a very good description of the dissociation of the molecule ion. It is possible that some of the re-

maining discrepancies are due to lacking knowledge of the dissociation processes. For that reason we have investigated two partially deuterated propanes.

Fig. 10 shows one breakdown curve of the deuterated propane [5]. The high peak at 12 eV has an isotopic composition that shows that the methane, lost during the dissociation, is formed from one methyl group and a hydrogen atom from the other methyl group.

At 12.1 eV a second process starts in which the methane is formed from one methyl group and a hydrogen atom from the CH_2 group. The second process is predominating at about 14 eV, but its maximum is low even here. The second process is responsible for about 25 % of the ethylene peak in the normal electron impact mass spectrum of propane, but using very low electron energies (13 eV), Ausloos and Lias [6] found the intensity of this fragment to diminish in agreement with our curve.

At about 20 eV the third process has a broad maximum. The isotopic composition is the same as for the first process, but the minimum at 15 eV proves that it cannot be the same process. In the third process the ethylene ion is probably formed from a propyl ion by loss of CH_3 . This hypothesis is supported by recent measurements on the breakdown curves of n-propyl iodide [5].

Fig. 11 shows first the formation of the ethyl ion by break of a carbon-carbon bond. Only very little rearrangement takes place in the molecule ion before this dissociation and only 5 or 10 percent of the ethyl ions have another isotopic composition. This small rearrangement is independent of energy.

The lower part of this figure shows the formation of vinyl ions from the ethyl ion by loss of a hydrogen molecule. In this case rearrangement takes place before the dissociation, and several authors (Kropf, Eyring, Wahrhaftig and Eyring [7] and Ausloos and Lias [6]) have assumed that the randomization is complete. This can easily be studied in our experiments as the vinyl ion is much more abundant than the ions with adjacent mass in this energy region so that the overlapping is less disturbing.

First we discuss the isotope effect. In the table the second process has intensity 0.5 and the third 0.25 as loss of H_2 is more probable than loss of D_2 . We then repeated the measurements with the mirror molecule $\text{CH}_3\text{CD}_2\text{CH}_3$ and obtained inverted order of the corresponding intensities as could be expected. We could therefore easily eliminate the isotope effect from our measurements.

Our intensities, now corrected for the isotope effect, could then be compared with a simple statistical computation. Assuming complete randomization of the ethyl ion, the intensities should be 6, 1, and 3 respectively. The agreement with our measurements is, however, not especially good. Our measured intensity of the second process, 0.5, is far too high, so the randomization of the ethyl ion is evidently not complete.

These results are valid only at the low energy part of the vinyl ion curve, at about 15 eV. At high energies, between 20 and 25 eV, the situation is quite different. There is no isotope effect at all and no agreement with the statistics. The explanation might be that in this region the vinyl ion is formed not from the ethyl ion as is presumed in the figure but from the propyl ion instead. Also this explanation is supported by our results with n-propyl iodide.

Fig. 12 shows the formation of propyl ions. The high and narrow peak is due to formation of secondary propyl ions, and the maximum of the normal propyl ion curve is much lower.

On the other hand, in hydride ion transfer mainly normal propyl ions are obtained.

In our measurements hydride ion transfer has often been a complication but with this observation we can easily eliminate this difficulty in the case of propane.

The ions C_3H_5^+ and C_3H_3^+ have also been measured with the deuterated propane but cannot be discussed until we know if the ions, from which they are formed, are normal or secondary propyl ions. We know the proportions between 12 and 14 eV but cannot extrapolate this result up to higher energies. Possibly, the problem can be solved by a comparison of the results with partially deuterated n-propyl iodide and isopropyl iodide.

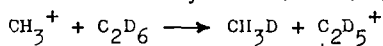
Ethane [5].

The breakdown graph of ethane was obtained in the same way and is shown in Fig. 13. Actually, C_2D_6 was used instead of ordinary ethane.

Hydride ion transfer from C_2D_6 was observed with incident CH_3^+ ions.

Incident ion	Velocity	Mass						
		36 $C_2D_6^+$	35	34 $C_2D_5^+$	33	32 $C_2D_4^+$	30 $C_2D_3^+$	28 $C_2D_2^+$
CH_3^+	2 eV	-	-	90	2	2	8	-
	30 eV	2	-	72	2	12	11	-
	900 eV	12	-	14	1	58	7	3

At low velocity of the incident ion the reaction



takes place and the $C_2D_5^+$ ion is predominating in the mass spectrum. At higher velocities the ion-molecule reaction becomes impossible and the intensity of this ion becomes lower. All fragments have, of course, even mass.

Also proton transfer to ethane was observed.

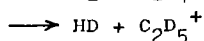
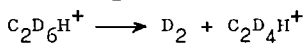
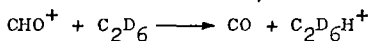
Incident ion	Velocity	Mass						
		36 $C_2D_6^+$	35	34 $C_2D_5^+$	33	32 $C_2D_4^+$	30 $C_2D_3^+$	28 $C_2D_2^+$
CHO^+	3 eV	2	-	77	47	9	8	-
	10 eV	3	-	72	34	11	9	-
	30 eV	4	-	63	19	13	13	1
	100 eV	6	-	39	6	29	16	2
	900 eV	8	-	18	1	49	11	4

It is very surprising that we now get a high intensity of an odd mass fragment (mass 33). As the intensity is small at high velocity the explanation must be an ion-molecule reaction. Fragment 34 shows the same velocity dependence and is evidently also due to a similar reaction.

When repeating the experiment with CDO^+ the fragment with odd mass disappeared.

Incident ion	Velocity	Mass						
		36 $C_2D_6^+$	35	34 $C_2D_5^+$	33	32 $C_2D_4^+$	30 $C_2D_3^+$	28 $C_2D_2^+$
CDO^+	3 eV	2	-	74	2	4	15	-
	30 eV	5	-	61	2	13	12	1
	900 eV	8	-	18	2	46	11	4

The explanation seems therefore to be that first a proton is added to the ethane molecule, and then the complex dissociates by loss of D_2 or HD



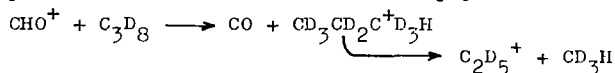
The probabilities of these two dissociation paths are approximately equal. This indicates that the intermediate ion has the structure $CD_3 - C^+D_3H$ and not for instance the structure of a protonated ethane. For in that case we would expect the intermediate ion to loose HD preferentially.

It seems then probable that the dissociation of the intermediate ion takes place by loss of a hydrogen molecule from the C^+D_3H group. If the

chemical bonds between the four hydrogens and the C^+ are equivalent, HD and D_2 will then be eliminated with equal statistical probabilities in agreement with our results.

This means, however, that the ionized carbon must be considered as having the valency five with all bonds of approximately equal strength. This idea is of course supported by the existence of CH_5^+ and similar ions.

As a further proof of the hypothesis the dissociation of propane after proton transfer can be mentioned [2]



If the bond between H and the rest of the intermediate ion had not been a strong bond, the dissociation would not have taken place in this way.

The concept of the valency five of C^+ in organic ions may possibly be of interest also in other cases.

Acetylene [8].

Fig. 15 shows the breakdown graph of acetylene.

In the earlier investigations from our laboratory on propane, ethane and alcohols, the main results were given in a breakdown graph in which the mass spectrum was plotted as a function of the energy. When we tried to do this for acetylene we could not obtain any consistent results. The reason seems to be that the probability for ionization of the acetylene molecule is very low between 12 and 15.5 eV but has large values at lower and higher energies. In the molecules investigated earlier, the distribution functions for ionization of the molecule were approximately constant in a large energy region, which simplified the interpretation.

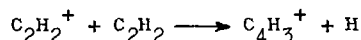
We have therefore found it necessary to present the results in a diagram in which the differential cross section for formation of a certain fragment is plotted as a function of energy.

The gap in the distribution function between 12 and 15.5 eV is very remarkable. This shows that the acetylene molecule ion can exist in two different electronic states, one at 11.4 eV and the other at about 15.5 eV. This fact is of fundamental importance for the statistical theory of the mass spectrum of acetylene. It is then necessary to consider each of these two electronic states separately. It is possible that the same can take place also in other molecules.

The interpretation of these two states can easily be given. The state at 11.4 eV is formed by ionization of one of the π -electrons that constitute the double bond in acetylene. The state at 15.5 eV is formed by ionization of one of the σ -electrons that constitute the third bond between the carbons. This interpretation agrees rather well with recent quantum-mechanical computations.

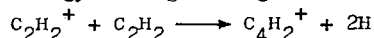
We could also observe some interesting ion-molecule reactions. We had rather high pressure in the collision chamber and observed condensation reactions between the acetylene molecules there and the ions that just had been formed in the charge transfer process. The condensation reactions give then ions with masses 49, 50, or 51. Usually one of them is more abundant than the others.

Starting with a $C_2H_2^+$ ion in the low energy state at 11.4 eV the process is



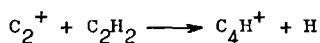
The energy is so low here that only one hydrogen can leave and the ion that we observe has mass 51.

If we start with a $C_2H_2^+$ ion in the high energy state at 15.5 eV the energy is high enough so that two electrons can leave:



The condensed fragment has therefore mass 50.

If finally we start with ions obtained in bombardment with He^+ the energy is so high that altogether three hydrogens can leave:



In this case the condensed fragment has mass 49.

References.

- [1] H. von Koch and E. Lindholm, Arkiv Fysik 19, 123 (1961).
- [2] E. Pettersson and E. Lindholm, Arkiv Fysik 24, 49 (1963).
- [3] M. Vestal, A.L. Wahrhaftig, and W.H. Johnston, Theoretical Studies in Basic Radiation Chemistry, ARL 62-426, 1962.
- [4] W.A. Chupka and E. Lindholm, Arkiv Fysik, in press.
- [5] H. von Koch, to be published.
- [6] P. Ausloos and S. Lias, J. Chem. Phys. 36, 3163 (1962).
- [7] A. Kropf, E.M. Eyring, A.L. Wahrhaftig, and H. Eyring, J. Chem. Phys. 32, 149 (1960).
- [8] E. Lindholm, I. Szabo, and P. Wilmenius, Arkiv Fysik, in press.

A MASS SPECTROMETRIC STUDY OF HOMONUCLEAR AND
HETERONUCLEAR RARE GAS MOLECULE IONS

M. S. B. Munson, J. L. Franklin, and F. H. Field
Research and Development
Humble Oil & Refining Company
Baytown, Texas

ABSTRACT

The homonuclear and heteronuclear diatomic ions of all the rare gases except radon have been studied by mass spectrometry. Appearance potentials of all except the HeXe^+ have been measured at pressures where three-body processes can be neglected. All are found to result from chemi-ionization reactions, and our appearance potentials agree well with those of other workers where they are available. Most of the heteronuclear ions have appearance potentials in the ionization continuum of the partner of lower ionization potential. Thus most of the heteronuclear ions exist at energies above one of their dissociation asymptotes, and presumably this is possible because of the non-crossing of potential energy curves. The appearance potential for HeAr^+ , 17.9 ev, and NeXe^+ , 16.0 ev, occur below the lowest excited state of He and Ne respectively and can only be understood as resulting from reaction of a long-lived discrete excited state of argon or xenon existing in their respective ionization continua.

MASS SPECTROMETRIC OBSERVATION OF ELECTRON AND PROTON TRANSFER
REACTIONS BETWEEN POSITIVE IONS AND NEUTRAL MOLECULES. PART II*

A. Henglein and G. A. Muccini[†]
Radiation Research Laboratories
Mellon Institute, Pittsburgh, Pa.
and

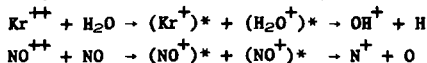
Hahn-Meitner Institut für Kernforschung
Berlin-Wannsee, Germany

*This work is supported, in part, by the U.S. Atomic Energy Commission.

[†]Present Address: Research Division, MELPAR, INC., Falls Church, Virginia.

SUMMARY

The method of Cermak and Herman has been applied to studies of unsymmetrical charge and proton transfer reactions. If the charge is transferred between atoms low cross sections are observed since part of the kinetic energy of the reacting system has to be converted into internal energy of the reactants. Large cross sections, however, have been found for the charge transfer between polyatomic species where apparently no resonance restriction exists. In several instances the unsymmetrical transfer $B^+ + A \rightarrow B + A^+$ has a higher rate than either of the processes $B^+ + B$ or $A^+ + A$. If the ionization potential of B is lower than that of A the cross sections are in general low. In certain cases exceptionally large cross sections are observed and can be explained by the excess energy of a long lived excited state of the donor B^+ . The process $H_2O^+ + CH_4 \rightarrow H_2O + CH_5^+$ occurs 10 times faster than in the reverse direction although one concludes from the generally accepted ionization potentials of methane or water that the process is endothermic. Dissociations following the transfer of one charge from a doubly charged ion to a neutral molecule such as



have also been observed. The results indicate that the doubly charged ion generally captures the electron into a high lying orbital.

Protonated cyclopropane is shown to be readily formed in ionized cyclopropane. In mixtures of water and methane, proton transfer has been observed in both directions. A large isotope effect on the secondary ion currents resulting from the transfer of a deuteron or a proton has been found in several simple systems. This isotope effect appears only if the secondary ions are observed in the Cermak-Herman method and is not found in the conventional operating of the ion source. This information provides considerable insight into the mechanistic details of the proton transfer since little isotope effect is expected if the reaction occurs via an inelastic collision complex while an isotope effect of the order of magnitude observed here is predicted by a stripping model.

INTRODUCTION

In the first part of this work,¹ the method of Cermak and Herman² was applied to studies of symmetrical electron and proton transfer processes in simple molecules. It was shown that essentially complete discrimination of primary ions formed between the chamber and electron trap of a conventional ion source can be achieved if the electron accelerating voltage between the filament and the chamber is kept at least two volts below the ionization potential of the gas. Secondary ions produced in the chamber were shown to be extractable into the analyzing section of the instrument as long as they do not possess significant kinetic energy in either the direction of the primary ion beam (< 2.5 ev) or perpendicular to this direction and the direction of analysis (< 0.34 ev). These conditions are fulfilled in ion-molecule reactions in which either the transfer of mass is small or which do not occur via long-lived complexes. Proton transfer reactions such as the process $H_2O^+ + H_2O \rightarrow OH + H_3O^+$ were postulated to occur via a "stripping" mechanism at least at kinetic energies above about 5 ev. These studies have been extended to investigations of electron and proton transfer processes between molecules of different structure and to dissociative charge transfer reactions induced by doubly charged ions.

EXPERIMENTAL

As has been described in the earlier report¹ the primary ions possess a spread of kinetic energies when they enter the ionization chamber. Most have energies near to the maximum value of eE_T where E_T is the voltage between the chamber and the trap. The lower energy limit of the primary ion beam is equal to $e(AP - E_e)$ where AP is the appearance potential of the primary ion and E_e the voltage between the filament and the ionization chamber. If E_e is kept constant the average kinetic energy of the primary ions increases with increasing E_T and so does the energy spread and the intensity of the beam. Since E_T and E_e determine the upper and lower limit of the primary ion energy, suitable combinations of these two voltages can be used to produce primary ion beams of a desired energy spread. For example, if the ionization potential of the gas amounts to about 13 ev (such as in water or methane) a beam of primary parent ions having kinetic energies between 3 and 5 ev can be produced by setting E_e equal to 10 and E_T equal to 5 volts. Other

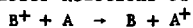
TABLE 1

Relative Cross Sections of Some Resonance Charge Transfer Reactions of the Type $A^+ + A \rightarrow A + A^+$

Ion	Relative Cross Section
CH_4^+	(1)
CD_4^+	1.0
$CD_2H_2^+$	1.0
H_2^+	1.7
CO_2^+	4.3
N_2^+	5.5
$n-C_3H_8^+$	3.9
$c-C_3H_8^+$	7.4
CH_3I^+	47
$C_2H_5I^+$	68

TABLE 2

Charge Transfer Reactions of the Type



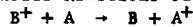
where $IP(B) > IP(A)$

No.	B	A	$IP(B)-IP(A)^*$	$\frac{\sigma_{BA}}{\sigma_{AA}}$	Reaction Partners
a	Ar	Kr	1.7	0.02	atom-atom
b	Kr	Xe	1.8	0.005	
c	N_2	Kr	1.6	0.06	atom-molecule
d	N_2	Xe	3.4	0.12	
e	H_2	Kr	1.4	0.47	
f	H_2	Xe	3.2	0.50	
g	Ar	H_2O	3.1	1.3	
h	Kr	H_2O	1.4	1.3	
i	H_2O	Xe	0.5	0.7	molecule-molecule
j	N_2	H_2O	3.0	1.8	
k	H_2	H_2O	2.8	4.0	
l	C_2H_2	CS_2	1.3	0.32	
m	H_2O	CS_2	2.5	0.48	
n	H_2O	C_2H_2	1.2	1.0	
o	CH_4	C_2H_6	1.2	1.2	
p	C_2H_2	C_2H_4	0.9	1.4	
q	C_6D_6	C_6H_5Cl	0.4	1.5	
r	H_2O	C_6H_6	3.4	1.6	
s	CS_2	C_6D_6	0.9	1.7	

*Values of the ionization potentials taken from reference (3)

TABLE 3

Charge Transfer Reactions of the Type



where $IP(B) < IP(A)$

No.	B	A	$IP(B)-IP(A)$	$\frac{\sigma_{BA}}{\sigma_{AA}}$	Reaction Partners
a	Kr	Ar	-1.7	0.03	atom-atom
b	Xe	Kr	-1.8	0.08	
c	Kr	N_2	-1.6	0.02	atom-molecule
d	Xe	N_2	-3.4	0.04	
e	Xe	H_2O	-0.4	0.3	
f	H_2O	Kr	-1.4	0.1	
g	H_2O	Ar	-3.1	< 0.001	
h	C_2H_2	Xe	-0.7	0.1	molecule-molecule
i	H_2O	N_2	-3.0	< 0.001	
j	C_6H_6	H_2O	-3.4	0.09	
k	C_6D_6	CS_2	-0.9	0.16	
l	CS_2	C_2H_2	-1.3	0.35	
m	CS_2	H_2O	-2.5	0.18	
n	C_2H_2	H_2O	-1.2	0.08	
o	H_2O	CH_4	-0.2 to -1.2	5.0	

combinations of E_T and E_e , as indicated in Fig. 5 and 6, have been used to produce beams of faster ions with a defined spread in energy. A drawback of this method is the unknown changes in the intensity of the primary ion beam when the different combinations are used. However, the method may well be applied to study the intensity ratios of two secondary ions resulting from competing reactions of the same precursor such as in the comparison of charge and proton transfer reactions. The results obtained by different sets of E_T and E_e are presented by the horizontal lines in Fig. 5 and 6 the length of which corresponds to the energy spread of the primary ion beam. The secondary ionization curves in all the figures have been normalized at an E_T of 40 volts in the case of singly charged primary ions and 150 volts for doubly charged ions.

In order to obtain relative cross sections of symmetrical charge transfer processes the ratio

$$\frac{\text{current of secondary ion at } E_e = 8 \text{ and } E_T = 40 \text{ volts}}{\text{current of primary ion at } E_e = 40 \text{ and } E_T = 40 \text{ volts}}$$

has been measured relative to the similar ratio for methane.¹ This procedure assumes that the primary ion current in the Cermak-Herman operation of the ion source (i.e. $E_e = 8$, $E_T = 40$ volts) is proportional to the current in the more conventional operation of the source ($E_e = 40$ volts). Since the primary current contained ions of kinetic energies between about 5 and 40 volts the value of the cross section obtained is an average over this range. A similar method was used to determine the cross section of unsymmetrical charge transfer reactions $B^+ + A \rightarrow B + A^+$ relative to that of the symmetrical process $A^+ + A \rightarrow A + A^+$. The compound A was at first introduced into the gas reservoir at a pressure of 40 - 100 μ and the currents $i_{A_1}^+$ at $E_e = 8$ and $E_T = 40$ volts and $i_{A_1}^+$ at $E_e = 40$ and $E_T = 40$ volts were measured. After the addition of compound B up to a total pressure of 550 μ the currents $i_{A_1}^+$ ($E_e = 8$, $E_T = 40$) $i_{A_2}^+$ ($E_e = 40$, $E_T = 40$) and $i_{B_2}^+$ ($E_e = 40$, $E_T = 40$) were determined. The ratio of the cross sections σ_{BA} and σ_{AA} of the unsymmetrical and symmetrical electron transfer processes was calculated from these data by using the relations $i_{A_1}^+ = k\sigma_{AA} i_{A_1}^+$ and $i_{A_2}^+ = k\sigma_{AA} i_{A_2}^+ + k\sigma_{BA} i_{B_2}^+ + i_{A_2}^+$ from which

$$\frac{\sigma_{BA}}{\sigma_{AA}} = \left(\frac{i_{A_2}^+}{i_{A_1}^+} - \frac{i_{A_2}^+}{i_{A_1}^+} \right) \cdot \frac{i_{A_1}^+}{i_{B_2}^+} \quad (1)$$

Relative cross sections of proton transfer reactions were calculated in a similar way.

Charge Transfer Processes

The relative cross sections of a few resonance transfer reactions are listed in Table 1 in order to complete the results obtained in the first part of this study. The largest cross sections found to date have been observed in methyl and ethyl iodide. Table 2 shows the relative cross sections of a number of unsymmetrical charge transfer reactions of the type $B^+ + A \rightarrow B + A^+$ where the ionization potential of the charge donor B is higher than that of the acceptor A. In the case of the transfer between atoms (reactions a and b) the cross sections are low, i.e., only about one per cent of that of the resonance process $A^+ + A \rightarrow A + A^+$. Here part of the internal energy of the reacting system has to be converted into kinetic energy of the reactants. If the charge is transferred between polyatomic molecules (reactions j-s) the ratio of the cross section σ_{BA}/σ_{AA} often is larger than unity, i.e., there is no resonance restriction for the unsymmetrical process at all. This is explained by the large number of rotational and vibrational levels in each electronic state of a polyatomic molecule so that there always exists a possibility for the two transitions $B^+ \rightarrow B$ and $A \rightarrow A^+$ to occur with equal energy differences. The charge transfer from B^+ to A may either occur as $B^+ + A \rightarrow B^* + A^+$ or $B^+ + A \rightarrow B + A^{*+}$, i.e., either the molecule B or ion A^+ (or both) will be in a higher vibrational level after the interaction. In a few cases in Table 2, the unsymmetrical charge transfer $B^+ + A$ occurs faster than both resonance processes $B^+ + B$ and $A^+ + A$. Typical examples are the reactions ($H_2^+ + H_2O$) and ($H_2O^+ + C_6H_6$). A comparison of the relative cross sections in Table 2 with those of the resonance processes listed in Table 1 and Table 1 of the first part¹ shows that ($H_2^+ + H_2O$) is 4 times faster than ($H_2O^+ + H_2O$) and 10 times faster than ($H_2^+ + H_2$), while ($H_2O^+ + C_6H_6$) is 1.6 or 5 times faster than the resonance transfers in benzene and water, respectively. No correlation between the cross section and difference in the ionization potentials of the reacting molecules seems to exist in the data of Table 2. Several reactions between atoms of the noble gases and molecules are also shown in this table (reactions c-i). The cross section often is markedly lower than that of the resonance process as is illustrated by the reactions between nitrogen and krypton or xenon, respectively. In other cases, such as the charge transfer from argon or krypton to water the cross sections become comparable with those of the resonance processes. It appears, therefore, that resonance restrictions can occasionally be severe when the charge is transferred between an atom and a molecule.

Fig. 1 shows how the shape of the secondary ionization efficiency curve of the $C_2H_2^+$ ion from acetylene is affected by the unsymmetrical charge transfer $H_2O^+ + C_2H_2 \rightarrow H_2O + C_2H_2^+$ when water is present. $C_2H_2^+$ appears at $E_e + E_T = 11.5$ volts in pure acetylene, i.e., at the ionization potential of acetylene. The $C_2H_2^+$ ion observed in pure acetylene is, therefore, formed by the reaction $C_2H_2^+ + C_2H_2 \rightarrow C_2H_2 + C_2H_2^+$. H_2O^+ appears in pure water at $E_e + E_T = 13.0$ and has to be attributed to the reaction $H_2O^+ + H_2O \rightarrow H_2O + H_2O^+$.

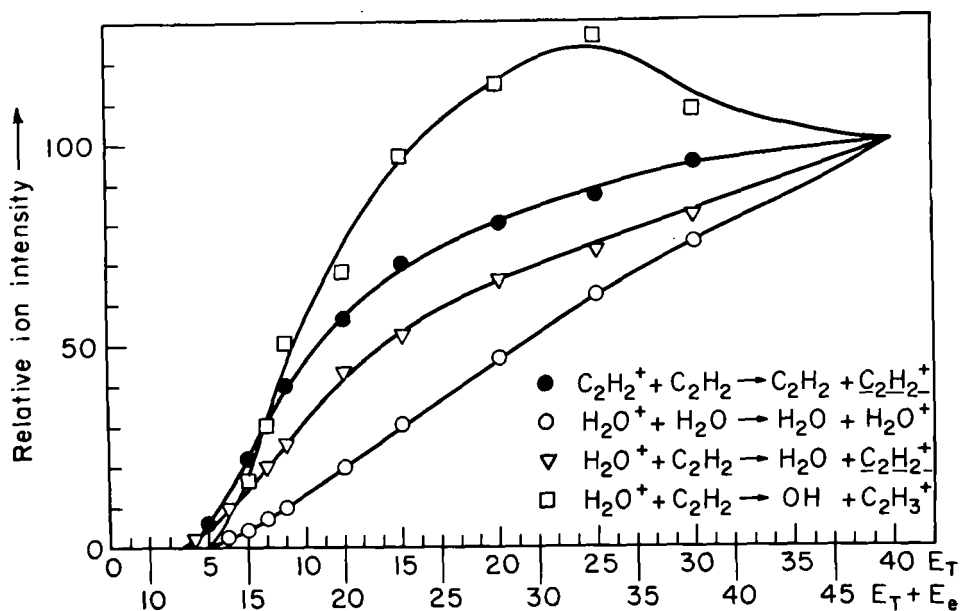


Fig. 1

Secondary ionization efficiency curves of C_2H_2^+ and H_2O^+ in pure acetylene and water (●,○) and of C_2H_2^+ and C_2H_3^+ (▽,□), in a mixture of acetylene and water (1:4)

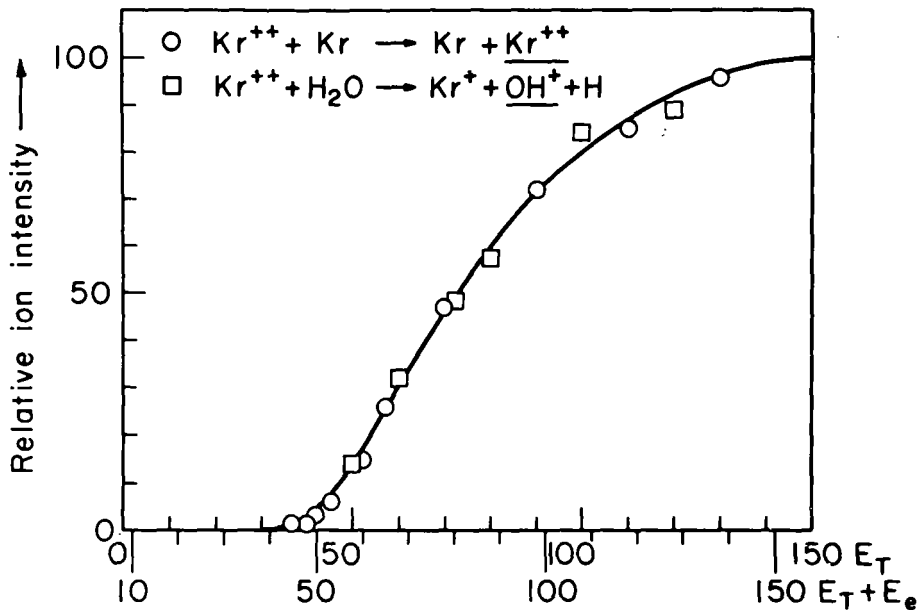


Fig. 2

Secondary ionization efficiency curves of Kr^{++} and OH^+ in a 1:1 mixture of krypton and water vapor

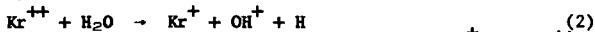
$C_2H_2^+$ appears at 11.5 volts in a mixture since the resonance process can still occur. However, at higher voltages the process $H_2O^+ + C_2H_2 \rightarrow H_2O + C_2H_2^+$ contributes to the formation of $C_2H_2^+$. This causes the secondary ionization efficiency curve of $C_2H_2^+$ to run between the curves of $C_2H_2^+$ and H_2O^+ formed in the pure compounds.

A number of unsymmetrical charge transfer reactions in which IP(B) is lower than IP(A) are listed in Table 3. In general, the cross sections are very much lower than those of the resonance processes since in order to satisfy the energetics part of the kinetic energy of the ion has to be converted into internal energy of the electronic system of A. In all cases where the calculated cross section σ_{BA} amounts to only a few per cent of σ_{AA} ions observed might be mainly due to simple scattering of primary ions. Relatively high cross sections, however, have been observed in the transfer from carbon disulfide to acetylene and to water as well as from xenon to water. These large cross sections are explained by the excess energy of the primary ion which makes these processes exothermic. Several reactions of an excited long-lived state of the CS_2^+ ion (AP = 13.3) have recently been observed.^{4,5} Similarly, the $^2P_{3/2}$ level of the doublet ground state of Xe^+ (1.3 eV of excess energy) may be responsible for the fast charge transfer to water.

Reaction o in Table 3, which describes the charge transfer from water to methane, occurs as a remarkable exception to the generalizations given above. The cross section is 5 times higher than that of the resonance transfer in methane, although this large factor should not be over-emphasized since the transfer in methane is relatively low (Table 1). The cross section of reaction o, however, is still about as large as that of the process $H_2O^+ + H_2O \rightarrow H_2O + H_2O^+$. It seems surprising that the largest ratio of σ_{BA}/σ_{AA} has been observed for a reaction that is endothermic if the ground level of the primary ion is involved. Various values of the ionization potential of water (12.6 - 13.1 volts) and methane (12.8 - 13.8) have appeared in the literature.³ The most probable values³ of the two potentials lead to the conclusion that reaction o must be endothermic. If we do not want to question this conclusion the only alternative explanation of the large cross section consists in a water ion entering reaction o with excess energy. However, there is no experimental evidence for a relatively long-lived ($> 10^{-6}$ sec) vibrational or electronic state of the H_2O^+ ion. It may be of interest with respect to the relative heights of the ionization potentials in water and methane that the charge transfer $CH_4^+ + H_2O \rightarrow CH_4 + H_2O^+$ occurs with a cross section about 10 times smaller than the reverse reaction as should be expected for an endothermic process.

Dissociative charge transfer from doubly charged ions

Dissociations following the transfer of the charge from a singly charged ion to a molecule have been reported by Cermak and Herman² as well as by Lindholm.⁶ We observed several reactions in which one positive charge from a doubly charged atom or molecule was transferred to a neutral molecule and in which the secondary ion subsequently dissociated. The first example of this reaction type has been found in a mixture of krypton and water. It was mentioned in the earlier paper that OH^+ is not present in the secondary mass spectrum of water.¹ However, in a mixture of krypton and water OH^+ appears at $E_T + E_e = 38$ volts, i.e., at the appearance potential of Kr^{++} . The following process is, therefore, postulated:



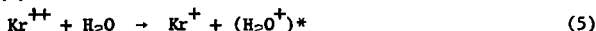
As can be seen from Fig. 2, the secondary ionization efficiency curves of OH^+ and Kr^{++} have the same shape. Kr^{++} ions which are observed under Cermak-Herman conditions in the ion source result from the resonance process



which competes with reaction (2). The current ratio OH^+/Kr^{++} was found to be equal to 1:4.3, i.e., the resonance process has a much larger cross section than the charge transfer from Kr^{++} to water. OH^+ has also been found as a secondary ion in a mixture of nitrogen and water. In this case, N_2^{++} is the precursor:



If the primary step of reaction (2) consists of



the water ion formed should have a total energy of 24.6 eV, i.e., the difference in the second and first ionization potentials of krypton. Since the appearance potentials of OH^+ and O^+ from water amount to only 18-19 volts the excited water ion formed by reaction (5) is expected to dissociate readily. Because of the large surplus of internal energy fragmentation to yield O^+ ions could occur with relatively large frequency. However, O^+ was not detected as a secondary ion.

As already reported¹ the resonance process



occurs with a low cross section. Reactions (7) and (8)



must also be postulated since the secondary ions N^+ and O^+ have been found to appear at

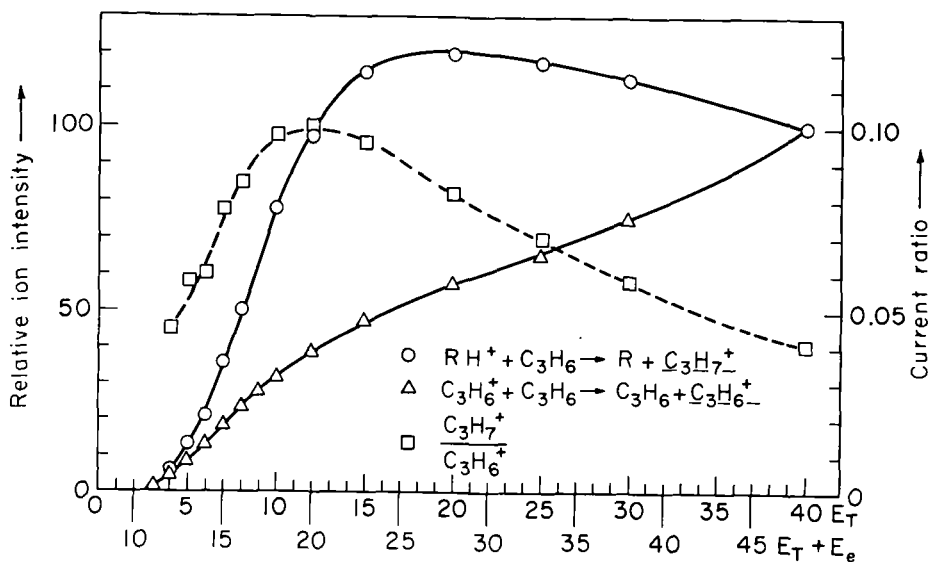


Fig. 3

Secondary ionization efficiency curves of $C_3H_6^+$ and $C_3H_7^+$ in cyclopropane as well as the current ratio $i_{C_3H_7^+}/i_{C_3H_6^+}$ as function of E_T .

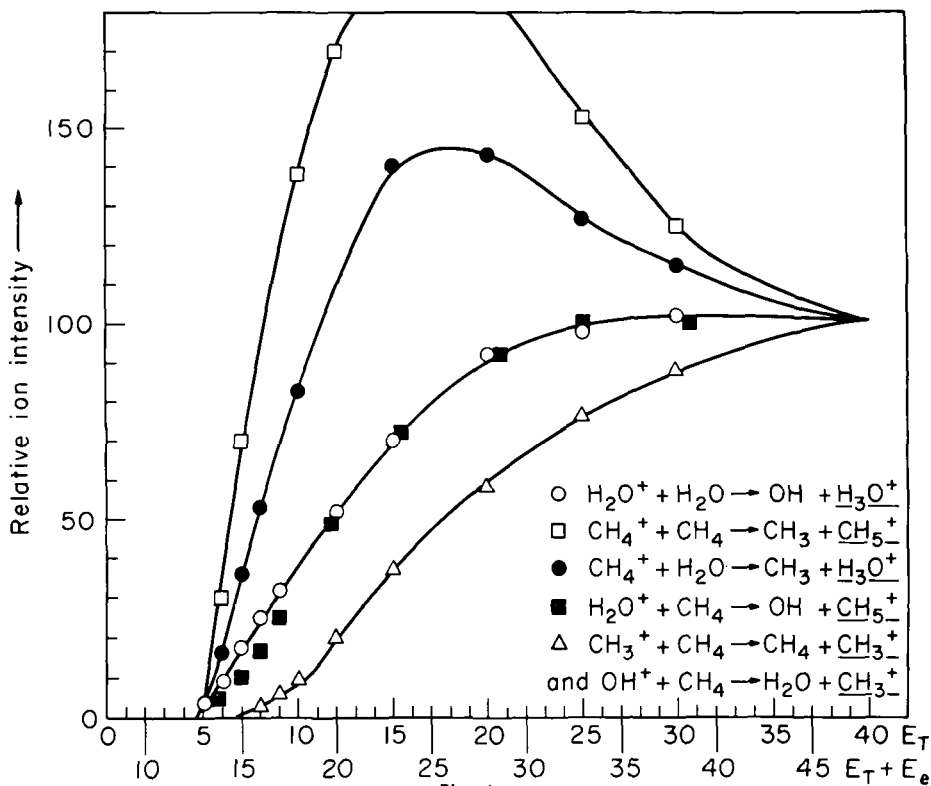


Fig. 4

Secondary ionization efficiency curves in pure methane ($\circ$) and pure water ($\bullet$) and in mixtures of methane and water (1:5- $\blacksquare$, $\triangle$) (5:1- $\circ$)

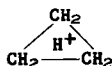
the second ionization potential of nitrous oxide (~ 42 volts). The intensity ratio $\text{NO}^{++}:\text{O}^+:\text{N}^+$ was found to be equal to 1:5:9 which shows that the resonance process (6) occurs less frequently than the dissociative charge transfer reactions (7) and (8). If the primary step of (7) and (8) is $\text{NO}^{++} + \text{NO} \rightarrow \text{NO}^+ \text{NO}^{++}$ (9)

the secondary ions resulting from the dissociation of the highly excited NO^+ ion could not be observed since their kinetic energy would be equal to about 12 eV (about 6 eV each), i.e., to the difference $\text{AP}(\text{NO}^{++}) - \text{AP}(\text{NO}^+) - \text{AP}(\text{N}^+ \text{ or } \text{O}^+)$ where $\text{AP}(\text{N}^+ \text{ or } \text{O}^+)$ is the appearance potential of N^+ or O^+ from NO . In order to explain why these ions can be observed it must be postulated that the NO^{++} ion captures the electron into a high lying electronic orbital and thus itself absorbs a large fraction of the excitational energy. The excess kinetic energy $\text{AP}(\text{NO}^{++}) - \text{AP}(\text{NO}^+)$ is therefore shared by either singly charged NO^+ ions formed in reaction (9). The higher frequency of the charge transfer (9) followed by (7) or (8) than that of the resonance double charge transfer (6) is explained by the large number of rotational and vibrational levels available in each of the NO ions and which makes reaction (9) resonance possible with respect to the energies involved in the transitions $\text{NO}^{++} \rightarrow \text{NO}^{++}$ and $\text{NO} \rightarrow \text{NO}^{++}$.

Similar results have been obtained in carbon dioxide where the secondary ions C^+ , O^+ , and CO^+ first appear at $E_T + E_e$ equal to about 40 volts. Their intensity ratio at $E_T \sim 150$ volts amounts to 1:4:8. They apparently result from dissociations as a consequence of the reaction $\text{CO}_2^{++} + \text{CO}_2 \rightarrow \text{CO}_2^{++} + \text{CO}_2^{++}$. Only traces of the CO_2^{++} ion from the double charge transfer $\text{CO}_2^{++} + \text{CO}_2$ could be observed. The C^+ ion was the only secondary ion found in carbon monoxide. Its formation is described by $\text{CO}^{++} + \text{CO} \rightarrow \text{CO}^{++} + \text{C}^+ + \text{O}$.

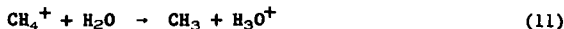
Proton and Hydride Ion Transfer

Protonated molecules formed by the process $\text{RH}^+ + \text{RH} \rightarrow \text{R} + \text{RH}_2^+$ have been observed in several hydrocarbons.¹ In the aliphatic series, CH_5^+ is formed with a large cross section in methane, while C_2H_7^+ could hardly be detected in ethane.¹ No protonated molecule has been found in n-propane and cyclohexane. The substitution of H atoms in methane by larger groups R apparently makes the formation of the protonated molecule more difficult. This does not necessarily mean that the proton transfer becomes endothermic but more likely that the reaction has a low steric factor due to the increased complexity of the higher hydrocarbons. A proton transfer with a rather large cross section has been observed in cyclopropane. This was not unexpected since the cyclopropane ring is known to be easily cationized and the C_3H_7^+ ion is one of the most abundant ions in the mass spectra of nearly all aliphatic hydrocarbons.⁷ Its structure may be described by



where the proton is embedded in a molecular orbital formed by the overlap of the three sp^2 orbitals protruding from the three carbon atoms.⁸ Fig. 3 shows the secondary ionization efficiency curves of C_3H_5^+ and C_3H_7^+ in cyclopropane as well as the current ratio $i_{\text{C}_3\text{H}_7^+}/i_{\text{C}_3\text{H}_5^+}$. Since both ions appear at $E_T + E_e$ equal to $\text{IP}(\text{C}_3\text{H}_5^+)$ the parent ion of cyclopropane must be a precursor of both secondary ions. The current ratio increases with decreasing E_T as has been found in many other comparisons of proton and charge transfer reactions.¹ However, at low values of E_T the ratio decreases again. This can be understood if C_3H_7^+ is not only formed by primary C_3H_5^+ but also by proton transfer from some other primary ion the appearance potential of which is higher than that of C_3H_5^+ . Because of their high mass spectral abundances, the ions C_3H_5^+ and C_3H_3^+ may also be precursors of C_3H_7^+ .

Proton transfer processes of rather large cross sections have been observed in water-acetylene and water-methane mixtures. The reaction $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_2 \rightarrow \text{HO} + \text{C}_2\text{H}_3^+$ is faster than the proton transfer between two acetylene molecules. C_2H_3^+ , therefore, appears at $\text{IP}(\text{H}_2\text{O}^+)$ in a mixture in which acetylene is present at low concentration as can be seen from Fig. 1. Fig. 4 illustrates that proton transfer in mixtures of water and methane can occur in both directions:



CH_5^+ is mainly formed by reaction (10) if methane is present at low concentration. In that case, its secondary ionization efficiency curve is completely different from that obtained in pure methane. The shape of its curve resembles that of the H_3O^+ ion in pure water. On the other hand, if methane is the major component of the mixture the curve of H_3O^+ is very similar to that of CH_5^+ in pure methane. The cross section of reaction (11) has been calculated to be about twice as large as that of reaction (10) at a value of $E_T \sim 40$ volts. Reaction (11) is as fast as the proton transfer in pure water under this condition. It has not been possible to detect reaction (10) if the more conventional techniques are applied in studies on ion-molecule reactions.⁹ Reaction (11), however,¹⁰ has been observed by Lampe although it was not possible to identify the precursor ion.

Other proton transfer reactions have been observed in the present work in acetylene (transfer in ethylene has previously been reported¹) and in carbon disulfide-water

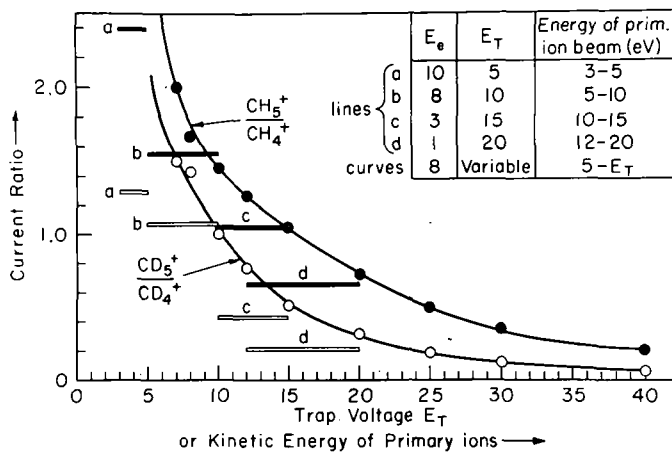


Fig. 5

Secondary ion current ratios in light and heavy methane as a function of E_T

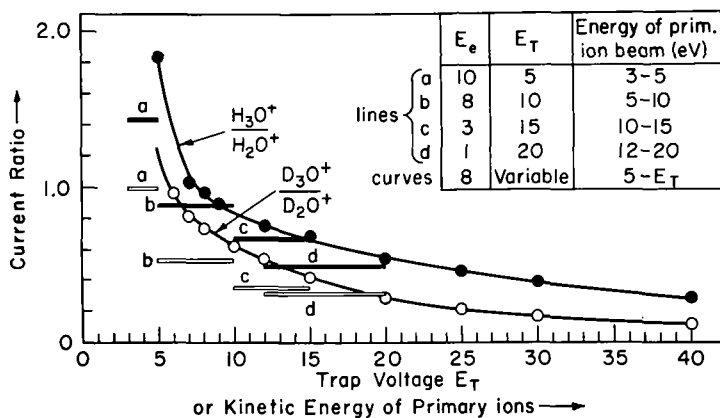


Fig. 6

Secondary ion current ratios in light and heavy water as a function of E_T

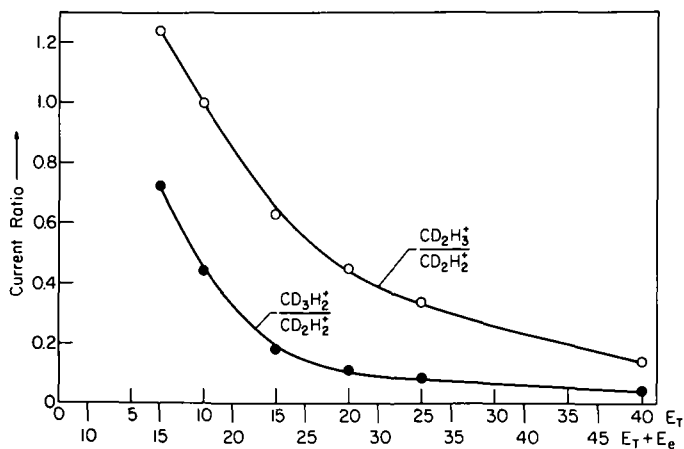
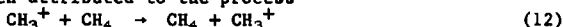


Fig. 7

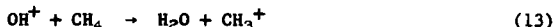
Secondary ion current ratios in methane- d_2 as a function of E_T

mixtures. Attempts to detect $C_6H_7^+$ in benzene and in benzene-water mixtures have not been fruitful.

Two examples of hydride ion transfer reactions are also illustrated by Fig. 4. The secondary CH_3^+ ion in methane has been attributed to the process



since this takes into account that the secondary appearance potential of CH_3^+ is equal to $AP(CH_3^+)$ from methane and that relatively little kinetic energy is transferred to the secondary ion.¹ This process can still be seen in a methane-water mixture since CH_3^+ appears at $E_T + E_e = 14.7$ volts, i.e., at $AP(CH_3^+)$. The ionization efficiency curve of CH_3^+ in Fig. 4 shows a rather sharp break at $E_T + E_e = 18.5$ volts. Since this agrees with $AP(OH^+)$ from water it is postulated that primary OH^+ ions contribute to the CH_3^+ formation at higher values of E_T :



This hydride transfer process occurs with a cross section 7 times larger than that of reaction (12) at $E_T = 40$ volts.

Observation and Interpretation of Isotope Effects

The ion intensity ratios CH_5^+/CH_4^+ and CD_5^+/CD_4^+ in pure methane and methane-d 4, respectively, are plotted as a function of the voltage E_T in Fig. 5 (E_e constant at 8 volts). These ratios have also been determined at the various combinations of E_e and E_T listed in the figure. The results of these measurements are presented by the horizontal lines the lengths of which indicate the spread in the kinetic energy of the primary ion beams. The decrease in the ratio CH_5^+/CH_4^+ with increasing E_T has been attributed¹ to the stronger discrimination of the protonated molecule over the product of the charge transfer reaction. Since protonated molecules can still be observed at values of E_T larger than 20 volts it has been concluded that the transfer of a proton does not occur via a completely inelastic collision complex. If a complex is formed the CH_5^+ ion would possess a large amount of kinetic energy in the direction of the primary ion. A stripping model has therefore been postulated to describe the reaction at least at higher kinetic energies.¹

If E_e is kept constant at 8 volts the primary ion beam will always contain a tail of low energy ions at higher values of E_T . It could therefore be argued that the secondary ions observed at higher values of E_T exclusively result from reactions of that low energy component of the primary beam. In this respect, the experiment carried out with the voltage combination No. d in Fig. 5 may be emphasized since only primary ions of rather high kinetic energy (between 12 and 20 ev) have been used here. The fact that the CH_5^+ ion could still be observed clearly shows that mass transfer in an ion-molecule reaction is still possible even if the relative kinetic energy exceeds the strength of the chemical bonds in the reactants. The CH_5^+/CH_4^+ curve runs through the right hand sides of the horizontal lines in Fig. 5. This result is not unexpected, for most of the primary ions will have kinetic energies near to the upper limit of the energy spread. Apparently, the contribution of the low energy tail in the primary ion beam to the observed ratio CH_5^+/CH_4^+ is not significant.

Fig. 5 shows that the current ratio CH_5^+/CH_4^+ is larger than the ratio CD_5^+/CD_4^+ . This isotope effect is more pronounced at higher values of E_T , i.e., at higher kinetic energies of the primary ions. Since the cross section of the symmetrical charge transfer in methane is not affected by the substitution of H-atoms by deuterium (Table I) there must be an isotope effect in the formation of the protonated and deuterated molecules, respectively. Apparently, the process



either has a lower cross section than



or the Cermak-Herman method more effectively discriminates against CD_5^+ than CH_5^+ ions. Experiments have also been carried out to study this isotope effect under the more conventional operation of the ion source, i.e., at E_e equal to 70 volts. The cross section of the proton transfer in methane was found to be 1.1 - 1.2 times larger than that of the deuteron transfer in methane-d 4. This isotope effect is small and not comparable to the large effect obtained in the Cermak-Herman operation where a factor of 4 is involved (at $E_T = 40$ volts).

Similar isotope effects have been observed when a proton or deuteron is transferred in other compounds. The reaction



in a mixture of methane and methane-d 4 was found to occur with the same cross section as the proton transfer in pure methane. The current ratio H_3O^+/H_2O^+ in water is shown by Fig. 6 to be higher than the ratio D_3O^+/D_2O^+ in heavy water. In the present work no isotope effect at all could be observed in water when these ratios were measured under the conventional conditions in the ion source. Lampe et. al.¹¹ report that D_3O^+ formation is slightly faster than that of H_3O^+ . In the case of methane-d₃, proton and deuteron transfer reactions could simultaneously be observed. As can be seen from Fig. 7, the intensity of the deuterated molecule again is smaller than that of the protonated one. The intensities of $CD_2H_3^+$ and $CD_3H_2^+$ were found to be equal under the conventional conditions in the ion source. As in methane itself the isotope effects in water and methane-d₂ became more pronounced as the kinetic energy of the primary ion was increased.

Although the experimental results obtained by the simple Cermak-Herman method are not sufficiently sophisticated to justify any detailed theoretical explanation of the isotope effects, a few brief remarks on what might be expected from our present knowledge of the mechanisms of ion-molecule reactions shall be made here. If a completely inelastic collision takes place the intermediate complex will move with the kinetic energy $E_p(M_1/M_1 + M_2)$ in the direction of the primary ion and will have internal rotational plus vibrational energy with amount equal to $E_p(M_2/M_1 + M_2)$. E is the kinetic energy of the primary ion, the neutral molecule is regarded to be at rest before the collision, and M_1 and M_2 are the masses of the ion and molecule. The complex will dissociate after a lifetime much longer than the time of an atomic vibration (10^{-13} sec). The secondary ion carries the kinetic energy

$$E_s = E_p \frac{M_1(M_2 + m)}{(M_1 + M_2)^2} \quad (17)$$

in the direction of the primary ion, if m is the mass of the transferred proton or deuteron, respectively. Where M_1 and M_2 are similar and m very much smaller, E_s will amount to about $1/4 E_p$ in both transfer processes. Thus the substitution of H by D in the reacting species is not expected to have any significant influence on either the formation of the intermediate complex or on the kinetic energy of the secondary ion if the reaction goes through a completely inelastic collision complex. As mentioned in part I, a secondary ion from such a collision can hardly be observed since its kinetic energy generally is much too high.

Isotope effects with respect to both the kinetic energy and the cross section for formation of the secondary ion have to be expected if the reaction takes place as a stripping process. In an ideal stripping reaction the neutral molecule is hit by only the proton or deuteron in the primary ion. Since the kinetic energy of the captured hydrogen ion is equal to $E_p(m/M_1)$ the kinetic energy of the secondary ion will amount to

$$E_s = E_p \frac{m^2}{M_1(m + M_2)} \quad (18)$$

i.e., it will depend very strongly on the transferred mass m . An ion resulting from the transfer of a deuteron will therefore have more kinetic energy perpendicular to the direction of analysis and be discriminated against more than one resulting from the transfer of a proton.

These simple considerations indicate that the stripping model provides a more suitable explanation of the experimental results than the activated complex mechanism, although it cannot be expected to be literally very applicable since the ideal stripping model requires the time of a collision to be much shorter than the time of one vibration of the hydrogen ion that is to be transferred. At low energies this supposition is not fulfilled since the times involved become comparable only at primary ion energies of 10-20 ev. It is therefore postulated that the proton transfer occurs through a loose collision complex $R \cdots H^+ \cdots M_2$ which acquires more and more the properties of a completely inelastic "activated" collision complex at lower kinetic energies. The stripping model becomes more and more useful to describe the process at higher energies. Perhaps many of the other known ion-molecule reactions occur even at rather low kinetic energies via non-completely inelastic collision complexes. This may explain why only a small fraction of observed ion-molecule reactions are known to involve persistent bimolecular collision complexes.¹²

LITERATURE REFERENCES

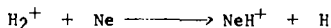
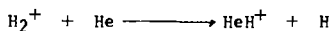
1. A. Henglein and G. A. Muccini, *Z. Naturforschung* **17a**, 452 (1962)
2. V. Cermak and Z. Herman, *Nucleonics*, **19**, No. 9, 106 (1961)
3. F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Acad. Press, Inc. Publ. N. Y. (1957)
4. V. Cermak and Z. Herman, *J. Chim. Physique* **57**, 717 (1960)
5. A. Henglein, *Z. Naturforschung* **17a**, 37 (1962)
6. B. Lindholm, *Proc. Roy. Soc. (London)* **66A**, 1068 (1953); *Arkiv Fysik* **18**, 219 (1960)
7. P. N. Rylander and S. Meyerson, *J. Am. Chem. Soc.* **78**, 5799 (1956)
8. J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.* **76**, 4501 (1954)
9. F. W. Lampe and F. H. Field, *J. Am. Chem. Soc.* **79**, 4244 (1957)
10. F. W. Lampe, *J. Am. Chem. Soc.* **79**, 6132 (1957)
11. F. W. Lampe, F. H. Field, and J. L. Franklin, *J. Am. Chem. Soc.* **79**, 6132 (1957)
12. R. F. Pottic and W. H. Hamill, *J. Phys. Chem.* **63**, 877 (1959)
A. Henglein, *Z. Naturforschung* **17a**, 44 (1962)
A. Henglein, G. Jacobs, and G. A. Muccini, *Z. Naturforschung*, **18a**, 98 (1963)

SOME RECENT EXPERIMENTAL MASS SPECTROMETER STUDIES
IN THE CHEMISTRY DEPARTMENT OF BROOKHAVEN NATIONAL LABORATORY*

L. Friedman
Chemistry Department
Brookhaven National Laboratory
Upton, L.I., New York

ABSTRACT

Contributions made by the author, Helge Von Koch, T. F. Moran, and A. P. Irsa will be reviewed. The subjects include studies on "endothermic ion-molecule reactions":



These reactions are examined from the standpoint of Gioumousis-Stevenson theory. Good agreement is obtained between experiment and theory if one assumes that vibrationally excited H_2^+ with sufficient energy to meet the thermochemical requirements of the reaction is the only ionized reactant. The data are used to obtain a value of the NeH^+ dissociation energy.

A brief description will be given of work with a short path length ion source used in a 60° sector mass spectrometer. Isotope effects in metastable transitions were investigated and will be discussed within the framework of the statistical theory of mass spectra.

- * Research performed under the auspices of the U. S. Atomic Energy Commission.

A STUDY OF SELECTED IONS IN THE MASS SPECTRA
OF BENZENETHIOL AND DEUTERATED BENZENETHIOL

by

D. G. Earnshaw,^{1/} G. L. Cook,^{2/} and G. U. Dinneen^{3/}

ABSTRACT

Partial mass spectra are presented for benzenethiol, C_6H_5SH , and deuterated benzenethiol, C_6H_5SD . The changes in ion intensities that result from deuterium labeling were studied to determine the structure of the parent ion before fragmentation. A 7-membered ring structure for the parent ion is proposed as precursor for some of the ions studied, whereas the 6-membered ring structure for the parent is proposed as precursor for the other ions.

Appearance potentials were obtained for several product ions from deuterated benzenethiol, C_6H_5SD , and were used to determine heats of formation of the ions and establish processes by which they are formed. The parent ion is the only intermediate between the molecule, C_6H_5SD , and the product ions at $m/e = 34, 45, 46, 67, 77, 84, 85, 109$, and 110 . A proposed process for the formation of each of the ions is discussed. When ring cleavage of the parent ion takes place, ring closure in one of the fragments also takes place.

INTRODUCTION

Part of the research done by the Bureau of Mines is concerned with sulfur compounds in petroleum and shale oil. Mass spectrometry has had an important role in this work (2, 9).^{4/} A study of benzenethiol is reported in this paper as an addition to this work.

^{4/} Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

Mass spectra of benzenethiol (C_6H_5SH) and deuterated benzenethiol (C_6H_5SD) were compared to determine which fragment ions contained the deuterium. From this information the structure of the precursor ion can be postulated. For example, the parent ion of benzenethiol might expand to a 7-membered ring before fragmentation, similarly to the ring expansion that has been proposed for alkylbenzenes (12) and alkylthiophenes (2).

Appearance potentials of selected ions were measured to determine heats of formation using the thermochemical equation:

$$\Delta H_f (\text{product ion}) = \Delta H_f (\text{precursor}) + \Delta H - \Delta H_f (\text{neutral fragment}) \text{ where:}$$

ΔH_f is heat of formation,

ΔH is heat of reaction, which is equal to the appearance potential of the product ion minus the appearance potential of the precursor.

It was assumed that substituting deuterium for hydrogen in benzenethiol had a negligible thermochemical effect. The proposed structure of the product ion, proposed structure of the neutral fragment, and the process of their formation were accepted if the value of ΔH_f (product ion), determined from the equation, agreed with the value of ΔH_f taken from the literature for the same ion.

EXPERIMENTAL

The benzenethiol used in this study was a standard sample prepared as a part of the work of American Petroleum Institute Research Project 48A at Laramie, Wyo. The deuterated benzenethiol was prepared by shaking 5 ml of the benzenethiol three successive times with equal volumes of D_2O . Conversion from C_6H_5SH to C_6H_5SD was 95 percent as determined by low-ionizing-voltage mass spectrometry and nuclear magnetic resonance spectrometry.

^{1/} Research Physicist.

^{2/} Project Leader.

^{3/} Project Coordinator.

All authors are with the Laramie Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Laramie, Wyo.

TABLE 1. - Partial spectra of C_6H_5SH and C_6H_5SD

m/e	Relative Ion Intensities			
	C_6H_5SH		C_6H_5SD	
	Polyisotopic	Monoisotopic	Polyisotopic	Monoisotopic
15	0.47	0.47	0.29	0.29
16	.03	.02	.17	.17
27	1.76	1.74	1.80	1.78
28	.07	.04	.39	.35
32	1.81	1.81	1.79	1.79
33	2.07	2.05	.30	.29
34	.47	.37	2.76	2.68
35	.12	.03	.49	.45
38	5.64	5.50	5.12	4.98
39	15.14	14.96	11.20	11.04
40	.93	.44	3.89	3.53
45	11.27	11.26	9.49	9.48
46	.35	.10	2.52	2.31
49	1.88	1.87	2.08	2.07
50	10.52	10.43	12.36	12.25
51	14.02	13.56	16.36	15.83
52	1.28	.68	2.25	1.52
65	10.38	10.36	6.13	6.09
66	27.90	27.33	3.13	2.80
67	1.67	.15	28.30	28.14
68	.62	.58	1.75	.20
69	11.43	11.41	9.46	9.42
77	13.78	13.68	9.32	9.22
78	2.45	1.55	7.13	6.52
79	.15	-	2.02	1.52
81	2.38	2.34	1.90	1.88
82	3.49	3.36	2.72	2.61
83	1.51	1.23	1.37	1.15
84	12.59	12.37	4.71	4.53
85	.77	.07	8.88	8.59
108	2.68	2.65	1.60	1.58
109	23.48	23.27	9.14	9.02
110	<u>100.00</u>	<u>98.16</u>	11.41	10.67
111	8.36	-	<u>100.00</u>	<u>98.78</u>
112	4.63	-	7.80	-
113	.34	-	4.60	-

The spectra of the thiols were obtained at 70 volts using a Consolidated Electro-dynamics Corporation 21-103C mass spectrometer with the sample inlet system at room temperature. Prior to obtaining the spectrum of the labeled thiol, the inlet system was conditioned to reduce the deuterium-hydrogen exchange. The spectrum of the C_6H_5SD was calculated by removing the contribution of C_6H_5SH from the spectrum of the impure sample.

Appearance potentials were obtained with repellers set at 2 volts and with the ionizing voltage meter replaced by a Hickok Model 534 voltmeter having 0-20 volt and 0-50 volt ranges. Appearance potential curves were obtained using a method similar to that of Lossing, Tickner, and Brice (11) except that the ionizing voltage which gave 0.1 percent ion abundance was taken as the appearance potential instead of the voltage that gave 1.0 percent.

The ionizing-voltage scale was calibrated using benzene as the primary standard. A mixture of benzene and benzenethiol was run, and appearance potential curves were plotted for both parent ions. The voltage scale was shifted so that the parent ion of benzene appeared at 9.2 eV (4). The appearance potential of the benzenethiol parent ion then was read directly from the voltage scale. In subsequent runs to determine the appearance potential of each fragment ion from C_6H_5SD , the appearance potential of the parent ion was used as a secondary standard.

RESULTS

Partial spectra of C_6H_5SH and C_6H_5SD are shown in table 1. Columns two and four show the polyisotopic patterns using the parent peak as a base. Columns three and five show the monoisotopic patterns after correcting the spectra for the isotopes C^{13} , S^{33} , and S^{34} .

All of the ions produced by a given process from C_6H_5SH appear at a single m/e , but some of the ions produced by the same process from C_6H_5SD appear at the next higher m/e because they contain a deuterium atom in the place of hydrogen. As the number of ions so displaced could not be determined directly, the method of Dibeler and Mohler (3) was used to determine the contribution of nondeuterated and deuterated ions to each selected m/e in the spectrum of C_6H_5SD . These data then were regrouped, as shown in table 2, to show the intensities for ions from C_6H_5SH and intensities for the same ions from C_6H_5SD divided into a nondeuterated and a deuterated portion.

The appearance potentials, proposed processes, and ΔH_f values for selected product ions from C_6H_5SD are shown in table 3. Accuracy of the values shown in the second column is estimated at ± 0.2 eV. The determined values of ΔH_f (product ion) shown in table 3 were obtained from the thermochemical equation using 1.1 eV as the ΔH_f for benzenethiol (13) and literature values of ΔH_f for neutral fragments from the processes shown. The ΔH_f values shown in the last column were taken directly from the literature or calculated by the method of group equivalents (5, 6, 7).

DISCUSSION

Several processes were considered for each of the ions from deuterated benzenethiol. The processes shown in table 3 gave determined values of ΔH_f (product ion) that agreed with the literature values to within 0.7 eV. All other processes considered gave values differing by at least 2.3 eV from the literature values. In every case the parent ion, $C_6H_5SD^+$, was the only intermediate between the molecule and the product ion; furthermore, ring cleavage in the parent ion was always followed by ring closure in one of the products, thus lowering ΔH for the process.

The data in tables 2 and 3 were used to postulate the structure of the parent ion before fragmentation. The observed appearance potentials and intensities for some product ions could be accounted for by a precursor with a structure similar to the conventional structure of the benzenethiol molecule, shown in figure 1A. However, the intensities and appearance potentials of other product ions could result only from a parent ion structure in which the 5 hydrogens and the deuterium were equivalent. One such structure is the 7-membered ring, figure 1B, analogous to the tropylium ion proposed by Rylander and Myerson (12). Although the deuterium is shown on a specific carbon in figure 1B, it could be associated with any carbon. In the subsequent discussion of specific ions, structure 1B will be used to represent structures in which the hydrogens and deuterium are equivalent.

$m/e = 33$ and 34. The m/e 34 ion, SD^+ , is produced by direct cleavage of the carbon-sulfur bond in structure 1A. Data in table 2 show the almost complete change from SH^+ production in $C_6H_5SH^+$ to SD^+ production in $C_6H_5SD^+$.

TABLE 2. - Ratios of intensities of nondeuterated to deuterated ions from C₆H₅SD

m/e	Empirical Formula	Intensity of ions from C ₆ H ₅ SH	Intensity of ions from C ₆ H ₅ SD	Ratio of intensities of ions from C ₆ H ₅ SD
33	SH ⁺	2.1	0.2	.11
34	SD ⁺	-	1.9	
45	CSH ⁺	11.3	9.1	4.14
46	CSD ⁺	-	2.2	
66	C ₅ H ₆ ⁺	27.3	-	-
67	C ₅ H ₅ D ⁺	-	27.3	
77	C ₆ H ₅ ⁺	13.7	8.0	1.40
78	C ₆ H ₄ D ⁺	-	5.7	
84	C ₄ H ₄ S ⁺	12.4	3.6	.41
85	C ₄ H ₃ DS ⁺	-	8.8	
109	C ₆ H ₅ S ⁺	23.3	10.2	.78
110	C ₆ H ₄ DS ⁺	-	13.1	
110	C ₆ H ₅ SH ⁺	98.2	-	-
111	C ₆ H ₅ SD ⁺	-	98.2	

TABLE 3. - Appearance potentials, proposed processes, and heats of formation for selected ions from C₆H₅SD

m/e	Appearance Potential, ev	Proposed Process	ΔH_f (product ion), ev		
			Determined	Literature	
45	12.7	C ₆ H ₅ SD ⁺ → CSH ⁺ + cyclo-C ₅ H ₄ D [·]	12.4	1/	12.4
46	12.7	C ₆ H ₅ SD ⁺ → CSD ⁺ + cyclo-C ₅ H ₅ [·]	12.4	1/	12.4
67	11.9	C ₆ H ₅ SD ⁺ → cyclo-C ₅ H ₅ D ⁺ + CS [·]	10.7	2/	(5)10.0
77	13.3	C ₆ H ₅ SD ⁺ → C ₆ H ₅ ⁺ + SD [·]	12.7		(5)13.1
84	11.8	C ₆ H ₅ SD ⁺ → cyclo-C ₄ H ₄ S ⁺ + C ₂ HD	10.5		(5)10.1
85	11.8	C ₆ H ₅ SD ⁺ → cyclo-C ₄ H ₃ DS ⁺ + C ₂ H ₂	10.5		(5)10.1
109	12.2	C ₆ H ₅ SD ⁺ → C ₆ H ₅ S ⁺ + D [·]	11.0		(6,7)11.0
110	10.8	C ₆ H ₅ SD ⁺ → C ₆ H ₄ DS ⁺ + H [·]	9.6		(6,7) 9.5
111	8.5	C ₆ H ₅ SD → C ₆ H ₅ SD ⁺	9.6		-

1/ An average of three values for the CSH⁺ ion reported by Hobrock and Kiser (see reference 8 in the bibliography).

2/ Underlined numbers in parentheses refer to items in bibliography at the end of this paper.

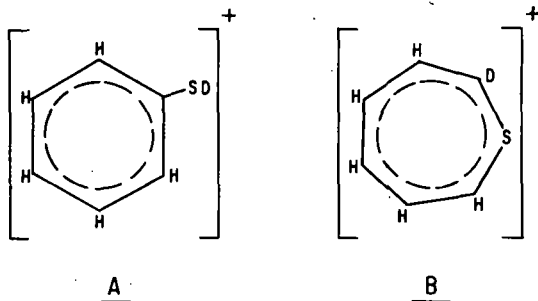


FIGURE 1.—Two proposed structures for the parent ion of C_6H_5SD

$m/e = 45$ and 46 . Simple ring cleavage of the structure 1A would produce CSH^+ ions only, but the data in table 2 show that the ratio of intensities of CSH^+ ion to CSD^+ ion from C_6H_5SD is 4.1. Ring cleavage of structure 1B would produce CSH^+ ions and CSD^+ ions in the intensity ratio of 5, which is close to the observed ratio of 4.1. The postulation of the same precursor for both ions is supported by the fact that they have identical appearance potential curves.

The values of ΔH_f for CSH^+ and CSD^+ shown in table 3 were determined using a ΔH_f for the cyclopentadienyl radical of 1.5 ev obtained by group equivalent methods. The good agreement between the determined values of the CSH^+ and CSD^+ ions and the literature value for the CSH^+ ion supports the process proposed in table 3.

$m/e = 67$. The 67 ion must be $C_5H_5D^+$, as all 5 hydrogens and the deuterium are required to produce it. A ΔH_f of 10.7 ev was determined for the 67 ion using a ΔH_f for the neutral fragment, $CS\cdot$, of 2.3 ev (4). This ion could have either a cyclic or non-cyclic structure, but the cyclic structure is more likely because the determined value of ΔH_f for the 67 ion was within 0.7 ev of the literature value for the cyclopentadiene ion, whereas, it differed by more than 2 ev from ΔH_f values for noncyclic structures calculated by group equivalents (5, 6, 7).

$m/e = 77$ and 78 . The 77 ion, $C_6H_5^+$, can be accounted for by simple bond cleavage of structure 1A. The resulting phenyl ion has a ΔH_f of 12.7 ev determined using a ΔH_f of 1.7 ev for the $\cdot SD$ radical (4). The good agreement shown in table 3 between the determined and literature value of ΔH_f indicates a simple cleavage of the carbon-sulfur bond to produce the phenyl ion at m/e 77 and the $\cdot SD$ radical.

One might expect very little production of 78 ions, $C_6H_4D^+$, from $C_6H_5SD^+$ because the production of 77 ions, $C_6H_5^+$, from structure 1A by loss of $\cdot SD$ seems to be straightforward. However, a relative intensity of 5.7 percent was observed for the 78 ions as shown in table 2. The appearance potential for the 78 ions was approximately 1 ev lower than that for the 77 ion. No process could be postulated for the formation of 78 ions.

$m/e = 84$ and 85 . The 84 ions, $C_4H_4S^+$, and the 85 ions, $C_4H_3DS^+$, have identical appearance potential curves showing that they have the same precursor. Both the 84 ions, $C_4H_4S^+$, and the 85 ions, $C_4H_3DS^+$, can be accounted for by simple cleavage of structure 1B, but only the 85 ions can be accounted for by simple cleavage of structure 1A. The observed ratio of the intensities of 84 ions to 85 ions is .42, in fair agreement with the ratio of .50, which would be expected from structure 1B.

The 84 ions, $C_4H_4S^+$, and the 85 ions, $C_4H_3DS^+$, have the thiophene structure, and the neutral fragment is acetylene. Using a ΔH_f of 2.4 ev (1) for acetylene, the determined value of ΔH_f for the 84 and 85 ions agrees well with the literature value of ΔH_f for the thiophene ion, as shown in table 3.

$m/e = 109$ and 110 . The 109 ion, $C_6H_5S^+$, is produced by loss of $D\cdot$ from $C_6H_5SD^+$. Using a ΔH_f for $D\cdot$ of 2.3 ev (4), the determined ΔH_f for the 109 ion is identical to the literature value shown in table 3. The 110 ion, $C_6H_4SD^+$, is produced by loss of $H\cdot$ from $C_6H_5SD^+$. Using a ΔH_f for $H\cdot$ of 2.3 ev (4), the determined ΔH_f for 110 ions agrees closely with the literature value shown in table 3.

It is believed that the 109 ions, $C_6H_5S^+$, and the 110 ions, $C_6H_4SD^+$, issue from structure 1A rather than from 1B as evidenced by the ratio of intensities of the two ions, their appearance potentials, and the shape of the appearance potential curve for the 109 ions. If all of the 109 ions were produced from structure 1B by loss of $D\cdot$, the corresponding loss of $H\cdot$ would yield 110 ions having the same appearance potential as the 109 ions and an intensity 5 times as great. Actually, the 110 ions have an appearance potential 1.4 ev lower than the 109 ions (table 3) and an intensity only 1.3 times as great (table 2). If the 109 ions were produced partly from structure 1A and partly from 1B, there should be a break in the appearance potential curve, but none was observed. Hence, structure 1A is the most probable source of the 109 ions, and the 110 ions also must come from this structure, because structure 1B cannot produce 110 ions without simultaneously producing 109 ions.

$m/e = 111$. The parent ion, $C_6H_5SD^+$, of deuterated benzenethiol, has a determined ΔH_f° of 9.6 ev, as shown in table 3. This value was calculated using a ΔH_f° of 1.1 ev for the compound (13).

CONCLUSIONS

For all the processes studied, two nonequivalent forms of the parent ion are the only intermediates between the molecule and the fragment ions. When ring cleavage occurs in the parent ion, ring closure occurs in one of the products thereby lowering the total energy required for the reaction. The processes and structures proposed are those which best fit the thermochemical data. It has been shown that some of the ions from C_6H_5SD issue from the 6-membered ring structure where the hydrogen and deuterium are not equivalent, but other ions issue from another structure, such as the 7-membered ring, where the hydrogens and deuterium are equivalent.

REFERENCES

1. American Petroleum Institute. Research Project 44. Selected Values of Properties of Hydrocarbons and Related Compounds. Table 12p, October 31, 1956.
2. Cook, Glenn L., and Norman C. Foster. Relation of Molecular Structures to Fragmentation of Some Sulfur Compounds in the Mass Spectrometer. *Proc. Am. Pet. Inst.*, Sec. III Refining, v. 41, No. III, 1961, pp. 199-214.
3. Dibeler, Vernon H., and Fred L. Mohler. Mass Spectra of the Deuteromethanes. *J. Research National Bureau of Standards*, v. 45, 1950, p. 441.
4. Field, F. H., and J. L. Franklin. Electron Impact Phenomena and the Properties of Gaseous Ions. Academic Press, New York, 1957, table 18, p. 129; table 45, Pt. 1, pp. 242-309.
5. Franklin, J. L. Calculations of the Heats of Formation of Gaseous Free Radicals and Ions. *J. Chem. Phys.*, v. 21, 1953, pp. 2029-2033.
6. _____. Prediction of Heat and Free Energies of Organic Compounds. *Ind. and Eng. Chem.*, v. 41, 1959, pp. 1070-1076.
7. Franklin, J. L., and F. H. Field. The Resonance Energies of Certain Organic Free Radicals and Ions. *J. Am. Chem. Soc.*, v. 75, 1953, pp. 2819-2821.
8. Hobrock, Brice G., and Robert W. Kiser. Electron Impact Spectroscopy of Sulfur Compounds. I. 2-thiabutane, 2-thiapentane, and 2,3-dithiabutane. *J. Phys. Chem.*, v. 66, 1962, pp. 1648-1652.
9. Kinney, I. W., and Glenn L. Cook. Identification of Thiophene and Benzene Homologs. *Anal. Chem.*, v. 24, 1952, pp. 1391-1396.
10. Lossing, F. P., A. W. Tickner, and W. A. Bryce. The Ionization Potentials of the Deuterate Methanes. *J. Chem. Phys.*, v. 19, 1951, pp. 1254-1258.
11. Rylander, Paul N., Seymour Myerson, and Henry M. Grubb. Organic Ions in the Gas Phase. II. The Tropylium Ion. *J. Am. Chem. Soc.*, v. 79, 1957, pp. 842-846.
12. Scott, D. W., J. P. McCullough, W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, and Guy Waddington. Benzenethiol: Thermodynamic Properties in the Solid, Liquid, and Vapor States; Internal Rotation of the Thiol Group. *J. Am. Chem. Soc.*, v. 78, 1956, pp. 5263-5268.

ORGANIC IONS IN THE GAS PHASE.
PHENYLATED CYCLOPROPANE ION IN THE DECOMPOSITION OF 3-PHENYLPENTANE

by

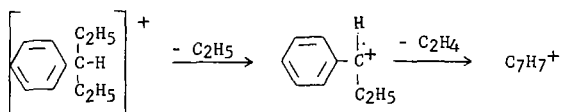
Seymour Meyerson
 Research and Development Department, American Oil Company, Whiting, Indiana

and

Harold Hart
 Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan

ABSTRACT

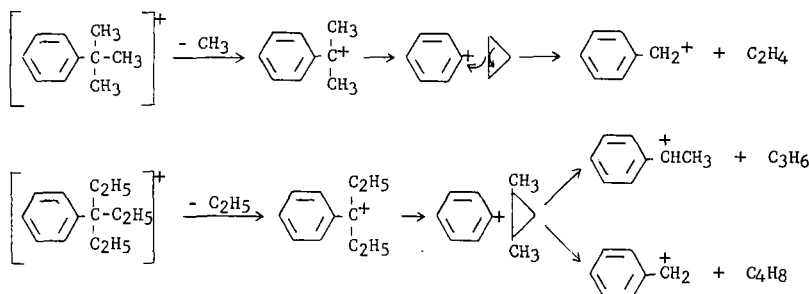
3-Phenylpentane breaks down under electron impact in the mass spectrometer by the path:



The spectra of 3-phenylpentane-1-d and -3-d reveal further details of this path. The C_2H_5 radical lost in step 1 consists solely of one of the original ethyl groups; thus no rearrangement of the parent ion precedes the primary cleavage. Step 2 apparently encompasses two separate reactions: I, beta cleavage and gamma hydrogen migration in the phenylpropyl ion; II, rearrangement to a phenylated cyclopropane ion, followed by shift of two electron pairs to give the observed products. II is the lower-energy process and accounts for 90% of the C_7H_7^+ ion yield obtained with 70-volt electrons.

INTRODUCTION

Evidence has been reported for cationated cyclopropanes as intermediates in gas-phase ionic decompositions in the mass spectrometer (1,2). Such species in which the coordinating cation is phenyl can account for the formation of C_7H_7^+ from t-butylbenzene, of C_8H_9^+ and C_7H_7^+ from 3-ethyl-3-phenylpentane, and for the label retentions observed in these ions when formed from labeled molecules (1,2):



The products can be formed simply by shift of two electron pairs (1-3), as shown in the first equation. Further evidence for such intermediates has been uncovered in a study of mass spectra of 3-phenylpentane unlabeled, -1-d, and -3-d.

EXPERIMENTAL

Unlabeled 3-phenylpentane was prepared by sodium-catalyzed ethylation of 1-phenylpropane (4,5). The 1-d species was isolated by fractional distillation from the synthesis of 3-ethyl-3-phenylpentane-1-d (1); the 3-d species was available from another investigation (6). Both labeled species were purified by gas chromatography. Isotopic composition of the labeled species was determined from the parent peaks in the 70-volt spectra:

	1-d	3-d
Unlabeled	12.0%	45.9%
$\underline{d}_1$	84.0	54.1
$\underline{d}_2$	4.0	0.0

The $\underline{d}_2$ material in the 3-phenylpentane-1-d suggests that the temperature during alkylation rose high enough to effect some dehydrogenation (4).

Mass spectra were measured on a modified (7) Consolidated instrument with 70-volt electrons. Table I shows partial spectra, corrected for the contributions of naturally occurring C^{13} and D (8) and of unlabeled 3-phenylpentane in the deuterated materials. That the fragment ions included arise in a common sequence is shown by the metastable peaks (2):

and

69.6	$(119^+) \rightarrow (91^+) + 28$
46.4	$(91^+) \rightarrow (65^+) + 26$

in the spectrum of the unlabeled species. More-diffuse metastable peaks at about the same masses in the spectra of the labeled species doubtless include unresolved components for metastable transitions of labeled ions:

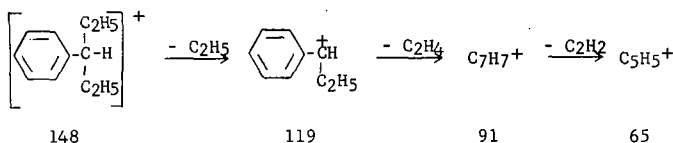
and

69.0	$(120^+) \rightarrow (91^+) + 29$
70.5	$(120^+) \rightarrow (92^+) + 28$
45.9	$(92^+) \rightarrow (65^+) + 27$
47.3	$(92^+) \rightarrow (66^+) + 26$

Measurements to determine dependence of label retention on ionizing voltage (9,10) were made with the repeller plates at an average potential of 3 volts; actual settings, adjusted for maximum ion current, were 3.55 volts on the inner repeller and 2.45 volts on the outer one.

DISCUSSION

The observed metastable peaks define the reaction path:



The ionic structure shown for $\text{C}_9\text{H}_{11}^+$ is nominal only. Label retentions in fragment ions from labeled species must reflect the nature of the decomposition steps and hence the structures of the reaction intermediates.

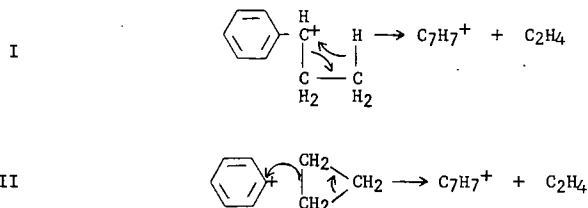
Retentions calculated (2) from the spectra are:

	1-d	3-d
$\text{C}_9\text{H}_{11}^+$	50.5 to 52.0%	100%
C_7H_7^+	16.3 to 19.8%	41.5%
C_5H_5^+	12 to 16%	46%

The uncertainties in the case of the ions from the 1-d species arise because of the unknown contributions of the $\underline{d}_2$ impurity. The lower limits shown were arrived at by assuming that the ions derived from 3-phenylpentane- $\underline{d}_2$ all contain at least one deuterium atom. The upper limits were arrived at by ignoring contributions of the $\underline{d}_2$ species.

Retentions in the $\text{C}_9\text{H}_{11}^+$ ions establish unequivocally that the C_2H_5 radical lost in the first step is one of the original ethyl groups. Thus no rearrangement of the parent ion precedes the primary decomposition.

Retention in the $C_7H_7^+$ ion from the 1-d species is about one-third that of $C_9H_{11}^+$. This value can be accounted for equally well by either of two mechanisms: I, cleavage of the beta carbon-carbon bond with concomitant hydrogen migration from the gamma carbon to the aryl moiety, as has been shown to occur in formation of $C_7H_8^+$ from 1-phenylbutane (11); II, rearrangement of $C_9H_{11}^+$ to a phenylated cyclopropane ion either concerted with or following the primary loss of C_2H_5 , followed by shift of two electron pairs, as in decomposition of t-butylbenzene, to give $C_7H_7^+$ and C_2H_4 :



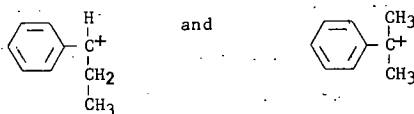
The 3-phenylpentane-3-d data furnish a basis for distinguishing between these mechanisms. Deuterium retention in $C_7H_7^+$ formed from this species by I should be 100%; by II, 33%. The experimental value is 41.5%, intermediate between the two predicted values.

The possibility that more than one path might be involved was explored by measuring the C7 spectral region at ionizing voltages varying from the appearance potential of $C_7H_7^+$ to 70 e.v. and examining the voltage dependence of label retention in the $C_7H_7^+$ ion (9,10). In the ion derived from 3-phenylpentane-1-d, retention was found to be independent of ionizing voltage over the entire range studied. In that derived from the 3-d species, retention is constant at about 35% over a range of some 3 volts immediately above the appearance potential; it then increases smoothly to a maximum of 41.2%, attained at about 40 volts, above which it is independent of ionizing voltage. The appearance potential apparently corresponds to the onset of II. The dependence of label retention on ionizing voltage implies that $C_7H_7^+$ arises by more than one reaction, and can be accounted for by contributions from the two mechanisms II and I in appropriate proportions: about 90:10 at ionizing voltages greater than 40 volts.

Neither the precise structure of the intermediate in path II nor the way in which it is formed is clear. The present data, coupled with those on t-butylbenzene- α - Cl_3 , require that the three carbon atoms and the six hydrogen atoms in the side-chain become indistinguishable as viewed from the phenyl group. A phenylated cyclopropane ion most simply represents $C_9H_{11}^+$ with the required symmetry.

The likelihood that $C_7H_7^+$ is formed from both 3-phenylpentane and t-butylbenzene mainly via a common intermediate poses an interesting problem. In the spectrum of the former compound, the ratio of intensities $C_7H_7^+ : C_9H_{11}^+$ is about 2 to 1; in that of the latter, it is about 1 to 2. Probability of losing C_2H_4 following primary beta cleavage is grossly different in the two compounds. Moreover, the difference in behavior is not limited to this specific pair of compounds, but is characteristic of the two classes of alkylbenzenes to which they belong (2)--secondary alkylbenzenes in which both substituents on the alpha carbon are larger than methyl, and 2-methyl-2-phenylalkanes.

The difference can be accounted for if the phenylated cyclopropane structure is assumed to arise largely by rearrangement of $C_9H_{11}^+$ ions formed initially in the less-stable classical structures (12):



The energy released by rearrangement of the secondary carbonium ion derived from 3-phenylpentane should be greater than that released by rearrangement of the initially more-stable tertiary ion derived from t-butylbenzene. The excess energy furnishes proportionately greater driving force for further decomposition.

TABLE I
PARTIAL SPECTRA OF 3-PHENYLPENTANES

<u>m/e</u>	<u>Unlabeled</u>	<u>-1-d^a</u>	<u>-3-d</u>
150	.0	4.6	.0
149	.0	95.4	100.0
148	100.0	b	b
147	.1	.0	.1
121	.0	7.1	.0
120	.2	149	297
119	287	140	14.9
93	.4	3.7	1.2
92	.0	101	222
91	533	408	303
67	.6	.7	.7
66	.6	4.3	11.9
65	26.0	23.6	16.9

^a Contains 4.6% 3-phenylpentane-d₂.

^b Assumed zero in calculating isotopic composition.

The C₇H₇⁺ ion derived from 3-phenylpentane decomposes further to C₅H₅⁺ to only a small extent, as indicated by the low intensity of the latter ion. In the spectrum of the 3-d species, label retention in C₅H₅⁺ is greater than that in C₇H₇⁺. This finding implies--if contributions from other, unknown precursors are not involved--that C₇H₇⁺ ions differing in label retention differ also with respect to further decomposition to C₅H₅⁺ and C₂H₂. Specifically, the data can be accommodated by a population of C₇H₇⁺ ions all having the symmetrical tropylium configuration (2,3) if the probability of further decomposition--as measured by the intensity ratio C₅H₅⁺:C₇H₇⁺--is assumed to be twice as great for ions arising by mechanism I as for those arising by mechanism II.

Thus, differences in energy content of molecule-ions, even those that decompose by nominally the same path, can be propagated through sequential reaction steps. Rearrangements, including particularly those to nonclassical structures, may well perform a critical function in the internal energy conversions responsible for the rich detail found in mass spectra of organic molecules.

REFERENCES AND FOOTNOTES

1. P. N. Rylander and S. Meyerson, J. Am. Chem. Soc., 78, 5799 (1956).
2. H. M. Grubb and S. Meyerson, in "The Mass Spectrometry of Organic Ions", F. W. McLafferty, ed., Academic Press, New York, 1963, p. 453.
3. The C₇H₇⁺ ion is shown here as having the nominal benzyl structure. It might be better represented, however, as the symmetrical tropylium ion (see ref. 2; also, P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc., 79, 842 (1957); S. Meyerson and P. N. Rylander, J. Chem. Phys., 27, 901 (1957)). The phenylethyl structure written for the C₈H₉⁺ ion is also to be regarded as nominal only.
4. H. Pines, J. A. Vesely, and V. N. Ipatieff, J. Am. Chem. Soc., 77, 554 (1955).
5. We are indebted to D. H. Esmay for this synthesis.
6. H. Hart and R. E. Crocker, J. Am. Chem. Soc., 82, 418 (1960).
7. H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, presented before 7th annual meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, May, 1959.
8. J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry", Elsevier Publishing Company, Amsterdam, 1960.

9. S. Meyerson, J. Chem. Phys., 34, 2046 (1961).
10. S. Meyerson, T. D. Nevitt, and P. N. Rylander, in "Advances in Mass Spectrometry," v. 2, R. M. Elliott, ed., Pergamon Press, New York, 1963, p. 313.
11. J. D. McCollum and S. Meyerson, J. Am. Chem. Soc., 81, 4116 (1959).
12. N. Muller and R. S. Mulliken, J. Am. Chem. Soc., 80, 3489 (1958).

IONIZATION AND DISSOCIATION PROBABILITIES
OF THE THREE NITROGEN MOLECULES INVOLVING
THE MASS 14 AND 15 ISOTOPES

Donald P. Easter and Amos J. Coleman
Basic Research Group
U. S. Army Engineer Research and Development Laboratories
Fort Belvoir, Virginia

Manuscript Withdrawn

Metastable Transitions in Small Molecules

V. H. Dibeler and H. M. Rosenstock

Physical Chemistry Division
National Bureau of Standards
Washington, D. C.

Introduction

The study of metastable transitions in mass spectra of polyatomic molecules has yielded much information concerning unimolecular ionic decomposition rates and mechanisms. Among other things, a quantitative explanation of the variety and abundance of metastable transitions has served as a powerful test of the validity of applying unimolecular reaction rate theory to the decomposition of isolated ions (or molecules). In the case of very small systems, such as triatomic or tetraatomic ions, particular interest attaches to the question of whether such a system can decompose with a rate slow enough (10^5 - 10^7 sec⁻¹) to be observable as a metastable transition in the conventional mass spectrometer.

There is little evidence for such transitions. In 1950, Dibeler and Mohler reported the occurrence of a metastable transition in the mass spectrum of CD₄⁺, corresponding to the loss of a deuterium atom from the CD₄⁺ ion. A later study of CH₄ by Melton and Rosenstock showed that only collision-induced dissociation peaks occurred in the CH₄ mass spectrum, although they did not investigate the deuteromethanes. Recently, there has been a brief controversy concerning the possible existence of a unimolecular metastable dissociation in N₂O. Because of this interest, we are carrying out an extensive mass spectrometric study on small polyatomic molecules to provide experimental information on this question. In this report we present detailed results on various isotopically substituted hydrogen sulfides and methanes, and mention some observations on H₂O and N₂O.

Experimental

Measurements were made by means of a 12-inch radius of curvature, 60° sector-field mass spectrometer. Both magnetic and electrostatic sweep were available, with a maximum ion accelerating voltage of 4000v. The ion repeller voltage was continuously adjustable from 0 to 40v. Source and collector slit widths were externally adjustable and, with proper attention to contributing parameters, permitted very satisfactory resolution of the C¹²O¹⁶ - N₂¹⁴ mass doublet. The ionizing electron beam was nominally trap-current controlled at 10 μ amp although some measurements were made at 50 μ amps. The nominal electron energy was variable from 5 to 100v in 0.1 v increments. The source housing and analyzer tube were separately pumped and could achieve a base pressure of 1×10^{-8} mm as measured with a Veeco ion gauge. However, pump-down between successive measurements usually reached about 5×10^{-8} mm. Ion current measurements in the range of 10^{-17} to 3×10^{-10} amps. were made by means of a 16-stage electron multiplier followed by a vibrating reed electrometer and recording potentiometer. Gas samples were introduced into the ion source through an all-metal inlet system using non-lubricated sylphon valves and a gold foil with a pinhole leak. Additional valves permitted the separate introduction of gases into the analyzer tube.

The hydrogen sulfide used in this study was Matheson C. P. Grade with a stated minimum purity of 99.5%. No other sulfur compounds were observed in the mass spectrum of this material. The deuterated hydrogen sulfide (D₂S) was kindly supplied by Professor B. DeB. Darwent of Catholic University. It was prepared by the repeated exchange of commercial H₂S with nearly pure D₂O. The purity was reported by the donor to be 97% D₂S. Unfortunately this could not be confirmed directly in the present studies because of a continuing isotope exchange in the sample system and the ion source. The HDS produced in the latter exchange was utilized for the study of that species.

The methane was Matheson CP grade with a purity greater than 99 percent, as stated by the manufacturer. The deuteromethanes were obtained from Merck, Sharpe and Dohme of Canada, Ltd. with a stated minimum isotopic purity of 98 atom percent deuterium. Mass spectrometric

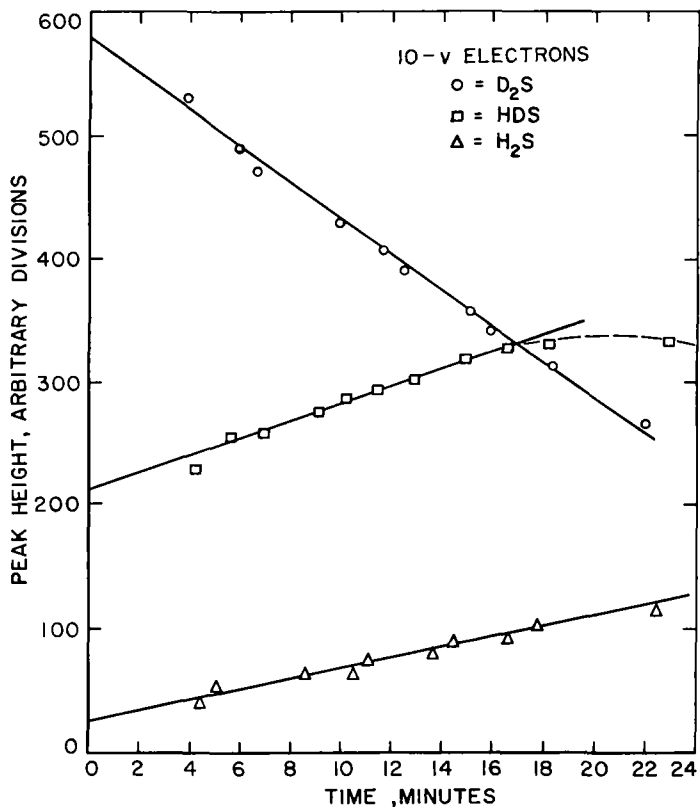


Fig. 1. Variation of peak height for D_2S^+ , HDS^+ , and H_2S^+ ions with time using a nominal electron energy of 10v.

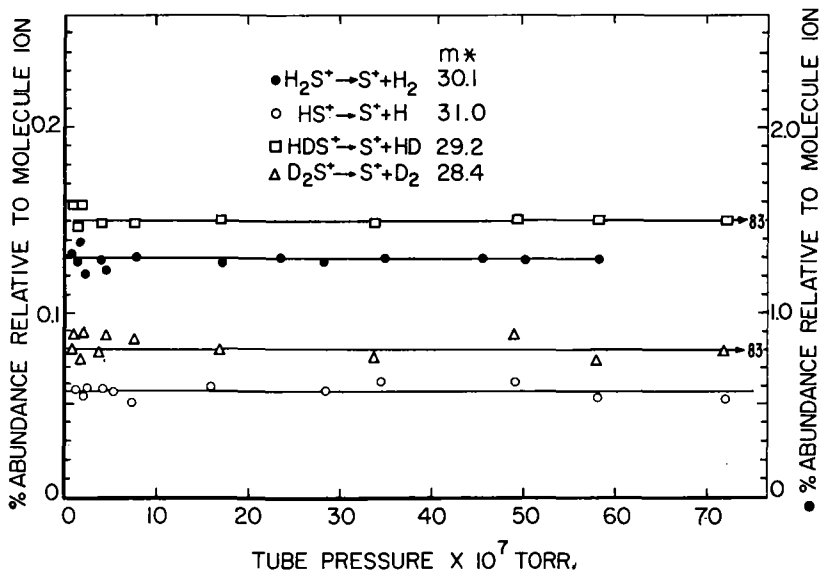


Fig. 2. Effect of variation in analyser tube pressure on relative abundances of metastable transitions in the hydrogen sulfides.

measurements indicated a comparable chemical purity.

Mass spectra were obtained in the usual manner using 70-v electrons. The relative abundances of the metastable transitions were also observed as a function of the analyzer tube pressure in order to determine whether the transitions were truly unimolecular or were collision-induced. The appearance potential curves were obtained with argon as a reference gas. The curves were normalized both at 70v and near threshold and plotted on a semi-logarithmic scale. In the case of D_2S , the continuing isotopic exchange was monitored and appropriate correction made as detailed below.

Results and Discussion

A. Hydrogen Sulfide

The study of ordinary H_2S in the mass spectrometer poses no unusual problems. Ionization and appearance potentials have been reported by a number of workers. The mass spectrum, however, is complicated by the presence of four sulfur isotopes of relative abundances $^{32}S = 1.0$, $^{33}S = 0.008$, $^{34}S = 0.044$ and $^{36}S = 0.00015$. In table I, the measured intensities at various mass positions are given together with their calculated contributions from various isotopic sources. In these calculations it was assumed that any sulfur isotope effect on fragmentation was negligible and that the contribution of ions containing deuterium in natural concentration ($\sim 1:6000$) could be ignored. The peaks at masses 30.1 and 31.0 are due to the metastable transition m_1 , $H_2^{32}S^+ \rightarrow ^{32}S^+ + H_2$ and m_2 , $H_2^{32}S^+ \rightarrow ^{32}S^+ + H$. At mass 32 there is a diffuse portion at the base of the peak, attributable to m_3 , $H_2^{32}S^+ \rightarrow H^{32}S^+ + H$. In addition there are significant contributions to the latter two of these transitions from other sulfur isotopes. These were also calculated assuming no sulfur isotope effect on dissociation probabilities. Contributions of less than 0.1 mv were ignored. The relative abundances of the different types of ions are summarized at the bottom of the table.

Table I
Summary of 70-v polyisotopic spectrum of H_2S and calculated contributions of the isotopic species of sulfur to the monoisotopic spectrum

m/e	Peak height (millivolts)	$S_{m_1}^+$	$S_{m_2}^+$	$S_{m_3}^+$	S^+	HS^+	H_2S^+	Residuals
30.1	17.1	17.1	-	-	-	-	-	-
31.0	0.9	0.1	0.8	-	-	-	-	-
32	651.	0.7	-	0.8*	649.5	-	-	-
33	567.	-	-	-	5.2	561.8	-	-
34	1353.	-	-	-	28.8	4.5	1319.7	-
35	35.3	-	-	-	-	24.9	10.6	-0.2
36	58.7	-	-	-	0.1	-	58.6	0
37	0.2	-	-	-	-	0.1	-	0.1
38	0.3	-	-	-	-	-	0.2	0.1
Totals		17.9	0.8	0.8	683.6	591.3	1389.	-
Relative Abundance		1.3	0.06	0.06	49.2	42.6	100.	

*Estimated total height of diffuse portion of the base of m/e = 32.0 peak was 1.5 mv.

In the case of D_2S , there is a problem of isotope exchange with residual hydrogenic compounds in the apparatus. In the present work, equilibration appeared impractical. However, the rate of the exchange was sufficiently slow and superficially simple enough to permit gathering of the desired information. At low electron voltages (ca 10 ev) the mass spectrum consists only of parent ions and Fig. 1 shows a typical variation of the composition with time as a result of the exchange. Thus, with suitable corrections for the S^{34} isotopes, a reasonable estimate of the various species can be obtained. This

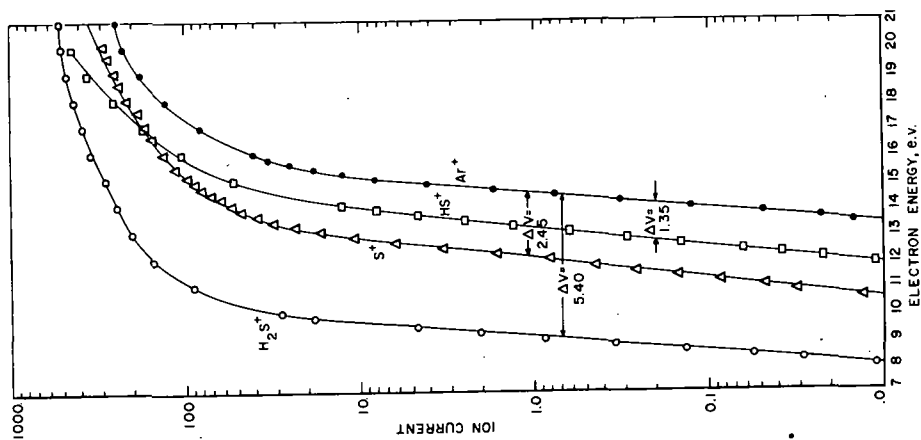


Fig. 3.

Semi-logarithmic plot of ion current versus uncorrected electron energy for H_2S^+ , S^+ , and Ar^+ ions.

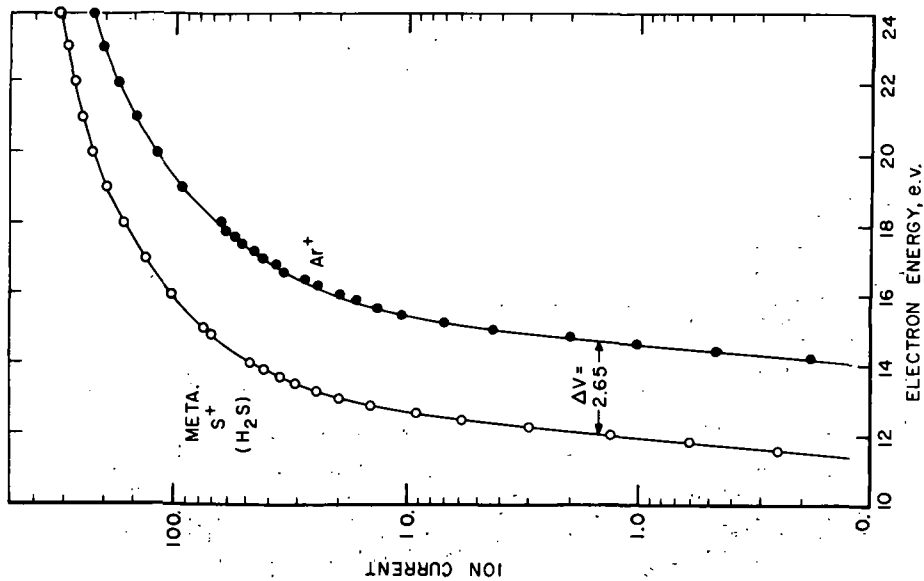


Fig. 4.

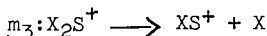
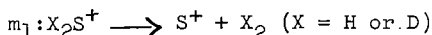
Semi-logarithmic plot of ion current versus uncorrected electron energy for S^+ from the metastable transition, $H_2S^+ \rightarrow S^+ + H_2$ and for Ar^+ .

estimate is limited, among other things, by the isotope effect on ionization potentials which causes a difference in the ionization cross section at low electron energies. This is indicated by the fact that the sum of the three parent ion intensities decreases slightly with time (see Fig. 1). With these limitations the HDS and D₂S cracking patterns can be determined by alternate scanning at 10 ev and at 70 ev. Correction for changes in concentration during a 70 ev scan results in nothing more than the mass spectra of several different mixtures of H₂S, HDS and D₂S the component mass spectra of which can be calculated by standard methods. The resultant mass spectra are listed in Table II.

Table II
Monoisotopic Spectra of Isotopic Hydrogen Sulfides
for 70-v Electrons

Ion	% Relative Abundance		
	H ₂ S	HDS	D ₂ S
S ⁺ (m ₁) ^{a/}	1.3	0.15	0.08
S ⁺ (m ₂)	0.06	b/	b/
S ⁺ (m ₃)	0.06	b/	b/
S ⁺	49.2	36.	36.
HS ⁺	42.6	12.	-
DS ⁺	-	27.	28.
H ₂ S ⁺	100.	-	-
HDS ⁺	-	100.	-
D ₂ S ⁺	-	-	100.

a/Metastable transitions:



b/Presently inseparable in mixed isotopic species. Probably ~ 0.01.

The dependence of the relative abundance of the metastable transitions on analyzer tube pressure was also determined. The results are shown in Fig. 2. It is clear that these decomposition processes are truly unimolecular and not collision-induced.

Figures 3 and 4 show typical semi-logarithmic plots of the ionization efficiency curves for the principal ions in the spectrum of H₂S. In Fig. 3, ion current versus uncorrected electron energy is plotted for the H₂S⁺, HS⁺, S⁺, and Ar⁺ ions. In Fig. 4, ion current versus electron energy is plotted for the metastable transition H₂S⁺ $\longrightarrow$ S⁺ + H₂(m₁) and for Ar⁺. In each case, the H₂S ion was matched to the Ar⁺ ion at 70v. The curves are essentially parallel and straight over 3 orders of magnitude in the case of the stable ions and nearly 2 orders in the metastable transitions. No significant change resulted in attempts to match curves near threshold. The voltage intervals between unknown and calibration gas were measured at arbitrarily selected points as indicated in the figures. Average values for three determinations together with the maximum deviation from the mean are given in Table III.

Similar curves were obtained for the molecule ions of HDS and D₂S and for the metastable transitions, HDS⁺ $\longrightarrow$ S⁺ + HD and D₂S⁺ $\longrightarrow$ S⁺ + D₂. The data, together with previously reported values are summarized in Table III.

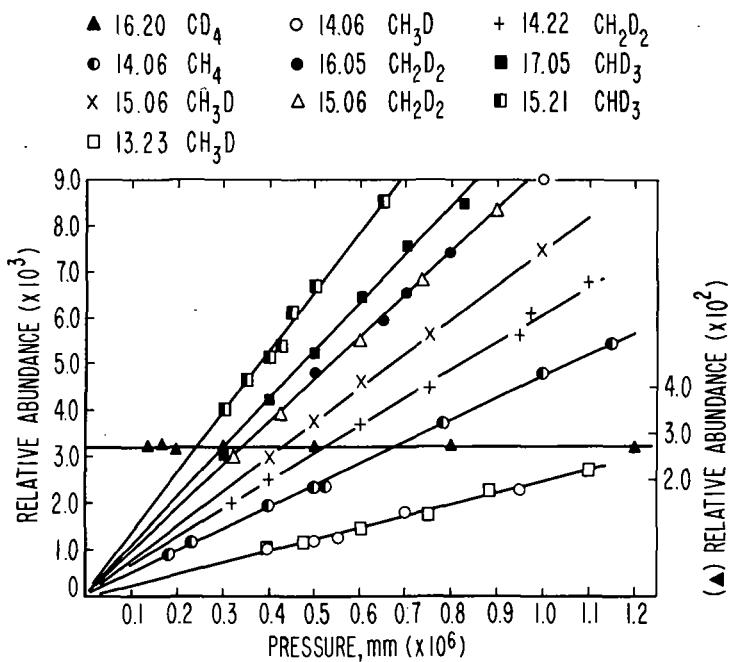


Fig. 5. Variation of relative abundance of metastable ions with pressure in the analyser tube.

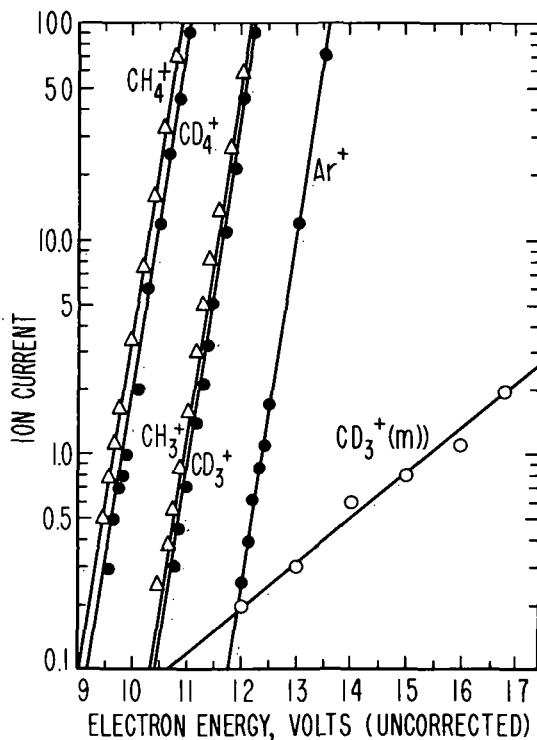


Fig. 6. Semilogarithmic plot of ion current versus uncorrected electron energy for Ar^+ , CH_4^+ , CD_4^+ , CH_3^+ , CD_3^+ , and the peak resulting from the metastable transition $\text{CD}_4^+ \rightarrow \text{CD}_3^+ + \text{D}$.

Table III
Ionization and Appearance Potentials for the Isotopic
Hydrogen Sulfides

Ion Process	Energy (ev)		Previous work
	This work		
$\text{H}_2\text{S} \longrightarrow \text{H}_2\text{S}^+$	10.4 ± 0.1	$10.45 \pm 0.03^{\text{a/}}$	$10.47 \pm 0.01^{\text{b/}}$
		12.46 ± 0.02	
		14.18 ± 0.04	
$\longrightarrow \text{HS}^+ + \text{H}$	14.4 ± 0.1	$14.43 \pm 0.1^{\text{c/}}$	$15.2 \pm 0.5^{\text{d/}}$
$\longrightarrow \text{S}^+ + \text{H}_2$	13.3 ± 0.1	$14.0 \pm 0.7^{\text{d/}}$	
		18.5 ± 1	
$\text{H}_2\text{S}^+ \longrightarrow \text{S}^+ + \text{H}_2 (m_1)$	13.1 ± 0.2	-	
$\text{HDS} \longrightarrow \text{HDS}^+$	10.3 ± 0.2	-	
$\text{HDS}^+ \longrightarrow \text{S}^+ + \text{HD} (m_1)$	12.9 ± 0.3	-	
$\text{D}_2\text{S} \longrightarrow \text{D}_2\text{S}^+$	10.2 ± 0.2	-	
$\text{D}_2\text{S}^+ \longrightarrow \text{S}^+ + \text{D}_2 (m_1)$	13.0 ± 0.3	-	

^{a/}D. C. Frost and C. A. McDowell, Can. J. Chem. 36, 39 (1958). These values are identified with $2B_1$, $2A_1$, and $2B_2$ states of the ion.

^{b/}K. Watanabe, J. Chem. Phys. 26, 542 (1957).

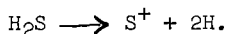
^{c/}T. F. Palmer and F. P. Lossing, J. Am. Chem. Soc. 84, 4661 (1962).

^{d/}H. Neuert and H. Clasen, Z. Naturforsch. 7a, 410 (1952).

The effect of isotopic substitution on the fragmentation of hydrogen sulfide is qualitatively the same as in other molecules.

The ionization potential of H_2S (10.4 ± 0.1 ev) is in good agreement with the first ionization potential of H_2S reported by Frost and McDowell and with photoionization measurements by Watanabe. Using the value $\Delta H_f(\text{H}_2\text{S})_g = -4.82$ kcal./mole, we calculate $\Delta H_f(\text{H}_2\text{S}^+) = 235$ kcal./mole. Similarly, the appearance potential of the HS^+ ion (10.4 ± 0.1 ev) gives $\Delta H_f(\text{HS}^+) = 275$ kcal./mole. This is in excellent agreement with the results reported by Palmer and Lossing and supports their thermochemical calculations of the heat of formation of HS^+ and of the bond dissociation energy $D(\text{H-SH})$. It would appear definitely to rule out the earlier value of 15.2 ± 0.5 ev reported by Neuert and Clasen.

The appearance potential of S^+ ion (13.3 ± 0.1 ev) is also considerably below that previously reported by Neuert and Clasen for the minimum energy of formation via the process: $\text{H}_2\text{S} \longrightarrow \text{S}^+ + \text{H}_2$. These authors also report a second ionization process appearing about 4.5 ev above the minimum onset and attribute this to the higher energy process:



No such break was observed in the present work either as shown in Fig. 3 or by a linear plot of the ionization efficiency curve.

Assuming that our value corresponds to the minimum energy process, we calculate the $\Delta H_f(\text{S}^+) = 302$ kcal./mole. Subtracting the ionization potential of S atoms gives $\Delta H_f(\text{S})_g = 64$ kcal./mole. This value combined with $\Delta H_f(\text{S}_2)_g = 30.8$ kcal. gives $D(\text{S-S}) = 98$ kcal./mole. The latter is entirely consistent with the calculations by Palmer and Lossing based on the ionization of the HS radical and, within the limits of uncertainty in the present work, is in agreement with the highest acceptable value for $D(\text{S-S}) = 102$ kcal./mole. obtained from spectroscopic and mass spectrometric studies.

The appearance potential of the metastable transition $\text{H}_2\text{S}^+ \longrightarrow \text{S}^+ + \text{H}_2$ is also clearly identified with the minimum-energy process of formation in which a hydrogen molecule is the neutral product. The observed appearance potential is equal to that of the normal S^+ ion within the estimated uncertainty. Useful appearance potential measurements of the other metastable ions in H_2S were precluded by the low abundance of these ions.

The ionization potentials of the HDS^+ and D_2S^+ ions are indistinguishable from each other and from the H_2S^+ ion within the estimated limits of error. Interpretation of appearance potentials of the fragment ions is also ambiguous. However, ions resulting from the principal metastable transition in each of these molecules are unambiguous. Appearance potential measurements indicate the formation of these ions is by a process entirely analogous to that in H_2S .

The relative abundance of the metastable transition $\text{H}_2\text{S}^+ \longrightarrow \text{S}^+ + \text{H}_2$ is remarkably high, 1.3%, compared to those found in other molecules. The drastic effect of deuterium substitution on the relative abundance parallels that found in larger molecules by Natalis where complete disappearance of a metastable transition is observed. In another small molecule, methane, the opposite effect was observed; i.e., a metastable transition of CD_4 completely disappears on substitution of one or more hydrogen atoms.

The existence of metastable transitions in a triatomic ion is of considerable interest. Our studies on H_2O with an estimated limit of detection of several parts per million showed no metastable transitions. Also, a study of N_2O showed only collision-induced transitions in agreement with a previous study by Friedman and Irsa. Simple application of the Kassel model as well as more elaborate models to the dissociation of vibrationally excited triatomic molecules, indicate that the lifetimes of these species are usually much shorter than 10^{-7} sec. Thus it is quite likely that the delayed decomposition processes observed in the present study are the result of electronic transitions as has been suggested by Friedman and Irsa.

B. Methane

At high detection sensitivity, "metastable" transitions were observed in the mass spectra of all five methanes under operating conditions usually considered as "normal" including analyzer tube pressures ranging from 1.3 to 4.0×10^{-7} mm. These transitions, the resulting apparent mass, and the percentage abundance relative to the molecule ion are given in Table IV. The variation in relative abundance with analyzer tube pressure is shown in Fig. 5 for all transitions except those numbered 5, 9, and 12 in the table. These peaks were of insufficient intensity to permit quantitative measurements.

Table IV
Summary of "Metastable" Transitions Observed in
Methane and the Deuteromethanes

<u>Molecule</u>	<u>($\times 10^7$ mm)</u>	<u>Metastable Transition</u>	<u>Apparent Mass</u>	<u>Abundance (%)</u> <u>Rel. to Mol. Ion</u>
CH_4	1.8	(1) $\text{CH}_4^+ \longrightarrow \text{CH}_3^+ + \text{H}$	14.06	0.0009
CH_3D	4.0	(2) $\text{CH}_3\text{D}^+ \longrightarrow \text{CH}_2\text{D}^+ + \text{H}$	15.06	0.003
"	"	(3) $\longrightarrow \text{CH}_3^+ + \text{D}$	13.23	0.001
"	"	(4) $\text{CH}_2\text{D}^+ \longrightarrow \text{CHD}^+ + \text{H}$	14.06	0.003
"	"	(5) $\longrightarrow \text{CH}_2^+ + \text{D}$	12.25	0.001
CH_2D_2	3.2	(6) $\text{CH}_2\text{D}_2^+ \longrightarrow \text{CHD}_2^+ + \text{H}$	16.05	0.003

Table IV (Continued)

Molecule	(x10 ⁷ mm)	Metastable Transition	Apparent Mass	Abundance (%) Rel. to Mole. Ion
	3.2	(7) $\longrightarrow$ CH ₂ D ⁺ + D	14.22	0.002
"	"	(8) CHD ₂ ⁺ $\longrightarrow$ CH ₂ ⁺ + H	15.06	0.003
"	"	(9) CH ₂ D ⁺ $\longrightarrow$ CHD ⁺ + H	14.06	0.001
CHD ₃	3.0	(10) CHD ₃ ⁺ $\longrightarrow$ CD ₃ ⁺ + H	17.05	0.003
"	"	(11) CHD ₂ ⁺ $\longrightarrow$ CHD ₂ ⁺ + D	15.21	0.004
"	"	(12) CHD ₂ ⁺ $\longrightarrow$ CD ₂ ⁺ + H	15.06	~ 0.002
CD ₄	1.3	(13) CD ₄ ⁺ $\longrightarrow$ CD ₃ ⁺ + D	16.20	0.027

In the figure, the right hand ordinate applies to the $m/e = 16.2$ peak in CD₄. No other transitions were observed. It is estimated that under present conditions the relative abundance of other possible transitions in CD₄ is less than five parts per million relative to the CD₄⁺ ion. The collision-induced transition observed in CH₄ is consistent with the results for that molecule as reported by Melton and Rosenstock.

It is apparent from Fig. 5 that all transitions except CD₄⁺ $\longrightarrow$ CD₃⁺ + D are collision-induced dissociations. The relative abundance of the latter transition is independent of the analyzer tube pressure up to about 3×10^{-6} mm. and is thus a true unimolecular process. Above 3×10^{-6} mm. the relative abundance increases with pressure due to a contribution from collision-induced dissociation.

Observations were also made of the peak shape and appearance potential of this transition. Contrary to the usually diffuse nature of metastable transitions, this peak had a half-width only 30% greater than that of the normal $m/e = 16$ or $m/e = 18$ peaks in CD₄.

Some appearance potential measurements were made of the CD₄⁺ and CD₃⁺ peaks, the CD₄⁺ $\longrightarrow$ CD₃⁺ metastable transition at mass 16.2 and, for comparison, the CH₄⁺ and CH₃⁺ peaks. The conventional semilogarithmic plot of ion intensity vs electron energy is shown in Fig. 6. With argon as a reference gas, the normal ion appearance potentials are in essential agreement with values reported in the literature. Further comparisons of CH₄ and CD₄ ionization efficiency curves indicate a difference of about 0.1 ev between the extrapolated onset energies of the two parent ions and the two methyl ions. This has been observed by a number of workers.

The intensity of the metastable transition of CD₄⁺ when plotted semi-logarithmically has a linear form, but with a slope considerably smaller than that of the integral mass peaks. In view of this, the "appearance potential" of this species cannot be given with the customary statement of the precision.

Applying another widely used technique of plotting ion current directly against electron energy leads to the conclusion that the onset energy of the metastable transition corresponds quite closely (ca 0.2 ev) to that of the daughter ions. This is in accord with the earlier results of Fox and Langer on metastable transitions in a number of larger hydrocarbons.

The disappearance of metastable transitions upon isotopic substitution has been reported earlier by Natalis for a variety of alcohols, nitroethane and some cyclic compounds. At this time we can propose no convincing explanation for those results or for the present observations. However, the following possibilities might be considered relevant to the phenomenon in general and to the methane case in particular. Neglecting electronic reorganization in the ion, the

second ionization potential of methane leading to an excited ion has been calculated to be approximately 25 ev. Frost and McDowell have experimentally observed the value to be 19.4 ev. The appearance potential data thus indicate that the metastable transition of CD_4^+ occurs from the electronic ground state of the ion. As a result of the Jahn-Teller effect, the equilibrium configuration of the methane ion is not tetrahedral. Consequently, the nominally triply degenerate electronic state is split into several levels. It is possible that the metastable transitions, and the unusual isotope effect, is associated with a crossing from one of these surfaces to another.

An alternative viewpoint is to consider the ion dissociation process as a unimolecular reaction describable by quasi-equilibrium theory. It is difficult to reconcile the experimental result with such a description. In particular, the similarity of shape and energy difference of the parent and methyl ionization efficiency curves give no suggestion of a significant gap in the excitation energy distribution function of CH_4^+ compared to CD_4^+ . Nevertheless, such a gap exists in the respective decomposition rate constants. Recent work has emphasized the discreteness of the vibrational levels in the problem of enumerating the states of the reactants and activated complex. This would lead to a corresponding discreteness in the possible values of the rate constants for unimolecular decomposition. The appearance or non-appearance of any parent ion metastable transition would then depend on whether the set of discrete rate constants included values in the range leading to mass spectrometric detection of metastable transitions. Vestal et al have shown how rapidly the rate constants vary with energy in the range of 10^0 sec^{-1} . However, Rice has concluded that such a set of discrete unimolecular rate constants, when viewed as lifetime of quantum states, lead by the uncertainty principle to a diffuseness of the level which is just sufficient to remove this discreteness completely. The experimental results are in conflict with this conclusion. It is not clear that a unimolecular decomposition rate constant arrived at from absolute reaction rate theory may be identified with and applied as a lifetime of a particular quantum state. This rate constant is, after all, an average over many states all having the same total energy.

The last and least enlightening possibility is that the isotope affect on metastable transitions is indicative of pronounced non-equilibrium effects. This is to say that the decomposition rate is determined not only by the energy but also by the initial phase and initial distribution of the energy among the degrees of freedom of the ion. This distribution might undergo drastic changes with isotopic substitution.

Further studies of the effects of isotopic substitution on metastable transitions, particularly in small molecules, are in progress.

STUDIES IN THE MASS SPECTRA OF SHORT-CHAIN ESTERS

By D. R. Black, W. H. McFadden, and J. W. Corse
Western Regional Research Laboratory,¹ Albany, California

Introduction

In the study of the rearrangement processes of short-chain aliphatic esters a series of deuterated butyl acetates and propionates have been synthesized. In previous correlation studies of short-chain esters both high and low resolution mass spectra of series of esters have been obtained (1,2). Deuterium labeled compounds have also been used (3,4,5). Mass spectral rearrangement processes are still not fully understood, however, and the mass spectra of these additional deuterated esters yields information not obtainable in previous studies.

Experimental

Sample preparation. Synthesis and NMR analysis of 4-deutero *n*-butanol and 3-deutero *n*-butanol have been described (6).

The 3-deutero *sec*-butanol was obtained as a byproduct in the synthesis of 3-deutero *n*-butanol above. The 1,1-dideutero *n*-butanol was obtained by reducing the acid chloride with LiAlD_4 (7). In the synthesis of 1,1-trideutero *sec*-butanol, CD_3I was added to magnesium and the CD_3MgI was reacted with propionaldehyde (8,9).

Acetic anhydride was obtained commercially and the acetyl and propionyl acid chlorides were made by refluxing the desired acid in phthaloyl chloride and distilling over the acid chloride (10). High purity commercial CD_3COOD was used in the preparation of CD_3COCl .

The esterifications were all carried out by adding an excess of either anhydride or acid chloride to the desired alcohol. The excess was subsequently hydrolyzed to the acid and then neutralized with carbonate. The ester was taken up in ether, dried, and then purified using a carbowax GLC preparatory column.

Mass spectrometry. The mass spectra were obtained with a Bendix Time-of-Flight Mass Spectrometer using continuous ionization current. The electron accelerating voltage was 70 e.v. Temperature was not measured in the ionization chamber but the source end of the mass spectrometer was $100 \pm 5^\circ$.

Isotopic purity. The isotopic purity of the compounds reported was checked by NMR and, where feasible, by the mass spectra of the deuterated alcohol or ester. Only compounds whose isotopic purity was better than 95% in the labelled position have been reported. No corrections were made for the isotopic impurities detected by NMR and no corrections were made for natural isotopic species. In all cases the conclusions are based on observed effects that exceed any contributions from isotopic impurities.

Results and Discussion

The principal features of the mass spectra of the deuterated esters are, for the most part, those which would be predicted from previous studies of the undeuterated esters (1,2). However, there are certain peaks in the former spectra which, in spite of their low intensities, give new information of the rearrangement processes of these esters. One of these is the well known rearrangement which involves the transfer of two protons from the butyl group in the formation of the $(\text{CH}_3\text{COO} + 2\text{H})^+$ ion. In another rearrangement there is apparently a loss of a CH_2O fragment from the center of the molecule with retention of the two end groups by the ion and a third rearrangement observed with secondary butyl acetate seems to involve an unexpected rearrangement in the formation of the apparently simple $\text{C}_4\text{H}_9\text{O}^+$ ion. Partial spectra are given to illustrate these rearrangements.

¹A. Laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Table I shows the partial spectra of the deuterated n-butyl acetates and n-propionates in the mass range 86 - 90 and 100 - 103. Table II shows

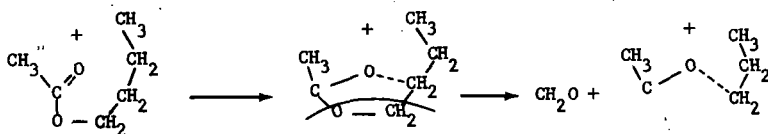
Table I. Partial Mass Spectra of Deuterated n-Butyl Acetate and n-Butyl Propionate

	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{CD}_3 \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$
	116	118	117	117	119	130	132
m/e	Percent of Total Ionization						
86	.31	.34	--	--	--		
87	.47	.02	.76	.79	--		
88	.05	.02	.08	.07	--		
89		.44	.04	.03	.33		
90					.47		
100						.21	.19
101						.44	.04
102						.05	.03
103						--	.42

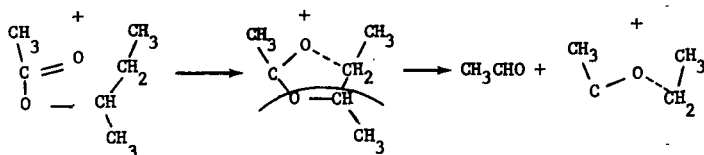
Table II. Partial Mass Spectra of Deuterated sec-Butyl Acetates

$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} - \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} - \text{C} \\ \\ \text{CD} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} - \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{CD} - \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} - \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{CD}_3 \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} - \text{C} \\ \\ \text{C} \end{array}$		
Ion		Percent of Total Ionization					
m/e	(ref. #1)	(T.O.F.)	(T.O.F.)	(Magnetic) <u>Ref. 11</u>	(Magnetic) <u>Ref. 11</u>	(T.O.F.)	(T.O.F.)
72	$\text{C}_4\text{H}_8\text{O}^+$	.46	--	--	.34	.48	
73	$\text{C}_4\text{H}_9\text{O}^+$	2.55	.43	.34	.16	1.60	.77
74		.18	2.30	1.94	1.23	.12	.60
75			.14	.15		.12	.47
76						1.75	1.00

partial spectra of the deuterated sec-butyl acetates. The spectra obtained with the magnetic instrument were taken from McLafferty and Hamming (11). Both sets of data give evidence for the second rearrangement mentioned above. The ions of interest are those which result from loss of 30 mass units from the molecular ions of the undeuterated n-butyl esters at mass 86 and mass 100, and that which results from loss of 44 mass units from the molecular ion of undeuterated sec-butyl acetate at mass 72. From the mass spectra of those compounds deuterated in the 3 or 4 positions of the butyl groups, the ionization normally observed at masses 72 or 86 is seen to be absent indicating retention of the terminal ethyl group. However, in the spectra of those esters with deuterium on the #1 carbon of the n-butyl group or on either the #1 or #2 carbon of the sec-butyl group, there is no shift of the ionization at masses 86 or 100 in Table I, or of mass 72 in Table II thus indicating loss of these carbons. Furthermore when the acetyl group is completely deuterated there is a corresponding mass shift of three mass units in the spectra although this is somewhat speculative in the spectrum of sec-butyl acetate. Evidently this mode of ionization results from cyclization of the molecular ion followed in each case by loss of the group immediately adjacent to the carbonyl group, CH_2O from the n-butyl esters and CH_3CHO from the sec-butyl acetate. One possible mechanism for this rearrangement would be:

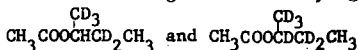


and:



Other cyclic intermediates are also possible. Similar rearrangements have been detected in the mass spectra of long-chain esters by Guriev et al. (12,13), Ryhage and Stenhagen (14,15,16), and Dinh-Nguyen et al. (4). The suggestion of cyclical intermediates has been previously made to explain observations in the mass spectra of many other compounds (5,6,17,18).

In addition to the above rearrangement, the spectra of the deuterated *sec*-butyl acetates given in Table II indicate that an unexpected exchange process occurs prior to the formation of the mass 73 ion in the undeuterated compound. From high resolution mass spectra (1) this ion is known to have the formula $\text{C}_4\text{H}_9\text{O}^+$. The mass spectral data of the esters in which the 2, 3, or 4 position of the *sec*-butanol have been deuterated would seem to confirm the expectation that this ion occurs by a simple bond break. However, the data obtained from the ester deuterated on the #1 carbon of the *sec*-butanol show the ionization due to this mode in two places; thus, approximately one-half the ions retain the deuterium (mass 76) and one-half lose the deuterium (mass 73). Since very little ionization is observed at masses 74 and 75 H-D exchange cannot explain this observation and it appears that by some mechanism an exchange of the methyl groups is occurring. The mass spectra of



(data not presented here) also confirm this observation and as shown in the last column of Table II, deuteration on the acetyl moiety is also only partly lost to give the mass 73 ion and partly retained to give the mass 76 ($\text{C}_4\text{H}_6\text{D}_3\text{O}^+$) ion. (In this case there appears to be some H-D exchange leading to the m/e 74 ion and in addition the ion formed by loss of CH_3CHO presumably occurs at m/e 75 as previously discussed.) Thus, it appears that the formation of the $\text{C}_4\text{H}_9\text{O}^+$ ion involves a complex intermediate in which the acetyl methyl and the *sec*-butanol methyl (#1 position) become indistinguishable. This could result from a variety of processes including part of the $\text{C}_4\text{H}_9\text{O}^+$ ions being formed by a simple mechanism, part by a complex rearrangement mechanism, possibly by a cyclization followed by relatively simple H-D rearrangements, or even by the rearrangement of an entire CH_3 group onto an adjacent oxygen. Further study seems to be indicated.

In the rearrangement process resulting in the formation of the $(\text{CH}_3\text{COO}+2\text{H})^+$ ion, the origin of the two protons of *n*-butyl acetate is of interest and is indicated in the mass spectra of the deuterated esters shown in Table III. The ionization resulting from transfer of the protons is seen at mass 61 in the spectrum of the undeuterated ester and that ionization resulting from transfer of the deuterium is seen at masses 62 in the other spectra. The mass 62 peak in the second spectrum represents only 8% of the total ionization due to this process and shows that the availability of the protons on the terminal methyl group is less than statistical. In the third spectrum the mass 62 peak is more intense, making up 37% of the total ionization due to the rearrangement process indicating that the protons on the carbon delta to the carbonyl group are favored. The mass 62 peak in the last spectrum represents only 16% of the

Table III. Effect of Deuteration on the Acetate Rearrangement Peaks of n-Butyl Acetate

	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \text{D} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \\ \\ \text{C} \text{D} \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{C} \text{D}_2 \\ \\ \text{C} \\ \\ \text{C} \end{array}$
m/e	Percent of Total Ionization			
59	.08	-	-	
60	.16	.14	.15	.10
61	5.42	5.09	3.45	5.14
62	.16	.48	2.03	1.01
63	.05	.08	.07	.10

total intensity of the mass 61 and mass 62 peaks. This result indicates that direct transfer of a proton to the adjacent oxygen is not highly favored, a result also indicated by the data of McLafferty (19) on deuterated secondary butyl acetate. The 2-mono-deuterated n-butyl acetate was not available but the intensity of the mass 62 peak in its spectrum can be surmised. If it is assumed that the intensity of the mass 62 peak in the spectra of the other deuterated acetates would be greater if each position were fully deuterated then transfer of a proton (deuteron) from the #2 carbon would not seem to be significant. These results indicate that in the case of the butyl acetates the protons on carbon #3 are more important than those on the beta and gamma carbons (positions 1 and 2 on n-butyl acetate) as indicated by Colomb et al. (5) from the mass spectra of deuterated hexyl butyrate and valerate. In addition data exist for deuterated ethyl acetates which indicate that deuteration on the #1 carbon of the ethanol (3) or the #2 carbon (19) lead to a nearly statistical selection of deuterium in formation of this rearranged ion. Thus, it is possible that for some molecules the two-proton transfer process may proceed by a different mechanism than that proposed by McLafferty (20). The present data suggest a selective transfer of one proton from carbon #3 followed by a random selection of the second proton from the other protons in the alcohol moiety. Such a random selection will always occur if the second transfer proceeds at a rate significantly less than the rate of H-D exchange within the alcohol group.

Acknowledgment. We wish to thank Dr. R. E. Lundin for the very necessary NMR analysis of the deuterated esters.

Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

References

- (1) J. H. Beynon, R. A. Saunders, and A. E. Williams, Anal. Chem., **33**, 221 (1961).
- (2) A. G. Sharkey, J. L. Shultz, and R. A. Friedel, Anal. Chem., **31**, 87, (1959).
- (3) E. W. Godbole and P. Kebarle, Trans. Faraday Soc., **58**, 1887 (1962).
- (4) N. Dinh-Nguyen, R. Ryhage, S. Stenhagen-Stalberg, and E. Stenhagen, Arkiv. Kemi, **18**, 393 (1962).
- (5) H. O. Colomb, B. D. Fulks, and V. A. Yarborough, 10th Annual Meeting ASTM Committee E-14, New Orleans, June 1962.
- (6) W. H. McFadden, D. R. Black, and J. W. Corse, J. Phys. Chem., (in press).
- (7) R. F. Nystrom, W. G. Brown, J. Am. Chem. Soc., **69**, 1197 (1947).

- (8) N. L. Drake and G. B. Cooke, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York and London, 1943, pp. 406-407.
- (9) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., J. Am. Chem. Soc., **74**, 4283 (1952).
- (10) J. D. Cox and H. S. Turner, J. Chem. Soc., 3197 (1950).
- (11) F. W. McLafferty and M. C. Hamming, Chem. and Ind., **42**, 1366 (1956).
- (12) M. V. Guriev and M. V. Tikhomirov, Zhur. Fiz. Khim., **32**, 2731 (1957).
- (13) M. V. Guriev, M. V. Tikhomirov, and N. N. Tunitsky, Doklady Akad. Nauk. S.S.S.R., **123**, 120 (1958).
- (14) R. Ryhage and E. Stenhagen, Arkiv. Kemi, **15**, 333 (1960).
- (15) R. Ryhage and E. Stenhagen, Arkiv. Kemi, **15**, 291 (1960).
- (16) R. Ryhage and E. Stenhagen, Arkiv. Kemi, **15**, 523 (1959).
- (17) W. H. McFadden, M. Lounsbury, and A. L. Wahrhaftig, Can. J. Chem., **36**, 990 (1958).
- (18) J. H. Beynon, R. A. Saunders, A. Topham, and A. E. Williams, J. Chem. Phys., **65**, 114 (1961).
- (19) Unpublished data of authors.
- (20) F. W. McLafferty, Anal. Chem., **31**, 82 (1959).

MASS SPECTRA OF DIARYL SULFONES

by

Seymour Meyerson

Research and Development Department, American Oil Company

and

Harald Drews and Ellis K. Fields

Research Department, Amoco Chemicals Corporation

Whiting, Indiana

ABSTRACT

Mass spectra of 24 diaryl sulfones have been measured. These spectra are sensitive not only to differences in molecular weight but also to structural differences among isomers. Correlation with molecular structure furnishes a basis for deducing structural features when pertinent reference spectra are not available, and also suggests decomposition paths underlying the spectra. Mass-spectral analysis of the product mixture obtained by sulfonating toluene has revealed all six possible isomeric sulfones.

STUDIES ON THE STEREOCHEMISTRY OF ORGANIC MOLECULES BY MASS SPECTROMETRY
I. THE ERYTHRO- AND THREO-3-PHENYL-2-BUTYL-SYSTEM

P. E. Butler
Analytical Research Division
Esso Research and Engineering Company
Linden, New Jersey

and

C. H. DePuy
Iowa State University
Ames, Iowa.

Manuscript Withdrawn

F

Continuous Ion Source for a Bendix Time-of-Flight Mass Spectrometer*

Martin H. Studier

Argonne National Laboratory, Argonne, Illinois

Introduction

With simple modifications improved performance of continuous ion sources in a Bendix time-of-flight mass spectrometer(1) has been obtained. The system was developed for use with heated filament surface ionization sources(2); however, the advantages of its use with continuous electron bombardment seem more significant. With the electron gun operating continuously, a factor of three hundred increase in sensitivity over that of the pulsed mode of operation is attained with improved resolution and no increase in the ratio of noise to signal.

Electron Bombardment Sources

Two sources available with the commercial instrument are illustrated in Figure 1. The two-grid source is operated with a 0.25 microsecond pulse of electrons followed by a voltage pulse to draw the ions past the first grid where they are accelerated to 2.8 kilovolts. With the usual 10 kilocycle pulse rate the duty cycle for ion production is only 0.25%, but the noise level is low since no ions are produced during acceleration and drift down the flight tube. The three-grid assembly is designed to be used with a continuous source of ions. The positively charged ions are "trapped" on the first grid (bias - 0.2 volts) by the positive biases of the electrodes on either side until drawn away by the pulse on the middle grid. A coincident pulse is put on the backing plate to prevent ions from drifting through the trapping grid while the ion focus pulse (draw out pulse) is operative. This mode of operation with a continuous electron beam gives little increase in sensitivity over the pulse mode. Its use is not recommended by Bendix(1) when a pulsed electron beam can be used because of poorer resolution and greater noise of the trapping grid operation.

Our modifications are illustrated in Figure 2. A continuous electron beam produces positive ions with a duty cycle approaching 100%. The ions are believed to be held in the electron beam by a potential well created by the electron beam itself. The ions are drawn out when the ion focus pulse is applied to the first grid. This pulse destroys the well by deflecting the electron beam into the backing plate. To prevent unfocussed ions from reaching the flight tube before the well is re-formed, pulse shaping techniques and direct current biases are used. The drawout pulse is integrated through a resistor and condenser and applied to the backing plate. Since the effect on the ions of a voltage applied to the backing plate is opposite that of a voltage of the same polarity applied to the first grid, the effect of the pulse on the backing plate is an algebraic subtraction from the draw out pulse. The shape of the backing plate pulse is such that the tail of the draw out pulse is subtracted and the voltage gradient is actually reversed. This prevents the drift of positive ions past the first grid after the main group of ions has passed. The variable 100 K resistor from backing plate to ground is a direct current return to prevent build up of charge. It also shapes the backing plate pulse to some extent. The resistor and condenser in series to ground from the first grid reduce the tail of the draw out pulse by providing a low impedance return to ground. The direct current bias on the first grid has a focussing action through its effect on the location of the electron beam and the ions. The second grid, with the full draw out pulse applied by the 0.01 microfarad coupling condenser combined with a positive bias, is an effective filter for stray ions that drift past the first grid. The intermediate high voltage on the third grid minimizes current leakage and may have a marked effect on sensitivity.

A machine modified as described above, was tuned for high sensitivity, low noise and good resolution. Figure 3 is an oscillograph

photo of the pulse on the first grid with a two microsecond per cm. abscissa and a 100 volt per cm. ordinate. Figure 4 represents the pulse on the backing plate. Figure 5 is the resultant of the algebraic subtraction of the backing plate pulse from the draw out pulse. Figure 6 is the spectrum obtained for xenon and Figure 7 is that of mercury. Figure 8 is a recorder scan of the mercury spectrum.

Figure 9 is a mercury scan with the source tuned for maximum resolution without regard to noise.

The detection limit of the Bendix spectrometer with the modified source operated with a continuous electron beam was estimated to be about 5×10^{-16} mm. of Hg for a gas with a single isotope.

Observations which support the theory that the creation of a potential well plays an important part in the operation of the modified source are as follows:

1. The sensitivity, resolution and noise level are all very critically dependent on the position of the source magnets which collimate the electron beam. With pulsed electrons the magnet positions are not at all critical.
2. The fact that the increase in sensitivity in going from pulsed to continuous operation is nearly equal to the increase in duty cycle suggests that the ions must be held in the source region during the 100 microseconds between voltage pulses.
3. The excellent resolution obtained suggests that the bulk of the ions start from a very limited region in the source.
4. Ion molecule reactions were observed to occur at pressures as low as 5×10^{-6} mm. of Hg (3). With the ions held in the well for 100 microseconds between draw out pulses neutral molecules have time to diffuse into the well and react.
5. The unexpectedly poor performance of the "trapping grid" mode of operation can be explained by the ions being trapped in the electron beam instead of on the grid.
6. It was observed that when the modified continuous mode was used with negative ions the noise level was high and there was little increase in sensitivity over the pulsed or trapping grid modes. With negative ions the electron beam constitutes a potential hill instead of a well.

Surface Ionization Sources

Surface ionization sources consisting of electrically heated ribbons of rhenium, tungsten or tantalum have been used successfully with the modified source of Figure 2. In Figure 10 is shown a Bendix source with a filament assembly in place. A screw and two guide pins in the heavy structural "L" piece of the source hold the assembly in place so that the flat ribbon is at the top of the grid opening. Figure 11 is a more detailed picture of the filament assembly. Double, independently heated filaments are being used routinely. Samples are mounted on a 0.02 inch wide ribbon facing a 0.04 inch wide filament. The wider filament is usually heated much hotter than the sample filament to provide an efficient ionizing source for sample molecules striking it. Each of the filaments has a variable bias applied through the center taps of the filament transformers. These biases, combined with the controls described above, permit focussing of surface produced ions even though the temperature of the ionizing filament may be as high as 2500°K. Neutral species evaporated from a filament may be determined by turning on the electron gun since the presence of the filaments does not interfere with electron gun mode of operation.

Figure 12 shows a spectrum of the alkali metals lithium, sodium and potassium. Figure 13 shows the spectrum from a uranium sample equimolar in U²³⁵ and U²³⁸ produced from a double rhenium filament.

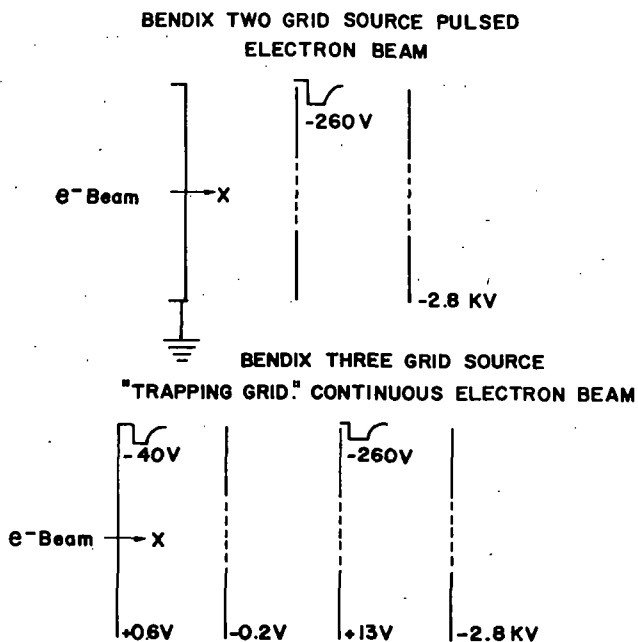


Figure 1. Bendix Ion Sources.

The ions are Re^+ , U^+ , UO^+ and UO_2^+ .

Acknowledgments

The author gratefully acknowledges many stimulating discussions with Everett G. Rauh who also designed the filament assembly shown in Figure 10. Thanks are due Bert Ercoli and Leon P. Moore for technical assistance.

References

- * Based on work performed under the auspices of the U. S. Atomic Energy Commission.
1. D. B. Harrington, "Encyclopedia of Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1960, pp. 628-647.
 2. Martin H. Studier, Eric N. Sloth and Leon P. Moore, J. Phys. Chem., 66, 133 (1962).
 3. Paper No. 46.

MODIFIED (FOUR GRID) SOURCE

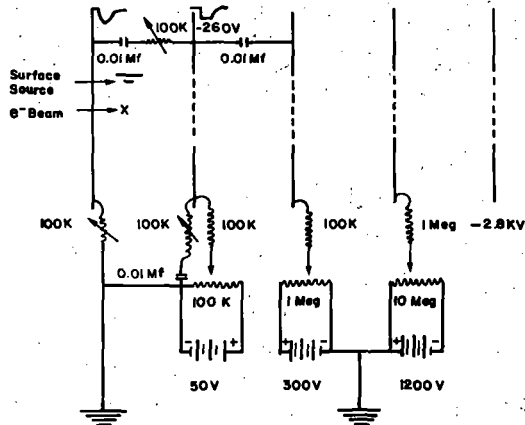


Figure 2. Modified Source For Continuous Ions.

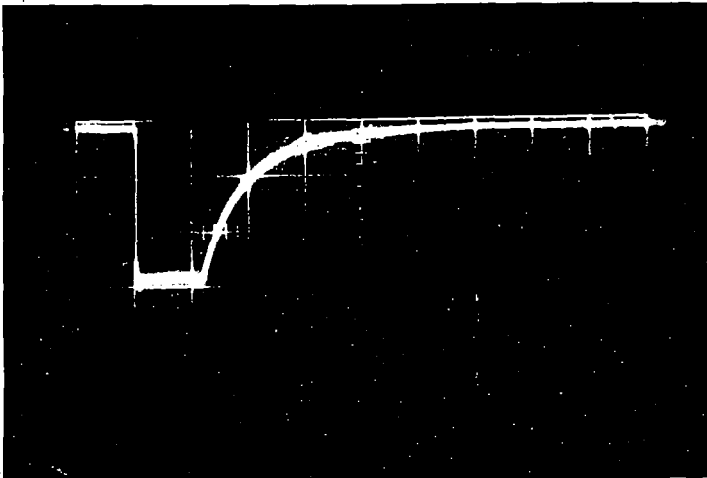


Figure 3. Draw out Pulse on First Grid.

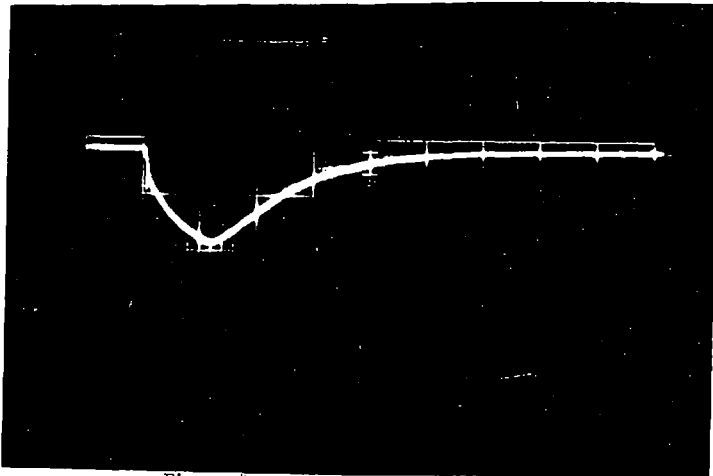


Figure 4. Backing Plate Pulse.

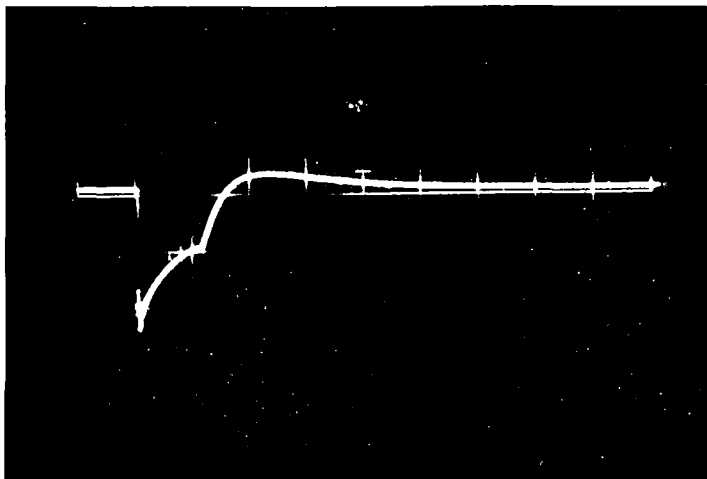


Figure 5. Resultant of Draw Out and Backing Plate Pulses.

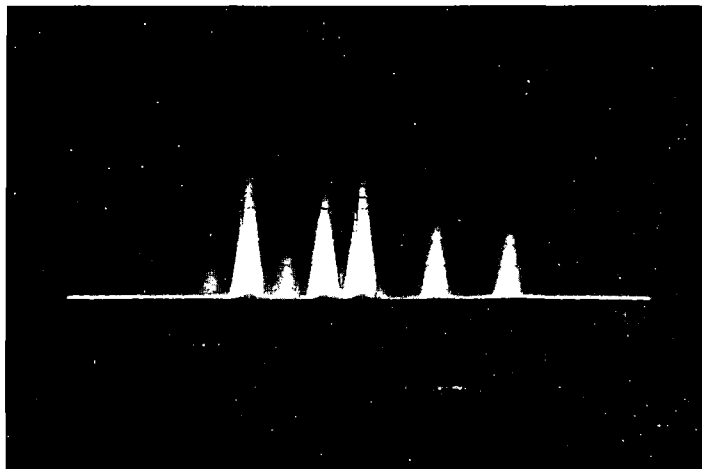


Figure 6. Xenon Spectrum.

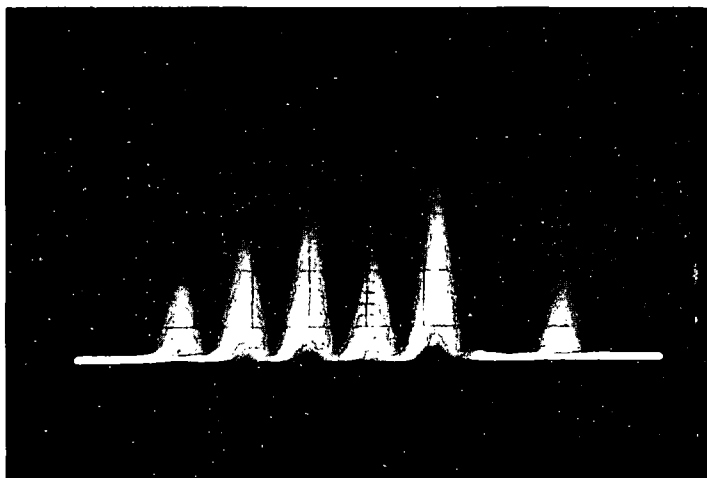


Figure 7. Mercury Spectrum.

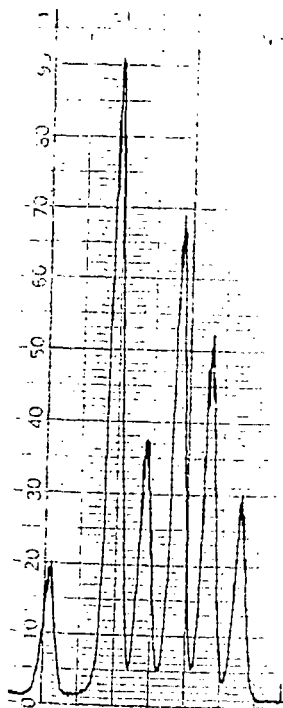


Figure 8. Mercury Recorder Scan with Source Tuned for High Gain and Low Noise.

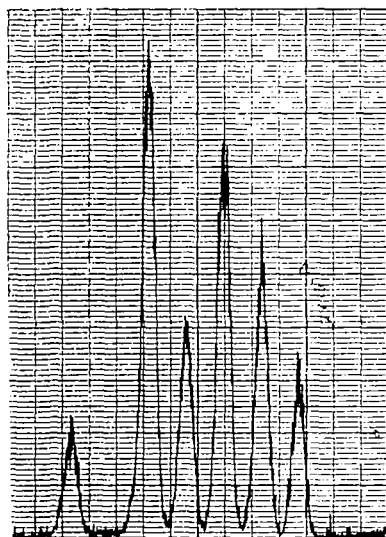


Figure 9.

Mercury Scan with Source Tuned for Maximum Resolution.

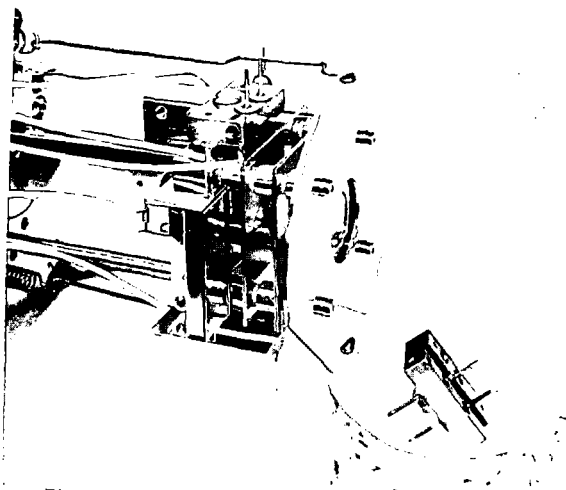


Figure 10. Bendix Source with Filament Assembly.

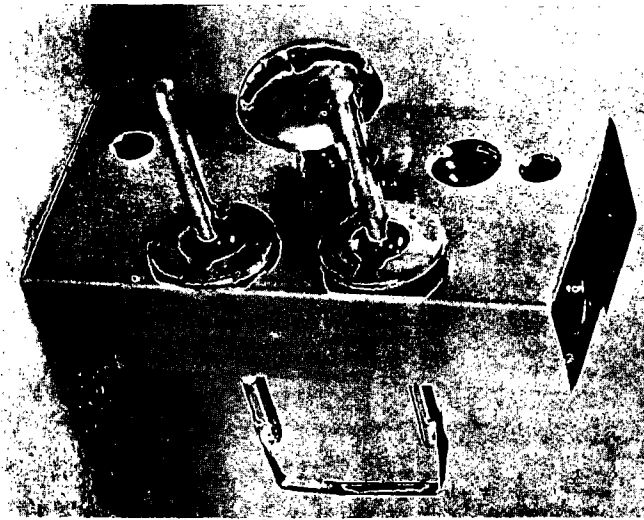


Figure 11. Filament Assembly.

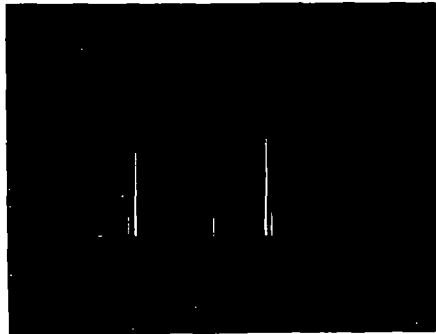


Figure 12. Spectra of Alkali Metals $\text{Li}^{6,7}$, Na^{23} and $\text{K}^{39,41}$.



Figure 13. Spectra of $\text{Re}^+(185,187)$, $\text{U}^+(235,238)$, $\text{UO}^+(251,254)$ and $\text{UO}_2^+(267,270)$.

A SIMPLE DISPLAY SYSTEM FOR RECORDING RAPID CHANGES IN MASS SPECTRA

Kenneth A. Lincoln
U. S. Naval Radiological Defense Laboratory, San Francisco, Calif.

Introduction

The time-of-flight mass spectrometer with its ability to present 10 or 20 thousand or more mass spectra per second lends itself quite well to the study of many types of fast reactions. However, a formidable problem often encountered is the complexity of the auxiliary equipment which is required to record all of the information available in the short interval of time. Most mass spectrometrists facing this situation have employed high-speed drum cameras to photograph the rapidly changing spectral patterns displayed on an oscilloscope.^{1,2} Described here is the convenient system we have devised at NRDL to record essentially the same information by employing two oscilloscopes and two still cameras.

Our studies have been concerned chiefly with obtaining the time-resolved spectra of the gaseous products evolved from solid materials which are pyrolyzed directly in the ion source of the mass spectrometer in an attempt to identify short-lived species. Fig. 1 is an artist's schematic conception of the entire system. Attention is directed first to the ion source and the flash equipment. The solid samples are positioned within the glass tube which opens directly to the ionizing beam (no slits or baffles lie between), and the samples are rapidly brought to a high temperature by the external xenon flashtube source of thermal radiation which has been described elsewhere.³ The approximately half-millisecond thermal pulses pyrolyze the sample into volatile products at a distance of a small fraction of a mean-free path from the ionizing beam from whence they are immediately mass analyzed.

Principle of Operation

In conventional time-of-flight operation one scope is used, and its sweep speed corresponds to the time of flight of the ions while the multiplier signals the time of arrival and intensity of the discrete ion bunches to the vertical amplifier; thus, the scope display is a continuous monitoring of the mass spectral patterns present. The display system to be described here is referred to as "simple" because the only equipment required in addition to that of the usual time-of-flight system is a large-signal, wide-band pulse amplifier, an additional oscilloscope, possibly an extra Polaroid camera, and a few added electrical cables.

For flash spectra recording the mass spectrometer remains in normal operation at a 10 or 20 kc repetition rate. Any spectrum signal present is fed to the vertical amplifier of the monitor scope, but prior to the flash this scope is not sweeping, and so the screen is blank. However, the vertical amplifier is continuously operating and supplies the spectral signal to the pulse amplifier which further amplifies and inverts it. Thus the spectral peaks produced at the multiplier are faithfully reproduced as large, negative peaks at the CRT cathode input terminal to z-axis modulate the raster scope (negative signals brighten the trace on the screen). Prior to the flash there is no vertical sweep on this scope, and because the horizontal sweep is synchronized with the mass spectrometer (as in conventional operation of the monitor scope), the resultant presentation on the screen is a horizontal row of dots corresponding to each peak of the spectrum and the dot brightness corresponds to the peak height. Of course, when there is no sample entering the inlet, the screen of the raster scope is also blank.

To initiate action the camera shutters are opened causing the synchronized switch to actuate the trigger circuit in the power supply which, in turn, fires the flashtube thus injecting sample gases into the ion source. Simultaneously, the monitoring scope is triggered and initiates a single, comparatively slow horizontal sweep. This horizontal sweep speed is set to match the time of the reaction under study. The horizontal sweep voltage is available at the "Sawtooth Output" terminal and is fed to the vertical input of the raster scope. This causes the horizontal row of dots to move vertically as a function of time. The net result is a picture of mass displayed in the x-direction, time displayed in the y-direction, and peak height in the z-direction (brightness).*

* This three-dimensional presentation of spectra has been independently suggested by L. P. Levine, Honeywell Research Center, Hopkins, Minn.

Although the x and y values are presented with good accuracy, the presentation of peak height is only semi-quantitative. To a certain extent this drawback is overcome by utilizing the monitor scope to display, quantitatively, peak height vs. time for any one of the preselected mass peaks. This technique has been described by Damoth;⁴ In brief, it uses the gating pulse from one of the analog output units (which ordinarily gates the multiplier) to pulse the CRT cathode of the blanked scope. Thus, when the gating pulse is timed to coincide with the chosen mass peak on each cycle of the mass spectrometer, only that one mass peak is displayed on the scope. Then as the horizontal sweep is applied, a number of line segments corresponding to the height of the peak are displayed side by side at 50 μ sec (or 100 μ sec) intervals. Now it can be seen that the reason for using the sawtooth output from one scope to provide the raster for the other is that an exact time correlation between the two records is automatically provided.

Performance

Evidence as to how the system performs is submitted in Fig. 2. This is a time-resolved spectrum of flash-heated glycolaldehyde exposed to a total energy of 2.6 cal/cm² delivered in about 0.6 milliseconds. The action recorded here is slow compared to the spectrometer repetition rate of 10 kc (100 μ sec apart); therefore, the rows of dots have merged into vertical lines. The dots along the bottom line are merely residuals remaining from some of the peaks after the vertical sweep terminated and returned to the reference position. The graticule image was included to facilitate the identification of mass numbers and, of course, to measure time along the vertical dimension. The raster technique is not limited to this speed, but can be increased by two orders of magnitude to follow faster events. It is quite evident that the time duration of some of the mass peaks is considerably shorter than others, and remaining ones make their appearance at a later time. For most of the peaks the decay rate appears to correspond to the evacuation rate of the vacuum system, but it is the short-lived ones which capture most of our attention. Note particularly the time sequence of masses 52 and 61, and then refer to Fig. 3 which displays both of these peaks quantitatively as a function of time. The mass 61 curve was photographed from the monitor scope simultaneously with the raster presentation of Fig. 2. The mass 52 curve is from the previous flash (same energy) and the instrument gain setting was twice that of the other two displays.

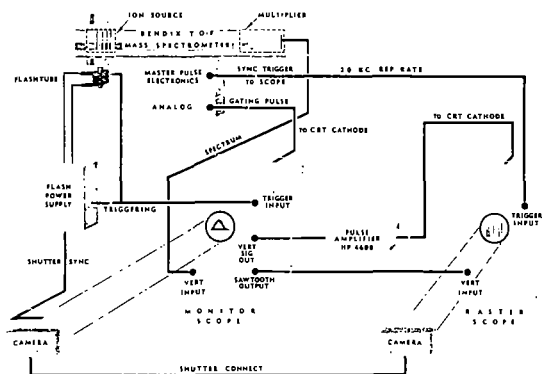
Other Options

With additional analog units or pulse generators in conjunction with double-beam scopes, it is possible to monitor simultaneously several mass peaks as a function of time.

A very useful fringe benefit of the same equipment can be outlined by again referring to Fig. 1. In conventional operation where only the monitor scope is used, the peaks of the mass spectral pattern can be brightened by simply using the pulse amplifier to z-axis modulate the monitor scope. A variable time delay (not shown) is inserted into the line to synchronize the brightening with the corresponding peak. Fig. 4 compares a mass spectrum with and without the z-axis brightening. This technique is helpful when the scope must be viewed in high ambient lighting and for some photographic applications where the flare from high intensity scope levels is objectional or where individual sweeps must be photographed.

Summary

This technique for recording rapid changes in mass spectra is a simple, integrated system which yields for each event one oscillogram showing semiquantitatively the height of mass peaks as a function of time for the entire spectrum plus one or more oscillograms showing, quantitatively, intensity vs. time for any preselected mass peaks. Thus, it may be counted among the advantages that the information is conveniently available on a small number of Polaroid prints instead of yards of movie film, and no special short-persistence CRT screens are required for this photography. Simplicity is, perhaps, the most important feature of the system; no special equipment need be built and the scopes plus the cameras are common models. Therefore, this technique places within the capability of any time-of-flight mass spectrometrists the means of recording rapid changes in spectra.

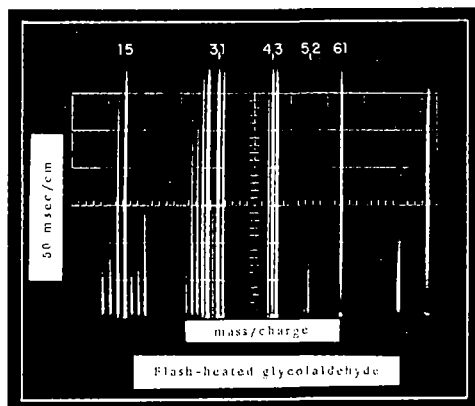


SYSTEM FOR RECORDING TIME-RESOLVED MASS SPECTRA

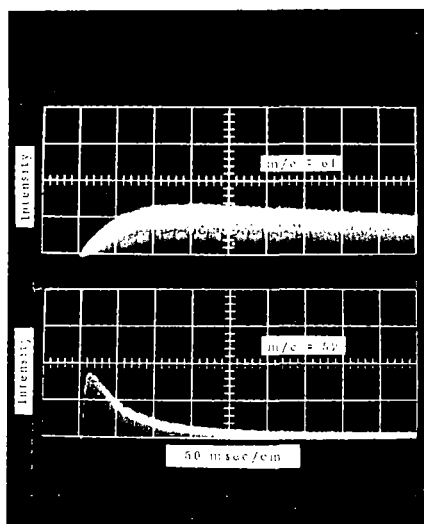
1. Block diagram of the entire system.

References

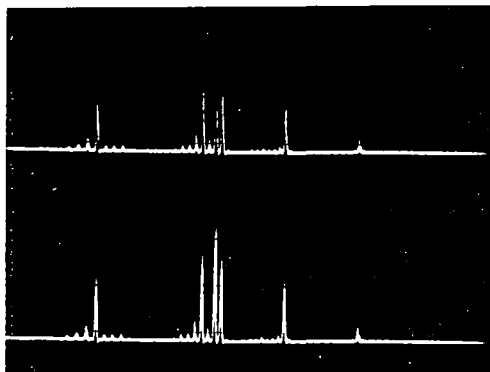
1. G. B. Kistiakowsky and P. H. Kydd, J. Amer. Chem. Soc., 79, 4825 (1957).
2. J. N. Bradley and G. B. Kistiakowsky, J. Chem. Phys., 35, 256 (1961).
3. K. A. Lincoln, U. S. Naval Radiological Defense Laboratory, USNRDL-TR-617 (Jan 1963).
4. D. C. Damoth, paper presented at Eighth Annual Meeting on Mass Spectrometry of A.S.T.M. Committee E-14, Atlantic City, N. J. (June 1960).



2. Typical time-resolved raster display.



3. Peak height vs. time of two of the glycolaldehyde peaks.



4. Top: typical oscilloscopic display of a mass spectrum.
Bottom: same spectrum with z-axis brightening of the peaks

A NEW DIGITIZER FOR MASS SPECTRA
By R. F. Klaver and R. M. Teeter
California Research Corporation, Richmond, California

At the meetings of this group three and two years ago in Atlantic City and Chicago, papers were presented from our laboratory describing some of the work we have done on the gas chromatograph-mass spectrometer (GCMS) combination. We discovered, as you may have too, that reduction of the data from this type of operation is a much larger job than its acquisition. We decided about two years ago that to help with this problem we would need a digital readout device for our CEC 21-103 instrument that would operate at a higher speed and more reliably than our commercial digitizer. Working in conjunction with Adage, Inc., of Cambridge, Massachusetts, we designed and built such a device and have been using the new instrument for the past year.*

The input information to the digitizer consists of the attenuated accelerating voltage and the output of the vibrating reed amplifier. Figure 1 shows a block diagram of the equipment. The peak height digitizer is the heart of the unit. It contains the input logic and circuitry for generating signals to control the other components.

The attenuated accelerating voltage is fed continuously to the mass number digitizer along with a reference voltage. Operating as a ratiometer, the unit converts the accelerating voltage to mass number, the mass range being selected by a switch and adjustable from the front panel. The mass number accuracy is better than 0.1% over a 10 to 1 mass ratio range. On the occurrence of a peak in the spectrum, a hold-command is issued by the peak height digitizer to the mass number digitizer and a print-command to the printer which then prints mass number and relative peak height. It should be noted at this point that the complete unit which Adage will sell will contain only one analog to digital converter, the peak height being held in a buffer register while the mass number is read. The two figures will then be printed simultaneously.

During normal operation, the digitizer output consists of a printed tape, as shown in Figure 2. The left-hand column is the mass number in tenths of a mass unit with an extra line drawn in by hand to indicate the decimal point. The right-hand column gives the peak height in arbitrary units. The molecular weight of this sample is 214, printed as 214.1, with a peak height of 5573. This figure is a photograph of only a portion of the record. The scan started at m/e equals 48. The instrument reads directly to four digits with no scale change required in order to cover a dynamic range of approximately 10,000 to 1. This makes the peak height easy to read and introduces no linearity problem between ranges. This partial spectrum was run at our normal speed of about 1 peak per second.

In the next figure, No. 3, we compare partial patterns for bis(trifluoromethyl)benzene at three different scan rates. The patterns are based on the sum of all of the ions above mass 100, calculated independently. The left columns compare the patterns from the galvanometer record to the digitizer record at our normal scan rate while the other sets were recorded at higher rates.

Encl. - Figures 1, 2, and 4

* Inquiries concerning the digitizer should be directed to Adage, Inc., 292 Main Street, Cambridge 42, Massachusetts, who will produce and sell the unit under license from California Research Corporation.

Figure 3

Patterns

m/e	0.99 Peak/Sec.		2.45 Peaks/Sec.		3.14 Peaks/Sec.	
	Galv.	Digi.	Galv.	Digi.	Galv.	Digi.
156	0.10	0.09	0.10	0.10	0.10	0.10
162	0.16	0.18	0.17	0.16	0.17	0.19
163	2.14	2.14	2.10	2.12	2.11	2.13
164	7.71	7.72	7.45	7.53	7.39	7.47
165	0.65	0.65	0.69	0.69	0.68	0.66
174	0.07	0.07	0.07	0.08	0.08	0.08
175	0.12	0.13	0.12	0.13	0.13	0.14
176	0.32	0.32	0.32	0.33	0.33	0.33
178	0.04	0.06		0.06		0.07
193	0.09	0.09	0.09		0.09	
194	0.97	0.97	0.98	0.98	0.99	1.00
195	20.51	20.57	20.65	20.83	20.89	20.97
196	2.01	2.00	2.08	2.09	2.05	2.06
197	0.12	0.13	0.20			
204	0.04	0.05	0.06	0.05	0.06	0.06
213	2.43	2.43	2.41	2.44	2.45	2.46
214	24.38	24.40	24.54	24.78	24.82	24.96
215	2.40	2.38	2.45	2.47	2.41	2.41
216	0.14	0.13	0.24			

The limiting factor on speed of our present equipment is frequency response of the vibrating reed amplifier. With a faster amplifier, the limit would be five peaks per second, determined by the 200-millisecond print cycle time of the printer. If a different sort of readout device were used, much higher speeds would be attainable since the analog to digital conversions are carried out at a rate of 1000 per second. (The digitizer, now available from Adage, is even faster.)

The minimum peak height readable by the digitizer depends on the mass spectrometer noise. The minimum height actually read is determined by a front panel bias level switch.

The operation of a mass spectrometer to analyze effluent from a gas chromatograph directly without trapping requires high speed operation of the spectrometer. The mass spectrometer scan rate is increased above normal so that each gas chromatography peak is scanned several times.

Most of the GCMS work that we have done lately has been handled by Mr. C. F. Spencer, and he has made a number of modifications and additions to our equipment. Among these are a cycle timer to control the mass spectrometer sweep and a clock on the digitizer. In GCMS operation the timer keeps the spectrometer sweep going so that it is necessary only to start the digitizer on the appearance of a peak in the gas chromatogram. The digitizer clock prints the time in minutes from the beginning of a run on both the digitizer tape and the gas chromatogram in order to aid synchronization of the two.

These two clocks have been used together also to automate effusion rate experiments. This is normally a time-consuming job, but the collection of the data is greatly simplified with the cycle timer to make the mass spectrometer scan the spectrum continuously and the digitizer with its clock to record mass number, peak height, and the time. Stability of the mass spectrometer still severely limits the applicability of the technique. But ignoring that phase of the problem, data collection is now simple. Figure 4 shows a small portion of a digitizer tape recorded during an effusion rate experiment on butylbenzene to check the inlet system leak rate. As before, mass number in tenths is the left column; and peak height is given on the right. The digital clock printed the time in minutes from the beginning of the run in the middle. The crossed off sections represent the rapid reverse scan. The sweep cycle timer was set on 15 seconds, giving four short sweeps per minute. A simple improvement in this system would be to have the digital clock

actuate the mass spectrometer sweep to ensure perfect synchronization. The sweep timer on the mass spectrometer would still be used for the GCMS applications.

One application that developed after we had been using the digitizer for a while is a rapid preliminary scan of the spectrum. Measurement of total ionization reveals nothing about the maximum peak height exhibited by any particular material, but a fast sweep using the digitizer shows immediately if any peaks are overloaded and if a higher mass range will be necessary.

With the mass number digitizer displaying mass numbers continuously on the front panel, it is very easy to locate specific peaks for focusing after a mass spectrometer shutdown. We then can use either the peak monitor on the mass spectrometer or the peak height digitizer, operating in continuous mode, to focus for maximum peak height.

The mass spectrometer to which the digitizer is connected was already equipped with an NMR magnetic field controller, and we feel that it has contributed considerably to the mass number accuracy. A stable magnetic field is necessary for this type of operation, and a stabilizer based on the Hall Effect should be satisfactory.

Since the output of our new unit is truly digital, the addition of a parallel-to-serial converter and a paper tape punch will be simple; and we plan to do this soon. This will permit direct entry to the electronic computer system without manual peak reading.

The high reliability of our mass spectrum digitizer has been demonstrated by over a year of almost trouble-free operation, with much of the operating time at the high speed required by the GCMS combination.

DEVELOPMENT OF A SOLID STATE DIGITIZER FOR MASS SPECTROMETERS

INTRODUCTION

This paper describes the development of an all solid state digitizer that collects ion peaks and acceleration voltage signals and presents the data on punched paper tape and printed output. The system uses one high speed analog to digital converter and switches from the ion signal to the acceleration voltage after a maximum peak amplitude has been detected. A digital comparator and pulse logic control system is used to identify the ion peak, to determine maximum amplitude, and to command the system to perform the other necessary functions.

The paper also describes how to install and start up the digitizer. An analysis of the digitizer's actual performance records is made in comparison to the Mass Spectrometer without a digitizer.

The need for a reliable digital data collection system for Mass Spectrometers has existed for several years. A large number of control laboratories operate their Mass Spectrometers on a round-the-clock, 7-day-a-week basis. An operation like this requires at least two people per shift, one to run the samples on the Mass Spectrometer and one to pick the peaks from the oscillographic chart and to log this data on calculation charts or to mark mark-sense cards for the computer. The justification for having an automatic data collection system is fourfold:

1. Reduction of personnel,
2. Increased accuracy from the data,
3. Elimination of the operation expense of the oscillograph and
4. An increase in the number of samples through the Mass Spectrometer.

After making an intensive study of available digital data collection systems, we decided that the equipment we needed was not presently available on the market.

From an electronic engineering standpoint the problem did not appear to be too complicated. We had two analog output signals from the Mass Spectrometer that needed to be digitized and presented in a format acceptable to a computer. Since most electronic engineering groups that we contacted had little or no knowledge of Mass Spectroscopy, it was necessary to define the nature of the output signals in great detail and to state our requirements specifically.

Included in our specifications were photographs of the D. C. amplifier output showing the various types of conditions that could exist. The data showed the effect of varying the response and damping circuits on the Mass Spectrometer as well as an analysis of the types of noise present. Those of you that are familiar with electrometer D. C. amplifiers realize that considerable high frequency noise is common in the output. The data gave the slopes in volts/sec of the various peaks encountered, from the sharp peaks at low magnetic fields to the broad peaks at high magnetic fields as well as metastable peaks. The data also included photographs of the acceleration voltage at different decay rates giving the volt per second decay rate throughout the decay range and showing the types of noise modulating the acceleration voltage signal.

After discussing our problem with several large companies that design and manufacture digital electronic equipment we found one company that was very interested in the job. We negotiated a tentative price and started to work on the project.

The first approach to the problem was to use a single high speed digitizer which would measure the ion signal voltages and then switch over to measure the acceleration voltage after the maximum peak amplitude had been determined. This design philosophy was fine except for the method of maximum peak identification. The first method was one of sample and compare on an analog basis. That is, the standard system whereby a sample of the analog signal is made and then converted to digital; held, converted back to analog and fed back to the input seeking a balance point. The peak height identification logic had to sense a change in voltage as a function of time. In other words, the comparison had to be made on some de/dt . If de/dt was too small the logic would identify noise as ion signals and ignore a slow ion peak. If de/dt was too large the logic would ignore fast peaks and cause considerable error on slow peaks. This system would work fine if the ion signals all had the same shape and same repetition rate. However, this is not one of the inherent characteristics of Mass Spectrometers. The system as developed is completely digital using a digital comparator for peak height identification.

the
Figure #1 is a block diagram of the all solid state Mass Spectrometer digitizer. The output of the Mass Spectrometer D. C. Amplifier labeled Ion Signal feeds through the single pole, double throw relay on the input through a buffer amplifier to the high speed M15 digital voltmeter. As the ion peak increases negatively in amplitude the M15 voltmeter is following this peak, the digital comparator is running and signals are being shifted into the "greater than" and "less than" registers. The digital comparator is now looking for a signal that is less than the last reading followed by five additional "less than" readings. As soon as this condition is met the logic of the system is satisfied for the criterion of the peak identification. The program register advance logic circuitry gives the command for the input relay to switch from the ion signal to acceleration voltage signal. The digital comparator is inhibited while the M15 voltmeter takes one reading of the acceleration voltage. As soon as this reading is complete the program register advance logic circuitry gives the command to read out. The ion signal which has been stored in the output of the digital comparator and acceleration voltage signal which is the output of the M15 is fed simultaneously to a binary coded decimal circuit where the binary information is converted to decimal form. From the BCD circuits we go straight to the printer and from the printer we go into a parallel to serial converter and thus to the tally punch to get the information back in binary form on a punched paper tape suitable for computer acceptance. At the completion of the print cycle the digital comparator is again energized and the logic circuit is now looking for the baseline, it is again looking for a signal that is greater than or equal to the last reading. As soon as the system sees one signal that is equal to or greater than the last signal followed by five consecutive equal to or greater than the system is now on the baseline and the circuitry is reset in preparation for a new peak.

The system is controlled by two clocks, a 60 cycle clock and 100 KC clock. The 100 KC clock controls the digitizing rate, the digital voltmeter, operates the digital comparator, the greater and less than logic gates and register. The 60 cycle clock is used to control the logic circuitry of the system and is a fundamental time base for decision making. In experimenting with several different clock speeds we came from a 1000 cycle down to 60 cycles where the error is negligible and where we get inherent rejection to 60 cycles pickup. This briefly covers the functional description of the unit. The details of the circuitry are rather complicated and will not be covered at this time.

Figure #2 shows the logic steps as they appear on a typical peak. All positive going peaks are rejected by the system.

Figure #3 shows the format of the output data from the unit. The tape punch is a standard Tally Model 420. The information is serial with 8 pieces of Mass Spectrometer data and an asterisk for end of work identification. The printer is a modified Hewlett Packard Model 155. The left hand column of data is the acceleration voltage and the right hand column is ion peak in direct voltage amplitude. There are no attenuation factors to consider.

INSTALLATION AND START-UP

The Mass Spectrometer Digitizer is quite easy to install. Inputs to the digitizer are the output of the D. C. amplifier and a 0-10V tap on the acceleration voltage. Both of these signals are filtered by a pi RC filter and provide signal to the digitizer with a total noise level of less than 1 millivolt peak to peak. After the digitizer has been connected and is operating properly the next step is to determine K factors for the different magnet ranges that will be used. The equation for mass number is: $M/e = \frac{R^2 B^2}{2E}$ which can be simplified to $M/e = \frac{K}{2E}$, where $K = \frac{R^2 B^2}{2}$ and B is fixed for a particular range. Therefore, $K = E \times (\text{mass number})$. In our operation we use three different magnetic field ranges which requires that we have three different K factors. Since the digitizer always reads only the acceleration voltage from 9.999 down to a lesser value, it is necessary for the operator to indicate which magnetic range he is on. The different K factors were determined by averaging the K factors from 10 known sample runs. The oscillograph^c charts were used to identify the individual peaks. An illustration of tabular values of mass numbers versus voltage is shown in Figure #4. After the K factors have been determined the system is ready for routine operation with all results being handled by a large digital computer.

PERFORMANCE

Thus far the performance of the equipment has been more than satisfactory. As an illustration of its performance the following data is based on the 91 day period of December 20, 1962, to March 20, 1963, (Figure #5):

1. Percent onstream 97.7%.
2. Percent utility 99% -- a few samples were run on the oscillograph at special request.
3. Labor savings -- 1 operator per shift.
4. Cost per sample reduced by 57%.
5. Capacity in samples per month 2000 -- an increase of 66%.
6. Estimated annual savings based upon savings thus far -- \$50,000.
7. Improvement in precision of results by a factor of 4.
8. Mass number identification $\pm$ 0.1 mass number up to mass 125 and $\pm$ 0.25 mass number up to mass number 250.

MAINTENANCE

We have had very few maintenance problems with the equipment. Out of the several hundred electronic components we have had one capacitor failure and one diode failure. We are not sure that we didn't cause the diode failure ourselves. I expect the MSD2 digitizer to operate with 99.98% onstream time. This is slightly better than our onstream time for the Mass Spectrometer.

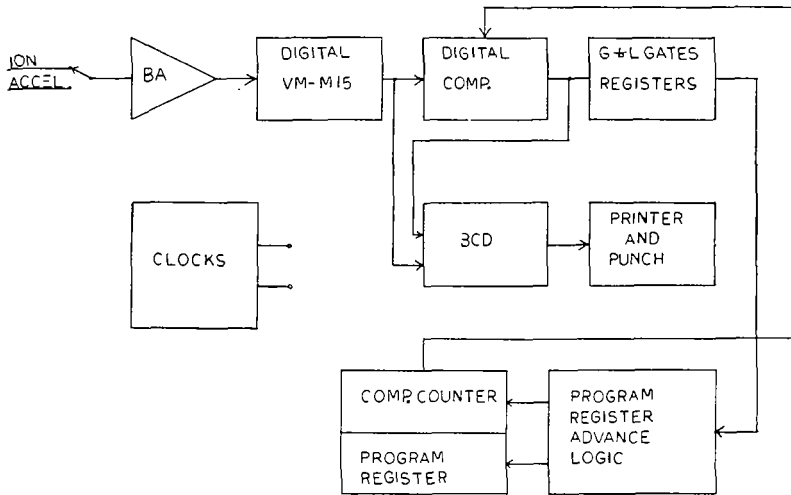


FIG. 1
BLOCK DIAGRAM

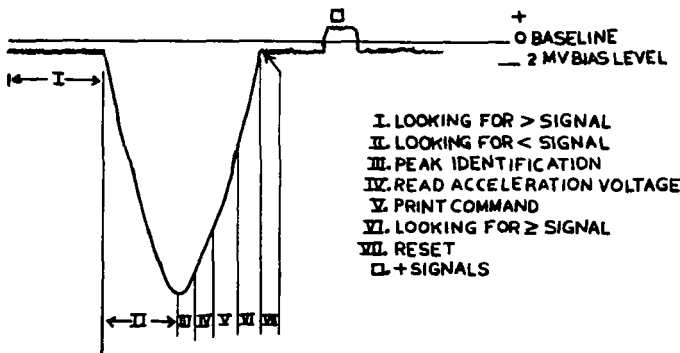


FIG. 2

SUMMARY

I have discussed the development of an all solid state digital data collection system for use primarily on Mass Spectrometers. It is obvious that the system can be used to log and correlate any two electrical signals that vary in amplitude from ± 10 volts and up to 10 cps. I have briefly discussed the principle of operation of this system and have pointed out the advantage of an all solid state digital system. The method used for peak height identification is especially reliable and accurate. The justification for using this digitizer is quite large with a payout of about 0.5 year.

DEVELOPMENT OF A SOLID-STATE DIGITIZER FOR MASS SPECTROMETERS

1. On-stream time = 97.7%
2. Utility = 99%
3. Labor savings = 1 operator per shift
4. Cost reduction per sample = 57%
5. Capacity in samples per month = 2,000
6. Estimated annual savings = \$50,000
7. Improvement in precision of results = 4
8. Mass number identification +.1 mass number up to mass 125 and +.25 mass number up to mass 250.

FIGURE 5
Performance Results

FIGURE 4

Acceleration Voltage to Mass Number Correlation

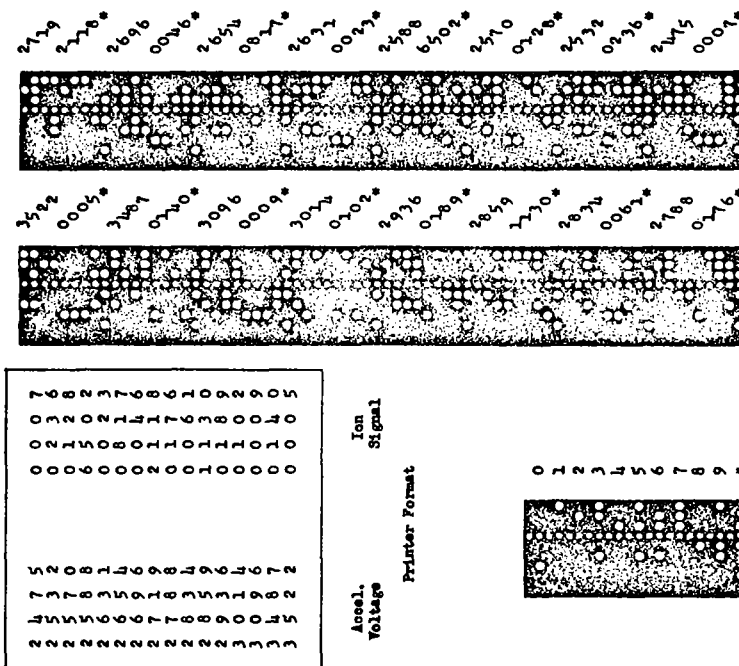


FIGURE 3 Record Format

THE MODEL 17-SERIES BENDIX TIME-OF-FLIGHT MASS SPECTROMETER

G. J. O'Halloran and W. R. Wyess

The Bendix Corporation
Research Laboratories Division
Southfield (Detroit), Michigan

An important requirement associated with future manned space travel concerns the availability of adequate laboratory-type instrumentation capable of analyzing the composition of breathable atmospheres. Additional information concerning the requirements and operational capabilities of breathable atmosphere supply systems, full pressure suit systems and "shirt sleeve" cabins is required to assist the scientists and engineers who are participating in the development of life support hardware for use in space. One approach to fulfilling these instrumentation requirements involves the use of a Bendix Time-of-Flight Mass Spectrometer.

We would like to describe for you the Model 17-series Bendix Time-of-Flight Mass Spectrometer. These instruments have been developed to provide gas analyzers with performance suitable for process control of all of the components vital to the physical well-being of an astronaut or laboratory test subject, while simultaneously supplying information about the performance of aerospace-type life support environmental supply systems.

The Model 17-series instruments have been developed with the view in mind of providing equipment of adequate quality and reliability to be used in long-term process control applications, sufficient versatility to provide the very rapid response characteristics required for pulmonary function research, and adequate sensitivity over the dynamic range required for residual gas analysis in a space simulator chamber.

A mass spectrometer is a very versatile tool for the analysis of gases, liquids, solids, and plasma (Reference 1). When properly designed, it can handle wide ranges of concentration accurately and provide very fast response. A mass spectrometer is often called a "omni sensor" by researchers in the breathable atmosphere composition analyzer area because it can handle all of the major atmospheric gases with relative ease and it is potentially capable of measuring the concentrations of the trace gases throughout the entire mass spectrum. Much of our recent activity has been associated with using the time-of-flight principle of mass spectrometry for applications in which stability, reliability, fast response, and unattended, multi-channel operation were of primary importance. This activity has been directed towards both miniaturized flyable hardware suitable for aerospace applications (References 2, 3, and 4), and the laboratory instrumentation (References 5 and 6) that forms the subject of this paper.

Our development efforts have concentrated on the application of the Bendix Time-of-Flight type of Mass Spectrometer through which basic advantages can be gained resulting from its inherent versatility, ruggedness, unusually high speed of analysis, simplicity of design, and high signal-to-noise ratio which lead directly to stability of operation adequate for process control applications.

The success of this type of instrument results directly from the application of two important inventions made at the Bendix Research Laboratories Division. One of these was the development of the double grid source (Reference 7) which focuses all peaks, regardless of mass, with but one setting of the instrument operating parameters. The other (Reference 8) was the development of a unique ion detector of simple and rugged construction which has an unusually high gain and extremely wide bandpass characteristics.

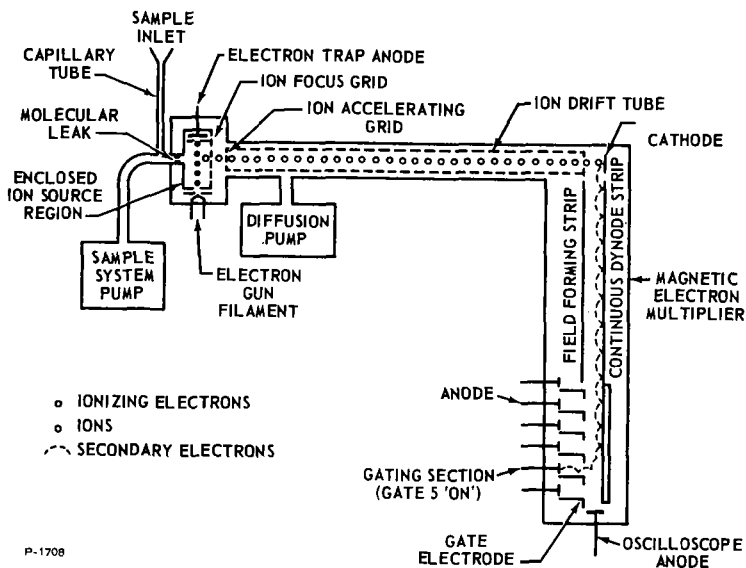
The focusing action of the source is such that the time interval during which a particular mass peak is detected is much shorter than the time interval during which the original ionization took place. This makes possible a very substantial increase in the signal-to-noise ratio over that which can be obtained using instruments that utilize

**TABLE 1 - RAW STABILITY DATA BENDIX MODEL 17-311
TIME-OF-FLIGHT MASS SPECTROMETER
(10 VOLTS FULL SCALE)**

TIME IN MINUTES	DIGITAL VOLTMEETER OUTPUT READINGS	TIME IN MINUTES	DIGITAL VOLTMEETER OUTPUT READINGS	TIME IN MINUTES	DIGITAL VOLTMEETER OUTPUT READINGS	TIME IN MINUTES	DIGITAL VOLTMEETER OUTPUT READINGS
0	5.690	24	5.680	48	5.681	88	5.681
2	5.690	26	5.670	50	5.678	90*	5.665
4	5.694	28	5.675	52	5.677	97	5.676
6	5.684	30	5.684	54	5.677	120	5.670
8	5.680	32	5.686	56	5.678	126	5.667
10	5.690	34	5.685	58	5.678	137*	5.659
12	5.685	36	5.679	60	5.678	143	5.666
14	5.691	38	5.682	63	5.681	160	5.671
16	5.689	40	5.680	67	5.677	167	5.670
18	5.700	42	5.681	73	5.674	172*	5.676
20	5.695	44	5.680	80	5.680	175	5.673
22	5.678	46	5.673	84	5.680	178	5.683

*MASS SPECTROMETER POWER INTERRUPTED TO DETERMINE EFFECTS

P-1708



P-1708

**FIGURE 1 - ESSENTIAL FEATURES OF THE BENDIX
TIME-OF-FLIGHT MASS SPECTROMETER**

continuous ionization and detection, and substantially greater resolving power than has heretofore been available in time-of-flight instruments.

The ion detector is a magnetic electron multiplier which employs crossed magnetic and electric fields to control the electron trajectories. The numerous dynodes of the more conventional multipliers have been replaced with a continuous dynode and a field forming strip each consisting of a high resistance coating which has been fired onto an insulating support. This eliminates the need for special cathode and dynode contours and provides for a straightforward mechanical design of a gating section which can be mounted at the output end of the multiplier. This multiplier provides a gain characteristic of sufficient stability that the result of an interruption and re-application of the supply potentials is a rapid decrease to zero in output current followed by its return to its original value. The output "pulse" caused thereby is exponential and characterized by a time constant of a few milliseconds for either rise or fall.

The value of the multiplier gain can be readily changed by changing the supply potentials used with it. This provides a convenient way of normalizing the sensitivity of equipment which makes use of this type of multiplier in its operation (Reference 9).

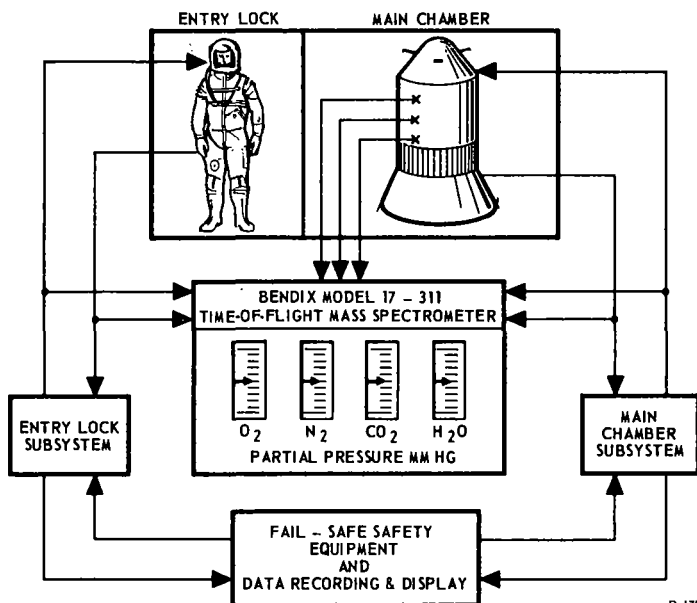
The essential features of a Time-of-Flight Mass Spectrometer designed for use as a gas analyzer are sketched in Figure 1. The gas to be analyzed is admitted into the mass spectrometer through the sample inlet, shown at the left side of the figure. The gas molecules enter the sample inlet and flow to the sample system pump under viscous conditions. A minute quantity of sample gas flows through the molecular leak orifice by random diffusion due to the thermal energy of the gas molecules. In this way, a representative sample of the gas to be analyzed is available for ionization in the source region of the spectrometer which is maintained at low pressure by the use of suitable vacuum pumping equipment.

The gas sample is ionized by an electron beam which is often operated in a pulsed mode. The resulting packet of positive ions is ejected from the source region by a negative pulse applied to the ion focus grid. By the time the packet of ions has reached the ion accelerating grid, they have all been accelerated to a common energy level. Consequently they emerge from the spectrometer source region with velocities which are proportional to $(M)^{-1/2}$. Upon leaving the ion source region, the ion packet enters a field-free drift region in which the ions separate into groups according to mass, with the separation increasing as the entire packet proceeds toward the detector.

At the far end of the drift tube, the ion pulses impinge on the cathode of the magnetic electron multiplier. The group of ions of lowest mass arrives first, followed in succession by ions of increasingly heavier mass. As each of the groups of ions strikes the cathode, a proportionate number of secondary electrons is emitted and multiplied through the continuous dynode-type magnetic electron multiplier.

The multiplier is ordinarily constructed with a multi-channel output gating assembly which permits the output electron pulses corresponding to a selected mass peak to be gated onto a selected anode. In the usual mode of operation, all other mass peaks in the spectrum will bypass this anode (though they may be gated onto the anodes of other channels). Gating is accomplished by applying a gate pulse to the gate electrode simultaneously with the arrival of the multiplier output pulse corresponding to the desired mass peak. Mass peaks which are not gated onto specific output channels will be collected by the oscilloscope anode which is mounted at the far end of the gating section. Of course, if none of the spectral peaks is gated into the fixed channels, then the entire mass spectrum appears as a succession of pulses on this ungated oscilloscope anode.

A complete mass spectrum is obtained in a period of a few microseconds. Therefore, the entire cycle can be repeated at a high repetition rate. Time-of-flight spectrometers have been produced with repetition rates as high as 100 kilocycles per second and as low as 2 kilocycles per second. However, for the more routine applications, repetition rates between 10 and about 50 kilocycles per second are ordinarily used. Since the complete mass spectrum is obtained in such a short period of time, a direct recording or telemetering of all of the information obtained by the instrument requires the use of very wide bandpass equipment.



P-1708

FIGURE 2 - BLOCK DIAGRAM OF COMPLETE ATMOSPHERIC SUPPLY SYSTEM

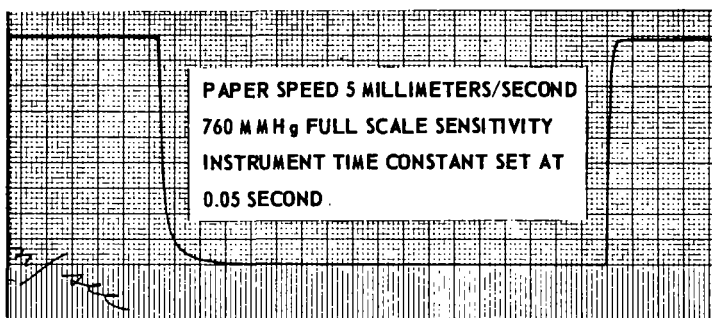


FIGURE 3 - RESPONSE OF INSTRUMENT TO A PRESSURE PULSE OF 760 mm Hg AMPLITUDE

It is possible to conveniently supply a complete spectral scan suitable for use with slow response equipment by scanning the mass spectrum with a gating pulse, which occurs slightly later in time, in each successive mass spectrum. This pulse can be made to sweep through the spectrum at a rate that satisfies the response capability of even the slowest recorders which are available. When using this technique, the entire spectrum appears at the sweeping gate anode with a repetition frequency corresponding to the sweep rate.

With a multi-channel output system, several mass peaks can be monitored simultaneously and continuously, while at the same time the scanning capability can be capitalized on to search the remainder of the mass spectrum for unexpected components or components which are of insufficient importance to require the assignment of a fixed, continuous channel.

Several types of output systems can be used with the time-of-flight instrument (Reference 10). The gated electron current is ordinarily measured by precision electrometers. The electrometer circuitry employs 100 percent feedback-type design with high open loop gain in order to provide low drift and to preserve fast response. The electrometer output can take any of several forms but is usually provided in a form suitable for use with commonly available telemetry and recording equipment.

The Bendix Model 17-series Time-of-Flight Mass Spectrometers usually incorporate these techniques to provide four output channels which are capable of continuously and simultaneously monitoring (for process control) the partial pressures of four components of the breathable atmosphere, and two channels which scan the remainder of the mass spectrum.

The instrument is completely self-contained, portable, and requires only primary power for operation. It is rather surprising to consider that though the instrument provides over 100 controls and adjustments, which an operator can use during the course of a given investigation, it is intended for continuous, automatic, and unattended operation.

The Model 17-311 provides a complete sample inlet system which is capable of remote, sequential sampling from eight different locations which can be over 50 feet from the instrument console. One of these channels is ordinarily used to allow automatic programmed recalibration of the equipment. Automatic recalibration can also be accomplished on a "press to calibrate" basis. The sequencing of the eight inlet system channels is accomplished through the use of paired, solenoid operated valves which are specially modified by Bendix for this application. The sequencing of the solenoid valves is controlled by electrical equipment which has been designed to provide maximum versatility in the inlet channel sequencing. This is accomplished through the use of an easily changed electrical "patch panel" which can be used in simple 1, 2, 3, 4, . . . , 7, recalibrate sequence or in a more complicated series such as 1, 2, 1, 3, 1, 4, . . . , 1, recalibrate. In addition, the inlet system can be programmed so that some of the channels are omitted. For example, the following sequencing can be readily programmed: 1, 2, 1, 2, 1, 2, . . . , 1, 2.

The instrument provides eight output channels, six of which are used directly for composition information. The other two are used for recalibration information and indexing readout for the sample inlet system.

The oxygen and nitrogen channels in the Bendix Model 17-311 Time-of-Flight Mass Spectrometer are used in a completely automatic, closed loop control system for maintaining the partial pressures of oxygen and nitrogen in a breathable atmosphere supply system. The water vapor and carbon dioxide channels, though they could be used in this same way, are used in a semi-automatic control loop which is closed through the supply system operator.

All of the output information from the spectrometer is available in a format suitable for slow response strip chart recorders. The complete breathable atmosphere supply system with which the spectrometer is normally used is shown in Figure 2 (Reference 11).

The four most important characteristics of a mass spectrometer when used as a gas analyzer in a process control application are: (1) stability, (2) sensitivity, (3) speed of response, and (4) resolution. The stability of the equipment is of crucial importance

and data which summarizes performance in this regard is presented later in this paper. As with most Bendix spectrometers, the sensitivity of the Model 17-series instruments is sufficient to provide a dynamic range in considerable excess of one million and a minimum detectable partial pressure of less than 10^{-14} mm Hg. The speed of response of the Model 17-series instruments is sufficient for pulmonary function studies; the output of the instrument will accomplish at least a 90 percent response to a step function change in input pressure within 0.1 second, and faster response speed can be provided. Resolution of 150 AMU appears adequate for breathable atmosphere applications and instruments of this type are often provided with this resolution. For special applications, the instrument can be provided with resolution in excess of 300 AMU.

PERFORMANCE DATA

The Bendix Model 17-Series Time-of-Flight Mass Spectrometers are designed to measure the absolute partial pressure of each of the gaseous constituents that are assigned to a fixed channel. Consequently, the absolute stability of the instruments is of primary importance.

The following discussion considers data taken while sampling from vessels containing gas at precisely regulated absolute pressures. The output data was taken by using both recorders, providing about ± 1 percent of full scale reading accuracy, and digital voltmeters, providing about 0.01 percent of full scale reading accuracy. The digital equipment was used since the absolute stability of these spectrometers is much better than ± 0.25 percent.

A definition of the terminology used in reporting the stability of these instruments is in order, since so many different meanings have been applied to the numerical stability of various analytical equipments.

Adjustments of the mass spectrometers were not permitted during any of the stability tests used for obtaining the data presented below. Almost all of the tests were run using "commercially bottled" oxygen so that the equipment would be subjected to high concentrations of an active constituent. For each run, one-half of the difference between the highest and lowest output amplitude, expressed as a percentage of full scale, is used as the stability. Using this rather severe criterion, the stability of the equipment is in general better than 0.25 percent in a one-hour period.

The stability tests were run in order to evaluate both the short term drift which immediately ensued a large amplitude pressure pulse, and the long term drift of the equipment.

The response of the instrument to a pressure pulse of 760 mm Hg is shown in Figure 3. The data shows the complete absence of overshoot and no detectable drift over the one minute periods before, during, and after the pulse. This "pressure pulse" is the most severe test associated with changes in inlet conditions and it is an extremely sensitive way of checking improper sample system operation.

Long term stability tests of the instrument produce raw data of the type included in Table 1. Worthy of special note is the fact that the instrument power was interrupted three times (denoted in Table 1 by *) during the three-hour test. No data points lie outside of the ± 0.25 percent of full scale interval.

These stability tests were run with the automatic recalibration subsystem disabled, so that the data applies to the basic Bendix Model 17-Series Mass Spectrometer.

The detection threshold for the recalibration subsystem comparator is set at 0.25 percent of full scale. The recalibration control loop employs a motor-driven potentiometer in a null-balance loop. The operation of the motor is audible to the test operator. Consequently, the instrument recalibration subsystem is an unmistakable "tattle tale" for drift exceeding 0.25 percent.

Perhaps the most easily run stability test, and certainly the one most often (practically continually) run, is to "listen for the motor." In several months operating time the motor has seldom been heard.

REFERENCES

1. O'Halloran, G. J., and Fluegge, R. A., "Plasma Analysis with the Bendix Time-of-Flight Mass Spectrometer," Presented at the Eleventh Annual Conference on Mass Spectrometry and Allied Topics, arranged by officers of the American Society for Testing Materials, Committee E-14, San Francisco, California, 19 through 24 May, 1963.
2. O'Halloran, G. J., "Two New Instruments for Breathable Atmosphere Control," Presented at the Closed Circuit Respiratory Systems Symposium, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio, 28 and 29 April, 1960.
3. O'Halloran, G. J., "A Breathable Atmosphere Composition Analyzer for Aerospace Applications," Presented at the 14th National Aerospace Electronics Conference, Dayton, Ohio, 14 through 16 May, 1962.
4. Betts, J. F., and O'Halloran, G. J., "Miniaturized Bendix Time-of-Flight Mass Spectrometers," Presented at the Eleventh Annual Conference on Mass Spectrometry and Allied Topics, arranged by officers of the American Society for Testing Materials, Committee E-14, San Francisco, California, 19 through 24 May, 1963.
5. Lee, W. L., Jr., Captain, USAF, MC, "Changes in Lung Volume and Alveolar Gas Concentration During Breath Holding after Breathing Oxygen at Reduced Barometric Pressures," Presented at the Aerospace Medical Panel of NATO (AGARD), the week of 24 July, 1961, Oslo, Norway.
6. O'Halloran, G. J., "A Rapid-Response Mass Spectrometer for Respiratory Function Analysis," Presented at the Clinic on Instrumentation Requirements for Psychophysiological Research, held at the Lafayette Clinic, Detroit, Michigan, 16-17 May, 1961.
7. Wiley, W. C., and McLaren, I. H., "Time-of-Flight Mass Spectrometer with Improved Resolution," The Review of Scientific Instruments, Vol. 26, No. 12, pp. 1150-1157, December, 1955, and U.S. Pat. No. 2,685,035.
8. Wiley, W. C., and Goodrich, G. W., "Resistance Strip Magnetic Electron Multiplier," The Review of Scientific Instruments, Vol. 32, No. 7, pp. 846-849, July, 1961.
9. Betts, J. F., Fluegge, R. A., and O'Halloran, G. J., The Bendix Corporation, Research Laboratories Division, and Narcisi, R. S. Air Force Cambridge Research Laboratories, "Development of a Balloon-Borne Time-of-Flight Mass Spectrometer," Presented at the Ninth Annual Meeting ASTM Committee E-14 on Mass Spectrometry, Chicago, Illinois, 4 through 9 June, 1961.
10. Betts, J. F., Paufler, E. H., and Wiley, W. C., "Output Systems for Time-of-Flight Mass Spectrometers," Applied Spectroscopy, Vol. 14, No. 5, pp. 119-123, 1960.
11. Scheppeler, R. H., Pioneer-Central Division, The Bendix Corporation, "Atmosphere Supply System for Man Inhabited Space Simulation Chambers," Presented at the Institute of Environmental Sciences, Los Angeles, California, 17 through 19 April, 1963.

PERFORMANCE OF AN ANALYTICAL MASS SPECTROMETER
By: C. M. Judson, R. F. Howard, and C. R. McKinney
Consolidated Electrodynamics Corporation
Pasadena, California

The design of an analytical mass spectrometer represents compromises between various performance requirements including speed, sensitivity, dynamic range, accuracy, resolution and mass range. An evaluation has been made of some ways in which a conventional instrument such as the CEC 21-130 cycloidal focussing mass spectrometer can provide improved performance for special purposes. This is generally accomplished at the expense of some other aspect of performance. A case of particular interest is the problem of monitoring gas chromatograph streams which requires high speed and sensitivity but permits lowered requirements for accuracy.

The scan times used in gas chromatograph monitoring are generally in the range of 1 to 30 seconds for a spectrum. One wishes to obtain a spectrum in 1/2 of the half-width of the chromatograph peak. A spectrum will seldom require more than 3 octaves (a factor of 2^3) in mass range. With a scan time of 1 second/octave or 3 seconds/spectrum, one can handle chromatograph peaks as small as 6 seconds half-width. One can calculate approximately that the bandwidth required in the detector system when using a logarithmic scan rate is

$$BW = 0.7 R \times S \quad (1)$$

where R is the resolution and S the scan speed in octaves/second. With a resolution of 200 in this instrument the bandwidth required for a speed of 1 octave/second is 140 cycles.

The limitations to the speed of scanning are as follows:

1. The scanning system must track, maintaining focus and maintaining logarithmic scan rate.
2. The amplifier and recorder must have sufficient bandwidth to follow the scan.
3. The chart drive of the recorder must be fast enough to make the record legible.
4. Sixty cycle ripple from the filament and from other sources must be minimized.

We have found that relatively simple modifications to the instrument can be made to permit operation at speeds up to 1 octave/second in spite of these difficulties. The limitations are taken care of as follows:

1. Tracking of the scan circuit is not a problem at these speeds.
2. The amplifier used in this instrument is readily adjusted to a bandwidth approaching 200 cycles, and a recording oscillograph is available from our Data Recorders Division with adequate bandwidth.
3. This fast recorder has a suitable range of chart speeds.
4. Modulation can be minimized by using a DC supply for the filament.
5. Increased noise and ripple somewhat reduce the sensitivity at high scan speeds but, as we shall see, operation at high pressure of carrier gas (generally helium) not only compensates for this but actually increases sensitivity over that obtained in normal operation.

It is possible to scan at rates faster than that which the available detector system will follow completely if one is willing to accept some loss in resolution, sensitivity, and accuracy. Actually a fast response system has increased noise over a slower system so that maximum sensitivity for a given scan speed is not necessarily accomplished with the highest possible detector bandwidth.

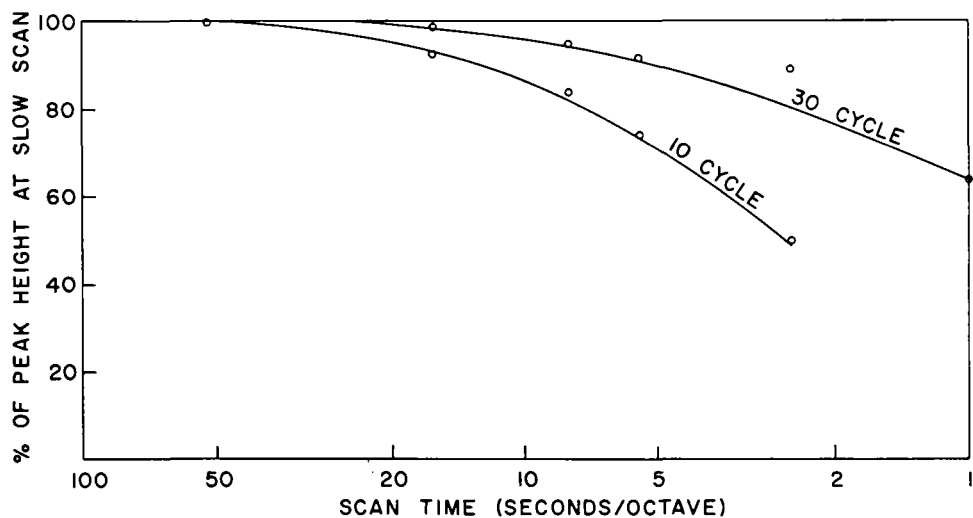


FIG. 1

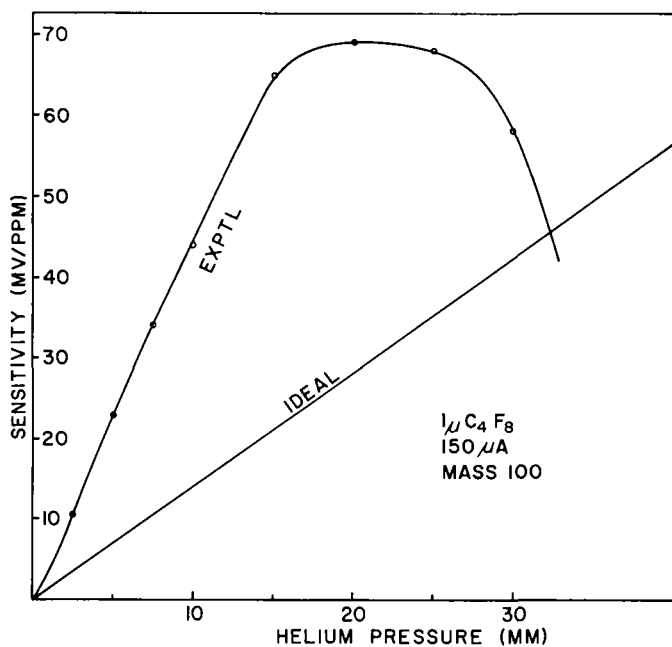


FIG. 2

Figure 1 shows the reduction in peak height which occurs as the scan rate is increased up to 1 octave/second with 10 cycle and 30 cycle detector bandwidth. With the 30 cycle system one can scan at 1 octave/second with a loss of a factor of two in sensitivity. Since peaks have constant widths using a logarithmic scan the pattern is little affected by the peak clipping. There is however, a loss in resolution when the recording system does not follow which is the main limitation to use of this speed with a 30 cycle system. To maintain resolution at this scan speed we use a 200 cycle system which follows the peaks with essentially no loss in sensitivity or resolution. With the 30 cycle system we generally scan at a speed of 1/3 octave/second requiring 10 seconds for a 3 octave spectrum.

The concentration of a component in the gas chromatograph effluent which will be present (measured in mol fraction in the helium stream) can be calculated from the equation:

$$MF = \frac{G}{\frac{MW}{T \times F}} \quad (2)$$

22,400

where G is the weight of a component present in the sample measured in grams, MW is the molecular weight, T is the peak half-width in minutes, and F is the helium flow rate in cc/min. For the case of a 1 mg. sample of MW 200, with a flow of 50 cc/min and a peak width of 30 sec., the calculated mol fraction in the effluent helium is 0.005. If we wish to identify a component at a concentration of 0.2% in the 1 mg. sample, we need to be able to obtain a spectrum at a mol fraction of 10^{-5} .

Modifications of the instrument which can be used to get this sensitivity are:

1. Increased helium pressure in the analyser. This has been successfully used and has been the major source of increased sensitivity.
2. Increased ionizing current. We have gotten only marginal improvement from increased ionizing current.
3. Larger grid resistor in the amplifier. We have not been successful so far in getting any large improvement in sensitivity for high speed scanning by this approach.
4. Low voltage. We studied the possibility that higher pressures could be used in low voltage spectra under conditions in which helium is not ionized but found no advantage with respect to the helium pressure which could be used.

Figure 2 shows the change in concentration sensitivity (expressed in signal/ppm with change in inlet pressure. The shape of this curve does not show any systematic variation with peak mass or compound molecular weight. At low pressures the signal for a given concentration increases linearly with pressure along the ideal curve of Fig. 2. At higher pressures the slope of the line increases as a result of changes in pressure conditions such that the higher molecular weight materials are swept through the leak with the helium at the faster leak rate of helium. At still higher pressures (about 20 mm) a maximum is reached and the signal then falls off quite substantially. These data were obtained with a batch inlet and a molecular leak. The gas chromatograph monitoring instrument is operated to provide the same leak rate to the analyser with the same analyser pressure, approximately 1/1000 of the inlet pressure.

The major adverse effect of operation at these helium pressures is the presence of a tail on the peaks. Figure 3 shows the xenon peaks with no helium and with 20 mm of helium present. The qualitative features of the spectrum are not in any way affected by the peak broadening.

The broadening is seen only in the tail of the peak. Fig. 4 shows the broadening at various heights from 1% to 25% of the total peak height. If we arbitrarily limit the allowed broadening to a factor of two at 10% height, we then set as an operating pressure 10 mm of helium rather than the 20 mm pressure at which maximum sensitivity was found.

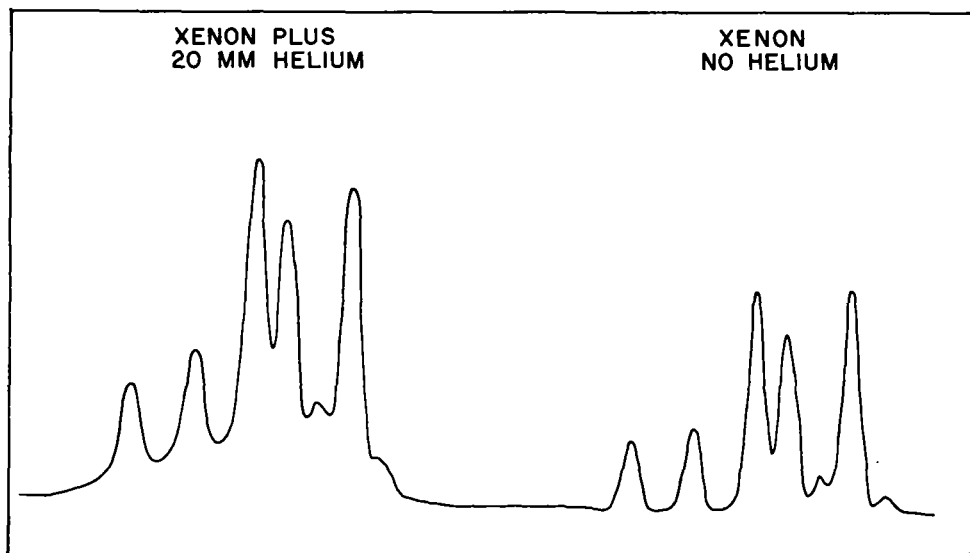


FIG. 3

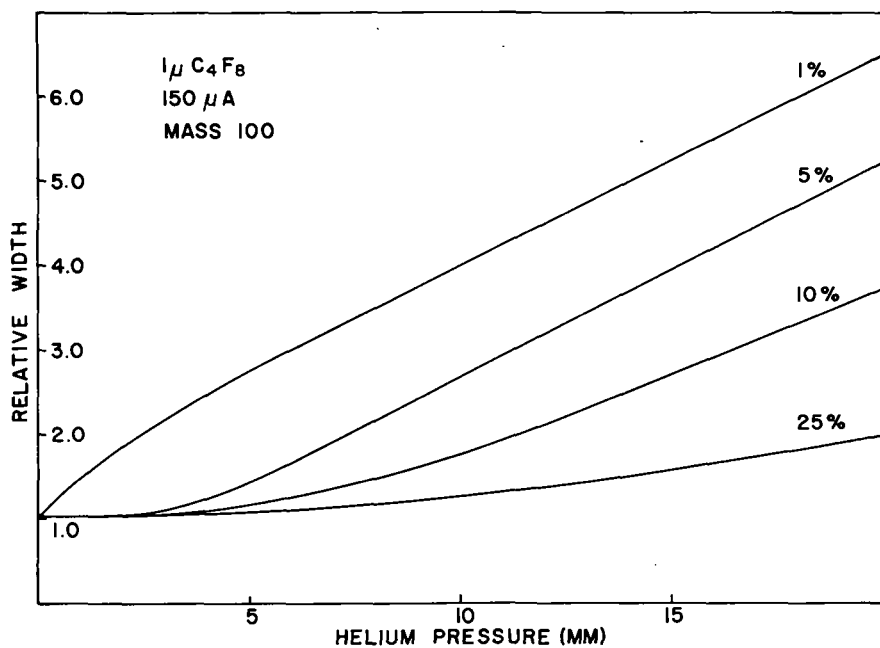


FIG. 4

Another limitation to use of high helium pressure is the necessity of limiting the concentration to avoid saturating the amplifier. It is necessary to provide means of attenuation other than recorder attenuation to handle high concentrations.

The instrument modifications which are needed for gas chromatography monitoring with a conventional instrument are:

1. Fast scan with continuous repetition.
2. Fast amplifier and recorder.
3. Fast recorder chart drive with variable speed.
4. DC filament to eliminate modulation of ion current.
5. Continuous monitoring by oscilloscope.
6. Dual inlet for batch and continuous introduction.
7. Increased dynamic range by adjustment of ionizing current, grid resistor, or analyser pressure.
8. Optional increased mass range using larger magnetic field.

The resulting performance obtained using 1/3 octave/sec. scan rate, 150 uA ionizing current, 10^{11} ohm grid resistor, and helium pressure equivalent to 20 mm in the batch inlet is such that we can detect 0.1 ppm of typical materials of moderate molecular weight. This is done with a flow rate of 0.4 atm.-cc/sec. Assuming that we require 50 times more to identify a compound we can identify a material at 5 ppm in the helium stream. Based on the calculation from equation (1) that we can expect 0.005 mol fraction for the major constituent, we can identify a component at 0.1% in the liquid sample introduced to the chromatograph. We have in fact run an unknown mixture of 30 hydrocarbons in a chromatograph using 0.020 inch capillary and identified all of the components from the mass spectra including components present at 0.1%.

We have also considered the general case of high sensitivity analysis, not necessarily using helium, and not necessarily scanning fast. The use of high gas pressures appears to be rather generally applicable for unreactive materials such as H_2 , N_2 , A and fluorocarbons and may be applicable to many other systems. The maximum sensitivity in the systems studied was in the 1-10 mm. region and did not show any systematic variation with molecular weight of the gas used.

If slower scan speed can be used we can use a larger grid resistor and lower bandwidth and get at least 10 times greater sensitivity, or alternatively we can get the same sensitivity at a lower total pressure. If the sensitivity at any specified pressure is increased much more than 10 times that which we have been achieving in the fast scan system, background will become significant and will limit further increase in sensitivity.

Another direction in which performance of this instrument can be extended is in the mass range. Using a 6000 gauss magnet instead of the normal 4500 gauss magnet the nominal mass range can be changed from 2-250 to 4-500. Actually we find that we can scan to mass 600 without a large loss in sensitivity. Resolution can also be increased by use of narrower slits. A standard narrow slit is available which increases the unit resolution from 220 to 310 with only a small reduction in sensitivity. It appears that some further improvement can be obtained with still narrower slits.

Finally we have shown applicability of this instrument for measurement of isotope ratios with a precision of 0.2% or better. There is not time to discuss the methods used, but it is relevant to indicate that this application involves quite different problems, precision, and accuracy being of major importance, sensitivity still being required, but speed being of minimum importance.

Acknowledgment

Acknowledgment is made to Heinz Boettger who carried out a major part of the experimental work reported.

A NEW TYPE OF POSITIVE ION DETECTOR
FOR THE SIMULTANEOUS MEASUREMENT OF TWO ION BEAMS

N. R. Daly
United Kingdom Atomic Energy Authority
Aldermaston, England

ABSTRACT

A new type of positive ion detector has been developed that is capable of simultaneously measuring two positive ion beams. It is made up basically of two scintillation detectors back to back. Two ion beams enter a chamber on either side of a thin 0.020" dividing position. They are attracted to two electrodes at 40 KV where they release secondary electrons. A magnetic field directed along the axis of the positive ion beam deflects the two electron beams so that they strike opposite walls of the ion detector. Two small organic phosphors situated in the walls at the electron impact points, produce light signals that are recorded using pulse counting techniques.

Visual observation of the electron images produced in the phosphors by large positive ion beams, show that there is good focussing and the phosphors collect all the secondary electrons. Background noise on both sides of the detector is less than 10^{-19} amps and equivalent. Measurements of isotopic ratios have shown that the stability of the system is such that the precision of measurements is defined almost entirely by the statistics of the number of ions counted. Since it gets over two of the difficulties associated with surface ionization techniques, i.e., instability and decay of ion beam intensity, it will give increased precision in the measurement of small samples. Its use with isotopic standards will also result in increased precision of measurements.

ION-COUNTING FOR RAPID MEASUREMENTS
WITH TIME-OF-FLIGHT MASS SPECTROMETERS

By

D. R. McAdams, L. Lane, and J. G. Lemley
Esso Research Laboratories,
Humble Oil and Refining Company
Baton Rouge, Louisiana

INTRODUCTION

The study of rapidly changing compositions, particularly those of effluents from capillary gas chromatographs, requires high speed and high sensitivity measurement systems. The technique known as ion-counting has been shown to have these features. Small samples sizes may be employed and 10-10 to 10-12 grams of many compounds may be detected.

SUMMARY

Ion-counting has been employed with a Bendix Time-of-Flight mass spectrometer in order to utilize the maximum available sensitivity of the instrument. The ion-counting technique utilizes an electron multiplier detection system in which the desired mass spectral signals are selected within the multiplier assembly. These signals, which exist as pulses resulting from single ions in the case of low sample concentrations, are amplified and summed in conventional electronic counters. Multiple channel operation permits determination of mass spectral peak intensity ratios. Absolute intensity levels are also measurable.

Performance of the equipment was evaluated by consideration of counting statistics and by comparison of operating parameters of the mass spectrometer with observed electron-multiplier pulse output rates for selected ions. Population theory was approximated under conditions wherein large fractions of the single-ion pulses were counted and switching signals were not counted. Linearity was demonstrated from low ion current levels to high values of about 1.2 average ions of selected weight per spectral scan.

Quantitative measurements of mass spectrometer ion currents with lower limits of 10-18 amperes and 100 ions have provided useful spectral information. Applications have been primarily studies of effluents from capillary gas chromatographs. High sensitivities have permitted studies of minor components without charging samples large enough to degrade the chromatographic resolution. As an example, 0.2 microliters of a blend containing 0.1% benzene was further split by a ratio of 1 in 400 before entering a capillary column 100 feet long. The benzene emerged in a peak with a width of five seconds. As many as 4000 ions (m/e 78) were observed in the mass spectrometer while sampling approximately 5% of the stream containing this 5×10^{-10} grams of benzene. Detectability limits of 10-12 grams of benzene are indicated with the observed background of 6 to 10 ions.

Observation of mass spectral peak ratios may be accomplished with rapidly changing sample compositions by counting ions over intervals of about 0.1 second. This simplified the adjustment of data demanded by existence of signal pulses resulting from multiple ions. The areas of gas chromatographic peaks with Gaussian shapes may be integrated with the ion-counting technique if consideration is given to the combination Gauss and Poisson functions involved.

Ion-counting has been observed to possess accuracy and speed better than other recording techniques particularly for low concentration components. The disadvantage of not being easily applied to major components is comparatively unimportant. Instrument background and other effects are also discussed.

DISCUSSION

Instrumentation. -- The conventional components employed were a Model 12 Bendix mass spectrometer with a mercury diffusion pump, liquid nitrogen trap and a Freon refrigerated baffle. The instrument background was minimized by heating the flight tube, particularly at the source end. A pumping restriction baffle was employed between the source and the pumping connection to the flight tube.

The gas stream being sampled was continuously pumped by a conventional mechanical pump. The sample portion admitted to the mass spectrometer was controlled by an experimental double-action metal valve possessing negligible

TABLE I
ION ABUNDANCE VERSUS IONIZING ELECTRON CURRENT

	<u>Ionizing Trap Current Arbitrary Units</u>	<u>True Ion Abundance</u>	<u>Ratio, Arbitrary Units</u>
Experiment A	2.6	10285	3956
	1.3	4950	3808
Experiment B	2.6	1536	591
	1.3	717	552

TABLE II
SELECTED VALUES FOR CALCULATING TRUE ION ABUNDANCES

<u>Peak Width (Seconds)</u>	<u>Maximum Ion Abundance (No. per Sec.)</u>	<u>Observed Counts</u>	<u>Total Ions Gaussian- Poisson</u>
0.2	1000	171	177
	10,000	1285	1773
	30,000	2377	5317
0.4	1000	342	354
1.0	1000	856	886
	10,000	6426	8862
	20,000	9863	17,724
4.0	1000	3422	3545
	10,000	25,702	35,449
	30,000	47,549	106,344

TABLE III
PEAK RATIO DATA
1% Normal Pentane
5 Second GC Peak Width
n-Pentane m/e 43 Abundance = 1.00

<u>Ion m/e</u>	<u>Ratio</u>	
	<u>Measured</u>	<u>Reported API</u>
41	0.38, 0.39	0.405
72	0.114, 0.119	0.088

internal volume at the point of sampling. A 1/8 inch tube sealed into the flight tube wall by use of a double-cone coupling carried the sample directly into the ionization region of the source.

The ion detector was a six-gated electron multiplier supplied by Bendix. A circuit for measuring total ion current by sampling alternate spectra⁽¹⁾ was incorporated. Other signal output provisions were (a) two channels of analog information recorded on a six galvanometer Minneapolis-Honeywell Model 1406 Visicorder, and (b) a Tektronix oscilloscope.

The ion-counting components provide for two channel operation. The signal pulses produced by the electron multiplier are selected by gate structures within the multiplier assembly under the control of timing circuits which permit choice of desired m/e value ions as in conventional analog recording. The selected pulses are passed through pre-amplifiers (Hammer Model N-356) of Nuovistor type having low noise levels and a voltage gain of slightly less than unity. Following this impedance transformation, the pulses are amplified with Hammer Model N-371 amplifiers adjusted to a gain of 3000 to 4000. Discrimination removed residual gating noise.

The accepted pulses were further discriminated and shaped in electronic circuitry originally designed by Bendix⁽²⁾ to permit time-sampling of the spectral signal after passage through a video amplifier. These circuits were used instead to provide gating pulses for the multiplier. This modification was found to be necessary for the detection of an adequate fraction of the single-ion pulses.

The signal pulses in each of the two channels were counted by the five-decade electronic counters supplied by Bendix. Rate and ratio measurements were permitted. A separate five-decade counter was used to determine accurately the total number of spectral scans occurring during the measurement periods.

Installation of Equipment. -- A degree of parallel operation of ion-counting with more conventional measurements was desired. An arrangement was used wherein (a) analog recording would not suffer interference from the ion-counting facilities, and (b) little or no cable re-arrangements would be necessary for changing from one mode to another. Therefore, the top priority gates in the electron multiplier were employed for analog recording. The two gates next in priority were used for ion-counting. The lowest priority was assigned to the total-ionization mode.

The most obvious problem encountered was excessive leakage of the master oscillator pulses from the mass spectrometer into the counting amplifiers. Conventional filtering was added to most of the DC power supply lines to cure this problem.

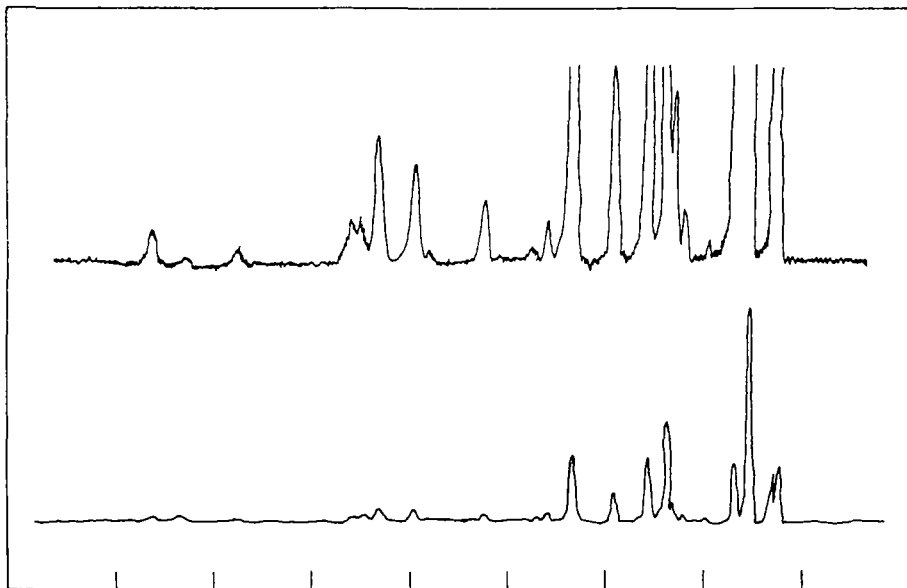
The gating pulses themselves presented certain problems. Their magnitude was 10^5 times as great as those of the single-ion pulses to be counted. Positioning of the electrical leads was critical both exterior to and within the vacuum housing. Excessive transfer of the channel 1 gating pulse into the channel 3 output was observed. Proximity of leads was the probable cause. No complete cure was found so channel 1 was inactivated during counting periods. Leakage from any other than #1 channel into adjacent channels was sufficiently low except with separations of 0.1 microsecond or less. Operation of the total-ionization switching circuit in its original form prevented use of the ion-counting facilities. This problem was eliminated by slightly damping the square-wave signal with a 20 pfd capacitor across the square-wave line at the multiplier connector.

Counting Statistics. -- Observation of pulses from the electron multiplier was a simple matter. The need, however, was for measurement of a very large fraction of the pulses resulting from only single ions and determination of the actual number of ions involved. Consideration of counting statistics permitted a useful criterion of equipment performance as well as study of integration of signals.

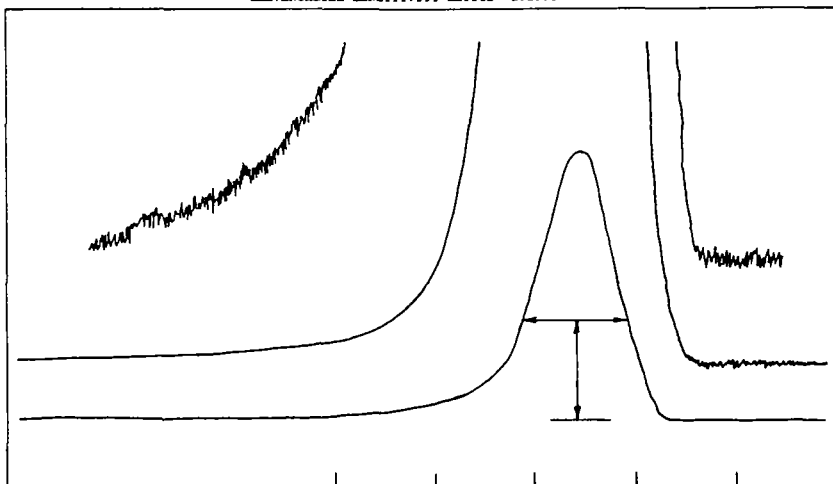
Reference was made by Betts, Pauve, and Wiley⁽²⁾ to the occurrence of pulses resulting from arrival of more than one ion of a given weight at the multiplier in a single spectral scan and hence at the same time. This was not a handicap because a statistical treatment⁽³⁾ of this phenomenon according to population theory provided a valuable means of determining whether the detection equipment had adequate sensitivity. Using the Poisson distribution as a simplification, the following equation was derived:

CAPILLARY GAS CHROMATOGRAPHIC EFFLUENT MONITOR BY MS USING TOTAL IONIZATION CIRCUITRY

GENERAL SCAN. RECORDING GALVANOMETERS HAVING RATIOS OF 10:1 SENSITIVITY.
MINUTE INTERVALS SHOWN ON TIME SCALE

MAJOR COMPONENT IN CAPILLARY GC EFFLUENT

MEASUREMENT OF PEAK WIDTH AT 36.8% OF PEAK MAXIMUM
INTERVALS ON TIME SCALE ARE 3 SECONDS
GALVANOMETER SENSITIVITY RATIOS 1:10:100



$$A = B(1 - e^{-T/B})$$

where A = the number of pulses observed

B = total spectral scans in the observation period

and T = total number of ions

For convenience a computer was employed in preparation of a table for conversion of observed pulse rates to "true-ion-abundances."

The above treatment was also applied to the special case of gas chromatographic peak shapes. In this, the Gaussian distribution was chosen as the approximation of the GC peak shape. Series of tables were prepared to permit adjustment of observed pulses to ion abundances for GC peaks of different widths measured at 1/e times the "peak maxima."

Applications

Detection of Single Ions. It was immediately observed that detection of large fractions of single-ion events was possible only after the elimination of extraneous pulse signals. This was accomplished by successive approximations. In each case plots were made of calculated ion abundances against mass spectrometer operating parameters such as ionizing-electron trap current. A too-rapid increase in "ions" with current signified insufficient observation of single-ion pulses. A too-gradual increase signified presence of extraneous pulses. These, of course, were observable in absence of ions. Proportionality nearly within limits of precision imposed by the statistics of random events was observed under conditions of proper adjustment of equipment, as shown in Table I.

The attainable performance was shown to have a noise level of less than one count per five seconds in the absence of ions. Linearity existed up to an average of 1.2 ions per spectrum, i.e. 12,000 ions of given m/e value per second for spectral repetitions of 10,000 per second. Lack of linearity at 15,000 ions per second and above may have resulted from insufficient amplifier recovery with large input pulses. In practice, the full dynamic range of 60,000 is seldom realizable on a single MS peak because of background ions.

The effluents from capillary gas chromatographs were especially interesting subjects for study by ion-counting techniques. Use of large samples by some investigators has been prompted by the natural desire to produce high concentrations of the compounds to be studied in the capillary effluent. The attendant loss of resolution when columns are loaded prompted the use of small samples in our work. Typical conditions were:

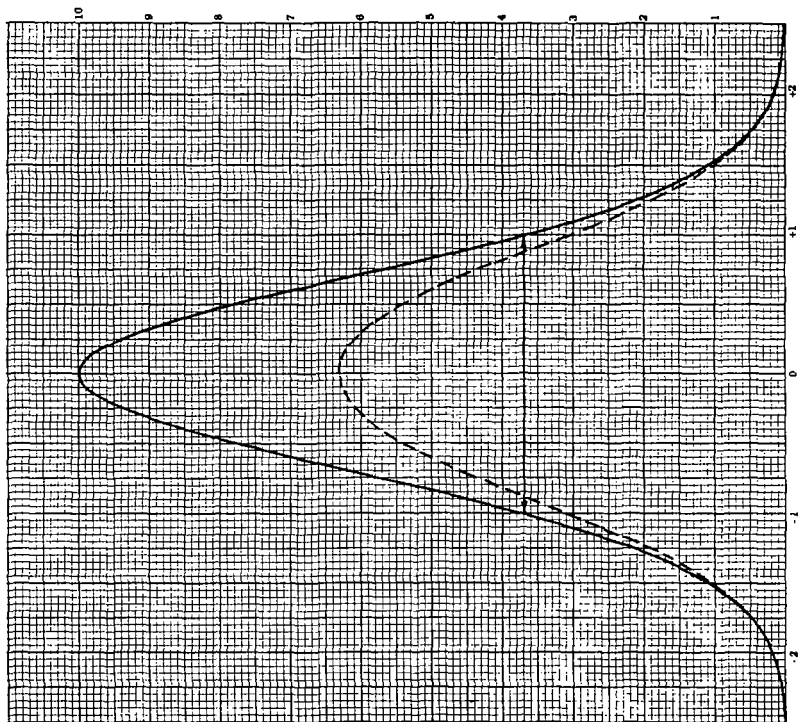
1. Helium carrier gas at 0.5 to 1.0 cc./minute.
2. Stainless steel 0.01 to 0.02 inch internal diameter capillary tubing.
3. 100 to 150 feet in length.
4. Sample size 0.2 to 0.5 milligram further split 1 in 400 before the capillary.

Other workers^(4,5) have described some results with mass spectrometric studies of capillary effluents. Their GC peak widths ranged from about 5 to 50 seconds. In our studies, the peak widths ranged from 1.3 seconds for short columns to 10 seconds, with most widths of about 5 seconds as measured at 36.8% (i.e., 1/e) of maximum height. These widths were usually determined by means of the total ionization circuitry. See Figures 1 and 2. Conventional analog scanning is feasible for the major components. The example in Figure 3 for n-pentane demonstrates the distortion introduced by simple scanning techniques.

Ion-counting also encounters a form of distortion, but this may be accounted for by means described in the section on statistics. The magnitude may be seen in Table II and in Figure 4. The latter is a case where the maximum of the curve represents an average of 1.0 ion per spectrum. The use of such corrections is desirable because the experimental steps are simple for integration of narrow GC peaks with a single measurement. As an example, small samples of air were repetitively injected into a capillary column producing GC peaks with 1.3 second widths. Oxygen ion measurements were 7514, 6711, 6784, 6789 and 6827. Reproducibility thus was excellent with a standard deviation of 114 to be compared with the expected value of 83 for this count level.

#253-2

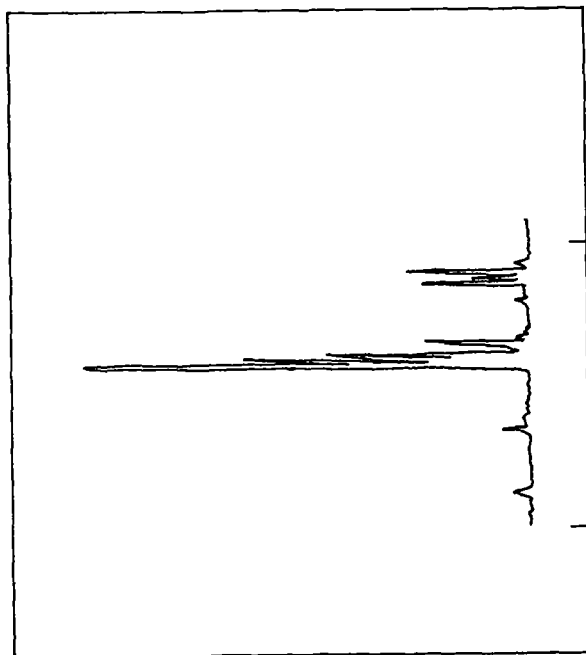
FIGURE 4
COMPARISON OF GAUSSIAN CURVE WITH A
COMBINATION POISSON-GAUSSIAN CURVE
—— GAUSSIAN
..... POISSON-GAUSSIAN



#253-2

FIGURE 3
MASS SPECTRAL SCAN OF n-PENTANE DURING
CAPILLARY GC EFFLUENT PERIOD

SCAN m/e RANGE 23-80. GC PEAK WIDTH WAS
ABOUT FIVE SECONDS. TIME INTERVAL INDI-
CATED IS 6 SECONDS.



The "saturation" in the count rate curve becomes more exaggerated as the maximum count rate value becomes larger. An experiment with a mixture containing one major and one trace component is shown in Figure 5. The elution times from a capillary GC column are noted by arrows above a time scale graduated in three second intervals. The electron multiplier pulses for one mass spectral peak were measured on an events-per-unit-time counter with intervals of 0.1 second and repetitions of about five per second. For presentation in this paper, the digital values were converted electronically to an analog signal and recorded on a Visicorder. The five galvanometers had relative sensitivities of 1, 3, 10, 30 and 100. The smallest step corresponding to one digit or 10 pulses per second is easily seen with the most sensitive galvanometer at low ion abundances. The background was approximately 20 ions per second. The top of the peak for the major component represents an indeterminate region wherein essentially all spectra contained at least one ion of the selected weight.

The width of the GC peak for a low concentration component may not be directly measurable from analog scans. The shape may then frequently be deduced from that of a neighboring GC peak of larger magnitude providing GC column overloading is avoided. With these assumptions as to shape and widths, integral pulse values may be adjusted to give integral ion numbers according to the method described above.

The corrections involved emphasize the caution needed in treating data from other ion sources such as solids-spark excitation wherein ions may be produced in high intensity bursts. The performance of the electronic counters will provide good indications of extremely large short-time variations.

Real peak shapes may be studied by ion-counting within limits imposed by statistics and by digital recording facilities. Figure 6 contains a point plot for the trailing edge of the extremely large GC peak shown in the analog scan of Figure 2. Short measurement periods were employed during rapid changes of ion concentrations to simplify adjustment of the count rates. Trailing of the peak in departure from Gaussian shape was verified.

The sensitivity of ion-counting techniques exceeds that of any other recording system with a mass spectrometer. Coupled with the feature of mass selectivity, a powerful tool is available. The maximum sensitivity level depends on (1) background, (2) pumping speeds, (3) sampling arrangements to optimize pressures in the mass spectrometer, and (4) interference from other sources. Experiments were conducted by passing 5×10^{-10} grams of benzene through a capillary column. This was done by splitting with a ratio of 1 in 400 a 0.2 milligram sample containing 0.1% benzene in normal pentane. With variations in sampling valve adjustments, total counts of the m/e 78 ion in a GC peak width of five seconds ranged from 400 to 4000. The background was 6 to 10 ions. The limit of detection of benzene would be approximately 10^{-12} grams under these conditions. Reliable measurements of the size of the sample actually entering the mass spectrometer were not possible. This was estimated to represent as much as 5% of the 1 cc. (STP) per minute effluent gas from the GC.

An increase in sensitivity of these systems was realized by increasing the concentration of the components in the carrier gas which composed the sample admitted to the MS. This was accomplished by operating the outlet end of the GC column below atmospheric pressure. The inlet pressure to the column was adjusted to give the desired pressure differential across the column. Ultimate sensitivities were then determined by the volatilities of the GC column coatings.

The sensitivity of ion-counting compares well with that of flame-ionization detectors used for GC detectors at the present stage of the art. The selectivity of ion-counting with an MS provides a powerful advantage over conventional GC detectors. The flame-ionization detector still has one important application where ion-counting cannot compete. Trace hydrocarbons in air may be detected by flame-ionization through use of very large samples. This is difficult with an MS.

Mass spectral peak ratio measurements are probably the most important application of ion-counting. They permit compound identifications. The attainable accuracy is high. Table III presents peak ratio data for normal pentane at 1% concentration injected into a capillary gas chromatograph. The relative intensity for the parent ion is higher than reported from other types

FIGURE 5

ION-COUNT-RATE CONVERTED TO ANALOG RECORD

GALVANOMETER SENSITIVITY RATIOS 1:3:10:30:100

APPROXIMATELY FIVE CONVERSIONS PER SECOND

TIME SCALE DIVISIONS EQUAL 3 SECONDS

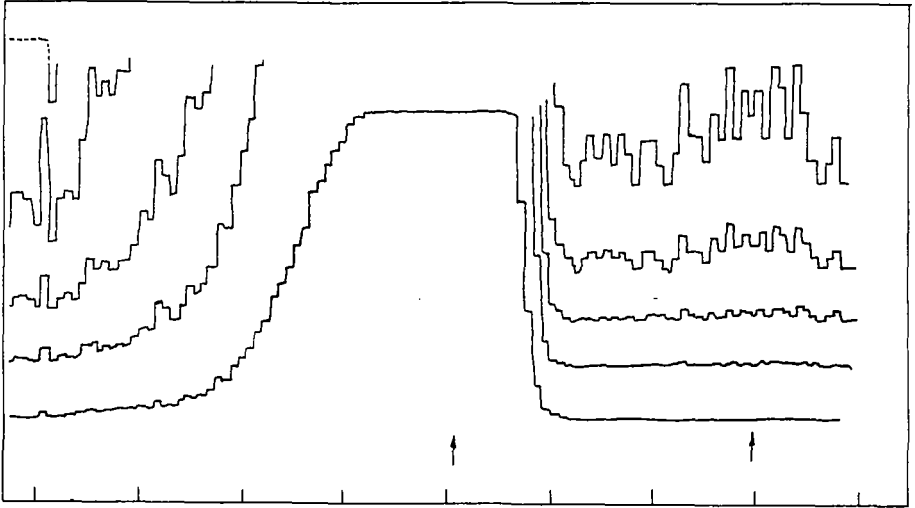
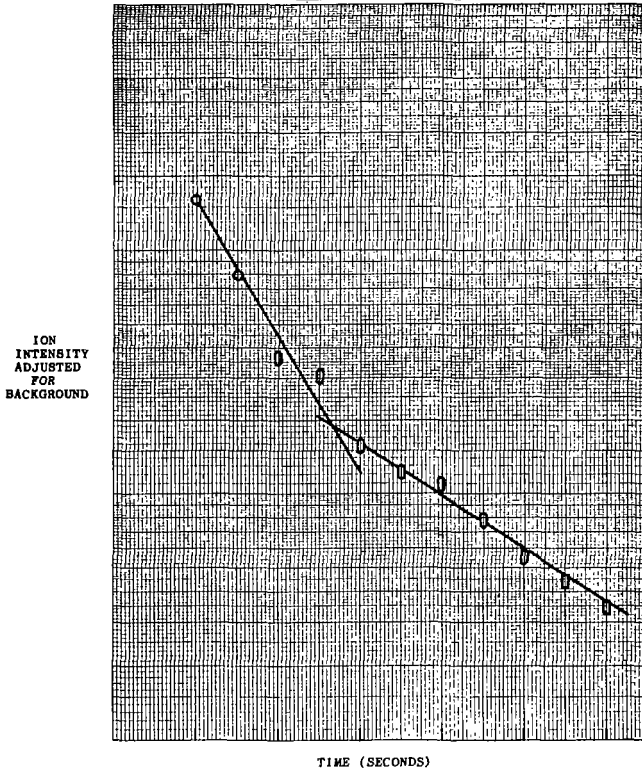


FIGURE 6

PLOT OF ION INTENSITY VERSUS TIME FOR

DECAY OF LARGE OC PEAK



of mass spectrometers. The lower effective temperature of the Bendix Time-of-Flight source is the cause. The 0.114 ratio for 72/43 ions was also observed under static conditions of n-pentane concentration.

For reasons noted above, ambiguous results will be obtained for peak ratios if the linear range for measurement of ions is exceeded. One method for avoiding this involves reduction of the ionizing electron beam intensity.⁽²⁾ A simpler approach is that of measurement of MS peak ratios during lower concentration periods of the GC peaks. The measurement periods may be maintained short relative to the concentration change to simplify calculations of the true ion abundances. Times of 0.03 to 0.1 second are convenient.

The composition change through regions of poor resolution by a gas chromatograph may be followed by ion-counting. Figure 7 shows a set of partially resolved components. Examination of the 43/41 mass ratios at one second intervals permitted differentiation of paraffinic from olefinic compounds for the four principal peaks which ranged in concentration from about one to five percent of a sample. Three other compounds with concentrations of 0.1 to 0.4 percent and locations as indicated by the shorter bars were not detected by this first simple approach. Study of other mass spectral peaks was required.

The effluents from conventional gas chromatographs may be studied even more easily than those from capillary columns because of the longer permissible times for measurements. Our studies employed a short length of capillary tubing as a sampling probe loosely inserted into the 1/4 inch diameter outlet connections of the GC instruments. The sampling lag was only about one second for a five foot length of capillary tubing because high flow rates were maintained by the mechanical pump downstream from the MS sampling valve.

Low ion abundances may be measured with the longer observation times with conventional columns. The lowest current level employed to date has been about 10⁻¹⁸ amperes. For this, approximately 100 ions were counted in a period of 25 seconds. These currents provide after electron multiplication signals of sufficient amplitude to provide deflections in analog recording systems using electrometer amplifiers. Figure 8 shows such a record with a detection system having a time constant of 0.1 second and with ion currents of 6 to 10 per second. Quantitative results were not obtainable by simple study of the records. At still lower ion currents some discrete pulses may be observed with high gains in the electrometer amplifier. This is, however, relatively inefficient for detection of single-ion pulses because of the wide range of pulse amplitudes.

CONCLUSIONS

Ion-counting has provided valuable mass spectral data for rapidly changing compositions at compositions lower than is possible with other systems. The data are easily obtained and interpreted. Further elaborations are obviously possible but the present system provides data sufficient for many applications.

REFERENCES

1. Roland S. Cohlke, "Use of a Total Ionization Monitor for Time-of-Flight Mass Spectrometry," ASTM E-14 - Meeting on Mass Spectrometry, New Orleans, 1962.
2. J. F. Betts, E. H. Pauve, W. C. Wiley, Appl. Spectr., **14** (5), 119-123 (1960).
3. William Feller, "An Introduction to Probability Theory and Its Applications," John Wiley and Sons (1950), Page 120.
4. W. H. McFadden, Roy Teranishi, D. R. Black and J. C. Day, "Use of Capillary Gas Chromatography with a TOF Mass Spectrometer," ASTM E-14, New Orleans, 1962.
5. P. F. Varadi and K. Ettre, Anal. Chem. **35** (3) 410-2 (1963).

FIGURE 7

UNRESOLVED COMPONENTS IN CAPILLARY GC EFFLUENTS

SIX SECOND INTERVALS ON TIME SCALE
GALVANOMETER RATIO 1:3:10

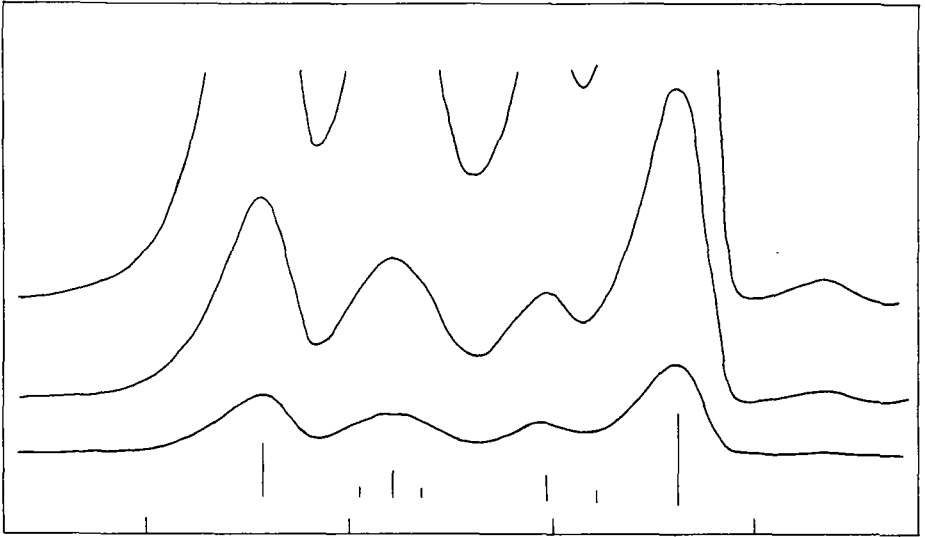
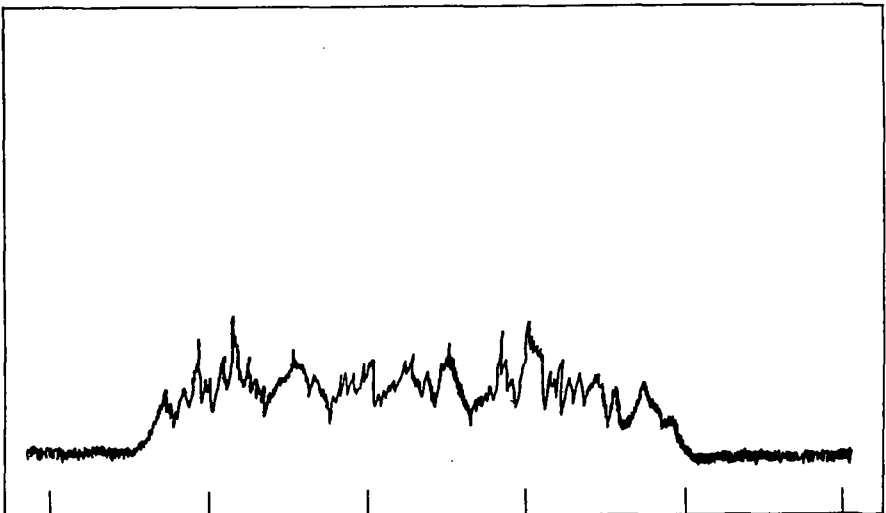


FIGURE 8

ANALOG TRACE AT 6 TO 10 IONS PER SECOND

TIME SCALE WITH THREE SECOND INTERVALS



A NEW CONTINUOUS QUANTITATIVE GAS ANALYSIS METHOD

W. J. Grubbs, G. H. Snider, F. I. Scott, E. I. Doucette Assoc. Inc.,
Chatham, N. J., and J. H. Bloom, AFCRL, Bedford, Mass.

Abstract

The system described measures the rates at which various gases are being drawn off the sample by two ion pumps. Throughput rates for the entire gas mixture are indicated by pressure differentials across calibrated orifices. (Pressures are measured with Bayard-Alpert type ion gauges which have been previously calibrated for each of the various gases individually). Once the orifice conductances and pump speeds are known, a single pressure measurement serves to indicate throughput since fixing the pressure at any point in the system determines the pressure at every point in the system. Thus, partial pressure measurements at the location of the mass spectrometer give the throughputs for all the various gases which are observed.

The requirements for additional knowledge about the nature and quantities of gases evolved from electron tubes have become more severe in recent years. A number of methods (1,3,4,5,6) for determining the amount or the composition of gases arising from tube components prior to assembly or from assembled tubes after exhaust and activation have been presented in the literature. Relatively little information exists, however, regarding the total quantity as well as the composition of gases evolved from assembled, unprocessed tubes.

To obtain more information in this regard, the present system was designed, built and calibrated. It allows continuous measurement of both quantity and composition of the gases evolved from an electron tube as a function of its materials, processing cycle, thermal treatment and level of operation.

Equipment Design

The objectives have been accomplished by designing a differentially-pumped vacuum system including an omegatron mass spectrometer. Six Bayard-Alpert type ionization gauges, four precision orifices, two ion pumps and a sorption pump in addition to the omegatron tube comprise the system. A block diagram is shown in Figure 1.

The calibrated orifices divide the flow of gas from the tube under test (or from the test gas supply) so that a small but constant fraction of the gas flows through the analyzer tube. Knowledge of the orifice conductances and the pump speeds permits determination of the throughput for a gas since fixing the pressure at any point in the system determines the pressure at every point in the system. The system has achieved total pressures in the range of 10^{-8} Torr (determined as the sum of partial pressures in the omegatron) and measured partial pressures down to 10^{-11} Torr.

Selection of the Omegatron

Although several types of mass spectrometers suitable for this application are available, the omegatron was chosen because it seemed to offer the best combination of simplicity, speed of response and resolution. Its relatively small volume, rugged construction and ability to be baked to 450°C and RF heated to 900°C were additional factors in its selection. The omegatron operates as a miniature cyclotron with crossed electric and magnetic fields and an ionizing electron beam. Gas molecules ionized by the electron beam follow a circular path in a plane which is perpendicular to the magnetic field. An RF field applied perpendicular to the magnetic field is parallel to the plane in which the ionized molecules are moving. This alternating electric (RF) field accelerates the ion over a portion of its circular path and retards it over the other portion unless the resonant frequency of the ion is exactly the same as the frequency of the applied RF field. In this case, the ion gains energy over its entire path and spirals outward. An ion collector at the bottom of the electrode box collects these ions and the DC current generated is subsequently amplified and read at the electrometer.

The work reported in this paper has been partially supported by the United States Air Force under Contract No. AF 19(628)-326.

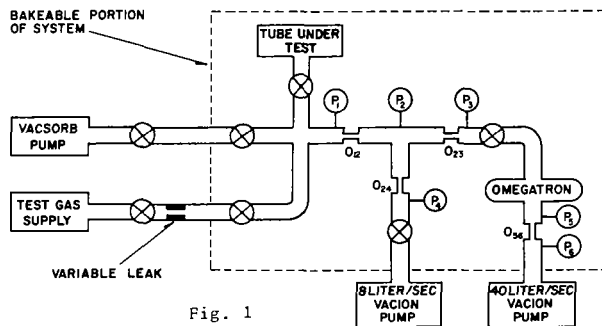


Fig. 1

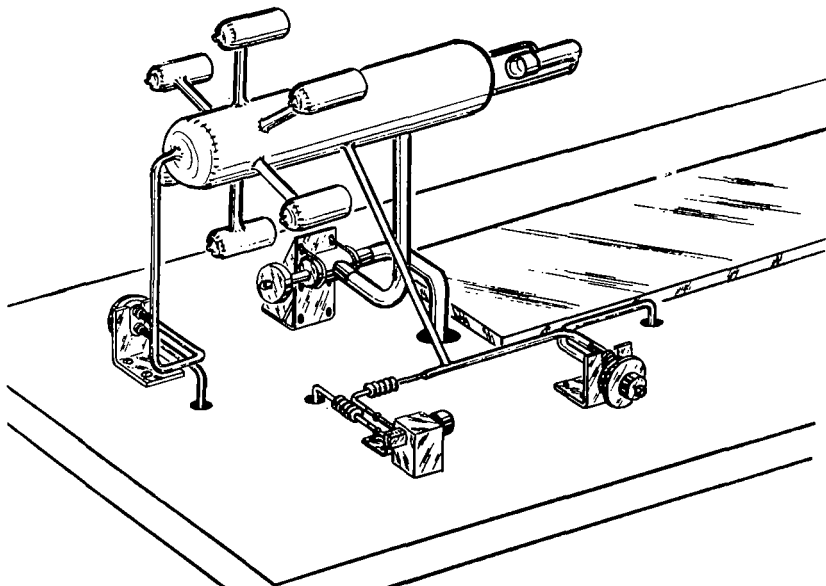


Fig. 2

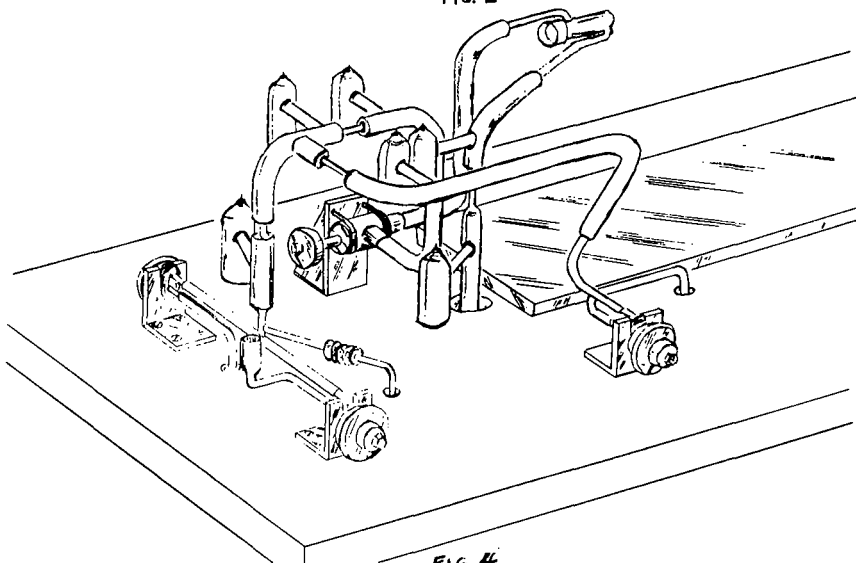


FIG. 4

The magnetic field collimates the electron beam and also causes the ions to move in a circular path. A small trapping voltage on the outer electrode structure (box) of the tube prevents ion loss in the axial direction. Qualitative information about the ion species collected is obtained from the frequency at which the ion current appears while quantitative information is obtained from the size of the ion current generated.

The requirement to develop a continuous quantitative gas analysis system strengthened the need for extreme accuracy in the partial pressure measurements. Connecting the omegatron tube to the system by a single tubulation would cause it to see a slightly different distribution of gases because the conductance of the tubulation varies inversely as the masses of the various gas molecules. The pumping action of the omegatron would also contribute to the distortion since the omegatron would see a lower total pressure than existed in the system. To minimize these sources of error, two tubulations were connected to the bulb to permit the gases to flow through the omegatron.

The Flow System

The continuous quantitative measurement of the gases evolved from the tube under test is accomplished by a system of calibrated orifices. These orifices divide the gases from the tube so that approximately 5% flows through the omegatron tube. The pressure drops across the orifices are measured by six ionization gauges which were individually calibrated for six gases. The five valves shown inside the dotted line (Figure 1) are all-metal bakeable valves. Because they must be left open during bakeout, two valves (with Teflon gaskets and O-rings) external to the dotted line serve to seal off the sorption pump and the test gas supply during baking.

The most important path the gas takes passes from the tube under test through O_{12} (the orifice between P_1 and P_2) then through O_{23} , the omegatron and O_{56} to the 40 liter/second ion pump. The second leg leading through O_{24} permits a larger throughput for the system.

Using the relationships:

$$Q = CP$$

$$Q = SP, \text{ where}$$

$$Q = \text{throughput in micron liters/second,}$$

$$C = \text{orifice conductance in liters/second,}$$

$$S = \text{pump speed in liters/second,}$$

$$P = \text{pressure in microns,}$$

The conductances of the orifices can be determined from knowledge of the pump speeds and the pressure drops across the orifices.

The orifice conductances may also be determined by their physical dimensions using Dushman's equation (2):

$$C = \frac{3.82 \cdot 10^3}{L + 1.33D} \left(\frac{T}{M} \right)^{1/2} \quad (1)$$

where D = orifice diameter in cm.

L = orifice length in cm.

T = temperature in $^{\circ}K$.

M = molecular weight of the gas in grams per mol.

Equation (1) holds when the gas flow through the orifice is molecular which is the case when the mean free path of the gas molecule exceeds the tube diameter; this requirement is fulfilled if $DP < 10$

where D = diameter in cm.

P = average pressure along the orifice.

Ion pumps do not remove all gases with equal speed. By inserting a low conductance orifice between the pump and the system, however, variations in pump speed for different gases can be greatly reduced. In the omegatron leg, for example, insertion of a suitable orifice between the 40 l/s. pump and the omegatron makes the pressure drop just equal to the omegatron pressure alone with a possible error of 1%. Increasing the pump speed by any factor cannot then affect the throughput of the orifice by more than 1%.

To assign values to the various pressures in the system, we begin by assuming that the minimum possible value for P_6 will be 10^{-6} Torr (mmHg). Assume also that P_2 will be essentially the same as P_6 . To reduce the effect of pump speed, let $P_4 = 100 P_6$, so $P_4 > 10^{-6}$, but the omegatron pressure should not exceed 10^{-5} , hence $10^{-8} < P_4 < 10^{-5}$ and $10^{-8} < P_6 < 10^{-7}$.

If we wish the omegatron to sample 5% of the total gas then

$$\frac{Q_{40}}{Q_6 + Q_{40}} = 0.05 \quad (2)$$

FIG. 5
TOTAL GAS RATE VS. OMEGATRON PRESSURE

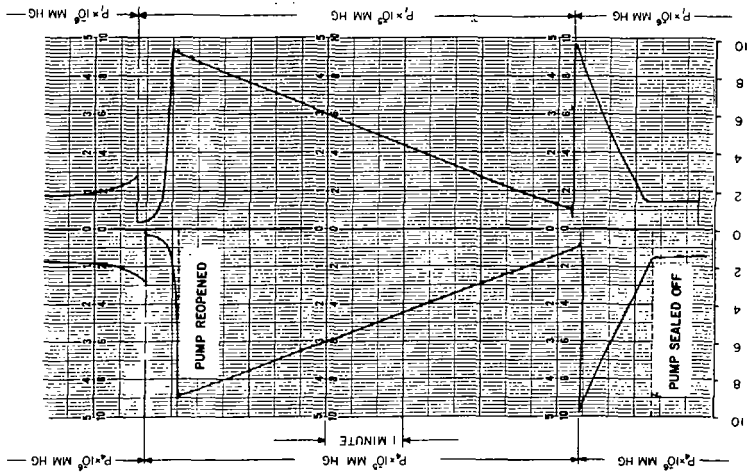


FIG. 3

FIG. 6
INDIVIDUAL THROUGHPUT VS. TIME
(SHOWING D₂ TRACER GAS)

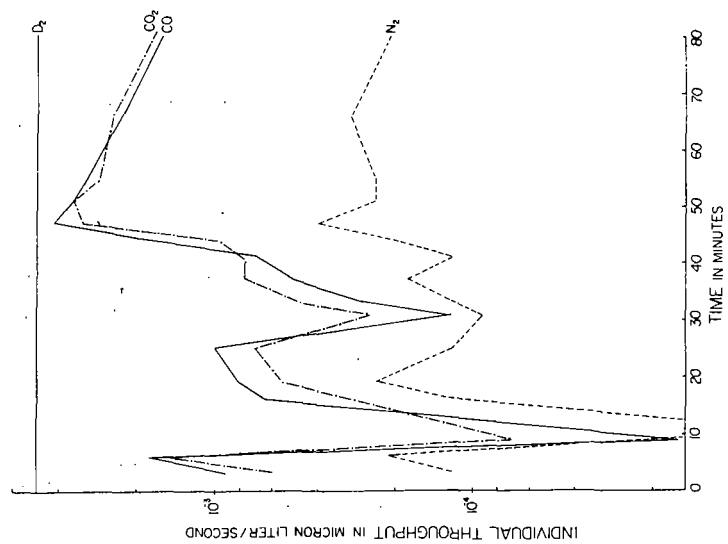


FIG. 6

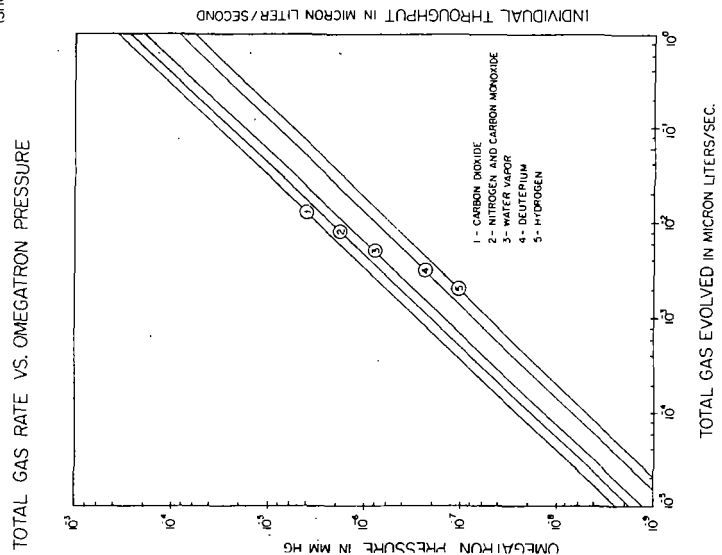


FIG. 5

where Q_{40} and Q_8 are the throughputs of the 40 l/s and 8 l/s pumps, respectively. Substituting

$$Q_{40} = S_{40} P_6$$

$$\text{and } Q_8 = S_8 P_4$$

where S is the pump speed. Then,

$$P_4 = P_6 \left(19 \frac{S_{40}}{S_8} \right) = 95 P_6 \quad (3)$$

For simplicity let $P_4 = 100 P_6$ in which case the omegatron sees 4.75% of the total gas. Thus, $4 \cdot 10^{-6} < P_4 < 10^{-5}$. To reduce the effect of variations in S_8 , design O_{24} to give $P_4 = 100 P_6$, and $10^{-4} < P_2 < 10^{-3}$. The pressure ranges obtained are then:

$$\begin{aligned} 10^{-4} &< P_2 < 10^{-3} && \text{Torr} \\ 10^{-6} &< P_2 < 10^{-5} && \text{Torr} \\ 10^{-6} &< P_3 < 10^{-5} && \text{Torr} \\ 10^{-8} &< P_6 < 10^{-7} && \text{Torr} \end{aligned}$$

P_1 , the pressure at the tube under test can take on values in any 10-to-1 pressure range consistent with the foregoing. The actual range being determined by O_{12} . At the time of system design, a few microns of Hg seemed a reasonable pressure to maintain at the sample and P_1 was set between 1 and 10 microns. The desired orifices, obtained through the use of equations (4) through (7) below, are given in Table I.

$$C_{56} (P_5 - P_6) = Q_{40} \quad (4)$$

$$C_{23} (P_2 - P_3) = C_{56} (P_5 - P_6) \quad (5)$$

$$C_{24} (P_2 - P_4) = Q_8 \quad (6)$$

$$\begin{aligned} C_{12} (P_1 - P_2) &= C_{23} (P_2 - P_3) + C_{24} (P_2 - P_4) \\ &= Q_{40} + Q_8 \end{aligned} \quad (7)$$

Equations (4-7) are the four independent relations which determine the four orifice conductances once the pressures and pump speeds are fixed; any four pressures can then be expressed as a function of the other two pressures.

The throughput as measured at O_{23} represents the total quantity of gas being analyzed in the omegatron per unit time; O_{24} meters the remainder of the gas. These two orifices indicate both the total gas through the system and the fraction of that gas going through the omegatron. The throughput at O_{12} gives an independent means of determining the total throughput.

TABLE I

Orifice	Diameter(cm)	Length (cm)	C (for N_2) l/s
O_{12}	0.100	1.24	.0100
O_{24}	0.3175	4.49	.0830
O_{23}	0.100	2.96	.0042
O_{56}	0.6350	7.09	.4020

To estimate the system response for two quite different gases, we admit the two gases in a known ratio and then determine their ratio at the omegatron. Assuming the two gases are admitted at the same partial pressure ($P_{1A} = P_{1B}$), the value of P_{3A}/P_{3B} is calculated according to equation (8) derived from equations (4-7).

$$\frac{P_1}{P_3} = \frac{1}{1 + 0.1125 \frac{S_8}{C_{12}}} \left[1 + 17.35 \frac{S_8}{C_{12}} \left(\frac{1 + 0.76 \frac{S_8}{C_{12}}}{1 + 0.1125 \frac{S_8}{C_{12}}} \right) \right] \quad (8)$$

To calculate P_1/P_3 for any gas, one needs only to evaluate S_8/C_{12} for that gas, and substitute the value of this ratio into Equation (8). Values of this and other ratios of interest are given in Table II.

TABLE II

Gas	M	S_8	$C_{12} \times 10^3$	S_8/C_{12}	P_1/P_3	$P_3/\text{gas}/P_3/N_2$
CO ₂	44	8	7.16	1118	1030	1.005
N ₂	28	8	9.00	889	1025	1.000
H ₂ O	18	8	11.2	715	1019	0.994
H ₂	2	21.6	33.7	641	1017	0.991
D ₂	4	15.2	23.8	639	1017	0.991
O ₂	32	4.55	8.41	540	1011	0.988
He	4	1.0	23.8	42	710	1.44

This table indicates that, with the present system design, all gas ratios remain constant while traversing the system to within 1 or 2% except when He is one of the gases. Other rare gases are pumped equally poorly by ion pumps but their masses are so great that the value of S_8/C_{12} for these gases should be such that they will be measured with sufficient accuracy.

Calibration Procedures

Calibration of the ionization gauges was performed on a system specially constructed to give essentially identical conditions. The six gauges were arranged symmetrically around a large glass(pyrex) vacuum chamber, connected to it through glass tubing of equal lengths and diameters. A sketch is shown in Figure 2. The omegatron with its two tubulations and the Granville-Phillips valves are also shown.

The sensitivity of an ionization gauge or an omegatron tube is generally expressed as: $p = i^+/S i^-$ where P is the pressure, i^+ is the collected positive ion current and i^- is the ionizing electron beam current. The ion gauges were operated at reduced grid current to minimize pumping action and grid-gas reactions. No data was recorded in the 10^{-3} Torr range.

Since the variable leak could not be reproducibly reset, a single setting was maintained for all calibrations. For nitrogen the inlet pressure was adjusted to 31 psja and the indicated pressure in the system allowed to rise from 1×10^{-6} to 1×10^{-4} Torr as measured simultaneously with two ion gauge tubes. The outputs from the ion gauge control units were recorded on both channels of a dual channel recorder. See Figure 3 for a typical plot. Five readings were made for each gauge in comparison with each of the other five gauges.

The assumption of a uniform sensitivity of 10 for N_2 for all gauges proved to be erroneous. Sensitivities were then assigned to each gauge by dividing the average pressure rise rate for each gauge by the average for all gauges and multiplying by 10. For N_2 , the sensitivities so determined were: $S_1 = 9.55$, $S_2 = 8.35$, $S_3 = 9.39$, $S_4 = 9.85$, $S_5 = 11.06$, $S_6 = 11.80$. Sensitivities for the other 5 gases, CO₂, CO, CH₄, H₂ and D₂ were obtained similarly.

Omegatron Calibration

Both the resolution and the sensitivity are important parameters of the omegatron. The resolution is defined as the ratio of the mass number of a peak to the width of the peak expressed in atomic mass units. It is a measure of the ability of the mass spectrometer to separate peaks occurring at adjacent mass numbers and may be stated as:

$$S = \frac{M}{\Delta M} = \frac{\text{peak location in a.m.u.}}{\text{peak width in a.m.u.}} \quad (9)$$

The theoretical relation is given by:

$$S = \frac{R_0 B^2 e}{2 E_0 M} \quad (10)$$

where R_0 is distance between the electron beam and the ion collecting plate, B is the magnetic flux density, E is the RF electric field, and e/M is the charge-to-mass ratio for the ion being observed.

The omegatron gauge calibration was made for the various gases following preliminary experiments to determine the optimum operating conditions. Magnet alignment and magnetic field uniformity proved to be the most important parameters.

The omegatron operating conditions used during calibration were: Filament Bias = -70 VDC, Collector Bias = 20 VDC, Trap Bias = 1.4 VDC, Beam Current = 1.0 μ amp, RF voltage = 1.5 Vrms. The sensitivities obtained for the various gases were:

CH₄: 9.5
CO₂: 4.2

CO: 9.7
N₂: 11.5

D₂: 3.5
H₂: 2.9

Orifice Calibration

Since the standard leaks proved unsatisfactory for the calibration experiments, the known speeds of the ion pumps were used to determine the orifice conductances. The test gas, nitrogen, was admitted to the system through the variable leak and allowed to reach equilibrium as indicated by constant ion gauge readings. At this point, all gauge readings were recorded along with pump current. Input (cylinder) pressure was then varied from 10 to 40 psig in 10 steps and the gauge and pump readings recorded at each equilibrium point. The average conductance values obtained were:

C₁₂ = 0.01682 l/s
C₁₂ = 0.129 l/s
C₂₄ = 0.0057 l/s
C₂₃ = 0.64 l/s
C₅₆

These values average about 50% greater than the calculated values. No satisfactory explanation of the differences has been determined. Possibly the actual pumping speeds of the ion pumps are lower than the values reported.

Determination of Quantities of Gases Evolved

A sketch of the gas analysis system is shown in Figure 4. Approximately 5% of the gas from the tube under test or from the test gas supply passes through the omegatron tube for analysis as determined by the ratio of orifice conductances in the two legs of the system. Knowing the total and partial pressures of the gases, their pumping speeds, and the total degassing time, the total amount of each gas evolved can be determined.

The actual ratio of throughput in the omegatron section to total throughput in the system is given by $Q_{40}/(Q_{40}+Q_8)$. The average value from 2 sets of ten readings is 0.0444 or 4.44% passing through the omegatron tube. Although this figure is based on the data for nitrogen, it is valid for all the gases encountered because both pumps are of the same type and pump equal fractions of each kind of gas.

To establish the relationship between the partial pressures determined by the omegatron and the total gas evolved, pump speed vs. pressure data were used to plot throughput as a function of pressure for the 40 l/s pump. The conductance between the omegatron and the 40 l/s ion pump was determined to permit calculation of the pressure in the omegatron, P_0 , against which the throughput, Q_{40} , could be plotted.

$$P_0 = Q_{40}/C_{0-40} + P_{40}$$

where C_{0-40} is the conductance between the omegatron and the 40 l/s pump.

From a plot of Q_{40} vs. P_0 , the throughput of the omegatron is obtained. Dividing the quantity so obtained by 0.0444 (the ratio of Q_{40} throughput to total throughput of the system) gives us the total degassing rate of the tube under test. This is plotted in Figure 5 as a function of the omegatron pressure for nitrogen.

Similar calculations and plots have been made for other gases expected in operation and they are included in Figure 5. The different plots reflect the differences in pump speed and conductance for the gases.

Equipment and Accessories

A Varian Vac-Sorb sorption pump produces the initial vacuum and permits an ultra-clean system free of oil contamination. The omegatron tube was made by Electron Technology, Inc. A power supply was built to provide and measure the required voltages for the omegatron. To permit continuous sweeping of any desired frequency range, a Hewlett-Packard oscillator was modified with a specially designed electro-mechanical sweep drive.

Ion current from the omegatron is measured with an Ekco vibrating reed electrometer and a Computer Measurements frequency meter monitors the oscillator frequency.

The ion gauges are Bayard-Alpert type with non-burnout filaments using Veece vacuum gauge power supplies. The 4000 gauss permanent magnet is manufactured by Arnold Engineering. Ion current readings are recorded on Westronix dual channel recorders. All equipment is mounted on two benches. The table top is 1/2" transite on 1" plywood. The oven for degassing the vacuum system was constructed using G. E. Calrod heaters and the insulation material is Marinite from John-Manville.

Preliminary Results

A commercial, high-quality electron tube, Amperex type 5894, was attached to the system for degassing. As planned, deuterium was admitted through the variable leak at a constant rate. An RF generator supplied power for heating the plates.

Upon admitting the D_2 to the system, a small but unmistakable peak appeared at mass 20. Since there was no peak at 40, the peak at mass 20 could not be doubly ionized argon. The peak at mass 20 was presumed to be D_2O . This presumption was essentially confirmed when a leak was subsequently discovered in the system. Apparently it existed at this time but was extremely small. The partial pressures existing at the omegatron were:

CO_2	1.52×10^{-8} mmHg
N_2	4.52×10^{-8} mmHg
CO	1.03×10^{-8} mmHg
D_2	3.12×10^{-7} mmHg

The throughput of D_2 (from Figure 5) was then 4.8×10^{-3} micron-liters/second. The throughputs of the four gases are plotted in Figure 6.

A number of additional experiments on several regular and modified tubes have confirmed the performance on the system according to design criteria. Additional results will be reported elsewhere in the literature.

REFERENCES

1. Collins, R. H. and Turnbull, J. C., Degassing and permeation of Gases in Tube Materials, 1960 Conference on Advances in Electron Tube Techniques, Pergamon Press, 1961, p. 186.
2. Dushman, S., Scientific Foundations of Vacuum Technique, 2nd ed., Wiley and Sons, New York 1962, Section 2.4.
3. Electron Tube Materials, Gases and Getters, Final Report, Signal Corps Contract No. DA 36-039-SC-87390, 31 January 1962.
4. Frost, H. B., Residual Gas Content As a Function of Tube Processing, Symposium on Materials and Electron Device Processing, STP300, ASTM, 1961.
5. Study of Failure Mechanisms in High Power Radio Frequency Generating Devices, First Quarterly Report, Air Force Contract AF 30(602)-2595, March 31, 1962.
6. Varadi, P. F., Thermal Degassing of Materials, 1960 Vacuum Symposium Transactions, Pergamon Press, 1961, p. 149.

SOURCE AND MULTIPLIER MODIFICATIONS OF A TIME-OF-FLIGHT MASS
SPECTROMETER TO INCREASE SENSITIVITY

W. K. Rohwedder, E. Selke, and E. D. Bitner
Northern Regional Research Laboratory, Peoria, Illinois

Abstract

The usefulness of a gas chromatograph and a mass spectrometer in tandem to analyze the odor constituents of soybean oil is limited by the sensitivity of the mass spectrometer and by the large amount of helium carrier gas compared with the amount of sample. The greatest possible sensitivity is necessary so that the least destructive method of odor collection can be used. A time-of-flight mass spectrometer was fitted with a tightly enclosed source and operated in a continuous ionization mode to increase instrument sensitivity. A gate pulse was applied to the front end of the magnetic electron multiplier to eliminate the electrons due to the helium pulse before they reached the multiplier dynode strips. This procedure prevented saturation of the multiplier by the helium carrier gas.

- - - - -

Introduction

Analysis of volatile odor components of soybean oil is greatly complicated by the very small amount of odor materials in the oil and by the great sensitivity of the oil to odor changes during collection procedures. The usefulness of a gas chromatograph and a mass spectrometer in tandem to analyze the odor constituents has been greatly limited by the small sample size obtained with collection methods, which are consistent with organoleptic evaluation requirements.

Source and multiplier modifications of a time-of-flight mass spectrometer have been made to increase the usable sensitivity so that an analysis can be made of small samples. The mass spectrometer source was totally enclosed to provide differential pumping in the source region, and the instrument was operated in a continuous ionization mode with high-trap current to achieve the maximum possible sensitivity. To prevent saturation of the magnetic electron multiplier by the mass four peak of the chromatograph helium carrier gas, a gate pulse was applied to the front end of the multiplier to prevent electrons due to the helium peak from reaching the multiplying surfaces.

The design of enclosed sources for use in magnetic deflection mass spectrometers has been described by Nier (1,2). The operation of the Bendix^{*} mass spectrometer has been described by Wiley and McLaren (3,4).

Experimental

The instrument used for this work was a Bendix Model 12 mass spectrometer with a Model 14 source. In all of the experiments *n*-butane was bled into the mass spectrometer through a molecular leak to determine the sensitivity

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

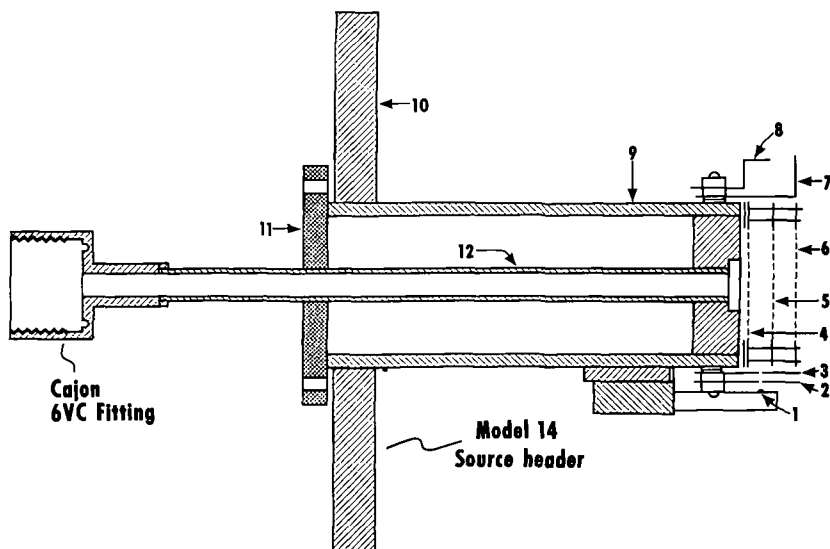


Figure 1. Modified Time-Of-Flight Mass Spectrometer Source

1. Filament
2. Electron grid 1
3. Electron grid 2
4. Backing grid
5. Ion grid 1
6. Ion grid 2
7. Trap shield
8. Electron beam trap
9. Source base
10. Source flange
11. Mykroy support
12. Inlet tubing

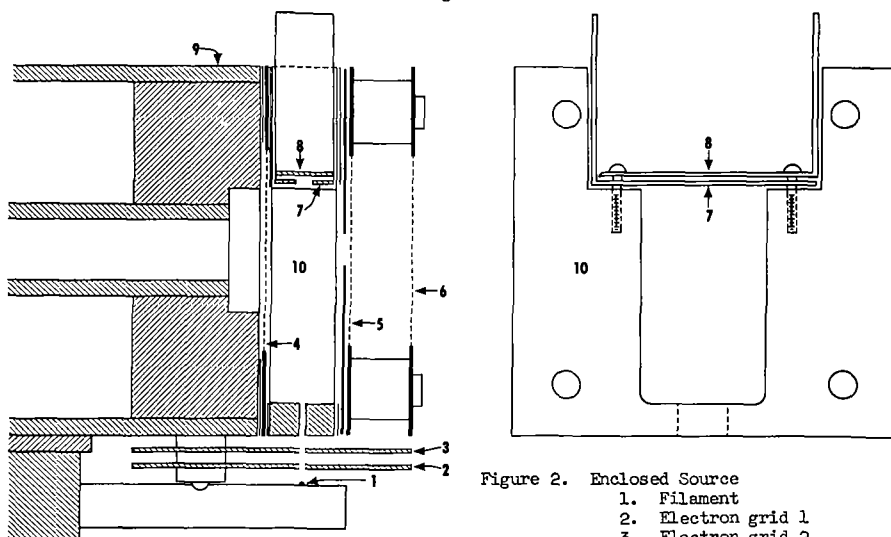


Figure 2. Enclosed Source

1. Filament
2. Electron grid 1
3. Electron grid 2
4. Backing grid
5. Ion grid 1 and baffle
6. Ion grid 2
7. Trap shield
8. Electron beam trap
9. Source base
10. Chamber enclosure

of the instrument under various operating conditions. The relative sensitivity was calculated by dividing the output of the mass spectrometer at the butane 43 peak by the butane sample pressure and by the electron beam trap current. All the sensitivities reported have been normalized so that the unmodified source operated in a pulsed mode has a relative sensitivity of 100.

The mass spectrometer, as supplied by Bendix, has two inlets, a 3/16-inch O.D. tubing through the source header and a 3/8-inch O.D. tubing through the cross header. The 3/16-inch tubing is very difficult to heat where it passes through the header due to its proximity to the electrical feed-through, which makes it impossible to use samples of low volatility; furthermore, the 3/8-inch tubing interferes with some of the accessories. A 3/8-inch O.D. stainless steel tube was soldered into the source base to provide a high conductance passage for the sample from the molecular leak to the ionization region without interfering with the mass spectrometer accessories. The tubing was wrapped with electrical heating wire, and a thermocouple was soldered into the source base so that the temperature of the ionization region can be controlled. Figure 1 shows the modified source base equipped with a Bendix standard grid system, except for the backing plate which was replaced by a grid. The relative sensitivity of the mass spectrometer with the three different inlet tubings was: 3/8-inch O.D. tubing through the cross header, 100; 3/16-inch tubing, 102; and the new 3/8-inch O.D. tubing through the source base, 104.

Figure 2 shows the modified header equipped with an enclosed source. The source is built up on the source base in the following order: a Teflon insulator, a grid, a Teflon insulator, the source chamber enclosure, a Teflon insulator, a baffle, a grid, a sapphire spacer, a grid, and the standard Bendix holddown, which is not shown in the diagram. The parts are aligned on sapphire rods that fit into holes in the source base. The grids, the sapphire rods and spacers, and the holddown are all standard Bendix parts. The filament structure and the filament grids are those supplied as standard by Bendix. The trap and trap shield close off the one end of the source completely, while the filament end of the chamber has a hole for passage of the electron beam. The filament structure was left out of the chamber area so that the heat from the filament would not dominate the source temperature and so that sample, pyrolyzed by contact with the hot filament, would not return to the ionization region. Several different size holes were tried in the first ion-grid baffle to find the optimum sensitivity. The hole sizes and sensitivities were as follows: 1/8-inch D hole, 28; 3/16-inch D hole, 220; 1/4-inch D hole, 236; 0.31-inch X 0.28-inch rectangular hole, 215; and baffle removed, 97. The long side of the rectangular hole was aligned with the electron beam. The 1/4-inch hole, which gives the maximum sensitivity, was used during the remainder of the experiments.

Studier reported (5,6) that when using a three ion-grid source that sensitivity is considerably increased if the second ion grid is held at -800 V and the third ion grid at -2800 V rather than having these two grids at -2800 V. The enclosed source was equipped with a third ion grid held at -2800 V, and the sensitivities were determined while the potential on the second ion grid was varied. The voltages and measured sensitivities were as follows: -2800 V, 93; -1040 V, 183; -415 V, 253; and the sensitivity decreased at still lower voltages. Apparently while an intermediate voltage on the middle grid of a three-grid source gives the greatest sensitivity with this source, the sensitivity of the source so wired is only slightly greater than that of the two-grid source. Since our work did not require the three-grid source, we used the two-grid source.

To obtain maximum output from the smallest samples, the instrument was operated in a continuous ionization mode. The filament was held at -70 volts, the electron energy potential. The first electron grid, which in the pulsed operation is negative with respect to the filament except for a short positive pulse, was held at a constant -50 volts. The second

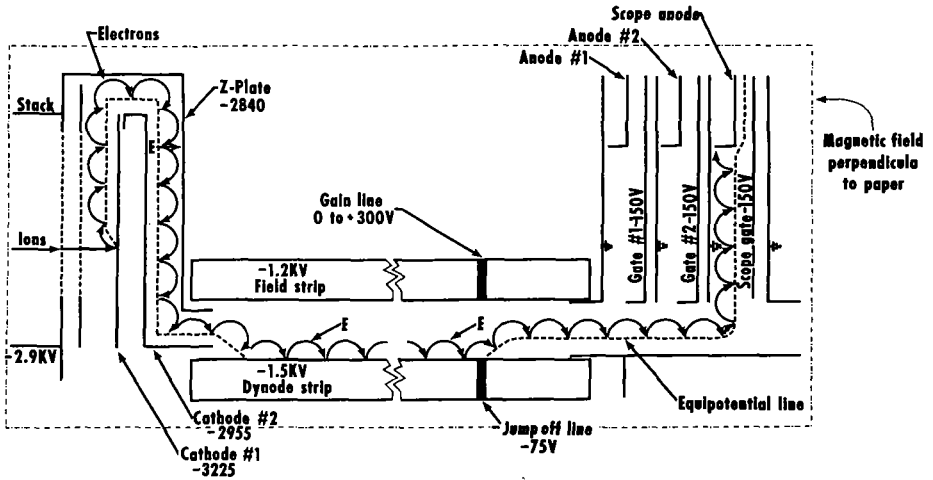


Figure 3. Magnetic Electron Multiplier Operation

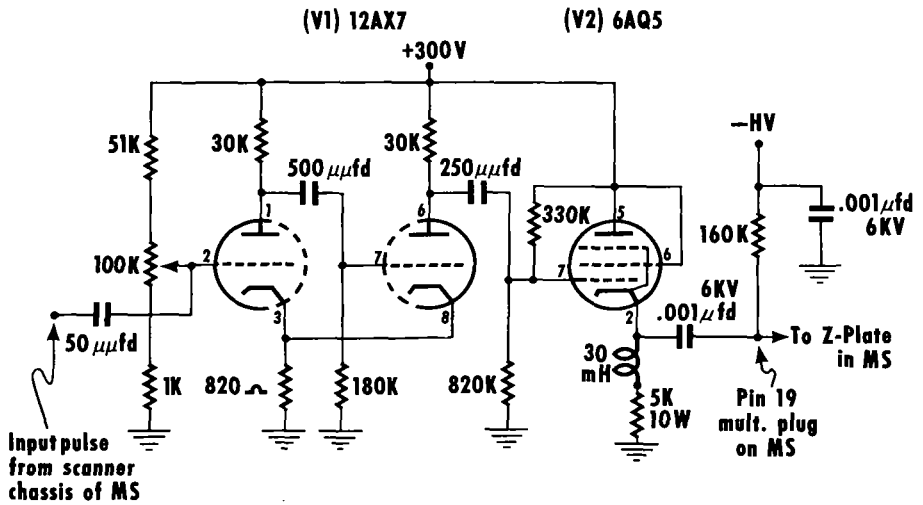


Figure 4. Pulse Generator Circuit

electron grid, the backing grid, and the source chamber were held at ground potential, and the ion grids were operated normally. Under normal pulsed operation the maximum trap current available is about 2 μ a. A trap current of 200 μ a was readily obtained in the continuous mode with some adjustment of the source magnets. At 200 μ a there was only a slight loss in the instrument resolution. Measurement of the sensitivity with a trap current of 200 μ a in the enclosed source gave a relative sensitivity of 223 as compared to 236 for standard pulsed operation for 2 μ a of trap current with the same enclosed source. Thus the increased sensitivity is real and usable.

Under normal pulsed operation, saturation of the multiplier takes place when a very large mass peak passes through the multiplier. A normal-size sample of normal butane was bled into the mass spectrometer through the molecular leak and the butane mass 43 peak was monitored. Helium gas was bled slowly into the mass spectrometer through a leak valve until the mass spectrometer pressure reached 5×10^{-5} torr. As the amount of helium increases, the multiplier becomes saturated and the butane 43 peak decreases until it is only about 70% of its original height. At the same time the sensitivity decreases, the output becomes distorted and the noise level increases.

In operating the Bendix electron multiplier, the ions from the field-free drift region hit cathode No. 1 (Figure 3) and generate secondary electrons that follow the line shown in the diagram through the electric and magnetic fields until they hit the dynode strip, which is the multiplying surface. The helium ions have an energy of 2,800 electron volts and are thus difficult to deflect. The best way to prevent the signal from the helium peak reaching the dynode strips appeared to be to upset the electric field between the Z-plate and cathode No. 2 so that the electrons from the helium ions are absorbed into cathode No. 2.

In early experiments if the voltage between the Z-plate and cathode No. 2 was set at 55 volts, the helium peak could be eliminated by applying a 90-volt high, 100-n sec. long pulse normally used to trigger one of the multiplier gates to the Z-plate. By use of delay circuits in the gate pulse chassis, the pulse applied to the Z-plate was made to coincide with the arrival time of the helium mass peak. With 55 volts between the Z-plate and the cathode No. 2 the overall instrument sensitivity decreased by about 20%. Since this reduction in sensitivity was not desirable, a separate pulse supply triggered by the gate pulse was made of sufficient size so that the peak could be eliminated with 110 volts between the Z-plate and cathode No. 2 and thus maintain normal sensitivity.

The circuit for providing this pulse (Figure 4) consists of a monostable multivibrator and a cathode follower, which produce a negative pulse 200 volts high and of variable length up to 1.5 μ sec. When this pulse is applied to the Z-plate, the helium peak is reduced by a factor of 9,000. A byproduct of the peak elimination is an unfocused haze in the mass 6 to 12 region, which is about 2 to 3% of the background peaks. Attempts to eliminate this haze by lengthening the pulse were futile because the haze merely moved out to higher mass numbers. Since the haze is of low intensity and appears in an uninteresting mass region, no further work was done to try to remove it.

Discussion and Conclusions

Under standard pulsed operating conditions with a standard source, a maximum of about 2 μ a of trap current is possible with a relative sensitivity of 100, whereas with continuous operation and an enclosed source about 200 μ a of trap current is available with a relative sensitivity of 223. The working or absolute sensitivity has been increased by a factor of $\frac{200 \times 223}{100} = 223$ over Bendix standard operation. With the modifications described it is now possible to identify as little as 10 ng. of an unknown in a chromatogram.

Literature Cited

- (1) A. O. Nier, Rev. Sci. Instr., 11, 212 (1940).
- (2) A. O. Nier, Rev. Sci. Instr., 18, 398 (1947).
- (3) W. C. Wiley and I. H. McLaren, Rev. Sci. Instr., 26, 1150 (1955).
- (4) W. C. Wiley, Science, 124, 817 (1956).
- (5) M. H. Studier, ASTM Committee E-14 Conference on Mass Spectrometry and Related Topics, May 1963, San Francisco, California.
- (6) M. H. Studier, Private communication.

REMARKS ON HIGH RESOLUTION MASS SPECTROSCOPY
Clifford E. Berry
Consolidated Electrodynamics Corporation
Pasadena, California

Abstract

For many years the technique of high-resolution mass spectroscopy has provided a fundamental method for the precise determination of the masses of the nuclides. More recently, the technique has been inverted so that unknown atomic or molecular species can be identified through precise measurements of their masses. The historical development of this latter technique, and its potential applications, will be discussed briefly.

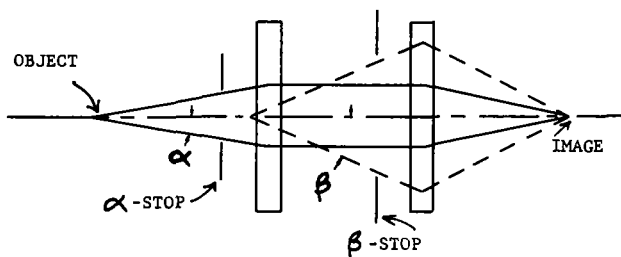
Because the instrumentation employed in high-resolution mass spectroscopy may take many forms, an attempt will be made to define a "figure of merit" by which various systems may be compared.

Instead of attempting to cover the entire subject matter mentioned in the abstract, I should like to restrict this paper to a discussion of the problem mentioned in the last sentence.

In a double-focussing mass-spectrometer it is not very meaningful to ask the question "What is the resolution?" The reason for this is that in a double-focussing machine all of the factors influencing resolution are under our control geometrically, so that in principle any resolution desired can be obtained by using sufficiently small slits and stops in the system. So the question really should be, "What is the relationship between the resolution and the transmission of the system?" A correlary question is "How do we optimize the transmission for a given resolution?"

Today I shall present a simplified analysis of this problem which allows us to derive the relationship between transmission and resolution, and which leads to a "figure of merit" for a given machine.

Figure 1 shows a schematic of a double-focussing machine ignoring dispersive properties.



At the left is an object slit which is imaged by a series of lenses onto an image plane at the right. A stop (α -stop) sets the angular aperture of the system. In addition, rays having a zero angle but with which there is associated a fractional velocity difference appear to originate at a virtual object on the optical axis and are brought to a focus at the image plane; a β -stop sets the angular aperture for these rays.

The dispersion relation of a magnetic sector is

$$D = Kr\Delta m/m, \quad (1)$$

where r is the radius and K is a constant depending on the object-image distance relationship. For a symmetrical sector of any angle $K = 1$. For the maximum asymmetry, e.g. the object at ∞ as in the Mattauch-Herzog double-focussing system, $K = 1/2$.

We have complete resolution of two ion beams when the beam width W_b plus the collector slit width W_c equals the dispersion;

$$W_b + W_c = D = Kr\frac{\Delta m}{m}. \quad (2)$$

Defining resolving power R as $m/\Delta m$ we have

$$R = \frac{m}{\Delta m} = \frac{Kr}{W_b + W_c} \quad (3)$$

Obviously, the smallest value of W_c that can be used with no loss of intensity is $W_c = W_b$. At this point

$$R = \frac{Kr}{2W_b} \quad (4)$$

As we let $W_c \rightarrow 0$, the intensity approaches zero and the resolving power approaches twice the above value. For the purposes of this discussion, however, we will assume that W_c is always kept equal to W_b so that the resolving power is that given by equation 4. Now, the beam width W_b is composed of two parts; first there is a portion equal to the product of the width of the source slit W_s and the optical magnification M of the system. The second portion W_a is due to various aberrations of the imaging system. Thus we can write

$$W_b = MW_s + W_a \quad (5)$$

Consider W_a ; in a double-focussing machine this is a function of $\alpha_{\max}$ and $\beta_{\max}$, the maximum values of α and β set by their corresponding stops. (We will ignore things of a practical nature such as stability of the electric and magnetic fields and non-parallel slits.) In a machine which is first-order focussed, W_a can be expressed as a function of $\alpha_{\max}^2$, $\alpha_{\max}\beta_{\max}$ and $\beta_{\max}^2$; if the machine is completely second-order focussed, the coefficients of these terms will vanish and W_a will be a function of third order terms. This paper will be restricted for simplicity to the situation where we have only first order focussing. The same basic treatment of the problem obtains if we have second order focussing, but the mathematics are more involved.

Now, obviously, if we specify a desired value for W_a , we can achieve this with an infinite set of pairs of values for $\alpha_{\max}$ and $\beta_{\max}$. For example, we could allow all of W_a to be accounted for by the $\alpha_{\max}$ aberration, which would force us to use a value of zero for $\beta_{\max}$. Similarly, we could allow the $\beta_{\max}$ aberration to account for all of W_a , forcing us to use a value of zero for $\alpha_{\max}$. In either case the transmission through the system will be zero. Our intuition then tells us that there should be a particular pair of values for which the product $\alpha_{\max}\beta_{\max}$, and thus the transmission of the system, is a maximum for a specified value of W_a . This is indeed found to be true, and it is shown in the appendix that $\alpha_{\max}$ and $\beta_{\max}$ must be linearly related by a constant which does not depend on W_a , but which involves only basic geometrical parameters of the machine. Thus we can write

$$\begin{aligned} \beta_{\max} &= C\alpha_{\max}, \text{ and} \\ W_a &= BC\alpha_{\max}^2, \end{aligned} \quad (6)$$

where B and C are dimensionless constants of the machine which can be evaluated for any given machine, and where it is understood that this relation applies only for the situation where $\alpha_{\max}\beta_{\max}$ is a maximum.

Now we can rewrite equation 5 as

$$W_b = MW_s + BC\alpha_{\max}^2 \quad (7)$$

To get a specified resolution we must achieve a certain value of W_b as given by equation 4. Obviously we can achieve this with an infinite set of pairs of values for W_s and $\alpha_{\max}$, but we can expect a particular pair of values to result in maximum transmission. The transmission is clearly proportional to the product of W_s , $\alpha_{\max}$, and $\beta_{\max}$; defining transmission as this product, and substituting $\beta_{\max} = C\alpha_{\max}$,

$$\begin{aligned} T &= W_s \alpha_{\max} \beta_{\max} \\ &= CW_s \alpha_{\max}^2. \end{aligned} \quad (8)$$

Substituting for $\alpha_{\max}^2$ from equation 7, we get

$$T = \frac{W_b W_s - MW_s^2}{B r} \quad (9)$$

Setting $dT/dW_s = 0$, we find

$$MW_s = \frac{W_b}{2}, \quad (10)$$

which says that maximum transmission occurs when half the beam width is due to the magnified object and half is due to the second-order aberrations. In a machine corrected to second order so that the aberrations are third order, three fifths of the beam width should be accounted for by the magnified object. (In general, for n-th order aberrations this fraction is $n/(n+2)$). Substituting equation 10 in equation 9 we get

$$T = \frac{W_b^2}{4MBr}, \quad (11)$$

and finally, substituting equation 11 in equation 4, we get a relationship between transmission and resolving power:

$$T = \frac{1}{16} \frac{K^2}{MB} \frac{r}{R^2}. \quad (12)$$

From this equation we can draw several important conclusions. First, for a given machine, i.e. for given r , K , M , B , the transmission varies inversely as the square of the resolving power if W_s , $\alpha_{\max}$, and $\beta_{\max}$ are maintained at their optimal values when R is changed. This relation represents the best we can do; it is an upper limit, and if W_s , $\alpha_{\max}$, and $\beta_{\max}$ are not maintained at their optimal values T will always be less than its theoretically possible value. Secondly, we see that the transmission varies directly as the radius of the machine. This makes sense because we have defined transmission as a two-dimensional thing. (If we take the Z dimension into account and scale a machine in all dimensions the transmission will vary as the square of the size.) Finally, equation 12 contains a dimensionless constant, K^2/MB which we can think of as a figure of merit. This constant depends only on the geometry of the machine, and not on its size or the sizes of any slits or stops. Thus the larger we make this constant, the more efficient will be the machine whatever its size or resolution.

Expressions for the constants B and C in terms of the second-order aberration coefficients for a Mattauch-Herzog system are given in equations 22 and 23 in the appendix.

Appendix

In order to optimize the relation between $\alpha_{\max}$ and $\beta_{\max}$ it is necessary to derive an expression for the aberration portion of the beam width, W_a , in terms of the angular widths of the α - and β - stops of the system. This will be done here for the Mattauch-Herzog geometry.

Assume that the β stop is at the entrance of the magnetic sector, which is at a distance d from the virtual β - object. The radius of the electric sector is r_e . Then the coordinate Y of a ray entering the magnet is given by

$$Y = r_e \alpha + \beta' d \quad (13)$$

where β' is the fractional velocity deviation of the ray in question. Solving for β' and substituting $\beta = Y/d$, we get

$$\beta' = \beta - \frac{r_e}{d} \alpha \quad (14)$$

where β represents the angular width at the point of entry into the magnet.

Now the point of intersection of the ray with the focal plane of the instrument can be written (1)

$$\frac{x}{r} = A_{20}\alpha^2 + A_{11}\alpha\beta' + A_{02}\beta'^2. \quad (15)$$

Substituting for β' from equation 15 and collecting terms, we have

$$\begin{aligned} \frac{x}{r} = & \left[A_{20} - A_{11} \frac{r_e}{d} + A_{02} \left(\frac{r_e}{d} \right)^2 \right] \alpha^2 \\ & + \left[A_{11} - 2A_{02} \frac{r_e}{d} \right] \alpha\beta + \left[A_{02} \right] \beta^2. \end{aligned} \quad (16)$$

Defining the brackets respectively as B_{20} , B_{11} , and B_{02} , we have

$$\frac{x}{r} = B_{20}\alpha^2 + B_{11}\alpha\beta + B_{02}\beta^2. \quad (17)$$

This does not look much different from equation 16, but the important thing to note is that α and β are not correlated, but are orthogonal to each other.

Next, for given stop sizes $\alpha_{\max}$ and $\beta_{\max}$, we must find $\frac{x_{\max}}{r}$ and $\frac{x_{\min}}{r}$. Then

$$\frac{W_a}{r} = \left| \frac{x_{\max}}{r} - \frac{x_{\min}}{r} \right|. \quad (18)$$

(In general, maximum and minimum values of $\frac{x}{r}$ do not occur when $\alpha_{\max}$ and $\beta_{\max}$ are simultaneously at their maximum values.) Performing this exercise, we find that

$$\frac{W_a}{r} = \frac{B_{11}^2 - 4 B_{20} B_{02}}{4 B_{20} B_{02}} \left(B_{20} \alpha_{\max}^2 - B_{02} \beta_{\max}^2 \right). \quad (19)$$

Now, if we maximize the product $\alpha_{\max} \beta_{\max}$ subject to the constraint imposed by equation 20, we find that

$$\begin{aligned} \beta_{\max} &= \sqrt{\frac{-B_{20}}{B_{02}}} \alpha_{\max} \\ &= C \alpha_{\max} \end{aligned} \quad (20)$$

and that

$$\left(\frac{W_a}{r} \right)_{\text{opt}} = \frac{B_{11}^2 - 4B_{20} B_{02}}{2B_{02}} \alpha_{\max}^2. \quad (21)$$

The constants B and C, when evaluated in terms of the aberration constants A_{ij} are given by

$$BC = \frac{A_{11}^2 - 4A_{20}A_{02}}{2 A_{02}}, \quad (22)$$

$$C = \left[\frac{A_{11}}{A_{02}} \frac{r_e}{d} - \frac{A_{20}}{A_{02}} - \frac{r_e^2}{d^2} \right]^{1/2}. \quad (23)$$

Reference

- (1) C. F. Robinson, R.S.I. 28, 777 (1957).

Instrumentation and Techniques of High Resolution Mass Spectroscopy

by

Heinrich HINTENBERGER

Max Planck-Institut für Chemie (Otto Hahn-Institut),
Mainz, Germany

1. Introduction

Instruments and methods of high resolution mass spectroscopy were originally developed for the precision determination of atomic masses. In the meantime, however, instruments and measuring techniques developed for this purpose have been applied in other fields also, i.e. in the domain of solid sample analysis (1), in the analysis of organic compounds (2,3) and in investigations concerning the structure of organic molecules (4). Nowadays, for the most part, those instruments and methods are used which have been employed for the precision determination of atomic masses some five or ten years ago. Therefore, it should be quite appropriate to consider a little more closely the instruments and methods applied to the precision determination of atomic masses at the present time, so that one might get an idea of some of the future instrumental developments in the other fields of high resolution mass spectroscopy.

The highest mass resolution obtained up to now was reported to be 900 000. It was obtained by OGATA and MATSUDA (5) with a double focusing mass spectrograph, the data of which are given in table I. The instruments to be discussed here do not need a resolution in the above order and the term high resolution mass spectroscopy will be applied to all investigations with machines having a resolution higher than 2000.

This resolution can be obtained by different types of mass spectrometers. Some workers have reported a resolution of more than 2000 which they obtained with the omegatron (6), the mass synchrometer (7), the quadrupole mass filter (8), and with single focusing sector field mass spectrometers under certain conditions (9,10). In general, however, in high resolution mass spectroscopy, double focusing instruments with static electric and magnetic deflection fields are employed. Sometimes these fields are superimposed, though ordinarily they are used as consecutive sector fields.

2. Resolution

In order to separate the lines of two neighbouring masses M and $M + \Delta M$ in the mass spectrum, their separation distance Δy must be greater than the line breadth b and the width s_2 of the exit slit. The distance Δy of the two masses on a screen perpendicular to the beam is $\Delta y = r \cdot D \cdot \Delta M / M$, where r means the radius of the ion path in the deflection field before the exit slit, and D the dispersion coefficient of the instrument. Therefore, the lines are separated if the following condition is fulfilled:

$$\Delta y = r \cdot D \cdot \frac{\Delta M}{M} \geq b + s_2 = s_1 \cdot G_e \cdot G_m + s_2 + \sum \Delta f_i \quad (1)$$

Here $b = s_1 \cdot G_e \cdot G_m + \sum \Delta f_i$ is expressed by the width s_1 of the entrance slit and the magnification G_e and G_m of the electric and the magnetic field, respectively. $\sum \Delta f_i$ is the line broadening resulting from the aberrations and other causes (for example scattering phenomena). The resolution is therefore given by:

$$R = \frac{M}{\Delta M} = \frac{r \cdot D}{b + s_2 + \sum \Delta f_i} = \frac{r \cdot D}{s_1 \cdot G_e \cdot G_m + s_2 + \sum \Delta f_i} \quad (2)$$

The ion optical theory of the sector fields yields the magnifications G_e and G_m as well as the dispersion coefficient D . The corresponding quantities of double focusing mass spectrometers are given by eqs. (4), (5), and (6) in section 3.

TABLE I

Double-Focusing Mass Spectrographs

No.	$\frac{l'_e}{r_e}$	ϕ_e	$\frac{l''_e}{r_e}$	$\frac{l'_m}{r_m}$	ϕ_m	ξ'	ξ''	$\frac{l''_m}{r_m}$	$\frac{r_e}{r_m}$	references
1	0.150	$\frac{\pi}{2}$	0.609	0	π	0°	0°	0	0.85	Dempster (23)
2	0	$\frac{\pi}{2}$	0	3	$\frac{\pi}{2}$	0°	0°	$\sqrt{3}$	1.00	Bainbridge, Jordan (24)
3	1.225	$\frac{2}{3}\pi$	0	1.00	$\frac{\pi}{3}$	0°	0°	3.73	0.909	Ogata, Matsuda (5)
4	0.35	$\frac{\pi}{2}$	0.35	2.28	$\frac{\pi}{3}$	0°	0°	1.36	1.23	Nier, Roberts (25)
5	0.406	$\frac{\pi}{2}$	0.299	1.426	$\frac{\pi}{2}$	0°	0°	0.701	1.25	Craig, Errock (26)
6	0.966	58°	∞	∞	70°	55°	-35°	-	var.	Reutensward (27)
7	0.707	$\frac{\pi}{4\sqrt{2}}$	∞	∞	$\frac{\pi}{2}$	0°	$-\frac{\pi}{4}$	0	var.	Mattauch, Herzog (20)

For explanation of the symbols see fig. 3.

however, the slit width responsible for the resolving power may, under certain circumstances, be smaller than the geometrical slit width of the apparatus. By means of the ion acceleration system of the ion source, the ion beam may, in special cases, be focused to a smaller cross section than the width of the entrance slit; furthermore, the effective width of the exit slit may be made smaller than its geometrical width, by the application of a retarding potential applied to the exit slit system (11).

In practice, the real resolution is deduced from the actually observed mass spectrum. Then the experimentally achieved resolution is understood to be the quantity $R = M/\Delta M$, where M is to be the mass number of the observed line and ΔM is the mass difference which another line of equal intensity must have in order to still be separated in the mass spectrum. Depending on the way in which separation of individual lines is characterized, different definitions for ΔM , and consequently for the resolution will result. As can be seen from the figure 1 the following quantities may be employed in characterizing the degree of separation of two mass lines. 1) The minimum intensity x between the two lines, 2) the intensity y which the one line contributes to the intensity of the other line and 3) the breadth ΔN_z of the line at z % of the maximum intensity. Each of these definitions yields a different value of resolution and, furthermore, the value depends on the choice of the parameters x , y , or z , respectively, as 50%, 10%, 1%, ... designating the degree of separation of the two lines. In case of two lines of equal intensity, the following relations can easily be derived from fig. 1:

$$R_x = R_z \quad \text{for } z = \frac{x}{2}, \text{ and}$$

$$R_y = 2R_z \quad \text{for } z = y.$$

Provided the intensity distribution of the individual lines is known, then both position and intensity of these lines may be determined also for unresolved spectra from their intensity distribution. A simple procedure to determine the breadth of the various lines is to singly or doubly differentiate the corresponding intensity distribution curve (12). An analysis of a spectrum can also be obtained by using a "resolution multiplier" which, by means of electronic components, separates the curve of the unresolved compound spectrum into its individual components (13).

But the "quality" of an instrument is not reliably characterized by the resolution alone. In addition, the transmission T of the instrument must be considered (14). The simplest way to mark the merits of an instrument consists in employing the product of resolving power R and transmission T . Each of the basic advances of mass spectrography has always been connected with an increase of the product $R \cdot T$. This was the case when the ideas of direction focusing and of double focusing were introduced, and this "figure of merit" may further be improved by stigmatic focusing and by correcting the image defects.

3. Double Focusing Instruments

a. Crossed Field Instruments

The first double focusing mass spectrometer was proposed by BARKY and DEMPSTER (15). These authors were able to show that the electric field of a cylindrical condenser with the deflection angle $\pi/\sqrt{2} = 127^\circ$, combined with a homogeneous magnetic field perpendicular to the electric field, yields simultaneous direction and velocity focusing. After the development of sector field ion optics, coincident field spectrometers could be designed, utilizing lower deflection angles as can be seen in fig. 2.

Instruments of this type have been used several times in high resolution mass spectroscopy (16). They have the advantage of a short ion path but their disadvantage lies in the fact, that the cylindrical condenser must be mounted between the pole pieces of the magnet. Consequently, the pole gap is wide and the stray field effects large. Furthermore, the plates of the cylindrical condenser will be exposed to a continuous ion bombardment by the separated beam. This will lead to contamination and disturbing charge-up effects, necessitating frequent cleaning or continuous baking-out of the deflection plates.

TABLE II
Mass Spectrometers for Precision Mass Determinations

A) Tandem-Sector-Field-Instruments									
$\frac{l'_e}{r_e}$	ϕ_e	$\frac{l'_e}{r_e}$	$\frac{l'_m}{r_m}$	ϕ_m	$\frac{l''_m}{r_m}$	ξ'	ξ''	$\frac{r'_e}{r'_m}$	L Laboratory
1 0.35	90°	0.35	2.28	60°	1.36	0°	0°	1.23	4 m Minneapolis (Nier-Roberts type ²⁸)
2 0.707	31.8°	∞	∞	90°	0	0°	-45°	var.	5 m Harvard (Mattauch-Herzog type ²⁹)
3 0.150	90°	0.609	0	90°	0	0°	0°	-	12 m McMaster University (Dempster ³⁰)
4 0.268	75°	∞	∞	110°	0.245	36.5°	-35°	1.00	10,4 m Argonne (z-focusing ³¹)
5 1.51	48°87'	∞	∞	167°	1.72	-38°	- 6.5°	var.	12.7 m MPI Mainz (32)
6 1.22	120°	0	1.00	60°	3.73	0°	0°	0.909	10 m Osaka University (5)
B) Other Types									
7	Toroidal Mass Spectrometer (Cyclotron Resonance Modification) (18, a, b)								
8	Synchrotron (7, 33)								
9	Quadrupole Mass Filter (8)								

For explanation of the symbols see fig. 3.

Crossed fields are also applied in the cycloidal mass spectrometer in which not only approximate, but exact double focusing is achieved (17). Instruments of this type have been built for many different applications (18). In a miniature design, utilizing permanent magnets, they are used for the determination of small amounts of rare gases as well as in the investigation of residual gases. ~~However, in the precision mass determination of small amounts of rare gases as well as in the investigation of residual gases.~~ However, in the precision mass determinations they are also rather advantageous and permit a very high resolution. This is particularly the case for the cyclotron resonance modification of this type of instrument (19, a,b). Unfortunately, the high resolution instrument, the construction of which was started at the National Bureau of Standards, has not been completed (19,b). This of course was due to other reasons and not to any fault in the principle of the instrument.

b. Tandem Sector Field Instruments

Much more frequently used in high resolution mass spectroscopy than the crossed field mass spectrometers are those instruments in which a cylindrical condenser and a homogeneous magnetic sector field in tandem are employed. The velocity dispersion of the electric field perpendicular to the main beam, is given by $y_e = K_e^2 \cdot \theta$. The velocity dispersion can be combined such, that after passing through both fields, velocity dispersion of the particles is zero at the point at which direction focusing appears. The condition for this "double focusing" in general form was first given by MATTAUCH and HERZOG (20). It is:

$$\begin{aligned} \pm K_e' &= \pm \sqrt{r_e(1-\cos \sqrt{2} \phi_e)} + l_e' \sqrt{2} \sin \sqrt{2} \phi_e \\ &= r_m (1-\cos \phi_m) + l_m' \sqrt{2} \sin \phi_m + (1-\cos \phi_m) \operatorname{tg} \varepsilon' = K_m' \end{aligned} \quad (3)$$

The meaning of the symbols can be seen from fig. 3. The upper sign is valid for deflection in electric and magnetic fields in the same direction, and the lower sign for deflections in the opposite sense.

Nowadays in high resolution mass spectroscopy, double focusing instruments of this type are generally employed. In table I the pertinent parameters of some of these instruments are collected. Machines No. 4, 5, and 7 in table I are also manufactured commercially.

In general, these instruments exhibit double focusing only for the mass adjusted to the exit slit of the apparatus. The curve along which direction focusing occurs for different masses is ordinarily different from the curve along which velocity focusing occurs (21) (see fig.3). Both curves will intersect at a point at which double focusing is then obtained, and at which the exit slit of the instrument is usually mounted. By suitable dimensioning of the fields it can be arranged, that the two curves intersect only in a grazing angle, or that they possess a common tangent. Simultaneous double focusing will occur for a somewhat larger mass range on a photographic plate mounted along this tangent. If the entrance slit of the mass spectrograph is mounted in the focal point of the electrical field, then double focusing is simultaneously obtained for all masses along a straight image curve (20). Both the image curve, along which the photographic plate is mounted, and the field boundary of the magnet at the exit side then form a straight line, the extension of which goes through the point C of entrance of the central beam into the magnetic field (fig.4). For the MATTAUCH-HERZOG mass spectrograph, having a deflection angle of $\phi_e = \pi/4 \cdot \sqrt{2} = 31.8^\circ$ and a magnetic deflection angle $\phi_m = 90^\circ$, the image curve coincides with the exit boundary of the magnet. Instruments of this type, equipped with a high frequency spark ion source and photographic ion detection, are now frequently used for trace analyses in solids (34, 35). In order to permit the alignment of the photographic plate a magnetic deflection angle amounting to somewhat less than 90° is often chosen. Then the image curves lie slightly outside the boundary of the magnetic field, and some space is gained for the alignment of the photographic plate.

At the distance l_m'' from the point of exit of the magnetic field, a beam of mass $N+\Delta N$ is separated from the main beam of mass N by:

$$\Delta y_m = r_m \cdot D_m \cdot \frac{\Delta N}{N}$$

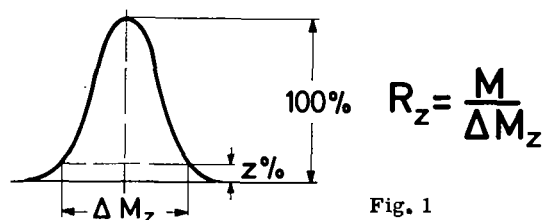
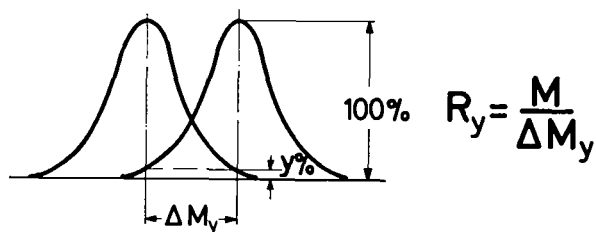
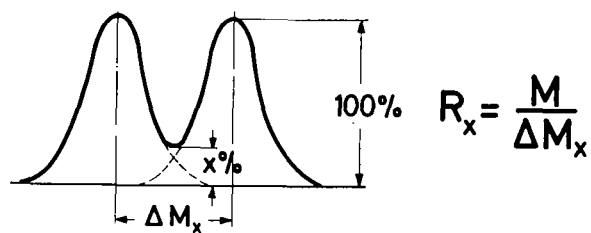
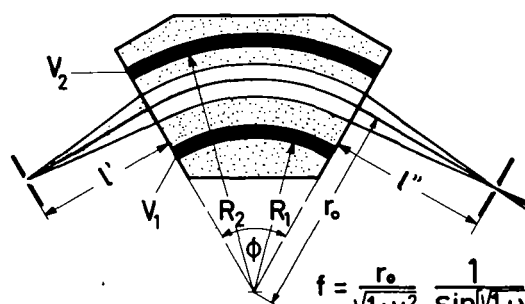


Fig. 1

Coincident Fields



Symmetrical case
 $l = l' = l''$ $l = g + f$
 (Bartly and Dempster)
 $l = 0$ $\phi = \pi/\sqrt{2}$

$$f = \frac{r_0}{\sqrt{1+y^2}} \frac{1}{\sin[\sqrt{1+y^2}\phi]}$$

$$g = \frac{r_0}{\sqrt{1+y^2}} \text{ctg}[\sqrt{1+y^2}\phi]$$

$$y = \frac{1}{m \cdot v_0^2} \frac{e(V_2 - V_1)}{\ln(R_2 - R_1)}$$

Fig 2

In order to obtain the distance between the intersections of the two beams with the image curve, this expression has to be multiplied by the factor $1/\cos \omega$, where ω equals the angle between the incident beam and the normal to the photographic plate (fig.4).

The mass dispersion coefficient, D_m , is, in the case of double focusing instruments with consecutive fields, given by:

$$D_m = \frac{1}{2} \left[(1 - \cos \phi_m) + \frac{l_m''}{r_m} (\sin \phi_m + (1 - \cos \phi_m) \tan \varepsilon'') \right] \quad (4)$$

The meaning of the various quantities above can be taken from fig.3.

The magnifications G_e and G_m are given by:

$$G_e = \frac{f_e + l_e'' - g_e}{f_e + l_e' - g_e'} = \frac{f_e}{l_e' - g_e'} = \frac{l_e'' - g_e''}{f_e} \quad (5)$$

and

$$G_m = \frac{f_m + l_m'' - g_m}{f_m + l_m' - g_m'} = \frac{f_m}{l_m' - g_m'} = \frac{l_m'' - g_m''}{f_m} \quad (6)$$

where the focal lengths f_e and f_m and the distances g_e' and g_m'' of the focal points from the corresponding field boundaries can be calculated by (36):

$$f_e = \frac{r_e}{\sqrt{2}} \frac{1}{\sin \sqrt{2} \phi_e} \quad (7)$$

$$g_e' = g_e'' = \frac{r_e}{\sqrt{2}} \cot \sqrt{2} \phi_e \quad (8)$$

$$f_m = r_m \cdot \frac{\cos \varepsilon' \cos \varepsilon''}{\sin(\phi_m - \varepsilon' - \varepsilon'')} \quad (9)$$

$$g_m' = r_m \cdot \frac{\cos \varepsilon' \sin(\phi_m - \varepsilon'')}{\sin(\phi_m - \varepsilon' - \varepsilon'')} \quad (10)$$

$$g_m'' = r_m \cdot \frac{\cos \varepsilon'' \sin(\phi_m - \varepsilon')}{\sin(\phi_m - \varepsilon' - \varepsilon'')} \quad (11)$$

Substitution of eqs. (4), (5), and (6) into eq. (2) yields the resolving power of double focusing consecutive sector field instruments.

The resolving power when using a photographic plate for ion detection is determined from equation (2) by setting $s_2 = 0$. Neglecting the image defects ($\sum \Delta f_i = 0$), one then obtains in this case $R = r_m \cdot D_m / 2s_1 \cdot G_e \cdot G_m$. This can be transformed into:

$$R = \frac{r_e}{2s_1} \left[1 + \frac{(l_e' - g_e)}{f_e} \right]. \quad (12)$$

For instruments having double focusing simultaneously for all masses along a straight image curve (MATTAUCH-HERZOG), the distance f_i of the line of the mass M_i on the photographic plate from the point C of entrance of the beam into the magnetic field (fig.4) is then:

$$f_i = \text{const} \cdot \sqrt{M_i}. \quad (13)$$

4. Instruments for Precision Mass Determinations

In the precision determination of nuclear masses, double focusing instruments with consecutive sector fields are used more than other types. In order to obtain a resolution of more than 100 000, the dimensions of these machines are considerably larger than those necessary for analytical purposes. While the ion path lengths in double focusing analytical spectrometers are on the order of 1 to 2 meters, the path length in modern instruments for precision mass determination amounts to 4 to 12 meters. The data of precision mass spectrometers presently in use are given in table II.

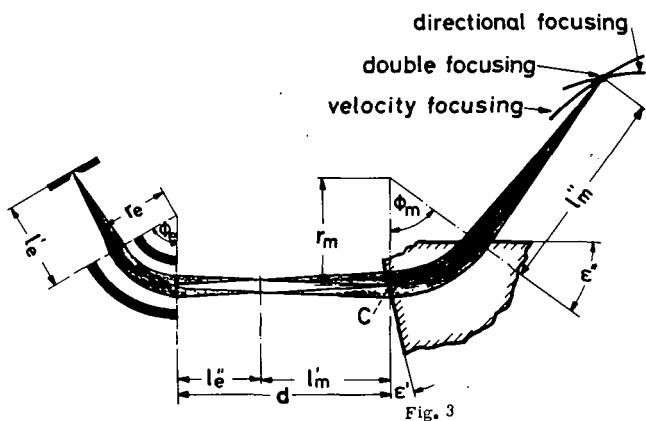


Fig. 3

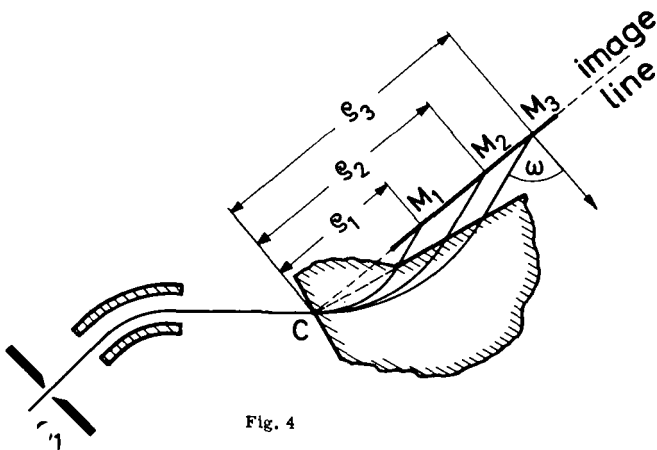


Fig. 4

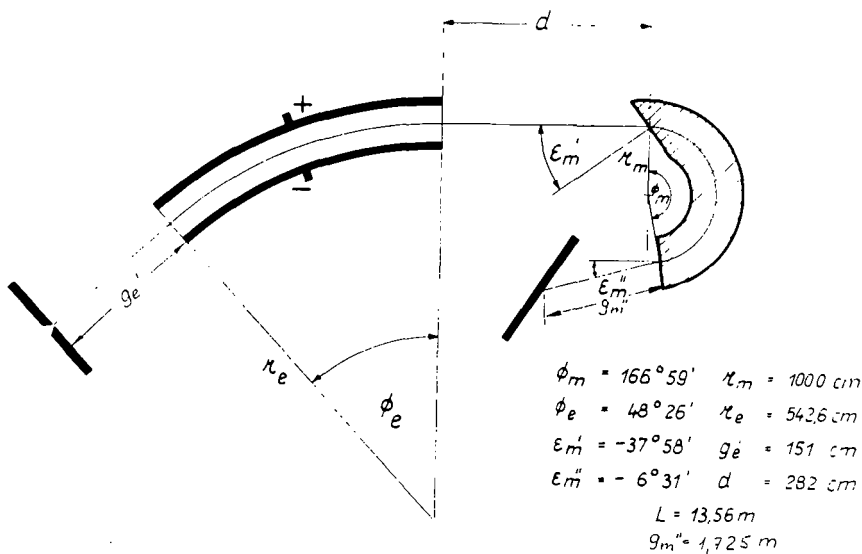


Fig. 5

Ion path in the high resolution mass spectrograph at the Max Planck-Institut in Mainz (32).

The Minneapolis instrument is an enlargement of the double focusing mass spectrometer by NIER and ROBERTS (28) which is already well known from its application in the analytical field. The ion path in the new instrument, however, amounts to 4 meters. The Harvard instrument (29) is a MATTAUCH-HERZOG type instrument and has an ion path of some 5 meters. The McMaster instrument (30) is an enlarged double focusing DEMPSTER type machine with an ion path length of about 12 meters. The instrument at Mainz (32) has an ion path of 12.5 meters. The resolution reached with each of these instruments is on the order of 300 000.

The data given as No.4 in table II apply to the instrument at Argonne National Laboratory (31). However, here a spherical condenser is used to enable focusing in z-direction also. Up to now this instrument was applied mainly to the investigation of isotopes of artificially produced elements employing wide slits in order to increase the detection sensitivity to the extreme. Fig. 5 shows a schematic diagram of the high resolution mass spectrograph at Mainz and fig. 6 a mass spectrum obtained with this apparatus. In fig. a resolution of 300 000 is demonstrated.

5. Image Defects

Double focusing instruments ordinarily exhibit image defects due to the apex angle α and the relative velocity aberration β . These quantities will lead to a line broadening given by

$$\Delta b = B_{11} \cdot \alpha^2 + B_{12} \cdot \alpha\beta + B_{22} \cdot \beta^2.$$

Neglecting the effect of stray fields, the aberration coefficient B_{ik} has been calculated (37). By suitable dimensioning of the fields a few or all of these coefficients can be made to be zero so that the corresponding image defects also vanish (37, 38, 39). For example, the apparatus designed by NIER and ROBERTS (25) has been corrected for angular aberration, that is $B_{11} = 0$. This is also the case at a certain point of the mass scale in the MATTAUCH-HERZOG mass spectrograph, that is for $r_2 = 1.68 r_m$ (40). The angular aberration is also corrected in the instrument at Argonne (31) and in our large mass spectrograph at Mainz (32). ROBINSON (41) described the conditions necessary to make the aberrations depending on $\alpha\beta$ and β^2 disappear in a MATTAUCH-HERZOG mass spectrograph, by applying a certain curvature to the magnetic field boundary at the entrance side. There are also instruments in which all three aberration coefficients vanish and which therefore exhibit complete double focusing in second order. In tables III and IV the data of a few other mass spectrometers with complete second order double focusing are given. The instruments marked with No.1 and 2 and the instruments

TABLE III

No.	ϕ_m	ε'	ε''	ϕ_e	d/r_m	r_e/r_m	l'_e/r_m	l''_m/r_m
1	55	0	0	81.510	3.4364	1.2762	0.4768	1.4239
2	60	0	-3	90.999	2.9930	1.2203	0.2835	1.2145
3	60	0	-15	56.569	4.5200	1.8143	1.8204	0.8377
4	60	-15	-15	97.849	2.8459	1.0081	0.0879	0.6637
5	70	15	-15	50.036	4.9392	2.6663	4.1875	0.9116
6	72	15	-15	59.101	4.0507	2.2773	2.5560	0.9082
7	80	15	-15	91.486	2.3494	1.5454	0.5406	0.8768
8	90	27	-15	94.650	1.5955	1.5938	0.7084	0.9477
9	105	32	-35	46.239	3.8878	4.5927	45.8907	0.4426
10	110	31	-35	109.276	1.3432	2.0185	0.7614	0.4424
11	111	31	-35	118.128	1.2136	1.8983	0.4473	0.4392
12	116	35.9	-45	129.238	1.1190	2.5988	0.7416	0.3174

For explanation of the symbols see fig. 3.

No. 3 and 4 in table IV have been calculated with α^2 , $\alpha\beta$, and β^2 term corrections. These instruments have practically the same deflection angles as the double focusing mass spectrometers of NIER and ROBERTS (25) and of the AEI mass spectrometer (26), respectively, but these spectrometers are corrected only for the α^2 term. However, the distances of the slits from the deflection fields are different in both types of instruments. Of the type No. 1 in table III we have built a small model at Mainz which is used for the measurement of isotopic abundances in minute amounts of rare gases. It works very well, but up to now a systematic investigation of image defects has not yet been performed on this instrument.

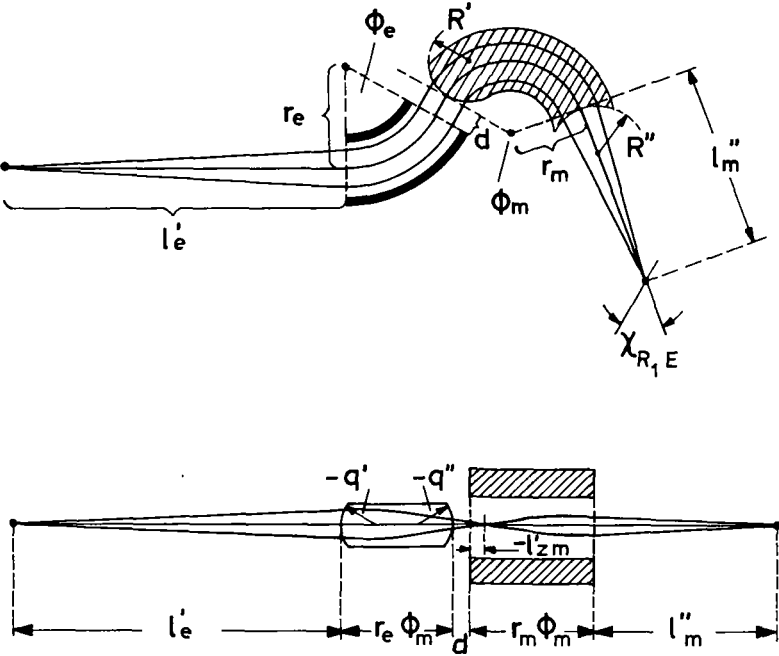
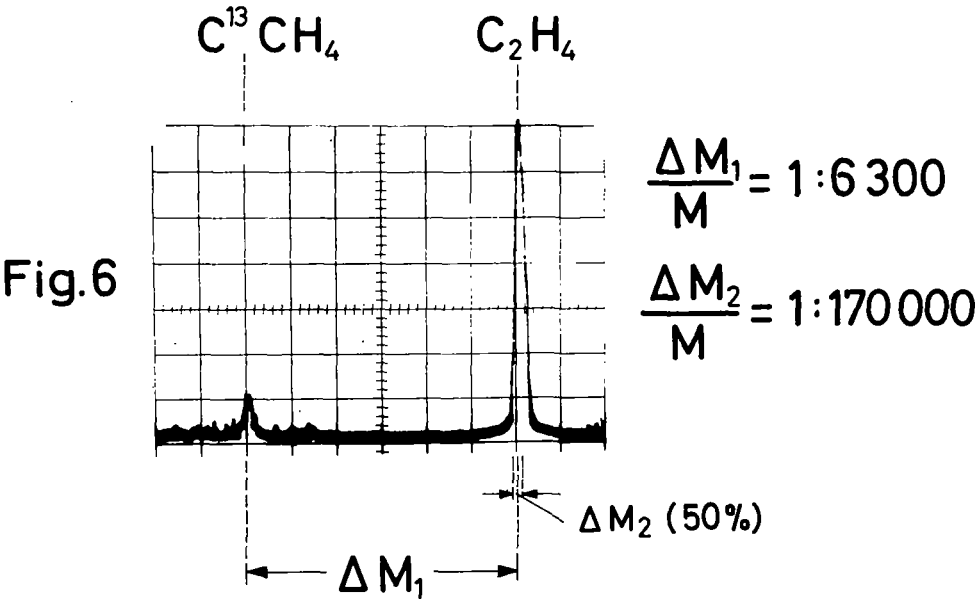


Fig. 7

Schematic diagram of the ion path of a stigmatic focusing mass spectrometer (48).

TABLE IV

No.	β_m	$\mathcal{E}'$	$\mathcal{E}''$	r_m/R'	r_m/R''	ϕ_e	d/r_m	r_e/r_m	l'_e/r_m	l''_e/r_m
1	60°	0°	-3.3°	0	0	90°	3.005	1.230	0.310	1.204
2	60°	0°	0°	0.200	-0.400	89.95°	2.723	1.132	0.286	1.399
3	90°	2°	-15°	0.360	1.500	89.72°	2.822	1.654	0.581	0.427
4	90°	2°	-15°	0.360	1.400	90.32°	2.790	1.639	0.559	0.431

For explanation of the symbols see fig. 3. R' and R'' are the radii of the field boundaries at the entrance and the exit side of the magnet.

6. Stigmatic Focusing

In both the cylindrical condenser and the homogeneous magnetic sector fields, the deflecting forces always act parallel to the middle plane (x - y -plane). As long as the stray fields can be neglected, no focusing takes place perpendicular to this plane (z -direction). Using spherical (42) or toroidal (43) condensers, or employing inhomogeneous magnetic fields (44, 45), focusing in the z -direction may be achieved. At equal ion path radii such fields permit a largely increased dispersion and a considerably greater resolution than a cylindrical condenser or a homogeneous magnetic sector field. When employing such fields, double focusing mass spectrometers and mass spectrographs may also be designed which exhibit focusing in the z -direction, and, under certain circumstances, even complete stigmatic focusing. In table V typical parameters of a few such instruments are presented.

TABLE V

No.	l'_e/r_e	ϕ_e	l''_e/r_e	l'_m/r_m	ϕ_m	$\mathcal{E}'$	$\mathcal{E}''$	l'_m/r_m	r_e/r_m	Ref.
1	2.39	29°42'	∞	∞	87°30'	0°	-46°15'	0.042	1.043	(42)
2	0.753	53°	∞	∞	106°	+26.5°	-37°	0.162	var.	(43)
3	0.268	75°	∞	∞	110°	+36.5°	-35°	0.245	1.00	(31)
									var.	

For explanation of the symbols see fig. 3.

Recently WACHSMUTH and EWALD (46) described a double focusing mass spectrometer with stigmatic focusing, employing a toroidal condenser and an inhomogeneous magnetic field between conical pole pieces (fig.7). At a path radius of 120 mm in the magnetic field and a slit width of $1/4$ micrometers a resolution of 50 000 was obtained.

Stigmatic focusing instruments require high precision in the manufacture of the field elements, and they also necessitate careful alignment. At equal radii of the ion paths such fields permit a largely increased dispersion and a considerably greater resolution than the conventional instruments employing a cylindrical condenser and a homogeneous magnetic field. It should be noted though, that with increasing dispersion, the aberration coefficients strongly increase, and thus it is rather essential to correct for image defects. In the above mentioned instrument of WACHSMUTH and EWALD the aberration coefficients of α^2 , $\alpha\beta$, and β^2 were corrected. However, instruments with stigmatic focusing exhibit further aberrations which are not present otherwise.

Ordinarily, stigmatic focusing can only be reached for one point of the mass scale. For mass spectrometers equipped with single collectors this restriction is insignificant. However, instruments with stigmatic focusing promise to offer particular advantages in the trace analysis of solids where the entire mass spectrum can be put simultaneously onto one photographic plate. Here, stigmatic focusing at a single point of the photographic plate, will lead to difficulties in the quantitative analysis of a sample. It should be pointed out here that R. MERZOG (47) described a double focusing mass spectrograph with stigmatic focusing as early as 1953 which uses a spherical condenser and exhibits double focusing along a straight line simultaneously for all masses. A double focusing mass spectrograph with partial focusing in the z -direction for all masses is given by HABFAST (49).

The large mass spectrometer at Argonne also incorporates a spherical condenser. There is, however, no complete stigmatic focusing. It has been generally used in nuclear physics investigations concerned with extremely small amounts of matter. With z -focusing a transmission of practically 100 % has been reached.

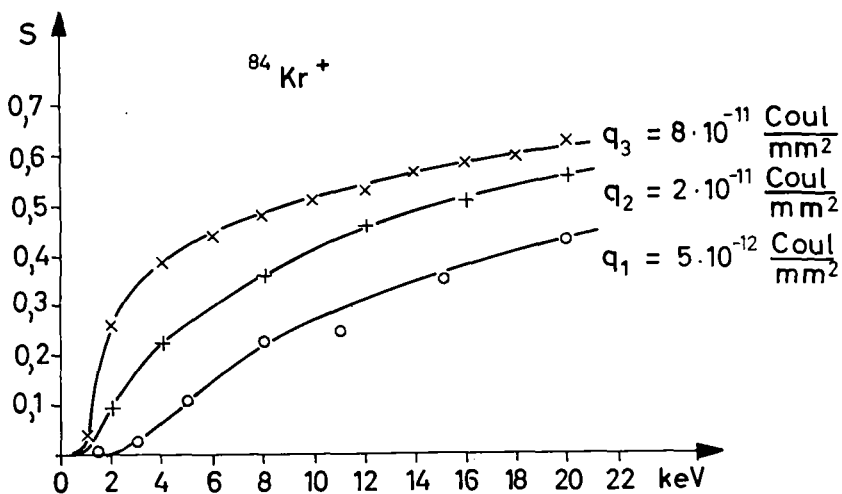


Fig. 8

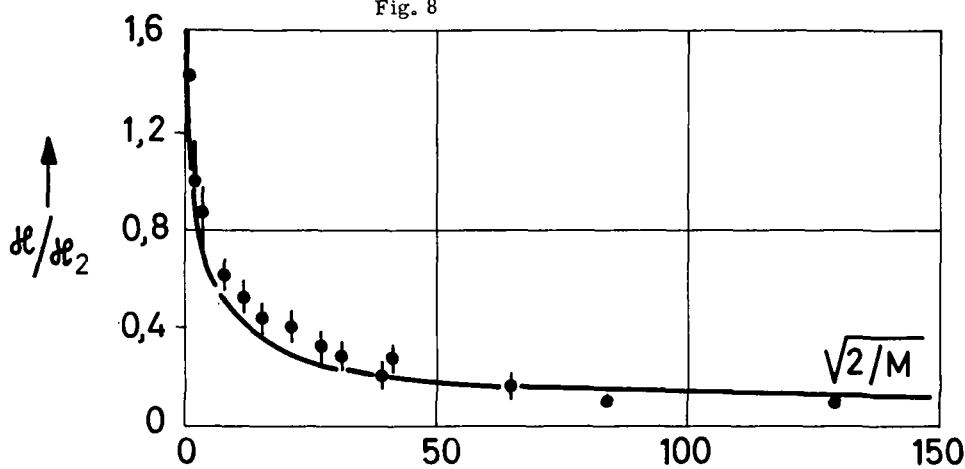
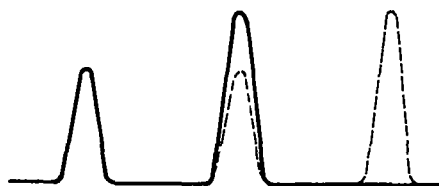
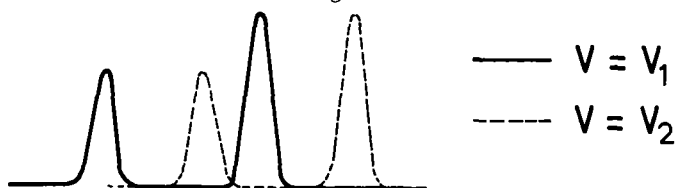


Fig. 9



Matched Peaks

$$\frac{\Delta M}{M} = \frac{\Delta V}{V} = \frac{\Delta R}{R}$$

Fig. 10

7. Ion Detection

a. Electrical Ion Detection

Using a single collector and a d.c. amplifier, ion currents as low as 10^{-15} to 10^{-16} A may still be detected, and the ratio of two ion currents can be measured to a precision of approximately 0.1 %. The precision of determining two ion currents can be increased to 0.01 % by employing a double-collector system in which two ion currents are compared with each other by means of a bridge circuit.

Using a multiplier, the detection sensitivity can be improved by a few orders of magnitude. Multipliers for ion detection are commercially available from mass spectrometer firms, but commercial types of photo-multipliers which had not previously been photo-sensitized by alkalis can also successfully be employed for this purpose (Dumont SP 114, Fernseh GmbH, Darmstadt FS 9). Ion currents of the order of 10^{-17} to 10^{-18} A can easily be detected by making use of a multiplier as a d.c.-pre-amplifier. By suitably selected electrode systems, arrangements can be found which make individual ion counting procedures feasible. For the purpose of ion counting, special equipment has been designed which employs scintillation counter techniques for the detection of the secondary electrons produced by incident ions striking a metal surface (51-54).

The most accurate method of ion detection consists of the electrometric measurement of ion currents by a collector system and a d.c.-amplifier. Multipliers often show discrimination effects, and their sensitivity alters with time by the presence of magnetic stray fields and by variations of the surface conditions of the multiplier electrodes.

With a given mass spectrograph a gain of resolution must always be paid for by a decrease of intensity. For this reason, in spite of the drawbacks mentioned above, the application of multipliers is particularly advantageous in high resolution mass spectroscopy. They make possible not only the detection of very weak lines, but they enable also the quick registration of the mass spectra. A combination consisting of a movable collector and a multiplier has proven most useful, since with an arrangement of this type, a simple sensitivity calibration of the multiplier can regularly and frequently be performed.

b. Photographic Ion Detection

Ilford Q-plates are almost exclusively employed to-day for photographic ion detection in mass spectroscopy.

Provided one remains in the low-density region, the linear relationship

$$S = k \cdot q$$

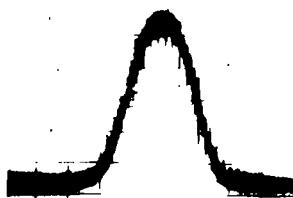
is valid between the blackening S ($S = \log$ of opacity) of a line and the current density q of the incident ion beam. This constant is given in table VI for ILFORD Q1-, Q2-, and Q3-plates, obtained for Ar^+ -ions of an energy of 9 keV. A line of blackening $S = 0.01$ is still distinctly visible; ordinarily, lines of half this density are still within the "just detectable" level. Using the values of table VI, one finds that for Q2-plates, a charge of $2 \cdot 10^{-13}$ C/cm² or $1.25 \cdot 10^6$ ions/cm² of H_2^+ -ions with 9 keV energy, will produce a clearly visible blackening on the Q₂-emulsion. In order to blacken a mass spectrographic line of dimensions 4 mm by .1 mm, a total of 5000 ions is necessary. At an exposure time of 2 hours this corresponds to an ion current of $1 \cdot 10^{-19}$ A. The emulsion sensitivity for ions of the heavy metals (elements) is lower by about one order of magnitude. Examples of the variation of line density with incident ion charge density, ion energy, and ion mass are shown in fig. 8 and fig. 9.

c. Mass Determinations

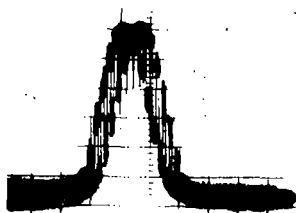
The determination of the masses corresponding to the individual lines of a mass spectrum is based on the following relation:

$$r = \text{const} \frac{\sqrt{MU}}{H}$$

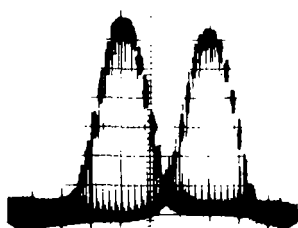
The mass M can be determined if the position of the line within the mass spectrum or the position of the final slit of the apparatus is known, (from this information r can be determined) and if the accelerating voltage U and the magnetic field strength H are given. Much more



$$\frac{\Delta V}{V} = 0$$



$$\frac{\Delta V}{V} = 2,9 \cdot 10^{-6}$$

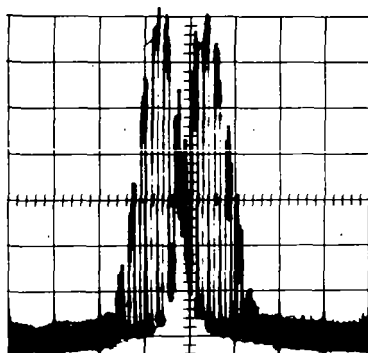


$$\frac{\Delta V}{V} = 1,4 \cdot 10^{-5}$$

Peak-Matching (CO-N₂)

Fig.11

Fig.12



$$\frac{\Delta V}{V} = 3,3 \cdot 10^{-6}$$

$$R_{50\%} = 300\,000$$

TABLE VI

M		Q_1 $\times 10^{-10}$	Q_2 $\times 10^{-10}$	Q_3 $\times 10^{-10}$	keV	Ref.
2	H_2^+	1.35	5.00	6.25	9	55
4	He^+	1.00			9	55
14	N^+	0.475	1.47	2.09	9	55
16	O^+	0.416			9	55
28	N_2^+	0.227			9	55
32	O_2^+	0.204			9	55
40	Ar^+	0.179	1.05	1.70	9	55
84	Kr^+	0.125			8	56
200	Hg^+		1.82		15	57
			0.39		10	57
144	C_{12}^+				14	58

Proportionality Factor κ [cm^2/amp] between blackening S and density of impinging ions q for different Ilford Q-plates and ions of different masses M and energy (keV).

accurate than such an absolute determination in grams is the mass determination in terms of atomic mass units, obtained by comparing the unknown mass M with a known mass M_0 . This can be done 1) at a given value of r and $\sqrt{U}$ by the measurement of H, 2) at a given value of r and H by the measurement of U, and 3) at a given value of U and H by the measurement of r, or of a quantity unambiguously dependent on r.

For the measurement of magnetic field strengths, induction coils, the field-dependent resistance of a bismuth-wire, or other magnetic field-dependent effects can be used. However, due to field inhomogeneities and hysteresis-effects, the field strength, averaged over the entire ion trajectory is usually not strictly proportional to the field strength measured at a given point. Therefore, an accuracy better than $1:10^3$ to $1:10^4$ is very difficult to achieve in a mass determination based on the H-measurement. For these reasons, the very high precision of magnetic field measurements offered by nuclear magnetic resonance techniques can not fully be utilized in high precision mass determinations.

Considerably more precise and also much simpler than the above, is the comparison of two masses by varying the accelerating voltage U and, therefore, the deflection voltage V which is proportional to U, keeping the magnetic field constant. The deflection voltages V_0 and V_x , at which the standard mass M_0 and the unknown mass M_x appears with maximum intensity, can be measured by a precision potentiometer, and the unknown mass M_x can be determined from a resistance ratio. This method increases in accuracy with decreasing relative mass difference $\Delta M/M = (M_0 - M_x)/M_0$. For $\Delta M/M = 10\%$, M can be measured to an accuracy of $1:1 \cdot 10^4$ to $1:1 \cdot 10^5$ (59).

In the precision determination of atomic masses the "peak matching" method first introduced by Lincoln SMITH (60) and further developed at Minneapolis (61) is exclusively employed nowadays. In this method, the deflection voltage V of the radial field is alternately adjusted to the one and then to the other line of the observed doublet. Each time, the mass spectrum of one of the members of the doublet is plotted on the screen of an oscilloscope. Both mass spectra will appear on the oscilloscope screen provided the latter shows sufficiently long persistence (fig. 10). By varying the difference ΔV of the two deflection voltages of the radial field, the two spectra can be mutually displaced on the oscilloscope screen until the two lines to be compared are superimposed. Then the relative mass difference $\Delta M/M$ is equal to the relative voltage difference $\Delta V/V$ and, therefore, equal to the relative difference of $\Delta R/R$ of the resistances from which the deflection voltages were taken. The fig. 11 and fig. 12 show mass spectra taken with the large mass spectrometer at Mainz (32). The upper section of figure 11 shows the N_2 -peak matched against the CO-peak at mass 28. In the middle part of the

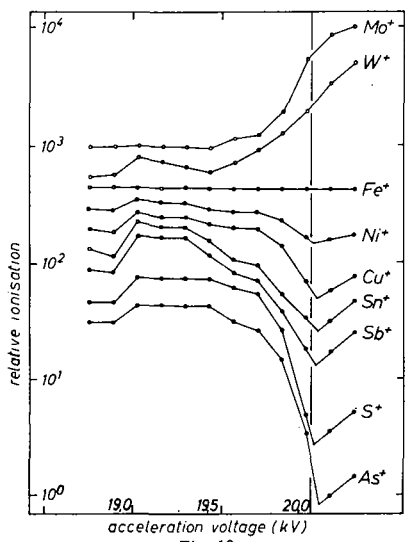


Fig. 13
Relative ionisation for different elements in a high frequency spark (62)

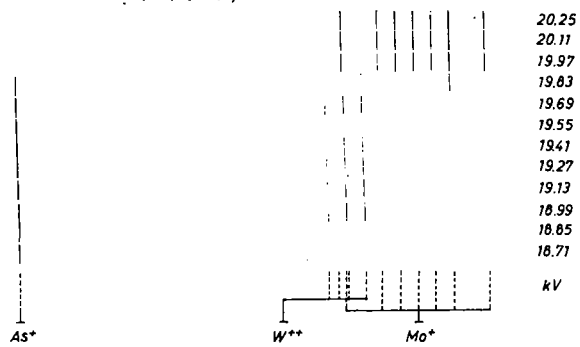


Fig. 14

Mass spectrum of a stainless steel sample containing As, Mo and W. The intensity of the lines depends on the acceleration voltage in different manner for each element (62).

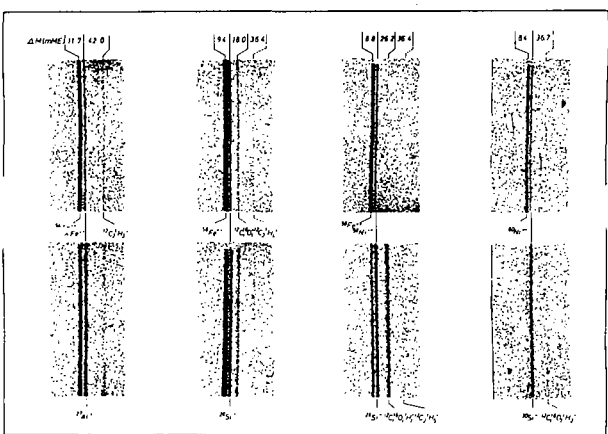


Fig. 15

High resolved mass spectrum of a stainless steel sample, taken with a d.c. spark source (66,68).

figure, the peaks are displayed by a voltage ΔV corresponding to a relative mass difference of $\Delta M/M = 2.9 \cdot 10^{-6}$. Fig. 12 demonstrates a resolution of 300 000 (at halfwidth). In these experiments a modification of the peak matching method has been employed. The deflection voltage V was switched 50 times from one peak to the other peak of the doublet during each single sweep.

This method is not only quite accurate, but the measurement can also be performed very quickly and without experimental difficulties. The peak matching method will surely also be adaptable with great advantage for the identification of peaks in investigations in the field of analytical chemistry. Although the application of the peak matching method has so far been almost exclusively employed in the measurement of very small mass differences, relative mass differences of $\Delta M/M = 10\%$ and more can also be determined. This means ΔM may amount to 10 mass units and more at mass 100. This is of interest for analytical applications.

A relatively easy but still accurate method of mass determination is offered by the measurement of the line position on a photographic plate obtained by a mass spectrograph of the MATTAUCH-HERZOG type. Here the distances ρ_i of the individual lines on the photographic plate, measured from the point of entrance C of the ion beam into the magnetic field, are proportional to the roots of the ion masses (see equation (13)). Since the point C does not lie on the photographic plate but on its extension, the distances ρ_i are not directly measured but only the distance y_i of a reference point P from this line. Let the distance between the points P and C be ρ_p then we have $\rho_i = y_i + \rho_p$ and, therefore, $y_i = \rho_i - \rho_p$. If $\sqrt{N_1}$ is plotted vs. y_1 for lines of known masses, then a straight line is obtained by means of which, from the position y_x , the unknown mass M_x can easily be determined with an accuracy of $1:1 \cdot 10^3$. For a more exact determination, two neighbouring lines of known masses M_1 and M_2 in the immediate vicinity of the line of unknown mass M_x must be chosen, and the distances $y_2 - y_1$ and $y_2 - y_x$ determined. From eq. (13) it follows that

$$M_x = M_2 \left(1 - \frac{y_2 - y_x}{y_2 - y_1} \cdot \frac{\sqrt{N_2} - \sqrt{N_1}}{\sqrt{N_2}} \right)^2$$

8. Ion Sources

In high resolution mass spectroscopy, up to now electron bombardment ion sources or radio frequency spark sources are almost exclusively employed. Electron bombardment sources have been widely used in the investigation of gases and vapors, but also, with a built-in oven, in studies of solid materials; their mode of operation has been thoroughly studied. The radio frequency spark source preferentially used in solid sample analysis, however, has not yet been investigated in great detail. Therefore, a few observations should be quoted here, which we have recently made with spark ion sources.

a. High Frequency Spark Source

Investigations with a MATTAUCH-HERZOG mass spectrograph had shown, that, when using a radio-frequency spark for ion production, a noticeably lower ion acceleration potential always had to be used, than when employing a thermal ion source with the same deflection voltage at the radial field (62). This shows that the ions from the radio frequency spark already possess initial energies which may be as high as a few kV. The energy distribution of the ions, however, shows very strong differences for different ion species. Fig. 13 shows the energy distribution of the singly-charged ions of a few elements. One can see that a variation of ion acceleration potential by only a few percent might produce a strong change of the ratio of two ion currents. For example, extremely different behaviour is exhibited by the elements arsenic and molybdenum. Increasing the acceleration potential by 2.5 % might change the abundance ratio of arsenic to molybdenum by a factor of 300. This will of course introduce serious errors in the analysis. This fact is also apparent from the mass spectrum shown in fig. 14. This figure shows a portion of a mass spectrum of a stainless steel alloy containing arsenic and molybdenum, obtained on a MATTAUCH-HERZOG mass spectrograph and a high frequency spark ion source. The various spectra differ from each other only by their different ion acceleration potentials. At high values of the acceleration potential, the molybdenum lines appear very strong in intensity, while arsenic can hardly be seen. At lower acceleration potentials, applied to produce the spectra in the lower part of the figure, the arsenic lines become very intense, while the molybdenum lines almost disappear. A variation of spark voltage

and electrode gap width causes similar effects (62, 63).

b. The Disjunctive Direct Current Spark, or Vacuum Vibrator

The above mentioned difficulties in quantitative solid ^{sample} ~~source~~ analysis introduced by the high frequency spark can be circumvented by using the disjunctive spark in vacuum. The disjunctive spark or vacuum vibrator was tested in 1935 by DEMPSTER as a possible tool for ion production from solids, but was rejected by him in favour of the radio-frequency spark (65). We have applied a d.c.-voltage to the electrodes in vacuum (66). A small solenoid, connected in series with the spark circuit, is mounted in one of the electrode supports. This solenoid produces disjunctive sparks between the electrodes, at a repetition rate of some 500 per s. The electrode connected with the solenoid is forced to remake contact with the other electrode after interruption of the current by a compression spring. The ions produced in the spark show only a very small energy spread. VENKATASUBRAMANIAN and DUCKWORTH (67) have made some electromagnetic measurements with the vacuum vibrator and found the energy spread of the ions from the spark to lie between zero and some 40 eV. Ion currents measured at the monitor prior to the magnetic sector field of the mass spectrograph are considerably higher than when using the high frequency spark (66). The intensity ratios of different ionic species are not noticeably influenced by a variation of the acceleration potential. Furthermore, the cost of the equipment is much lower than with the radio frequency spark. A small power supply capable of supplying some 10 A at 12 V dc served as voltage source for the spark current. Experience has further shown that, in general, it is possible to obtain a considerably higher resolution with the disjunctive spark than with the radio-frequency spark on the same apparatus. In addition, by suitably choosing excitation conditions, certain ion species, for example the multiply charged ions or the molecular ions, may be arbitrarily produced or suppressed. In this manner the mass spectra may be influenced in the desired manner (68). Fig. 15 shows, as an example, the separated lines of magnesium, aluminum and silicon in an iron alloy, which, when using the radio-frequency spark, we were never able to separate from the doubly charged iron ions.

References:

- 1) A.J. Ahearn, Conf. on Mass Spectrometry, San Francisco 1963, paper No. 42
- 2) J.H. Beynon, Advances in Mass Spectrometry I, p. 328, Pergamon Press 1959
- 3) E.G. Carlson, M.L. Andre, M.H. O-Neal, Advances in Mass Spectrometry II, p. 377, Pergamon Press 1963
- 4) K. Biemann, Conf. Mass Spectr. 1963, San Francisco 1963, Paper No. 43
- 5) K. Ogata and H. Matsuda, Nuclear Masses and Their Determination, p. 202, Pergamon Press, London 1957
- 6) J.A. Hipple, H. Sommer, H.A. Thomas, Phys. Rev. 76, 1877 (1949); 78, 332 (1950); 82, 697 (1951)
- 7) L.G. Smith, Rev. Sci. Instr. 22, 115 (1951); Proc. Conf. Nucl. Masses, p. 418, Toronto Press 1960
- 8) R. Köhler, W. Paul, K. Schmidt, U.v. Zahn, Proc. Conf. Nucl. Masses, p. 507, Toronto Press 1960.
- 9) J.T. Kerr, G.R. Bainbridge, J.W. Dewdney, H.E. Duckworth, Advances in Mass Spectrometry I, p.1, Pergamon Press, 1959
- 10) G.G. Wanless, G.A. Glock, Mass Spectrometry Conference 1962, New Orleans, Paper No. 47
- 11) C.E. Berry, Mass Spectroscopy in Physics Research, Nat. Bur. Standards (US) Circular 522, p. 99 Washington DC 1953
- 12) J.H. Beynon, S. Clugh, W.A. Williams, J.Sci.Instr. 35, 164 (1958)
- 13) B.R.F. Kendall, Rev. Sci. Instr. 33, 30 (1962)
- 14) C.E. Berry, Conference on Mass Spectrometry, San Francisco 1963, Paper No. 40
- 15) W. Bartky, A.J. Dempster, Phys. Rev. 33, 1019 (1929)
- 16) H.G. Voorhies, C.F. Robinson, L.G. Hall, Advances in Mass Spectrometry I, P. 44, Pergamon Press London 1959

- 17) W. Bleakney, J.A. Hipple, Phys. Rev. 53, 521 (1938)
- 18a) C.F. Robinson, L.G. Hall, Rev. Sci. Instr. 27, 504 (1956)
- 18b) L.G. Hall, C.I. Hines, J.E. Slay, Advances in Mass Spectrometry I, p. 266, Pergamon Press, London 1959
- 19a) J.A. Hipple, H.A. Thomas, Phys. Rev. 75, 1616 (1949)
- 19b) J.A. Hipple, H. Sommer, Mass Spectroscopy in Physics Research, NBS Circular 522, Washington DC 1953, p. 183
- 20) J. Mattauch, R. Herzog, Z. Phys. 89, 786 (1934)
- 21) R. Herzog, V. Hauk, Z. Phys. 108, 609 (1938)
- 22) J. Mattauch, Erg. exakt. Naturwiss. 21, 170 (1940)
- 23) A.J. Dempster, Phys. Rev. 51, 67 (1937)
- 24) K.T. Bainbridge, E.V. Jordan, Phys. Rev. 50, 282 (1936)
- 25) A.O. Nier, T.R. Roberts, Phys. Rev. 81, 507 (1951)
E.G. Johnson, A.O. Nier, Phys. Rev. 91, 10 (1953)
- 26) R.D. Craig, G.E. Errock, Advances in Mass Spectrometry, Pergamon Press, London 1959, p. 66
- 27) C. Reuterswärd, Ark. Mat. Astr. Fys. Svenska. Vet. Akad. 30 A, No.7 (1943)
- 28) A.O. Nier, Nuclear Masses and Their Determination, Pergamon Press, London 1957, p. 185
- 29) T.L. Collins, K.T. Bainbridge, Nuclear Masses and their Determination, Pergamon Press, London 1957, p. 213
- 30) N.R. Isenor, R.C. Barber, H.E. Duckworth, Proc. Int. Conf. Nuclidic Masses, Univ. Toronto Press 1960, p. 439
- 31) C.M. Stevens, J. Terande, G. Lobell, J. Wolfe, N. Beyer, R. Lewis, Proc. Int. Conf. Nuclidic Masses, Univ. Toronto Press 1960, p. 403
- 32) H. Hintenberger, J. Mattauch, W. Müller-Warmuth, H. Voshage, H. Wende Proc. Int. Conf. Nuclidic Masses, Univ. Toronto Press 1960, p. 387
- 33) L.G. Smith, Proc. Int. Conf. Nuclidic Masses, Univ. Toronto Press 1960, p. 418
- 34) R.D. Craig, G.A. Errock, J.D. Waldron, Advances in Mass Spectrometry, Pergamon Press, London 1959, p. 136
- 35) C.F. Robinson, G.D. Perkins, N.W. Bell, Proc. 5th International Instr. and Measurements Conf. 1960, Stockholm, Vol.1, New York 1961, p.260
- 36) R. Herzog, ZS. Phys. 89, 447 (1934)
- 37) H. Hintenberger, L.A. König, Z. Naturforschg. 12a, 140, 773 (1957)
- 38) H. Hintenberger, L.A. König, Nucl. Instr. 2, 133, 250 (1958)
- 39) H. Hintenberger, L.A. König, Advances in Mass Spectrometry, Pergamon Press, London 1959, p. 16 and 85
- 40) H. Hintenberger, H. Wende, L.A. König, Z. Naturforschg. 10a, 344 (1955)
- 41) C.F. Robinson, Rev. Sci. Instr. 28, 777 (1957)
- 42) R. Herzog, Z. Naturforschg. 8a, 191 (1953)
- 43) H. Ewald, H. Liebl, Z. Naturforschg. 10a, 872 (1955); 12a, 28 (1957)
- 44) H.A. Tasman, A.H.J. Boerboom, Z. Naturforschg. 14a, 121 (1959)
- 45) M.M. Bretscher, Atomic Energy Comm. Documents, ORNL-2884, UC-34-Phys. Math. TID-4500 (1960)
- 46) H. Ewald, H. Liebl, G. Sauermann, Z. Naturforschg. 14a, 129 (1958)
- 47) R. Herzog, Mass Spectroscopy in Physics Research, Nat. Bur. Stand. (U.S.) Circular 522, p. 191 (1953)
- 48) H.W. Wachsmuth, H. Ewald, Z. Naturforschg. 18a, 389 (1963)
- 49) K.E. Haffast, Conference on Mass Spectrometry, San Francisco 1963, paper No. 76
- 50) C.R. McKinney, J.M. McCrea, S. Epstein, H.A. Allen, H.C. Urey, Rev. Sci. Instr. 21, 724 (1950)

- 51) W. Schütze, F. Bernhard, Z. Physik 145, 44 (1956)
- 52) F. Bernhard, K.H. Krebs, J. Rotter, Z. Physik, 161, 103 (1961)
- 53) N.R. Daly, Rev. Sci. Instr. 31, 264 (1960)
- 54) F.D.S. Butement, N.P. Finkelstein, J.Sci.Instr.37 329 (1960)
- 55) W. Rudloff Z. Naturforschg. 17a 414 (1962)
- 56) P. Jansen, H. Hintenberger, Phys. Verhandlungen, Jg. 1961, 88;
P. Jansen, (Doctoral thesis, Univ.Mainz, Mainz, Germany 1963)
- 57) H. Wagner (Doctoral thesis, Univ. Jena, Jena, Germany, 1960); Acta
IMEKO, Budapest, 1961, 24-DDR-120
- 58) E. Dörnenburg, H. Hintenberger, Z. Naturforschg. 14a, 765 (1959)
- 59) R.D. Graig, G.A. Errock, Advances in Mass Spectrometry, Pergamon
Press, London 1959, p. 66
- 60) L. Smith, C.C. Damm, Rev. Sci. Instr. 27, 638 (1956)
- 61) K.S. Quisenberry, T.T. Scolman, A.O. Nier, Phys. Rev. 102, 1071(1956)
- 62) J.Franzen, H. Hintenberger, Z. Naturforschg. 18a, 397 (1963)
- 63) J. Franzen, Z. Naturforschg. 18a, 410 (1963)
- 64) J.R. Woolston, R.E. Honig, Private Communication (Rev. Sci.Instr.
1963in press)
- 65) A.J. Dempster, Rev.Sci.Instr. 7, 46 (1936)
- 66) K.D. Schuy, H. Hintenberger, Z. Naturforschg. 18a, 95 (1963)
- 67) V.S. Venkatasubramanian, H.E. Duckworth, Can.J.Phys. 41, 234 (1963)
- 68) K.D. Schuy, H. Hintenberger, Z. Naturforschg. 18a, (1963) in press.
- 69) E. Burlefinger, H. Ewald, Z. Naturforschg. 16a, 430 (1961)

VACUUM SPARK MASS SPECTROSCOPY OF SOLIDS

by

A. J. Ahearn
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

The double focusing Mattauch geometry mass spectrograph with the vacuum spark positive ion source is being widely applied to the analysis of solids. This ion source is popular in spite of its disadvantages, because it is relatively simple, relatively free of contamination and because it exhibits little discrimination. Consequently, nearly all elements in nearly any matrix can be detected with nearly the same sensitivity.

One disadvantage of this spark source namely the wide energy spread of the ions necessitates a double focusing instrument. A second shortcoming - the erratic nature of the spark makes photographic detection highly desirable. Consequently, the Mattauch geometry double focusing is widely used in work with the vacuum spark.

I would first like to discuss methods and problems involved in the calibration and sensitivity determinations of this instrument. With the instrument that was designed and built at Bell Telephone Laboratories several years ago we used standard samples in the form of semiconductors that were doped with known impurities in the concentration range 10^{-4} to 10^{-7} . Figure 1 shows the calibration obtained with such a series of germanium samples doped with known concentrations of antimony. The internal standard that was used was a germanium diatomic ion. Consequently the mass spectrographic determination of the antimony concentration is in arbitrary units and cannot be reduced to absolute values because the relation between the diatomic ions and the monatomic ions of germanium is unknown in this experiment.

Data like that of Figure 1 demonstrated that the detection sensitivity was ≤ 100 p.p.b. The scatter in the data of Figure 1 indicates an uncertainty of a factor of about 2. Uncertainties at least as low as ± 20 per cent are now reported by Hull¹ and Owens and Giardino² and perhaps others.

Of particular significance is the fact that in Figure 1 the spectrographic determination varies linearly with the known concentration. Two deductions can be drawn from this observation. The antimony ion beam varies linearly with the concentration. The departure from the reciprocity law* is negligible in the concentration range 10^{-4} to 10^{-7} . These deductions must be slightly qualified since it would be possible for a nonlinearity in the ion beam to be accidentally compensated by a departure from reciprocity, but this is unlikely.

The data of Figure 1 contributes no information about reciprocity in the concentration range 1 to 10^{-4} .

Recent measurements on Ilford Q2 plates by Franzen and Hebeda³ have been made using 30 KV Argon Neon and Krypton ions in which the exposure time was varied by a factor of about 3300. They interpreted their data to mean that over this range the departure from reciprocity was negligible. However, it does not necessarily follow that this departure would be negligible when the exposure range is ten million to one hundred million.

Mass spectrographs are further calibrated using standard samples as follows. The density of a minor component mass line is matched to

*The reciprocity law states that the photographic response is determined only by the total amount of exposure independent of the exposure rate.

Table 1. Relative Sensitivity Coefficients for
Vacuum Spark Mass Spectroscopy of Solids

Reference Matrix	15 Alloys	4 S.S.	16 Al	5 Cu	16 Any	17 Bx	2 S.S.	2 III-V	10 Ga	18 Al
Element										
Li						6.5				
Be				.21		1.3				
B					1-3	6.5				
C					1-3					
Mg	2.9				> 3	1.3				
Al	1.1					.32				1
Si			1.8	.56	1-3					
P				.63	1-3					
S					> 3					
Cr	1.7	1.68		.98	1-3	1.0	1.9			
Ti			1.2		1-3	1.0				
Va					1-3		1.5			
Mn	2.5		2.0	1.12	1-3		3.3			
Fe	1.2	1.12	1.1	.84		1.3	1.12			
Ni	1.0	1.0	1.0	1.0	1.0	1.0	1.0			
Co				.56	1-3					
Cu	1.25		0.9			1.9	2.0		.6	1
Zn	2.3		6.1		> 3	2.2			.8	
Ga				1.03				~1	1.0	
As				1.20				~1		
Zr					1-3	.39				
Nb							.44			
Mo					1-3		.55			
Te				1.40						
Ag				2.28	1-3					
Ind								~1		
Sn				2.32	> 3					
Sb				1.76				~1		
Ta					1-3					
W					1-3					
Hg						3.2				
Pb				.94	> 3					
Bi				.61	1-3					

that of a major component. The ratio of the corresponding exposures multiplied by the appropriate isotope abundance factors gives the concentration. A mass analysis made in this way yields concentrations which at least for some elements disagree with the known composition of the standard. This discrepancy is interpreted to mean that the ion beams of these elements are not representative of the standard samples due to selective volatilization, differences in ionization efficiency and other factors.^{1,2} This discrepancy is corrected by introducing a relative sensitivity coefficient where

$$S = \frac{\text{mass spectroscopic concentration}}{\text{known concentration}}$$

The necessity for this correction factor S first appeared in the mass spectroscopic analysis work of Gorman Jones and Hipple⁴ using electrical detection.

Table 1 summarizes data on relative sensitivity coefficients S by different workers using both electrical and photographic recording and with different matrices. The coefficients are normalized to S = 1 for nickel where that element is among the constituents. The coefficients for chromium are quite consistent as are those for iron but in general the disagreement seems quite serious. Perhaps the disagreement indicates that the relative sensitivity coefficient is a function of the matrix.

In some of the data of Table 1 derived from photographic detection the factor S unwittingly may cover a departure from reciprocity as well as the now known effect of ion mass on photographic plate sensitivity.²

In the meantime the detection sensitivity of modern instruments has been pushed down into the parts per billion⁵ region by improving vacuum conditions so that less scattering and consequently lower background occurs. Again as in earlier work, trace impurity concentrations are calculated from the exposure ratio derived from density matching. This determination generally assumes that the relative sensitivity coefficient is one, that there is no mass effect on plate sensitivity and that the departure from reciprocity is negligible.

This general problem is further compounded by the possibility of small scale inhomogeneities in samples and the likelihood of photographic plate sensitivity inhomogeneities.

Because of these uncertainties, there is an urgent need for standard samples with concentrations down into the p.p.b. range and there is almost a complete lack of such standards.

To begin to meet this need, I would like to suggest two possibilities. Semiconductor suppliers are now able to supply silicon doped with selected impurities at concentrations down to about 10 p.p.b. in which the degree of compensation is not more than 5%. If such samples were sufficiently homogeneous they should prove most useful.

The second potential standard consists of a dilute solution of platinum in gold. The wide spread in relative abundance of the various platinum isotopes carries two advantages. The total platinum content can be high enough to be determined accurately by the spectrochemical technique but the individual isotopic concentrations extend into the p.p.b. region. For instance with a total content of 100 p.p.m. we have platinum isotopes at 34, 33, 25, 7, and 0.8 p.p.m. and one at 13 p.p.b. atomic.

We have made some preliminary studies on such alloys and I am indebted to the Associated Electrical Industries, Ltd. for graded series of mass spectra recorded on their MS7 mass spectrograph.

Table 2

Mass Spectrographic Detection of Impurities
Introduced into Deionized Water⁹

<u>Impurity</u>	<u>Isotope</u>	<u>Mass Line m/e</u>	<u>Density of Mass Line</u>	<u>Concentration, Atom Fraction</u>
Beryllium	9	9	0.44	1.1×10^{-9}
Chromium	53	53	0.12	1.0×10^{-9}
Copper	65	65	0.06	0.9×10^{-9}
Arsenic	75	75	0.33	1.0×10^{-9}
Silver	107	107	< 0.02	1.2×10^{-9}
Lead	207	103.5	0.04	5.8×10^{-9}
Sulfur	32	10.67	0.11	22.0×10^{-9}

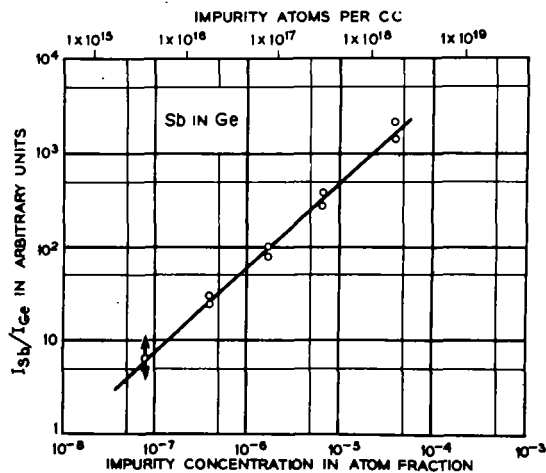


Fig. 1 Determination of Antimony in Germanium.¹⁹

Spectrochemical tests made in our laboratory by Mr. E. K. Jaycox on two alloys gave platinum contents of 0.11% and 0.019% respectively. The corresponding platinum 190 isotope concentrations were 130 and 23 p.p.b.

In both cases the platinum 190 isotope was recorded on the mass spectra. For the .019% platinum alloy the mass spectra yielded a platinum content of .008% (low by a factor of 2.4). This could mean that the departure from reciprocity over this range from 1 to 10^{-8} concentration is a factor of 2.4. The more likely explanation is that the relative sensitivity of gold is 2.4 times that of platinum and that the departure from reciprocity is negligible. More tests are needed to resolve this ambiguity and also to be more certain of the homogeneity of these alloys.

One of the advantages of this mass spectrographic technique derives from the simple spectrum that is obtained — simple by comparison with that of the spectrochemical technique. Nevertheless with this vacuum spark ion source, which produces many multiply charged ions, many elements have mass lines of the same nominal mass as other elements and masking occurs unless the resolving power is adequate.

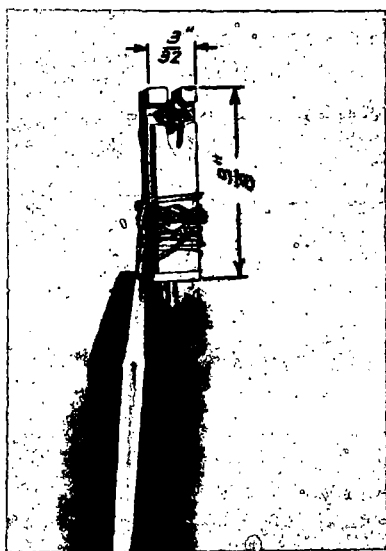
Now if you asked anyone working in this field what elements in what matrices he wanted to be able to study in the foreseeable future, I suspect he would answer that he wanted to be able to study almost any element in almost any matrix.

The mass differences that need to be resolved for this purpose have been compiled from the Sandia Corp. Monograph "Table of Atomic Masses."⁶ This table compiled with the spark source in mind, includes ion masses of most but not all isotopes up to 6 electronic charges and includes the singly-charged ions of most but not all isotopic polymers up to mass 210.

Figure 2 shows the percentage of the elements as a function of this $M/\Delta M$ value or to put it in a different way the graph shows the percentage of the elements resolved from their nearest neighbor as a function of the resolving power $M/\Delta M$ that is available. Here I did not insist on using the most abundant isotope. I arbitrarily sacrificed abundance by a factor of not more than 3; if by so doing a more remote nearest neighbor was obtained.

Figure 2 shows that with a resolving power $R = 1000$ only 10 per cent of the elements are resolved from their nearest neighbors. With $R = 2000$, 35 per cent are resolved from their nearest neighbor, etc. Now with today's modern equipment, resolutions in the 2000 to 3000 range are available. It is evident that the separation of additional elements requires large increases in resolving power. For instance with a resolution of 5000, only 52 per cent of the elements would be separated from their nearest neighbor.

In Figure 2 the elements and their nearest neighbors are listed in columns according to their mass difference $M/\Delta M$. For example with $R = 1000$ only hydrogen, lithium, beryllium, boron, dysprosium, erbium, holmium and thulium are resolved from their nearest neighbors indicated. Many of the cases calling for high resolving powers correspond to nearest neighbors in the form of oxides. One might argue that their inclusion is unrealistic but since we here are concerned with p.p.b. concentrations this presumes either a very low oxide concentration or a very high degree of dissociation in the spark. Figure 3 presents the curve of Figure 2 along with that obtained when these oxides are excluded from consideration. This exclusion does not markedly alter the general shape of the curve but it does indicate a higher percentage of resolved elements at any given resolving power.

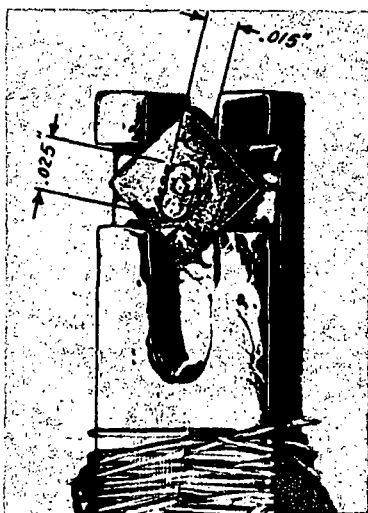


FRONT VIEW

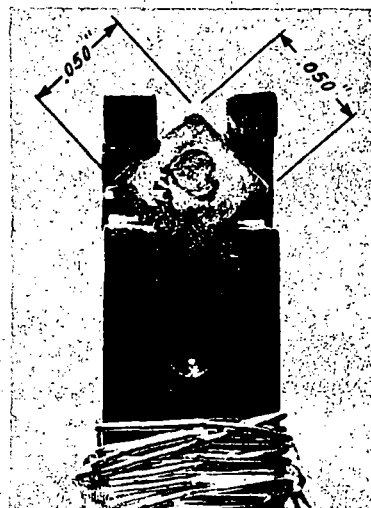


SIDE VIEW

Fig. 5 Silicon holder for vacuum spark to small sample.⁹



BEFORE



AFTER

Fig. 6 Photographs showing area explored by spark using pointed electrode.⁹

The decision to sacrifice abundance by not more than a factor of 3 where necessary is arbitrary but not unrealistic. Even this reduction by only 3 cannot be allowed in the 27 per cent of the elements that are monoisotopic. Consequently when higher resolving power is available, I'm sure it will be gratefully received by people working in this field.

This mass spectrographic technique is already being used for a wide variety of analytical problems. Many of these problems are reasonably straightforward while others require special techniques. I should like very briefly to outline some of the kinds of problems that have been studied and some of the special techniques that have been employed along with typical examples and results.

The analysis of most metals seems to be relatively straightforward. The sample requirement is modest - two rods about 1/2 inch long by 1/32 inch in diameter. The only requirement here is that the sample be long enough so that its holder doesn't contaminate the spark. Sometimes such ideal electrodes are shaped in a particular way at the spark end to minimize self-shielding and thus promote a satisfactory ion current from this source. The above specific dimensions while ideal are not necessary. Irregular shaped pieces with considerable variation in size can be used.

The problem of a metal powder has been handled by applying it as a wet⁷ paste to dry on a graphite electrode or by applying the dry powder to a rough⁸ carbon electrode. Probably an alternative way would be to compound a metal powder with pure graphite.⁷

In our own laboratory we first faced the problem of a liquid metal in the form of gallium which melts at 29.8°C. Liquid gallium readily wets a clean silicon surface and with the aid of supersonic agitation it also wets a germanium surface. By forming a spark between such gallium tipped electrodes the gallium spectrum, accomplished unfortunately by that of the base electrode, was obtained and some qualitative comparisons of gallium samples were made.⁹ At this E14 meeting a year ago Waldron and Wolstenholme¹⁰ described a cooling technique whereby the gallium was maintained in the solid state during the sparking thereby avoiding selective distillation of certain impurities such as zinc. This cooling technique might profitably be employed for the analysis of mercury, indium and other low melting point elements.

The analysis of semiconductors like silicon, germanium and most of the III-V compounds is as straightforward as metals in general. However, Owens and Giardino² found that a prolonged sparking of GaAs caused a loss of the more volatile arsenic from the area sparked which resulted in gallium rich spectra subsequently recorded.

In our own first attempts to analyze insulators we formed a spark between two short metal tubes that were completely filled with the insulator after the latter had been ground up to a powder. This method of testing insulators suffers from a number of disadvantages the most important of which is the erratic contribution to the spark and therefore to the mass spectrum on the part of the insulator.

The limitations inherent in this powder technique were largely circumvented by the setup shown in Figure 4. When the conductor electrode is brought near the insulator a spark is formed and the mass spectrum is a mixture of the conductor and the insulator. The conductor spectrum alone can of course be obtained by forming the spark between the two conductor electrodes. Insulators like steatite have been analyzed using the setup of Figure 4a whereas Figure 4b was used for quartz.

In the analysis of insulators James and Williams⁸ employed auxiliary conducting electrodes each of which had a piece of the insulator sample in contact with its sparked end. This method has been used for the analysis of synthetic silica and fused quartz.

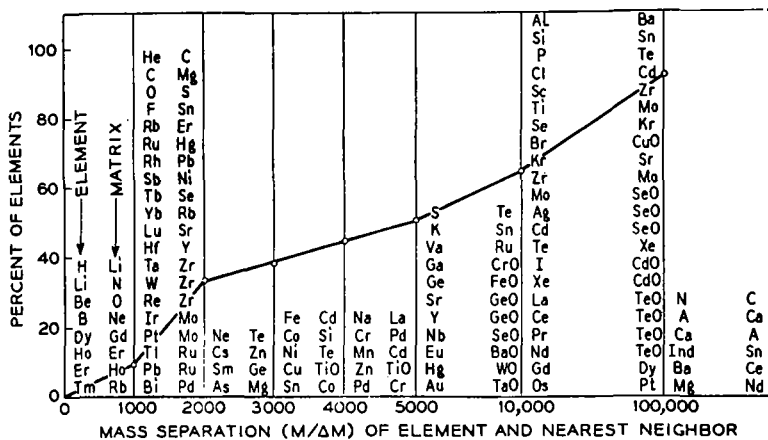


Fig. 2 Resolving power needed to separate elements from nearest neighbors in vacuum spark mass spectroscopy. Isotopes within 33 per cent of optimum abundance accepted.

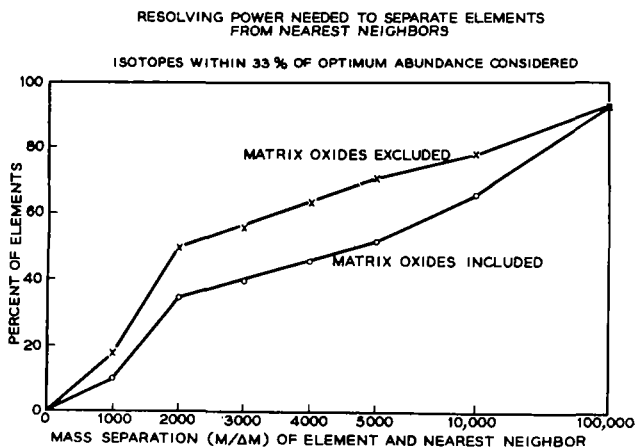


Fig. 3 Resolving power needed to separate elements from nearest neighbors in vacuum spark mass spectroscopy. Isotopes within 33 per cent of optimum abundance accepted.

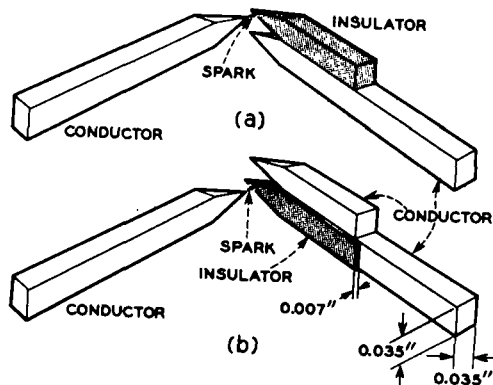


Fig. 4 Electrodes for vacuum spark positive ion source for mass spectrographic studies of insulators.⁹

Whether we are dealing with metals, semiconductors or insulators, we frequently are presented with cases in which the total sample available is so small that conventional methods of analysis even for major components become difficult or even impossible. The higher detection sensitivity available in this mass spectrographic technique fills an important gap in the analysis of such microsamples.

Microsamples might be roughly grouped into two categories - the first consisting of isolated particles of small mass such as tiny crystals, whiskers, filings, etc. while the second consists of singularities in large bodies such as inclusions or segregations at grain boundaries or other localized inhomogeneities. With the first category the problem is largely one of mounting the tiny sample in a manner so that the contribution to the spectrum from the holder is minimal and correctable. With the second category of microsample the problem is largely one of confining the spark to the localized area principally to avoid wastage of the spark - this amounts to minimizing the loss in sensitivity.

Small samples have been mounted in a number of different ways. Purified natural graphite crystals¹¹ weighing as little as 2 mg have been mounted in high purity indium electrodes. Equally small radar diodes have been mounted in split electrodes¹² of pure graphite.

Small crystals of diodes or other semiconductor devices in general cannot be analyzed satisfactorily "in situ" because the spark cannot be completely confined to the crystal. In our own case, this limitation was avoided by removing the minute crystal in question and mounting it in the holder shown in Figure 5. These photographs show a silicon crystal in a holder consisting of two pieces of high purity silicon mounted in a standard pin vise.

Donor and/or acceptor impurities detected in silicon crystals from a number of semiconductor devices included boron, arsenic, aluminum, gallium, antimony and indium in concentrations ranging from 1 to 1000 p.p.m. This sample holder is not limited to holding square or rectangular shaped samples. It could be used to hold a wide variety of irregularly shaped small samples.

Figure 6 illustrates the case where the spark needs to be limited to a small area. This again is a silicon crystal held in a silicon holder like that of Figure 5. In this particular case the area of interest was this detail right in the center of the crystal. By using a reasonably sharply pointed counter electrode, the spark was confined as shown in the photograph taken after the mass spectra were recorded. It is apparent that in this simple way, most of the spark can be confined to a diameter of about .025 inches.

It is possible to examine a much smaller region of a sample by this microprobe technique. This was demonstrated by Hickam and Sweeney.¹³ The sample was in the form of a copper plate with a 25 micron (1 mil) diameter niobium wire embedded therein and flush with the copper surface. When the sharply pointed gold counter electrode was positioned directly over the niobium wire and a few sparks of 20 microseconds duration were passed, 50 per cent of the ions in the mass spectrum recorded could be associated with the 25 micron diameter niobium wire. When the counter electrode was positioned about 50 microns away from the center of the wire, niobium was not detected in the recorded spectrum.

Such direct sparking to a specific predetermined area of this dimension is achieved in 50 per cent of the samples examined. Failure to achieve 100 per cent is believed to be due to mechanical limitations of alignment rather than to an electrical phenomenon.

In order to measure the quantity of material sputtered, Hickam and Sweeney¹³ used a setup in which the sample was in the form of a

10 mil diameter iron wire. After a spark was drawn to the surface of the wire and the mass spectrum recorded, the sparked wire was placed in an electron microscope and oriented with the electron beam perpendicular to the axis of the wire and to the axis of the counter electrode. The electron micrograph showed a very shallow crater and the deposit at its perimeter. Assuming the sparked area to be circular, this micrograph shows that its diameter is 25 microns and the thickness of the removed layer is less than 3 microns. This implies the detection of a 30Å film on a specified area of only $6 \times 10^{-6} \text{ cm}^{-2}$.

This vacuum spark microprobe technique for analyzing microsamples localized in solids should prove to be a most valuable supplement to the electron microprobe technique.

So far this discussion has been concerned with the detection of impurities that are more or less homogeneously distributed throughout the sample in question. But the mass spectra obtained with the vacuum spark distinguish between these so called bulk impurities and those that are present largely as contamination on the surface of the sample electrode. This differentiation arises since the spark first samples the electrode surface and subsequently it samples the interior of the electrode. Consequently a surface contamination is revealed by impurity mass lines that decrease in intensity in successively recorded spectra.

This identification of surface impurities when the contamination amounts to as little as 0.01 monolayer⁹ has been very fruitfully employed many times in our laboratory. For instance, tests demonstrated that deleterious p (acceptor) layers grown on vacuum heated silicon in a borosilicate glass vacuum system were due to boron¹⁴ from the borosilicate glass.

This surface contamination sensing ability of the vacuum spark has been employed to study trace impurities in liquids. This is done by exposing a suitable surface to the liquid in question in one of a number of ways.

Figure 7 illustrates one way in which impurities in water were detected. One drop of water was put on the tip of this shaped electrode. The drop is smaller than the optimum that the tip will support so it climbs as shown in (a). By applying an appropriate electric field it was pulled down to the tip as shown in (B). (C), (D), (E), and (F) show the remaining drop held in position by progressive increase in the voltage as the water evaporated. In this way the residue from the water is confined to the tip where it is available to the spark.

A deionized water sample was doped simultaneously with beryllium, sulfur, chromium, copper, arsenic, silver and lead. One drop of this multiply doped water was dried on an electrode as shown in Figure 7. All were detected in the mass spectrum subsequently recorded. Table 2 lists the concentration of a specific isotope of each of these doped impurities along with the density of the corresponding mass line used for detection of this impurity. The density of the doubly charged mass line of lead suggests that the singly charged ion would be detected at about 1×10^{-9} atom fraction if the latter were recorded. Similarly the density of the sulfur triply charged line suggests that if the singly charged line were resolved from the oxygen background line it too could be detected at about 1×10^{-9} atom fraction. Thus the data of Table 2 indicates that impurities in water can be detected at or below concentrations of 10^{-9} .

The single drop of water about 3 mm in diameter that was used contained about 10^{-11} gm of beryllium and 10^{-10} gm of silver. These small quantities needed for detection by this mass spectrographic technique compare favorably with the quantity of about 10^{-7} gm needed by spectrophotometric methods at optimum sensitivity.

This method of detecting impurities is not limited to the case of water but should be applicable to any liquid that evaporates more rapidly than do the impurities in solution in the liquid. The analysis of body fluids, the detection of nuclear fragmentation by-products in water, the identification of inorganic impurities in air by dissolving in a suitable solvent are examples that indicate the wide range of studies to which this technique should be applicable.

CONCLUSIONS

The Mattauch geometry double focusing mass spectrograph with the vacuum spark positive ion source is proving to be quite a versatile instrument for analytical studies. This technique complements that of emission spectroscopy by extending this general analytical capability to lower impurity concentrations.

Now that satisfactory techniques are at hand for testing almost any insulator, this instrument can test for most impurities in almost any solid of a wide variety of sizes and shapes.

The microsample and microprobe techniques now available open up yet another field where the high sensitivity of this mass spectrographic method can be profitably used.

Since the vacuum spark initially samples the surface of a solid, surface contaminants can be distinguished from bulk impurities. This surface sensing ability has added greatly to the usefulness of the instrument. Not only has it been used to study surface contamination per se, but this surface sensing ability can be employed to study liquids.

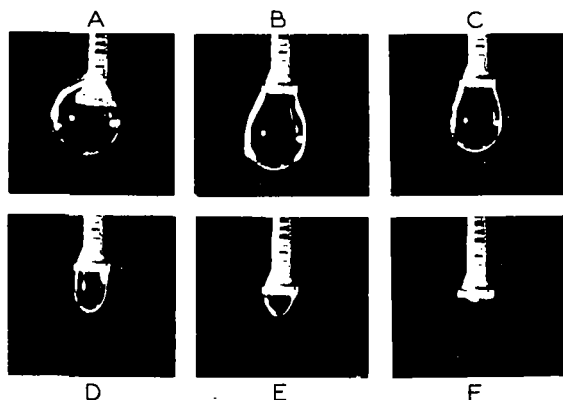


Fig. 7 Evaporation of water drop to electrode tip by electric field.⁹

REFERENCES

1. Hull, C. W., ASTM E14, Mass Spectrometry Conference, New Orleans, June 3-8, 1962.
2. Owens, E. B. and Giardino, N. A., Lincoln Laboratory, Massachusetts Institute of Technology Report No. J.A. 2091.
3. Franzen, J. and Hebeda, E., Z. Naturforsch, 17a, 476-8, June 1962.
4. Gorman, J. G., Jones, E. J. and Hipple, J. A., Anal. Chem. 23, 438, 1951.
5. Elliott, R. M., Craig, R. D. and Errock, G. A., Instruments and Measurements, Vol. 1 edited by Helge von Koch and Gregory Ljungberg, 1960, p. 271.
6. Compiled by R. Heath and edited by J. W. Guthrie.
7. Brown, R., Craig, R. D. and Elliott, R. M., Advances in Mass Spectrometry, Vol. 2 edited by R. M. Elliott, 1963, p. 141.
8. James, J. A. and Williams, J. L., Advances in Mass Spectrometry Vol. 1 edited by J. D. Waldron, 1959, p. 157.
9. Ahearn, A. J., Xth Colloquium Spectroscopicum Internationale edited by Ellis R. Lippincott and Marvin Margoshes, 1962, p. 769.
10. Waldron, J. D. and W. A. Wolstenholme, ASTM Committee E14 Mass Spectrometry Conference. New Orleans, June 3-8, 1962.
11. Fitzsimons, R. G., Fletcher, W., and Tushingham, R., ASTM Committee E14 Mass Spectrometry Conference, New Orleans, June 3-8, 1962.
12. Brown, R., Craig, R. D., James, J. A. and Wilson, C. M., Ultrapurification of Semiconductor Materials edited by M. S. Brooks and J. K. Kennedy, 1961.
13. Hickam, W. M. and Sweeney, G. G., Private communication.
14. Allen, F. G., Buck, T. M., and Law, J. T., J. Appl. Phys., 31, 979, 1960.
15. Chakravarty, B., Venkatasubramanian, V. S. and Duckworth, H. E., Advances in Mass Spectrometry, Vol. 2 edited by R. M. Elliott, 1963, p. 128.
16. Craig, R. D., Errock, G. A. and Waldron, J. D., Advances in Mass Spectrometry, Vol. 1 edited by J. D. Waldron, 1959, p. 136.
17. Jensen, A. V., Goshgarian, B. B. and Dane, N. E., Rocket Propulsion Laboratory Technical Documentary Report No. RTD-TDR-63-1.
18. Duke, J. F., Ultrapurification of Semiconductor Materials edited by M. S. Brooks and J. K. Kennedy, 1961, p. 294.
19. Hannay, N. B. and Ahearn, A. J., Anal. Chem., 26, 1056, 1954.

The Use of High-Resolution Mass Spectrography in the Determination of the Structure of Organic Molecules

K. Biemann

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Mass.

Of the presently commercially available high resolution mass spectrometers, the CEC 21-110 and the MS-9 of AEI, the former allows the simultaneous recording on a photographic plate of the ions of all mass-to-charge ratios formed on electron impact. The double focussing principle of Mattauch and Herzog used in this spectrometer permits accurate mass measurement, the principal usefulness of which in organic mass spectrometry had been clearly demonstrated by Beynon (1) using a high resolution mass spectrometer of different design (MS-8, the predecessor of the MS-9) which employs magnetic scan and electronic recording.

The term "mass spectrography" used in the title of this paper is the more correct one for the technique involving registering ions with the aid of a photographic emulsion as contrasted to successive electronic recording of the individual ion currents. We shall, however, continue using the term mass spectrometry also in this paper to simplify the terminology, as we use in our laboratory various kinds of spectrometers and the application discussed here is merely a special aspect of our work.

For the work in our laboratory, the high resolution mass spectrometer is used almost exclusively for measurement of the accurate mass of many ions in a spectrum for the purpose of either determining (or confirming) the elemental composition of a molecule or of fragments thereof, or both. The former is the necessary starting point of any structure determination, the latter confirms the elemental composition of the fragments or helps in the elucidation or corroboration of the fragmentation process which organic molecules undergo on electron impact.

For this perhaps somewhat specialized situation--as contrasted to the possibly more general one, namely the desire to record mass spectra with medium or low resolution and only occasional necessity of accurate mass measurement on selected peaks--the simultaneous and instantaneous recording of all the data, with the highest resolution the spectrometer is capable of, has many advantages:

(1) The recording of the primary data in permanent form (i.e. positions of lines on the plate) eliminates the necessity of making actual measurements while the substance is in the instrument, a factor of particular importance if the residence time of the sample in the ion source is short (e.g. if a compound of low vapor pressure or of low thermal stability is introduced directly into the ion source).

(2) It is not necessary to know before or while determining the spectrum, the mass of which ions is to be measured accurately. These decisions can be made at any later date as the actual mass measurement requires determination of the position of the line on the plate with reference to two calibration lines. For this purpose a comparator (a microscope equipped with horizontally moving stage, accurate to ± 1 micron), rather than the mass spectrometer itself, is used.

(3) Introduction (simultaneous with the sample) of a calibration compound giving lines distributed over the entire mass range provides reference lines suitable for measuring any desired mass. (Care has to be taken to select a compound of quite different elemental composition, e.g. a fluorocarbon for the work with compounds containing a reasonable number of hydrogen atoms but no fluorine).

The major disadvantage of the photographic plate as a means for recording mass spectra is the difficulty of determining accurately the abundance of the various species, because of the non-linear relationship of the intensity of the ion beam vs. the density of the resulting line, and the small dynamic range of the photographic emulsion. While reasonably good abundance data can be obtained upon

careful calibration with standards and making a series of exposures of different duration, rough abundance data obtainable with less elaborate calibration frequently suffice for our work. An alternative solution to this problem is found in electronically scanning the spectrum (after the necessary plate exposures have been made) with a scan speed and paper speed just sufficiently slow to resolve all multiplets of interest and thus permitting abundance measurements directly.

As most of the compounds we are interested in are solids, it was necessary to modify the all-glass inlet system available with the instrument for the introduction of solid samples either into the reservoir or directly into the ion source (for compounds of very low volatility). This was accomplished using two vacuum locks, one of which permitting insertion of the sample into a heated side arm of the inlet system while the other one enables us to place the sample directly into the high-vacuum line behind the ion source. The vacuum locks employ stainless steel ball valves and teflon gaskets and are similar to the one which we have been using for sometime with the CEC 21-103C spectrometer for placing the sample into the ion source. Details of this design, which would go beyond the purpose of this paper, can be found elsewhere (2). The spectra of all three compounds discussed below were obtained by introducing the sample directly into the ion source.

Before discussing any of the results we have obtained recently, it is necessary to indicate the accuracy and reliability of the mass measurement with our present equipment and technique. Table I summarizes the data obtained when 143 lines in the mass range from 43 to 230 were measured once and a spacing of reference lines 10-25 m.u. apart was chosen. Over 3/4 of all lines were found within ± 2 millimass units from the theoretical value while a few were off up to ± 5 millimass units and at present we are therefore considering all elemental compositions falling between ± 5 millimass units of the found value. Repetitive measurement of both the reference lines and our unknown line would improve the accuracy but it is felt that this is justified only if really necessary (i.e. for the molecular ion of a new compound). As the distance of a line from the position of mass zero is proportional to the square root of mass the calculation of the accurate mass of an ion giving rise to a particular mass is, in principle, simple and straightforward and can be done on a desk calculator. Because of the great number of data obtained with each spectrum, we prefer the use of a computer to convert line positions into masses. In principle it is possible to use a direct relationship of distance vs. mass over a narrow range (1% of mass) which simplifies the calculations but requires, on the other hand, the choice of a specific--rather than a general--reference compound in most cases and is thus in contrast to our aim namely to devise a general procedure equally applicable to a wide variety of substances.

Table I

149 lines between 43 and 230

$\bar{X} = 1.6$ $\sigma = 1.34$

81 deviate 0 - 1 mmu

32 -" - 1 - 2 mmu

20 -" - 2 - 3 mmu

13 -" - 3 - 4 mmu

3 -" - 4 - 5 mmu

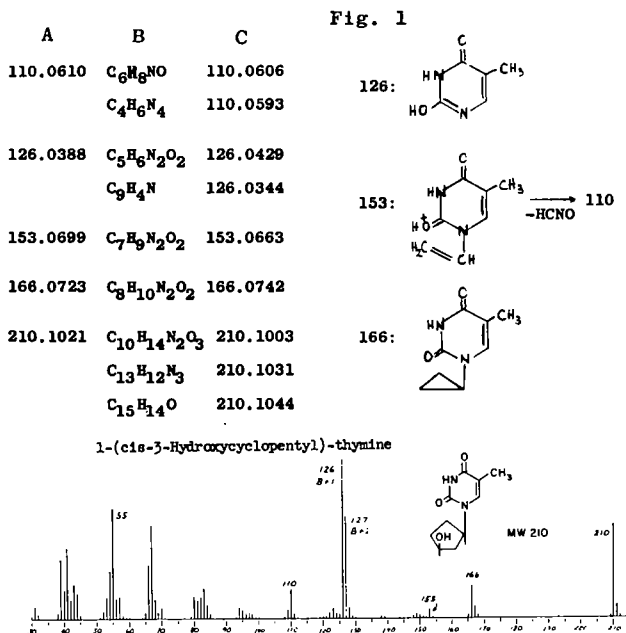
While these data have some bearing on the accuracy of the mass measurement, they do not indicate the resolution of the instrument as these two characteristics are only indirectly related. As long as there is no interference with adjacent ion beams, the accuracy of the mass

measurement is not greatly influenced by changes in resolving power, as long as the center of the ion beam (peak or line) can be accurately located. Incompletely resolved multiplets make this difficult and it is here where the resolving power becomes important. Presently we have obtained clearly distinguishable lines for ions differing 12.5 m.m.u. at mass 182 ($C_{12}H_{10}N_2$ and $C_{13}H_{12}N$) corresponding to a mass difference of 1 part in 14,600. When recording electronically a resolution of 1 part in 10,000 (10% valley) has been obtained with a collector slit 0.3 mil wide. We are presently using a detector system that contains both the photographic plate and a slit with electron-multiplier, a combination important for the successful use of the photographic plate as the multiplier facilitates tuning the instrument to optimum performance before taking an exposure on the plate.

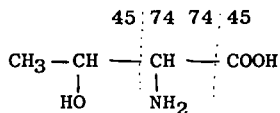
A few specific examples shall now be discussed as an illustration of the kind of investigations we are presently pursuing in our laboratory and of the situations in which high resolution mass spectrometry yields information beyond that obtained with "low resolution" (unit mass) spectra as well as cases in which accurate mass measurement does not provide any additional clue.

In an endeavour to confirm the fragmentation processes of nucleosides and related compounds the high resolution spectrum of 1-(cis-3-hydroxycyclopentyl)-thymine (low resolution spectrum shown in Fig. 1) was taken and the mass of the ions at m/e 110, 126, 153, 166 and 210 was determined accurately. The values found (column A) correspond to the elemental compositions shown in column B (theoretical mass in column C) if a range of ± 5 m.m.u. is considered for reasons outlined earlier.

While there are three possible combinations of C,H,N and O for the species of mass 210, all but $C_{10}H_{14}N_2O_3$ are eliminated because all the fragments contain nitrogen and some (m/e 153 and 166) must contain oxygen. Such considerations aid in the selection of a unique empirical formula for the molecular ion, particularly as the number of possible combinations increases rapidly with increasing molecular weight and number of elements considered. On the basis of the accurate mass of the ions of m/e 110, 126, 153 and 166 the fragments shown on the right of Fig. 1 are proposed (2) in agreement with earlier data (3).



The interpretation of the mass spectrum of the amino acid threonine (I) is complicated by the fact that some of the rather prominent peaks (m/e 45, 57 and 74) in its low-resolution spectrum can arise in at least two different ways (as indicated in I) which cannot be distinguished by deuterium labeling, so useful in most other cases, because the number of labile hydrogen atoms are the same for each one of the alternatives (2). The peak at mass 57 can arise in principle both from m/e 74 (loss of NH₃) or from m/e 75 (loss of H₂O). The high resolution spectrum indicated that all the expected fragments are formed.



I
threonine

Mass 45 found to be COOH and CH₃CHOH

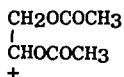
Mass 57 found to be C₂H₃ON, CH₃-C=CH and CH₃-CH=CH
 $\begin{array}{ccc} \text{OH} & & \text{NH}_2 \end{array}$

Mass 74 found to be CH₃CH(OH)CHNH₂ and CH(NH₂)COOH

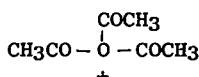
Mass 75 found to be H₂N-CH=C(OH)₂

In addition, the peak at m/e 57 turned out to be a triplet, the third species (C₃H₇N) being due to loss of H₂O and CO₂ from threonine.

The above example should by no means imply that high resolution spectra will eliminate the need of isotope-labeling. To the contrary, there are many instances in which the opposite is true. The spectra of polyacetates of carbohydrates exhibit, for example, an intense peak at m/e 145 which could in principle be fragment II, but its appearance at m/e 154 in the corresponding trideuteroacetates eliminated this



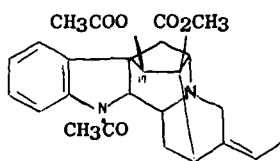
II



III

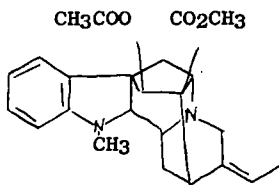
possibility in favor of III (4). Both species are isomeric (C₆H₉O₄) and can thus not be distinguished by even the most accurate mass measurement. It should not be overlooked that this is a frequent problem in the interpretation of mass spectra.

Finally, an example from our work on the structure of alkaloids may be cited, which illustrates the additional information obtained from high resolution spectra. The structure of quebrachidine was deduced (5) by comparison of the low resolution mass spectrum of its diacetate (IV) with the spectrum of vincamedine (V), an alkaloid of known structure (6). Determination of the accurate mass of the more important peaks (for the low resolution spectra see ref. 5) shows (Table II) that the elemental composition of these peaks reflects the structural difference between IV and V, namely a CH₃CO-group at the dihydroindole-nitrogen in IV vs. a CH₃-group in V. Thus the elemental composition of the species of mass 130, 143 and 144 from IV contain CH₂ less (H instead of CH₃; the acetyl group in these indole fragments is predominantly lost) than the 144, 157 and 158 ions of V. The species of mass 192, 222 and 264 are, in fact of identical composition, while the ions of mass 377 and 436 in IV contain CO more than the ions of mass 349 and 408 in V, reflecting the difference between COCH₃ (in IV) and CH₃ (in V). The ion of mass 185 in the spectrum of IV has no counterpart in V and its composition indicates that it is due to the fragment of mass 143 having retained the acetyl group. A detailed interpretation of the fragmentation process leading to these ions can be found elsewhere (5) as its discussion here would go beyond the scope of this paper.



Diacetylquebrachidine
IV

Table II



Vincamedine
V

130.0606 (-4.9) C ₉ H ₈ N	144.0802 (-1.1) C ₁₀ H ₁₀ N
143.0717 (-1.9) C ₁₀ H ₉ N	157.0902 (+0.9) C ₁₁ H ₁₁ N
144.0432 (-1.6) C ₉ H ₆ NO	158.0605 (+0.1) C ₁₀ H ₈ NO
144.0783 (-3.0) C ₁₀ H ₁₀ N	158.0946 (-2.4) C ₁₁ H ₁₂ N
185.0869 (+2.9) C ₁₂ H ₁₂ NO	
190.0870 (+0.3) C ₁₁ H ₁₂ NO ₂	190.0854 (-1.3) C ₁₁ H ₁₂ NO ₂
222.1095 (-3.3) C ₁₂ H ₁₆ NO ₃	222.1149 (+2.1) C ₁₂ H ₁₆ NO ₃
264.1241 (+0.8) C ₁₄ H ₁₈ NO ₄	264.1233 (0.0) C ₁₄ H ₁₈ NO ₄
377.1892 (-3.4) C ₂₃ H ₂₅ N ₂ O ₃	349.1917 (-0.9) C ₂₂ H ₂₅ N ₂ O ₂
436.2023 (+3.3) C ₂₅ H ₂₈ N ₂ O ₅	408.2041 (-2.7) C ₂₄ H ₂₈ N ₂ O ₄

It is worth pointing out the doublet at m/e 144 in IV and the corresponding one at m/e 158 in V. Their elemental compositions require the presence of both two carbon atoms as well as one carbon atom plus one oxygen atom attached to the dihydro indole moiety. This doublet is thus indicative of compounds oxygenated at C-17 of this carbon skeleton.

The few examples outlined above illustrate the utility of high resolution mass spectrometry in the interpretation of the spectra of natural products and related compounds. Because of the complexity of the spectra and their interpretation, which frequently requires some time, and the number of ions formed from large molecules, the permanent record of the primary data stored on the photographic plate makes high resolution mass "spectrography" an attractive technique from the practical point of view.

I should like to thank my associates, particularly Dr. P. Bommer, Mr. D. Desiderio, Dr. J. A. McCloskey and Dr. W. McMurray for their collaboration in many phases of the work discussed in this paper.

References

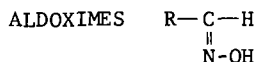
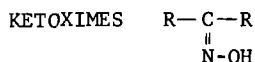
- (1) J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry", Elsevier Publishing Company, Amsterdam, 1960 and references cited therein.
- (2) J. A. McCloskey, Ph.D. Thesis, M.I.T., 1963.
- (3) K. Biemann and J. A. McCloskey, J. Am. Chem. Soc., 84, 2005 (1962).
- (4) K. Biemann, D. C. DeJongh and H. K. Schnoes, J. Am. Chem. Soc., 85, 1763 (1963).
- (5) M. Gorman, A. L. Burlingame and K. Biemann, Tetrahedron Letters, No. 1, 39 (1962) and a forthcoming paper.
- (6) M.-M. Janot, J. Le Men, J. Gosset and J. Levy, Bull. Soc. Chir. (France), 1962, 1079.

MASS SPECTROMETRY OF OXIMES

By H. R. Harless

Research and Development Department
Union Carbide Chemicals Company
South Charleston, West Virginia

A study of the mass spectra of oximes involving five ketoximes and four aldoximes presents a number of interesting aspects which will be discussed here today. The general formula for these oximes and the specific compounds studied are presented in the first slide.



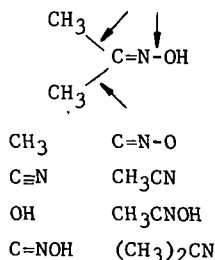
Acetoxime
Methyl Ethyl Ketoxime
Methyl Isopropyl Ketoxime
Methyl Sec-Butyl Ketoxime
Methyl Neo-Pentyl Ketoxime

N-Butyraldoxime
Iso-Butyraldoxime
2,2-Dimethyl-4-pentenaldoxime
Trichloroacetaldoxime

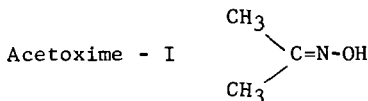
These nine compounds have exhibited some unusual ionization modes which should be of interest to mass spectroscopists as well as advocates of other disciplines. Some simple dissociations and a remarkable array of reformations and electronic stabilizations have been observed.

The spectra were obtained on a General Electric Mass Spectrometer operating at 70 electron volts, ionizing potential and 2,000 volts accelerating potential with variable magnetic scanning. Detailed spectra were recorded and relative intensities were calculated for all ions as small as 0.01% of the most intense peak. For spectrum-structure correlations abbreviated spectra have been used with abundant ions listed in order of intensity.

The lower molecular weight members of the series show a lesser degree of fragmentation and less rigorous atomic kinetics (to reach equilibrium) than do the more complex members, but even acetoxime shows severe rearrangement modes. Obvious bond ruptures are suggested by arrows, on slide two, for acetoxime and some expected ion forms are listed.



The observed abundant ions of acetoxime are shown on slide three.

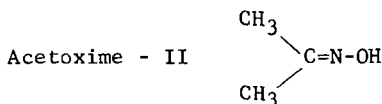


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	73	Molecule
2	58	$\text{CH}_3-\text{C}=\text{N}-\text{OH}$
3	42	$\text{C}=\text{NO}-$ or $\text{N}=\text{C}=\text{O}$
4	41	$\text{CH}_3\text{C}\equiv\text{N}$
5	39	C_3H_3

The first four most abundant ions are formed as normally predicted, or approach the anticipated form.

Ion number five (mass 39) is rather unusual, calling for severance of the carbon-to-nitrogen double bond and a stripping of atoms to a near-skeletal form.

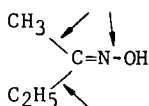
Slide four shows the next most abundant ions and four of these are states hardly predictable from a cursory examination of the acetoxime structural formula.



<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
6	54	$\text{CH}_2=\text{CH}-\text{CH}=\text{N}-$
7	40	C_3H_4 or $\text{C}_2\text{H}_2\text{N}$
8	56	$(\text{CH}_3)_2\text{C}=\text{N}-$
9	55	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{N}- \\ \diagup \\ \text{H}_\text{C} \\ \\ \text{H} \end{array}$
10	38	C_3H_2

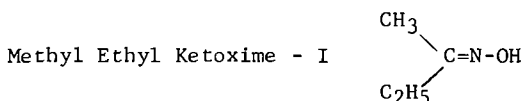
Little effort will be made to reconcile these ions with appropriate equilibrium states, either known forms or reasonable forms. The discussion that follows may help clarify some of the more obvious rearrangement modes.

Next let us study the fragmentations of methyl ethyl ketoxime, the second member of the series. Slide number five shows the typical structural formula and suggests obvious bond ruptures which would yield the listed ions and possibly others.



CH_3 CH_3CN
 C_2H_5 $\text{C}_2\text{H}_5\text{CN}$
 CN CH_3CNOH
 CNOH $\text{CH}_3\text{CNC}_2\text{H}_5$

This four-carbon ketoxime, slide number six, shows four of the six most abundant ions (numbers 1, 3, 4 and 6) to be of an unexpected degree of intensity.



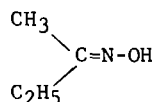
<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	42	$\cdot\text{C}\equiv\text{N}=\text{O}$
2	87	Molecule H
3	28	C_2H_4 or $-\text{C}=\text{NH}$
4	27	C_2H_3 or $\text{CH}\equiv\text{N}$
5	29	C_2H_5
6	41	C_3H_5 or $\text{CH}_3\text{C}\equiv\text{N}$
7	58	$\text{CH}_3\text{C}=\text{NOH}$

This is the first of three members of the series to show an extremely abundant $\text{C}\equiv\text{N}=\text{O}$ ion at mass 42. Valence reversion either occurs to form the mass 42 ion, or it may exist as the $\text{N}=\text{C}=\text{O}$ form, wherein valence characteristic are maintained and atomic rearrangements are brought about. The third largest peak, at mass 28, is somewhat unusual and no satisfactory arrangement for it has yet been found in oximes or where it is seen in other types of nitrogen compounds. The postulation of an imine radical, as shown on the slide (ion number three) is possibly the most likely explanation to-date, (N_2 can probably be discounted).

The number four peak is an easily imagined rearrangement since the HCN ion is often found in stabilizations of molecular fragments containing nitrogen. The number six peak is apparently a reversion to the form of acetonitrile and is seen in several oximes.

The eighth through the fourteenth largest peaks for this compound are shown on slide seven.

Methyl Ethyl Ketoxime - II

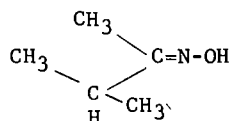


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
8	15	CH_3
9	55	$\text{C}_2\text{H}_5\text{C}\equiv\text{N}$
10	43	$-\text{C}=\text{N}-\text{OH}$
11	39	C_3H_3
12	26	$\text{C}\equiv\text{N}$ or C_2H_2
13	31	NOH
14	40	C_3H_4 or $-\text{CH}_2-\text{C}=\text{N}-$

Peak number nine is a form similar to peak six, a reversion to the nitrile. Peak number eleven, C_3H_3 , also present in acetoxime, as peak number 5, is rather unthinkable for such an abundant state until you consider the reactivities of propene, propenyl derivatives, and butadiene. In these a three carbon skeletal with varying numbers of protons form prominent ions, and C_3H_3 , mass 39, is one of the dominating figures.

Methyl isopropyl ketoxime, presents some anomalous characteristics but its spectrum does not show a great departure from the methyl ethyl compound. (slide eight please)

Methyl Isopropyl Ketoxime - I

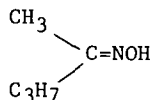


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	42	$-\text{C}\equiv\text{N}=\text{O}$
2	41	CH_3CN
3	73	$(\text{CH}_3)_2\text{C}=\text{NOH}$
4	43	$-\text{C}=\text{N}-\text{OH}$
5	27	HCN
6	39	C_3H_3
7	86	p-minus-15

Three of the seven most abundant ions are rearrangement forms, but are similar to those discussed for the previous compound. However, peak number three represents a reversion to acetoxime, a frequent rearrangement of oximes in which they display a tendency to form the lowest number of the series.

Slide number nine presents the eighth through the fourteenth most abundant ions.

Methyl Isopropyl Ketoxime - II

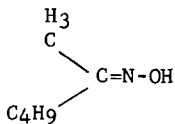


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
8	28	C_2H_4 or $-\text{CH}=\text{NH}$
9	84	Parent minus OH
10	58	$\text{CH}_3\text{C}=\text{NOH}$
11	40	C_3H_4
12	29	C_2H_5 or CH_2NH
13	15	CH_3
14	55	$\text{CH}_3\text{CHC}\equiv\text{N}$

The C_2H_5 ion (number 12 on the slide) can be formed by a rearrangement from the propyl group and indeed this may be sufficient explanation. But the intensity of this ion would appear large for an alkyl reformation and methylene imine is shown as a contribution at this mass position.

Methyl secondary butyl ketoxime (slide ten) offers greater opportunity for alkyl fragments to obscure probable atomic rearrangements, but even in this case only three of the most intense ions are a result of completely normal, or expected bond rupture.

Methyl sec-Butyl Ketoxime - I

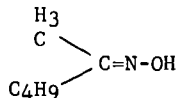


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	42	$-\text{C}\equiv\text{N}=\text{O}$
2	41	CH_3CN
3	87	Parent-minus-ethyl
4	29	C_2H_5
5	27	HCN
6	28	C_2H_4 or $-\text{CH}=\text{NH}$
7	39	C_3H_3
8	43	C_3H_7 or $-\overset{ }{\text{C}}=\text{NOH}$

The forms displayed here are not unusual when compared to the first three members of the series.

Slide eleven shows peaks number nine through sixteen.

Methyl sec-Butyl Ketoxime - II

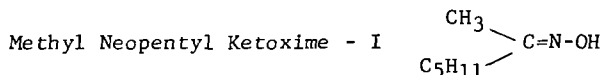


<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
9	56	C_4H_8
10	55	C_4H_7
11	45	$\text{CH}_2=\text{NOH}$
12	1000	Parent-minus 15

13	18	OH ₂
14	40	C ₃ H ₄ or -CH ₂ -C≡N
15	57	C ₄ H ₉
16	73	(CH ₃) ₂ C=NOH

Here we see the acetone oxime rearrangement is not as pronounced (peak number sixteen) as in methyl isopropyl ketoxime, where it was the third largest peak. A greater degree of proton shifting is required to saturate the secondary carbon of this butyl isomer.

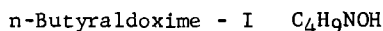
Methyl neopentyl ketoxime (slide twelve) shows eight of nine most abundant ions formed by other than simple bond rupture.



<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	57	C ₄ H ₉ or CH ₃ C=N-O-
2	73	(CH ₃) ₂ C=NOH
3	41	C ₃ H ₅ or CH ₃ CN
4	29	C ₂ H ₅ or CH ₂ =NH
5	42	C≡N=O
6	39	C ₃ H ₃
7	27	HCN

The acetoxime form (the number two ion) is again very abundant as available hydrogens diminish the required "kinetics-of-stabilization."

Aldoximes are no less susceptible to rearrangement. For the sake of brevity the first members of the series are not reported and n-butyl aldoxime is shown on slide 13.



<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	59	CH ₃ CH=NOH
2	41	CH ₃ CN
3	42	C≡N=O or C ₃ H ₆
4	72	P-15
5	27	HCN
6	29	C ₂ H ₅
7	28	C ₂ H ₄ or -CH=NH

Here is the first example of dominant stabilization to the simplest form of the species. The most abundant ion is of the acetaldoxime form. However, the cyano form is the second most abundant ion and third is the familiar cyanate radical. The C₃H₆ group may contribute to this mass 42 body but relegation of C₃H₇ (a more stable form) to the number nine position would hardly permit major contribution to mass 42 by the C₃H₅, propenyl group, plus a proton. Studies under higher resolution would, of course, differentiate the slight variation in the precise a.m.u. of these two groups.

The eighth through the fourteenth most intense ions of n-butyraldoxime are shown on slide 14.

n-Butyraldoxime - II C_4H_9NOH

<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
8	39	C_3H_3 or $-CHC\equiv N$
9	43	C_3H_7
10	46	$-CH_2NH-OH$
11	55	$CH_3CH_2-C\equiv N$
12	44	$CH=H-OH$
13	40	$CH_2-C\equiv N$
14	54	$CH_2=CH-CH=NH$

Four of these seven ions take interesting forms. Number eight is probably contributed to by a cyano arrangement. Number ten is best satisfied by a hydroxylamine rearrangement, eleven by a cyano form and 14 by an imine rearrangement.

Isobutyraldoxime, slide 15, ionizes somewhat differently from the normal isomer.

Iso-Butyraldoxime - I

<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	70	Parent minus OH
2	41	C_3H_5 or $CH_3C\equiv N$
3	42	C_3H_6 or $C\equiv N=O$
4	28	C_2H_4 or $-CH=NH$
5	72	Parent minus 15
6	43	C_3H_7
7	39	C_3H_3 or $-CHC\equiv N$
8	55	$C_2H_5C\equiv N$

The most abundant ion from the iso form, the parent minus hydroxyl at mass 70, was not seen in the spectrum of the normal isomer. The mass 59 ion, the acetaldoxime form, which was most intense for the normal isomer is only the sixteenth most abundant ion of isobutyraldoxime.

The beta-carbon of the iso form has a deficiency of protons, as compared with the normal isomer, making it more difficult to achieve the acetaldoxime state by shifting protons to the major fragment.

On slide 16 is seen the first part of the abbreviated spectrum of an olefinic aldoxime, 2,2-dimethyl-4-pentenalaldoxime.

2,2-Dimethyl-4-pentenalaldoxime - I

<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	41	C_3H_5
2	86	$(CH_3)_2-C=NOH$
3	39	C_3H_3 or $-CHC\equiv N$
4	42	$C\equiv N=O$
5	28	C_2H_4 or $-CH=NH$
6	27	HCN
7	68	$CH_2=CH-CH_2-C-CH_3$

One halogenated oxime has been studied and on slide 17 the first part of the spectrum of trichloroacetaldoxime is presented.

Trichloroacetaldoxime - I $\text{CCl}_3\text{C}=\text{N}-\text{OH}$

<u>Order of Intensity</u>	<u>Mass</u>	<u>Ion Form</u>
1	44	$-\text{CH}=\text{NOH}$
2	126	Parent minus 35
3	30	$\text{N}=\text{O}$
4	82	$-\text{CCl}_2$
5	47	$-\text{CCl}$
6	60	$\text{ClC}=\text{CH}$
7	29	$-\text{CHO}$

Ions number 3, 4, 5, 6, and 7 are quite unexpected, especially with such great intensity. They need considerable effort and study to reconcile their existence in such an abundant state.

Ion number four (the CCl_2 form) being so abundant, illustrates the ease of rupture of a single chlorine from the molecule. The ion CCl_3 is not formed in any abundance and the parent minus one chlorine is the second most intense peak. Ion five, the CCl state, and ion six, the C_2HCl state, then may be postulated by this mode of severe stripping of the nitrogen-oxygen central body.

In summation, ionic species of a series of oximes have been shown in some detail. Ketoximes and aldoximes exhibit severe rearrangement phenomena and acquire extreme stabilization forms after electron bombardment in the mass spectrometer. The chemical reactivity of these molecules has then been indicated by the large amount of fragmentation shown in their mass spectra. Certain typical rearrangements have been shown, such as the tendency to form abundant mass 39, C_3H_3 , and mass 45, CH_2NOH , ions. Valence reversion of nitrogen from the plus three state to N (V) state is a frequent occurrence. Perhaps the most important feature of these compounds are their tendency to form an ion representing the charged molecule of the lowest member of the family, acetoxime in the case of ketoximes and acetaldoxime in the case of the aldehyde derivatives. However, in spite of their severe fragmentation, this broad class of compounds are amenable to mass spectrometry and can be studied and analyzed readily by existing commercial equipment.

THE MASS SPECTRA OF DIPEPTIDES*

Gregor A. Junk and Harry J. Svec

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

The crucible source technique was used in this investigation of the mass spectra of dipeptides. A General Electric Analytical mass spectrometer was modified so that the solid samples could be placed directly into the ionization chamber. The modified source assembly is shown in Fig. 1. The details of the design and fabrication of this assembly will not be discussed. The ion chamber, trap, trap holder, filament, filament holders and the first shield plate were substituted for the original General Electric ionization chamber assembly. The collimating slits and alignment studs were not altered or changed in any manner.

The solid sample is pressed into a small glass crucible. The crucible is then lowered into the ion chamber and the chamber is capped. After the system is evacuated, the filament of the mass spectrometer is turned on. Radiation from the hot filament heats the ion chamber and the dipeptide sample vaporizes. Slots on the side of the chamber allow for passage of the ionizing electrons from the filament, through the chamber and onto the trap electrode.

The preferred fragmentation of a molecule-ion from an amino acid is shown on the left in Fig. 2. The amine fragment ($\text{RCH}=\text{N}^+\text{H}_2$) is readily formed by rupture of the bond which is β to the charged nitrogen. The ionization at the nitrogen position and the listed fragmentation have been established from earlier work with a series of amino acids and deuterated amino acids.¹ Based on this work, the expected dominant ionization and fragmentation of a dipeptide is shown on the right. Ionization should occur preferentially at the free amino nitrogen as shown. Fragmentation identical to that which occurs with the free amino acids is expected.

The observed spectra of a number of isomeric dipeptides are reported in Table I. Only selected peaks, that is, those due to the various possible amine fragments, are shown. The designations used are those recommended by the International Union for Pure and Applied Chemistry. In this system, gly-al α is glycyl-alanine, al α -gly is alanyl-glycine and so on. The amino acid which is listed first is that which has the free amino group and is commonly called the N-terminal amino acid. Isomeric dipeptides are in adjacent columns to show the difference in the spectra. Note that the base peak is at mass 30 whenever glycine is in the N-terminal position. When alanine is in this position the base peak shifts to mass 44. With proline the base peak is at 70, with valine at 72, with leucine at 86, and when phenylalanine is in the N-terminal position, the base peak is at mass 120. Thus, the base peak is characteristic of the amino acid which is in the N-terminal position. The mass spectra are quite unique and their value for qualitative identification of dipeptides has been predicted and is quite evident.²

The two most probable molecule-ions from dipeptides are shown at the top of Fig. 3. The possible fragments which can be formed by rupture of one of the bonds β to the charged nitrogen are listed. The bond designated by (a) is β to the charge on the free amino nitrogen. This bond (a) is also β to the charge on the imido nitrogen. The fragment (A) is formed when the charge is on the free amino nitrogen. The fragment (A') is formed by bond rupture when the charge is on the imido nitrogen. Rupture at (b) produces the fragment (B). Rupture at (c) the fragment (C) and so on.

The intensities of the ion currents due to each of these charged fragments from several dipeptides are given in Table II. Note that the amine fragment (A) occurs with a much higher frequency than do any of the other possible fragments due to β bond rupture. Thus, there is some experimental evidence that the

*Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Diagram illustrating the components of a vacuum furnace assembly, showing an exploded view of the parts:

- CAP
- CRUCIBLE
- ION CHAMBER
- TRAP
- TRAP HOLDER
- FILAMENT
- FILAMENT HOLDER
- SHIELD PLATE
- SPACERS
- DRAWING OUT PLATE
- ALIGNMENT STUDS
- GLASS INSULATORS

Fig. 4 - Ion chamber reactions.

$$\begin{array}{ccc}
 \text{AMINO ACIDS} & & \text{DIPEPTIDES} \\
 \begin{array}{c}
 \text{R} \\
 | \\
 \text{H}_2\text{N}-\text{CH}-\text{COOH} \\
 | \\
 \text{H}
 \end{array}
 & \xrightarrow{\quad} &
 \begin{array}{c}
 \text{R}_1 \\
 | \\
 \text{H}_2\text{N}-\text{CH}-\text{C}(=\text{O})-\text{NH}-\text{CH}-\text{COOH} \\
 | \quad | \\
 \text{H} \quad \text{R}_2
 \end{array}
 \end{array}$$

Fig. 2 - Ionization and fragmentation of amino acids and dipeptides.

$$\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-CH-COOH \\ | \\ H \end{array} \quad (I)$$

$$\begin{array}{c} R_2 \\ | \\ O \\ || \\ C-NH-C(=O)-COOH \\ | \\ H \end{array} \quad (II)$$

Pathway (A): $(I) + (II) \xrightarrow{a}$ Product (A): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Pathway (B): $(I) + (II) \xrightarrow{b}$ Product (B): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Pathway (C): $(I) + (II) \xrightarrow{c}$ Product (C): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Pathway (D): $(I) + (II) \xrightarrow{d}$ Product (D): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Pathway (E): $(I) + (II) \xrightarrow{e}$ Product (E): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Pathway (F): $(I) + (II) \xrightarrow{f}$ Product (F): $\begin{array}{c} R_1 \\ | \\ H_2N-C(=O)-NH-C(=O)-NH-C(=O)-COOH \\ | \\ H \end{array}$

Fig. 3 - Beta bond ruptures of dipeptides.

$$\begin{array}{c} \text{SOLID DIPEPTIDE} - d_4 \\ \xrightarrow[\text{from filament}]{\Delta} \\ \text{DIPEPTIDE} - d_4 \text{ VAPOR} \end{array} \quad \begin{array}{c} \text{CYCLO(DIPEPTIDE)} - d_2 + D_2 \text{ OI} \\ \xrightarrow{\Delta} \\ \text{CYCLO(DIPEPTIDE)} - d_2 \text{ VAPOR} \end{array}$$

$$\begin{array}{c} \text{R}_1 - \text{CH} \\ \vdots \\ \text{---} \text{C} = \text{O} \\ \vdots \\ \text{ND} - \text{CH} - \text{COOD} + 2\text{H} \\ \vdots \\ \text{R}_2 \end{array} \quad \begin{array}{c} \text{ND} \\ \vdots \\ \text{---} \text{C} - \text{R}_2 \\ \vdots \\ \text{ND} \end{array} \quad \begin{array}{c} \text{R}_2 \\ \vdots \\ \text{---} \text{C} = \text{O} \\ \vdots \\ \text{ND} - \text{CH} - \text{COOD} \\ \vdots \\ \text{R}_1 \end{array} + \text{DHN} = \text{CH} + \text{O} = \text{C} - \text{ND} - \text{C} = \text{O}$$

Fig. 4 - Ion chamber reactions.

ionization and fragmentation of dipeptides is similar to that which occurs with the free amino acids.

If one stops in the explanation of the mass spectra at this point, the interpretation is correct but very incomplete. Only those parts of the entire mass spectra which agree with our pre-conceived ideas concerning the ionization and fragmentation mechanisms have been shown. The results from this limited amount of data look good, but close inspection and analysis of the data given in Table II reveals that the processes which occur in the ion chamber are not as simple as proposed. The listed peaks are given in percent of total ionization. As stated above, the only peaks of significant intensity are caused by the amine fragment (A) and these same amine fragments are observed in the mass spectra of free amino acids. However, the intensity from the amino acids is much higher (see bottom of Table II). For example, the amine fragments from the free amino acids gly, ala, pro, val, leu, and phe average 44% of the total ion yield¹. When these same amino acids are tied up in the N-terminal position of a dipeptide the average intensity of the amine fragments is only 21%. Because of this large difference one suspects that at least one other significant process is occurring in the ion chamber when dipeptides are being assayed. The actual ion chamber reactions were resolved after a consideration of the entire mass spectra of the dipeptides, the mass spectra of several deuterated dipeptides, and the spectra of two cyclo-dipeptides. The conclusion drawn from these studies is that the observed spectrum from a sample of pure dipeptide is the summation spectra of the pure dipeptide and a product of thermal cyclization. The processes which occur in the ion chamber once temperature and pressure equilibrium are established are summarized in Fig. 4.

A dipeptide, deuterated at the active sites, is used in the example. Some of the solid dipeptide cyclizes thermally. Both the dipeptide and the cyclo-dipeptide vaporize but the cyclic product has the higher vapor pressure. Molecule-ions are formed from both vapors. The dipeptide dissociates to produce large amounts of the di-deuterated amine fragment while the cyclo-dipeptide dissociates to produce the mono-deuterated amine fragment. Other fragmentations of the molecule-ions occur but the two listed processes are dominant.

All of the experiments which were used to prove the explanation of the mass spectra of dipeptides cannot be presented here. However, some of the more interesting and vital experiments can be discussed briefly. One of the initial puzzling observations was a large peak due to a monodeuterated amine fragment when the sample in the ion chamber was a dipeptide completely deuterated at the active sites. The mono-deuterated amine fragment cannot form from the dipeptide since the decomposition to form the amine fragment involves only one β bond rupture of the parent dipeptide ion and no significant hydrogen-deuterium mixing is expected in this low energy process. The mono-deuterated amine fragment can, however, form from the cyclo-dipeptide in the manner shown in the figure. This fragmentation mechanism has been proven by studying the mass spectra of two pure symmetrical cyclo-dipeptides--cyclo (gly-gly) and cyclo (ala-ala).

The spectra of these samples are given in Fig. 5. Note that the base peak in each spectrum occurs at the mass of the amine fragment; at mass 30 from cyclo(gly-gly) and at mass 44 from cyclo (ala-ala). This observation proves that the amine fragments are readily formed from cyclo (dipeptides). The mechanism proposed in Fig. 4 for the formation of the mono-deuterated amine fragment was also proven. The mass spectrum of cyclo(gly-gly), deuterated

Table I. RELATIVE FRAGMENTATION PATTERNS OF DIPEPTIDES AT
THE MASSES UNIQUE FOR AMINO ACIDS

M/e	GLY-ALA	ALA-GLY	GLY-VAL	VAL-GLY	GLY-LEU	LEU-GLY	GLY-PRO	PRO-GLY
30	100	29	100	17	100	67	100	13
44	39	100	7	7	13	61	12	14
70	1	1	9	2	2	7	90	100
72	--	--	1	100	--	2	--	1
86	2	2	1	1	6	100	--	1
120	--	--	--	--	--	--	--	--

M/e	GLY-PHE	PHE-GLY	ALA-LEU	LEU-ALA	ALA-PRO	PRO-ALA	VAL-LEU	LEU-VAL	VAL-ALA
30	100	42	3	65	5	3	47	45	5
44	60	17	100	75	100	24	45	49	14
70	12	3	2	6	237	100	17	7	2
72	7	1	--	--	2	2	100	30	100
86	3	1	3	100	3	1	5	100	--
120	6	100	--	--	--	--	--	--	--

Table II. SELECTED PEAKS--% TOTAL IONIZATION

	GLY-ALA	ALA-GLY	GLY-VAL	VAL-GLY	GLY-LEU	LEU-GLY	GLY-PRO	PRO-GLY
A	21.7	26.9	28.3	35.9	32.3	15.2	6.8	15.8
A'	--	--	--	0.1	--	--	--	--
B	--	--	--	0.7	--	0.3	--	--
C+P	--	--	--	--	--	--	--	--
D	--	--	0.1	--	0.1	--	0.4	0.3
E	--	--	0.1	--	1.8	--	--	--

	GLY-PHE	PHE-GLY	ALA-LEU	LEU-ALA	ALA-PRO	PRO-ALA	VAL-LEU	LEU-VAL	VAL-ALA
A	6.8	8.3	51.8	13.8	6.4	28.1	6.6	9.4	42.3
A'	--	0.1	0.1	--	--	--	--	--	--
B	--	2.2	--	--	--	--	--	--	--
C+P	--	--	--	--	--	--	--	--	--
D	0.4	0.1	0.1	--	--	0.1	--	--	0.4
E	0.2	--	0.4	--	--	--	--	0.4	--

Average of Σ_A from all dipeptides is 21%

Weighted average of Σ_A from free amino acids is 44%

Table III. EXPERIMENTAL EVIDENCE OF CYCLIZATION

SAMPLE	Σ^a Cyclo (dipeptide)	$\frac{R_1CH = \overset{R_2}{N}HD^b}{R_1CH = ND_2}$	N-terminal $R_1CH = NH_2$	C-terminal ^c $R_2CH = NH_2$
Leu-ala	8	0.5	100	6
Ala-leu	8	--	100	3
Val-gly	12	0.8	100	5
Val-ala	13	--	100	12
Gly-leu	14	1.0	100	7
Ala-gly	15	1.3	100	28
Pro-ala	15	--	100	23
Leu-gly	15	--	100	7
Gly-ala	16	1.8	100	34
Gly-phe	19	--	100	6
Leu-val	19	--	100	30
Gly-val	21	2.3	100	9
Phe-gly	21	--	100	37
Pro-gly	22	--	100	9
Gly-pro	32	--	100	90
Ala-pro	44	--	100	237
Val-gly	48	5.9	100	5

a - % of total ionization

b - from deuterated dipeptide data

c - relative to a value of 100 for the N-terminal amine fragment

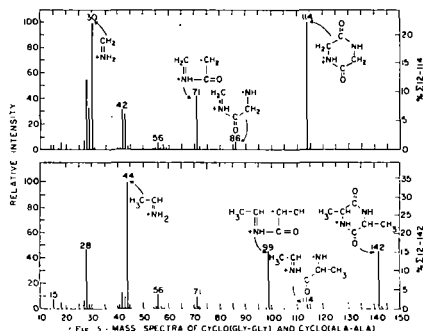


Fig. 5. MASS SPECTRA OF CYCLO(GLY-GLY) AND CYCLO(ALA-ALA)

at the nitrogen positions, has the base peak shifted to mass 31 and the mass spectrum of deuterated cyclo (ala-ala) has the base peak shifted to mass 45. Both base peaks, mass 31 and mass 45, are caused by mono-deuterated amine fragments.

The mass spectra of the symmetrical cyclo (dipeptides) can be used to predict qualitatively the spectra of unsymmetrical cyclo (dipeptides) such as those which are formed in the ion chamber when dipeptides of mixed amino acids are being assayed. Some of these predictions are:

1. Amine fragments which contain R_1 and R_2 will be observed since ionization can occur at either nitrogen positions.
2. The parent ion intensity will decrease as the molecular weight increases.
3. Peaks will be observed 28 and 43 mass units below that of the parent due to the elimination of neutral CO and CONH from the parent ion.
4. Peaks will be observed due to the further fragmentation of these ions.

Peaks were observed at these predicted passes for each dipeptide which was assayed. These peaks, which are characteristic of the cyclo (dipeptide) have been summed and the sums are reported in column 2 of Table III.

The comparison of the sums gives one an idea of the relative amount of cyclic product which is present in the vapor phase. The smaller sums at the top of the column indicate lesser amounts of cyclo (dipeptide) contamination. The larger sums, towards the bottom of the column indicate relatively larger amounts of contamination.

The ratio of the amount of mono-deuterated to di-deuterated amine fragments from several deuterated dipeptides is reported in column 3. This ratio also reflects the amount of cyclo (dipeptide) which is present in the vapor phase. Good correlation between the two sets of data exists. The observation of a large peak due to the R_2 fragments can be used as evidence for cyclization. However some preferred ionization and fragmentation occurs with the cyclo (dipeptides). For this reason comparative intensities of the R_1 and R_2 amine fragments shown in columns 4 and 5 from different dipeptides cannot be used to indicate the relative amounts of cyclic product.

In conclusion, this research can be very briefly summarized. The mass spectra of dipeptides can be fully explained when one realizes that cyclo-dipeptides are present in the vapor phase. All the large peaks are accounted for by ionization at one of the nitrogen positions of either the dipeptide or the cyclo-dipeptide and at least one bond rupture $\nearrow$ to the charged nitrogen. Ionization and fragmentation of both dipeptides and cyclo dipeptides are very similar to that which has been observed with amino acids.¹

REFERENCES

1. G. A. Junk and H. J. Svec, J. Am. Chem. Soc. 85, 839 (1963).
2. G. A. Junk and H. J. Svec, Anal. Biochem, submitted March 1963. Accepted April 1963.

MASS SPECTROMETRIC STUDIES OF NOBLE GAS COMPOUNDS(1)

Martin H. Studier and Eric N. Sloth

Chemistry Division, Argonne National Laboratory
Argonne, Illinois

Observations on the vapor phase of xenon compounds in a modified Bendix Time-of-Flight Mass Spectrometer(2,3) have demonstrated the existence of independent xenon oxyfluorides and have verified the existence of several stable xenon fluoride species (Table I).

Table I. Independent Gaseous Xenon Compounds

Species	Ref.
XeF_2	4,5,6,7
XeF_4	4,5,7
XeF_6	7,8
XeOF_4	5,7,9
XeO_2F_2	This Work

Numerous samples prepared by others(4,5,6,8,9) were examined for xenon compounds and impurities. Each sample was cooled in liquid nitrogen and evacuated with an auxiliary vacuum system. Small portions of gaseous species were introduced into the spectrometer as the sample was warmed and the vapors were recondensed in a cooled U-tube. This technique was used to identify independent species from mixtures as various fractions of the samples were sublimed.

Ions produced by electron bombardment of sample vapors were identified by their masses and the characteristic xenon isotopic abundance pattern (Plate 1)(10). Since fluorine is monoisotopic, this pattern is preserved in fluorides of xenon. The isotopes of xenon and mercury as well as hydrocarbon peaks (which occur at every mass from impurities in the spectrometer) were used to determine precise masses. The observed fragmentation patterns of the xenon fluorides were typical of those of other fluorides. Doubly charged species were also observed.

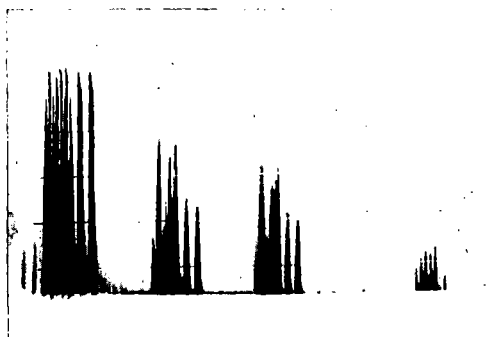
Plates 2, 3 and 4 are the mass spectra obtained from samples of xenon difluoride, xenon tetrafluoride and xenon hexafluoride respectively. As in the case of uranium hexafluoride, the ion of the parent molecule, XeF_6 , is difficult to observe. However, in Plate 5, where the peaks of the fragments are so large that their images are distorted, the ion XeF_6^+ is barely visible.

The formula of the oxyfluoride, XeOF_4 , was deduced from its mass and the complexity of the fragmentation pattern caused by loss of either oxygen or fluorine atoms as shown in Plates 6, 7 and 8. The compound XeOF_3 from a xenon tetrafluoride sample was first thought to be an independent species(5,7) because of some apparent change in the ratio $\text{XeOF}_3^+/\text{XeOF}_4^+$, and the absence of a detectable XeF_4^+ mass spectrum even though XeF_3^+ , XeF_2^+ , XeF^+ as well as XeOF_2^+ , XeOF^+ and XeO^+ were observed. More careful studies on samples of XeOF_4 prepared from xenon hexafluoride(9) show about 2% XeF_4^+ present and a constant $\text{XeOF}_3^+/\text{XeOF}_4^+$ ratio of about 100/1. In addition, negative ion spectra of the same sample(Plate 9) show XeF_4^- to be of greater intensity than XeOF_3^- indicating that a parent with four fluorine atoms exists. It is probable, therefore, that in samples of XeOF_4 prepared from XeF_6 little or no independent XeOF_3 exists.

Plate 10 illustrates the presence of XeO_2F_2 and its fragmentation products. This compound was prepared by distilling xenon hexafluoride into a nickel weighing can containing water. Subsequent evacuation,

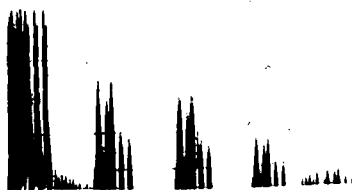


Plate 1. Mass Spectrum of Xenon
(Courtesy of J. Phys. Chem.)



Xe^+ XeF_1^+ XeF_2^+ Hg^+

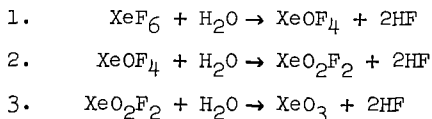
Plate 2. Mass Spectrum of Xenon Difluoride



Xe^+ XeF_1^+ XeF_2^+ XeF_3^+ Hg^+ | XeF_4^+

Plate 3. Mass Spectrum of Xenon Tetrafluoride
(Courtesy of J. Phys. Chem.)

heating and distillation of the products of the reaction into the spectrometer revealed XeO_2F_2 to have an independent existence. It appeared and persisted after warming above room temperature. No spectrum attributable to xenon trioxide was observed although copious evolution of xenon and oxygen suggested the presence of an oxide. Also, an explosion which ruptured the nickel can implied its presence (11,12,13). These observations suggest as a possible mode of formation the following reactions:



A number of charged species containing two atoms of xenon were observed at pressures as low as 5×10^{-6} mm of Hg (Table II).

Table II. The Observed Dinuclear Species From Samples of XeF_2 and XeF_4

<u>XeF_2</u>	<u>XeF_4</u>
Xe_2F_3^+	Xe_2F_7^+
Xe_2F_2^+	Xe_2F_5^+
Xe_2F^+	Xe_2F_3^+
Xe_2^+	

Variations of intensity with pressure demonstrated that these are formed in the spectrometer by ion-molecule association but the independent existence of one or more of these was not ruled out by the experiment. At least four additional dinuclear species were observed in samples containing XeOF_4 and XeF_6 but the exact formulas for these have not been determined. Plate 11 shows a spectrum of Xe_2F_3^+ compared with the calculated isotopic intensities for a molecule with two xenon atoms.

In preparation for the mass spectrometric analysis of radon compounds(5,14), one millicurie of $\text{Rn}(222)$ was analysed in the mass spectrometer(Plate 12) and found to give a mass peak roughly ten thousand times the limit of detection of the instrument.(15)

REFERENCES AND NOTES

1. Based on work performed under the auspices of the U. S. Atomic Energy Commission.
2. D. B. Harrington, "Encyclopedia of Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1960, pp. 628-647.
3. M. H. Studier, Presented at the Eleventh Annual Conference (May, 1963) of the A.S.T.M. Committee E-14 on Mass Spectrometry.
4. H. H. Claassen, H. Selig and J. G. Malm, J. Am. Chem. Soc., 84, 3593(1962).
5. C. L. Chernick, et al., Science 138, 136(1962).
6. J. L. Weeks, C. L. Chernick and M. S. Matheson, J. Am. Chem. Soc. 84, 4612(1962).
7. M. H. Studier and Eric N. Sloth, J. Phys. Chem. 67, 925(1963).
8. J. G. Malm, I. Sheft and C. L. Chernick, J. Am. Chem. Soc. 85, 110(1963).
9. C. L. Chernick, H. H. Claassen, J. G. Malm and P. L. Plurien, J. Am. Chem. Soc. (In Press).
10. Plates were obtained by photographing the mass pattern displayed on an oscilloscope.
11. D. F. Smith, J. Am. Chem. Soc. 85, 816(1963).
12. D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, J. Am. Chem. Soc. 85, 817(1963).
13. N. Bartlett and R. R. Rao, Science 139, 506(1963).

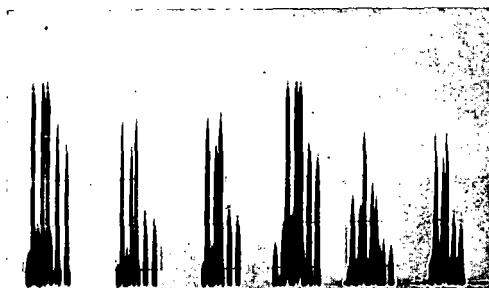


Plate 4. Fragmentation Pattern from
Xenon Hexafluoride

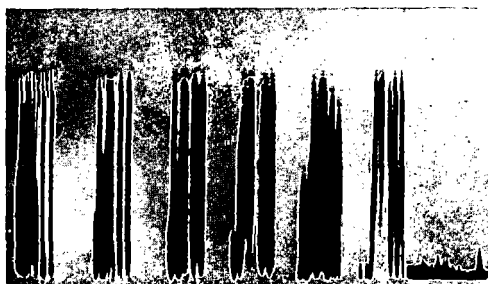


Plate 5. Mass Spectrum of Xenon Hexafluoride

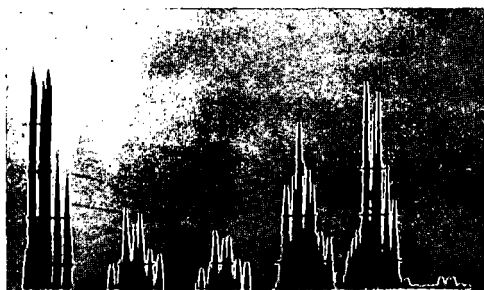
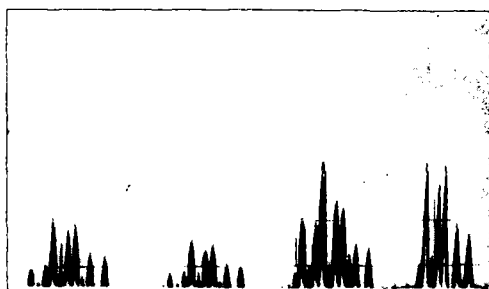


Plate 6. Mass Spectrum of XeOF_4

14. P. R. Fields, L. Stein and M. Zirin, J. Am. Chem. Soc. 84, 4164 (1962).
15. The authors gratefully acknowledge the technical assistance of Leon P. Moore.



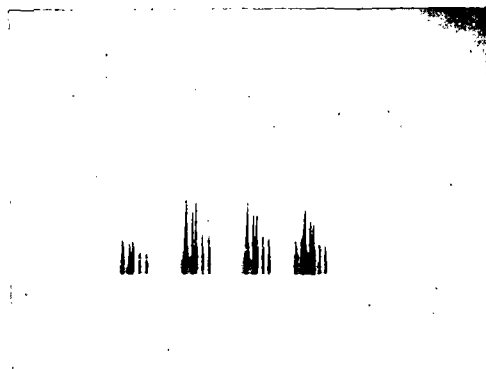
XeO^+ XeOF^+ XeOF_2^+ XeOF_3^+
 XeF^+ XeF_2^+ XeF_3^+

Plate 7. Fragmentation Pattern from XeOF_4



XeOF_2^+ XeF_3^+ XeOF_3^+

Plate 8. Fragmentation Pattern from XeOF_4
at XeF_3 Position



XeF^- XeF_2^- XeF_3^- XeOF_3^-
 XeF_4^-

Plate 9. Fragmentation Pattern from
 XeOF_4 ; Negative Ions

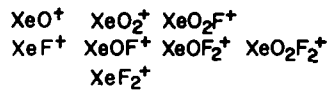
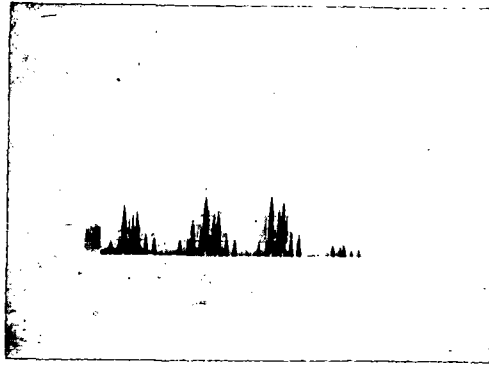


Plate 10. Mass Spectrum of XeO_2F_2

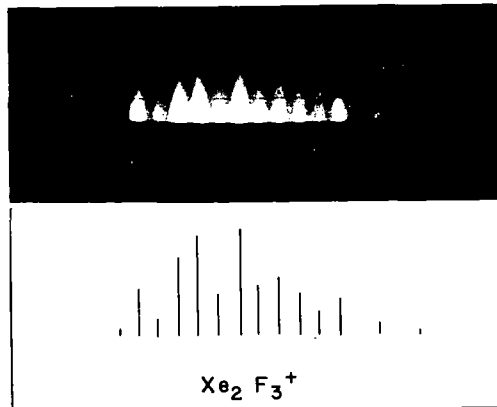


Plate 11. Calculated and Observed Intensities in Mass Spectrum of Xe_2F_3^+

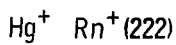
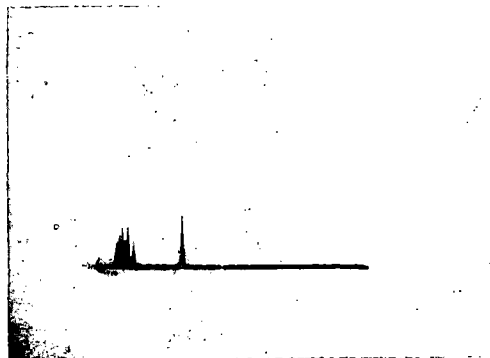


Plate 12. Mass Spectrum of Radon(222)

by

H. E. Lumpkin and Thomas Aczel
Humble Oil & Refining Company
Research and Development
Baytown, Texas

Abstract

A new set of low voltage calibration data is presented for aromatic hydrocarbons, including compound types from alkylbenzenes to chrysenes. Separate data are provided for alkylbenzenes and naphthalenes with different degrees of substitution, and for average coefficients for these compound types obtained by using determined and calculated average isomeric distribution values.

Ionization efficiency curves also have been obtained for a number of alkylbenzenes and naphthalenes in an effort to correlate ion current magnitudes at a given ionizing energy level with molecular structure. Preliminary data indicate that the degree of substitution on the aromatic ring affects the slope of the ionization efficiency curves.

Introduction

The low voltage method for identification and analysis of hydrogen deficient materials has continued to be one of the most powerful techniques in mass spectrometry since its inception in 1955⁴. A set of calibration data for a number of olefinic and aromatic compound types published in 1958⁵ is widely used in industrial research.

Revision and extension of the coefficients obtained originally is justified by the availability of a larger number of pure compounds and increased knowledge about the constitution of petroleum. The recent shift in emphasis to chemicals and chemical precursors makes a recalibration on a weight, rather than volume per cent basis desirable. Concurrently, the scope of low voltage analysis is being augmented by the advent of instruments featuring resolving powers of the order of 1 in 5000 and above and thus capable of differentiating among the parent peaks of more than seven compound types. These factors furnished the incentive for obtaining a new and consistent set of calibration coefficients for aromatic hydrocarbons, which is presented and discussed in the following paragraphs.

Correlations between molecular structures and low voltage ion current intensities have been sought and established for several classes of compounds by Crable and co-workers³. Their data have been corroborated and extended by the presentations of ionization efficiency curves for a number of alkylbenzenes. Discussion of the conclusions derived from these data constitutes the second part of this paper.

Calibration Coefficients for Aromatic Hydrocarbons

Calibration data were obtained on a 180° magnetic deflection (Consolidated Electrodynamics Corp. Model 21-103) mass spectrometer, adapted for low voltage work as reported previously⁶. Solid materials were introduced through the solids inlet system devised by Lumpkin and Taylor⁷. The availability of this system made calibration possible for four and five-ring condensed aromatics. The magnitude of the effort expended is illustrated in Table I, where the compounds used for calibration are summarized. These included API standards whenever available, and materials from various other commercial sources. Purity was at least 95 per cent in all cases and above 99 per cent for most compounds, as established by mass spectrometric techniques. Significant numbers of alkyl-substituted compounds were available only for benzenes and naphthalenes, but the data obtained in this and previous studies justified the extension of some of the results to other compound types.

Data on the reproducibility of the measurements are reported in Table II. These data were obtained for an ethylbenzene standard in the course of one week during which the ionization curves for 24 alkyl benzenes were determined. The coefficient of variation found was around three per cent at 7.6 volts, two per cent at 15.0 volts and 1.5 per cent at 70.0 volts. The reproducibility of the instrument is around one per cent, and thus accounts approximately, together with errors due to different amounts of sample introduced, for the deviation observed at 70.0 volts. The poorer reproducibility at 15.0 and 7.6 volts was caused by additional factors, including the instability of the low voltage circuitry and the inaccuracy of reading the voltmeter. Considering also the fact that the ionization curve is very steep in this region, causing large changes in the ion

Table I

Pure Compounds Used in Study

<u>Compound Type</u>	<u>Number of Compounds</u>
Alkylbenzenes	62
Indanes and Tetralins	9
Naphthalenes	22
Non-condensed 2-ring aromatics	5
Condensed 3-ring aromatics	9
Condensed 4-ring aromatics	10
Condensed 5-ring aromatics	1
Miscellaneous	<u>9</u>
Total	127

Table II

Reproducibility of Ethylbenzene Sensitivities

<u>Electron Volts</u>	<u>Divisions/Micromole</u>		
	<u>7.6 Volts</u>	<u>15.0 Volts</u>	<u>70.0 Volts</u>
Range for 21 runs	18.2-19.6	128.5-138.6	241.6-256.2
Average	18.73	132.53	247.6
Standard Deviation	0.55	2.85	3.66
Coefficient of Variation (%)	2.94	2.15	1.48

Table III

Isomeric Distribution of Alkylbenzenes in Petroleum

<u>Carbon Number</u>	<u>Substitution</u>						
	<u>Mono</u>	<u>Di</u>	<u>Tri</u>	<u>Tetra</u>	<u>Penta</u>	<u>Hexa</u>	<u>Average</u>
C ₇	100						1.0
C ₈	10	90					1.90
C ₉	8	31	61				2.53
C ₁₀	6	18	40	36			3.06
C ₁₁	4	13	33	28	22		3.51
C ₁₂	2	11	30	26	17	14	4.05

Table IV

Determination of the Average Degree of Substitution
in Alkylbenzenes by NMR

<u>Synthetic</u>	<u>Average Degree of Substitution</u>		<u>Deviation</u>	
	<u>Known</u>	<u>Determined</u>	<u>Absolute</u>	<u>Relative (%)</u>
A	3.06	3.03	0.03	0.1
B	2.29	2.38	0.11	4.8
C	1.72	1.87	0.15	<u>8.7</u>
			Average	4.5

current in response to relatively small changes in the applied electron energy, the standard deviation observed at lower voltages is considered excellent.

All the calibration coefficients reported or plotted in this work were reduced to a standard ratio with respect to a fixed value of ethylbenzene sensitivity. The latter was introduced into the mass spectrometer together with or immediately after each calibration run.

The data obtained on all the alkyl-substituted compounds confirmed the dependence of low voltage sensitivities on the degree of substitution, as pointed out by Crable and co-workers³. Additional effects due to the position of the substituents in alkylbenzenes and particularly in alkylnaphthalenes were also evident. The decrease in intensities with increasing molecular weight agreed with that established by Lumpkin⁶. Calibration data were obtained therefore by drawing smoothed curves obtained when individual compound sensitivities for each type were plotted versus reciprocal of the molecular weight. The sensitivities were expressed in divisions per milligram. On our instrument one division corresponds approximately to 2×10^{-14} amperes.

Values for individual compounds or carbon numbers can be easily determined from these curves. The curves for alkylbenzenes are given in Figure 1. Since a sufficient number of alkyl-substituted compounds were available in this case, separate curves could be drawn for the different degrees of substitution. Such a set of curves does improve greatly the accuracy of the low voltage method, if the degree of substitution is known from independent sources. For most problems encountered in petroleum chemistry, this parameter is, however, not known beforehand. One is therefore faced with the task of extrapolating or determining an average value which can be used for the selection of the appropriate calibration coefficients. The dotted line in Figure 1 represents such an average for alkylbenzenes derived from petroleum products. This curve was obtained by considering the average isomeric distribution for alkylbenzenes (Table III). Monosubstitution is obviously the only possibility for C_7 benzenes. Data obtained by Rossini and co-workers on Ponca City petroleum indicate that C_8 monoaromatics consist of about 90 per cent xylenes - disubstitution - and ten per cent ethylbenzene - monosubstitution. Experimental data of this nature are available also for C_9 and C_{10} alkylbenzenes and are tabulated in Table III. The regularity of the values thus obtained allowed their extrapolation, by means of curves connecting points representing a determinate type of substitution, to C_{11} and C_{12} alkylbenzenes. Average data have been obtained similarly for alkylnaphthalenes and were used in the construction of the correspondent calibration curve given in Figure 2.

This method led to a value of about 4.0 for the average degree of substitution in alkylbenzenes of molecular weight 162 and above. This number is however at variance with data obtained recently by J. M. Barnewall¹ who found that the mononuclear aromatic material (230-305°C) separated from the representative petroleum of the American Petroleum Institute Research Project 6 contained prevalently di- and tri-substituted compounds.

Nuclear magnetic resonance is capable of furnishing rapid and accurate determination of the per cent of unsubstituted hydrogens on an aromatic ring and therefore of the average degree of substitution². This is achieved by measuring the ratio between aromatic proton intensity and the intensities of protons located on carbon atoms α to the aromatic ring. Since the latter can be primary, secondary, or tertiary, an appropriate correction has to be introduced to take care of this parameter. Reliability of the NMR method is illustrated by the values reported in Table IV, obtained on synthetics of more than 20 components. It is suggested that this approach be used as a criterion in selecting calibration coefficients whenever justified by accuracy requirements. Calibration data for fractional values of alkylsubstitution can be easily derived from Figure 1.

Curves comprising a consistent set of calibration data for 13 aromatic compound types are given in Figures 2 and 3. The general shape of the curves for compound types with fewer data points was patterned after those obtained for alkylbenzenes and alkylnaphthalenes. It was reassuring to note that the newly obtained data differed only slightly from those published previously⁸.

Ionization Efficiency Curves

The relationship between ion current intensity at a given electron energy level and the energy necessary to ionize a molecule (ionization potential) has been investigated by several authors^{3,5}. It is generally assumed that knowledge of the ionization potential, if it can be determined with sufficient accuracy, will allow the determination of the ion current intensity at a given electron energy level, thus furnishing calibration coefficients for compounds which cannot be examined directly. It has, however, been noted in these laboratories, and also by Crable³ and Sharkey⁹, that isomeric methyl-naphthalenes and methyl-naphthols give considerably different ion current intensities at

Table V

Analytical Expressions for Ionizing Efficiency Curves
Between ca. 0.6 and ca. 2.0 e V Above the Ionization Potential

Compound	Ionization Potential (e Volts)	Standard Error of Approximation		Slopes (using linear fit)
		Linear Fit	Quadratic Fit	
Benzene	9.58	2.78	2.08	15.9
Toluene	9.20	4.94	1.68	21.8
Ethylbenzene	9.17	2.53	2.10	21.5
n-Propylbenzene	9.14	1.58	1.45	21.5
n-Butylbenzene	9.13	2.60	2.06	21.4
n-Pentylbenzene	9.12*	2.96	3.03	22.4
i-Propylbenzene	9.13	1.76	1.09	20.3
o-Xylene	8.97	4.02	1.65	26.0
m-Xylene	9.02	3.97	0.88	27.6
p-Xylene	8.88	4.65	1.53	25.5
1,3-Diethylbenzene	8.99	2.91	1.74	27.4
1,2,3-Trimethylbenzene	8.75	4.01	2.27	31.6
1,2,4,5-Tetramethylbenzene	8.48*	5.95	1.55	36.9

* Extrapolated values

Table VI

Low Voltage Sensitivities of Some Aromatic
Compounds at 10.1 and at 11.5 e Volts

Compound	Parent Ion Intensities Ratios 11.5/10.1 e Volts	Total Fragment Ion Intensities (per cent of parent peaks)	
		10.1 e Volts	11.5 e Volts
Benzene	3.48	1.31	0.39
Naphthalene	2.30	-	-
α -Methylnaphthalene	2.29	-	-
β -Methylnaphthalene	2.25	-	-
1,4-Dimethylnaphthalene	2.28	0.81	0.65
2,3,5-Trimethylnaphthalene	2.45	0.66	0.48
1,3,7-Trimethylnaphthalene	1.89	0.52	0.49
2-Methylfluorene	2.24	-	0.33
1-Methylphenanthrene	2.19	-	-
1-Methylpyrene	1.93	-	-
4-Methylpyrene	1.79	-	-
Perylene	1.90	-	-

the voltages generally used for low voltage work. Since the ionization potentials of α - and β -methyl naphthalenes are identical⁶, this difference must be correlated to the shape of the ionization efficiency curve, the knowledge of which should also be necessary for predicting low voltage calibration coefficients. It is interesting to note at this point that the higher sensitivity values observed for β -methyl naphthalene (and for other methyl naphthalenes substituted in analogous positions) can be correlated to molecular properties depending on the π electron distribution.

In order to investigate better this phenomenon, as well as the reasons for the dependence of the ion current intensities on the degree of substitution, ionization efficiency curves have been obtained for 24 alkylbenzenes and nine alkyl naphthalenes. Preliminary data indicate that the correlation found for alkylbenzenes is valid also for the alkyl naphthalenes. The following discussion is restricted however to the former type.

The ionization efficiency curves were obtained by determining the values of the ion currents at intervals of 0.5 volts between 17.5 and 12.5 volts and at intervals of 0.2 volts between 12.5 and 8.9 volts. Each measurement was repeated several times and a correction factor was introduced to compensate for sample pressure decrease during the experiment. The standard used was ethylbenzene, because the ion pump installed on the mass spectrometer could not handle noble gases. Reproducibility of the ethylbenzene sensitivities has been already discussed. The data obtained were expressed in micromoles per division.

The dependence of the shape of the ionization efficiency curves on degree of substitution is immediately evident from Figure 4. While the curves are similar for all the compounds with the same degree of substitution, there is essentially no overlap between the curves given by compounds possessing different numbers of alkyl substituents. The nature of the substituting group has little or no effect at all, except in the case of highly branched groups, such as tertiary butyl, which tend to flatten the curve sooner than in other compounds. This effect can be ascribed to the competitive processes leading to the formation of fragment ions, which are presumably more significant for these molecules.

The portion of the curve, which presents the highest interest for the purposes of this investigation, is the quasi-linear portion observed slightly above the ionization potential. Linearity of the curves was determined in this interval, that is, between ca. 0.6 and ca. 2.0 volts above the ionization potential, by the least squares method, using first and second order expressions. The limits chosen included the energy level at which low voltage analyses are usually made. Some standard errors of approximation between experimental and calculated data are reported in Table V. Although the quadratic fit appeared to be slightly more accurate in particular for the polysubstituted compounds, the deviations from the linear fit were still very small, proving the essentially linear character of the curves between the intervals studied. The ionization potentials used were those available in the literature⁶ from electron impact studies. When electron impact values were not available, they were estimated from values for lower molecular weight compounds or from values obtained by other methods. It was noted that, while ionization potentials obtained by different methods differ considerably, the average change from a given compound in a homologous series is nearly constant. Agreement of the values thus derived with those obtained in the course of this study was satisfactory.

Dependence of the slopes on the degree of alkyl substitution is also evident from the data reported in Figure 4. Quantitative data supporting this statement are reported in Table V, column 5, and Figure 5. The slopes were calculated on the linear portions of the ionization efficiency curves, in the same interval selected for the determination of linearity discussed above. It can be concluded from these data that these slopes are nearly identical for compounds possessing the same degree of alkyl-substitution but that they increase linearly as the number of alkyl-substituents on the ring increases (Figure 5).

Any prediction of low voltage coefficients from theoretical data must thus take into consideration both the ionization potential and the slope of the ionization efficiency curve. If these two parameters can be determined or extrapolated, a satisfactory prediction of ion currents at a given electron energy level can be made. In the course of this work, such predictions were made for n-hexyl and n-heptyl benzenes. The predicted values differed from the experimental values, obtained at a later time, by about seven per cent on the average. Considering the over-all reliability of low voltage measurements, the predicted values are considered acceptable. The constancy of the slope for compounds with the same degree of alkyl substitution, together with the asymptotic behavior of the ionization potential curve for homologous substances, will also result in the construction of theoretical low voltage calibration curves compatible with experimental data.

Table VII

Partial Spectra of 1,3,5-Triethylbenzene
Obtained at Various Ionizing Voltages and Currents

Ionizing Voltage, V	Ionizing Current (μ A)	Parent Peak Sensitivity (relative to that at 10.1 V, 11 μ A)	Fragment Peak Sensitivities (in per cent of parent peak sensitivity)									
			$\Sigma 105 + 119 + 133$	106	120	134	148	106	120	134	148	(Isotope corrected)
10.1 e/V	11	1.00	1.06	-	-	-	-	-	-	-	-	-
	35	1.63	1.12	-	-	-	-	-	-	-	-	-
	45	1.11	-	-	-	-	-	-	-	-	-	-
11.5 e/V	11	2.15	12.10	-	-	1.35	0.61	-	-	0.46	0.11	-
	35	5.23	5.64	-	-	0.66	0.36	-	-	0.24	0.15	-
	45	5.09	3.64	-	-	0.64	0.33	-	-	0.18	0.19	-
14.5 e/V	11	3.66	81.90	-	-	6.30	4.59	-	-	1.46	0.21	-
	35	11.45	69.11	-	-	5.49	3.72	-	-	1.30	0.18	-
	45	13.18	64.61	-	-	5.30	3.41	-	-	1.26	0.22	-
17.5 e/V	11	4.37	156.03	0.70	0.42	10.08	8.87	0.09	0.10	2.10	-	-
	35	13.93	142.90	0.62	0.34	9.40	8.25	0.08	0.07	1.87	0.33	-
	45	16.79	136.21	0.56	0.24	9.19	7.76	0.97	0.07	1.95	0.23	-
70.0 e/V	11	6.48	407.09	5.10	1.73	20.87	23.74	0.59	0.25	4.46	0.98	-

An application of the work discussed in the preceding paragraph lies in the recognition of the possibility of analytical work at slightly higher voltages than the limit of 10 e Volts adopted generally. At 10 e Volts the ionization process produces primarily aromatic and olefinic parent ions, and less intense ion currents are accepted in order to maintain a simple spectrum. At least for aromatic concentrates, the ion current intensity may be greatly enhanced by increasing slightly the electron voltage without affecting adversely the selectivity towards molecule ions.

The data reported in Tables VI and VII show that two to three fold increases can be achieved in this way accompanied by still negligible fragmentation processes. The most abundant fragment peaks are those at odd mass numbers and their interferences at parent peaks of lower molecular weight homologs can be further reduced by isotope correction. Simultaneous increase of ionizing currents leads to further increases in sensitivity as illustrated by the partial spectra of 1,3,5-triethylbenzene (Table VII) obtained at various ionizing voltages and currents. At about 11.5 e V and 35 μ A of ionizing current, the parent peak sensitivity for this compound is comparable to that obtained in normal high voltage work (70 e V, 11 μ A), while the fragmentation is still negligible.

The parent peak sensitivity values reported in column 3 of Table VII indicate that the ion current increases obtained by increasing the ionizing current approach linearity only at the higher voltage settings. This fact is attributed to the presence of space charges diminishing the collection efficiency. This difficulty might be obviated by operating at higher repeller voltages. In spite of these deviations from linearity, the reproducibility data obtained thus far on parent peak sensitivities are satisfactory. Analyses of synthetics of triethylbenzene in isoparaffins have shown that the former can be determined at an 0.04 per cent level with the accuracy of ± 10 per cent.

Another anomaly is the change in pattern caused by variations in ionizing currents. The diminution of the fragment peak sensitivities with respect to that of the parent peak is, however, an obvious advantage.

Acknowledgment

An expression of appreciation is due G. R. Taylor and J. L. Taylor for obtaining and tabulating the experimental data discussed in this article. The authors also wish to thank Dr. K. W. Bartz for obtaining and interpreting the nuclear magnetic resonance spectra.

Literature Cited

- ¹ Barnewall, J. M., Unpublished data on research sponsored by the American Petroleum Institute Research Project 6 at Carnegie Institute of Technology, Pittsburgh, Pa.
- ² Chamberlain, N. F., *Anal. Chem.*, 31, 56 (1959).
- ³ Crable, G. F., Kearns, G. L., and Norris, M. S., *Anal. Chem.*, 32, 13 (1960).
- ⁴ Field, F. H., Hastings, S. H., *Anal. Chem.*, 28, 1248 (1956).
- ⁵ Honig, R. E., *J. Chem. Phys.*, 16, 105 (1948).
- ⁶ Kiser, R. W., "Tables of Ionization Potentials", page 53 (U. S. Atomic Energy Commission, 1960).
- ⁷ Lumpkin, H. E. and Taylor, G. R., *Anal. Chem.*, 33, 476 (1961).
- ⁸ Lumpkin, H. E., *Anal. Chem.*, 30, 321 (1958).
- ⁹ Sharkey, A. G., Jr., et al, ASTM Committee E-14, New Orleans, May, 1958.

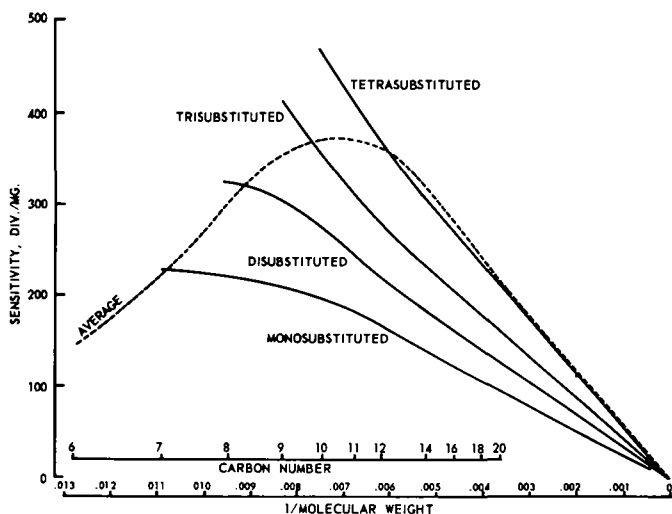


Fig. 1. LOW VOLTAGE CALIBRATION DATA FOR ALKYL BENZENES.

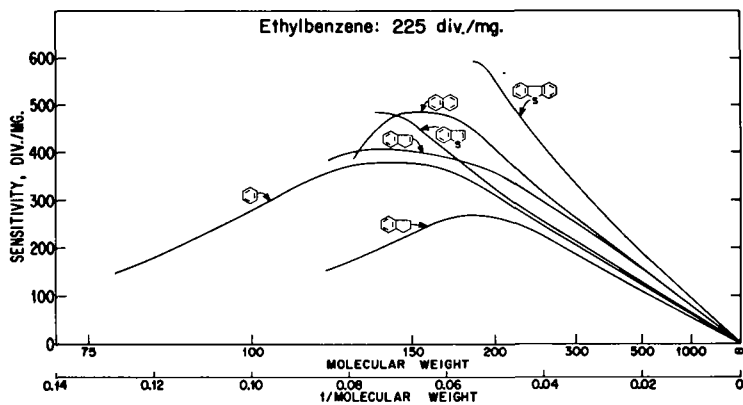


Fig. 2. LOW VOLTAGE CALIBRATION DATA No. 1.

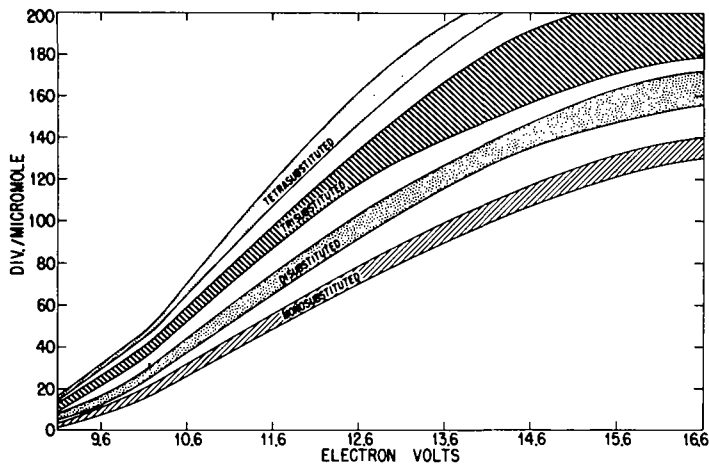


Fig. 4. IONIZATION EFFICIENCY CURVES FOR ALKYL BENZENES.

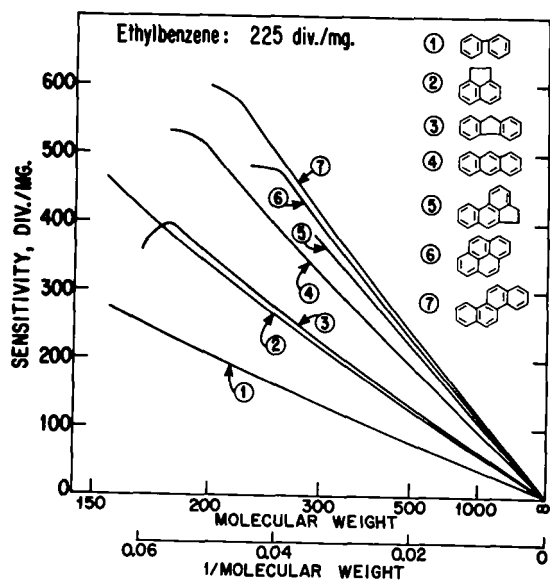


Fig. 3. LOW VOLTAGE CALIBRATION DATA No. 2.

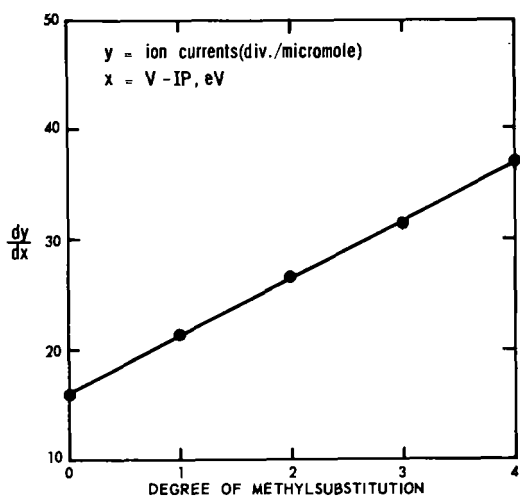


Fig. 5. SLOPES OF IONIZATION EFFICIENCY CURVES IN ALKYL BENZENES.

A STUDY OF THE IONS PRESENT IN ACTIVE NITROGEN USING A QUADRUPOLE MASS SPECTROMETER

By G. Neil Spokes and Bert E. Evans
Stanford Research Institute
Menlo Park, California

Introduction

Gaseous nitrogen at a pressure of several Torr which has been activated by flowing it through an electrical discharge may glow with a yellow-green color. There is a considerable body of evidence summarized by Jennings and Linnett¹ that the chief active component of such a gas is atomic nitrogen in the 4S state. In addition to its chemical activity, active nitrogen shows electrical conductivity.² Kunkel and Gardner³ found that the electron density in such active nitrogen, as determined by a microwave method, was dependent on the presence of a small quantity of oxygen impurity in the nitrogen. The low ionization potential of molecular nitric oxide (9.25 eV) points to NO^+ as being the most likely positive ion.

Studies of fast flowing active nitrogen streams⁴ brought to light an apparently new phenomenon--the "pink afterglow" of nitrogen.* Broida and Tanaka⁶ found the gases in this pink glow to be highly ionized. R. A. Young⁷ suggested that the high energy spectral emissions (up to 21.5 eV excitation above the molecular ground state and up to 10.6 eV of atomic excitation) could be due to reactions of nitrogen ions with electrons or atomic nitrogen.

So far as we are aware, there has been no previous determination of the mass numbers of the ions present in active nitrogen. The present work was undertaken in the hope of accomplishing this. A quadrupole mass spectrometer was used for the ion analysis.

Experimental

A typical experimental apparatus is illustrated in Fig. 1. Briefly, Matheson prepurified nitrogen passes through a microwave plasma where "activation" occurs. Ultraviolet radiation from the discharge is prevented from entering the mass spectrometer by a light trap. This prevents excessively high background signals due to such an origin.

Various reaction cell configurations have been used and Figs. 1, 2, and 4 show three different kinds of chamber. Figure 1 illustrates a method of introducing NO gas to study its effects on the ionization. Another method used, but not illustrated, was to inject nitric oxide gas into the active nitrogen stream several decimeters upstream from the sampling chamber. There is no electron gun in our mass spectrometer.

Ions in the sampling chamber are sampled through a small aperture in the end-plate of the high-vacuum apparatus. Details are given in Fig. 2. The sampling aperture was formed by piercing the aluminum foil with a fine wire.

A powerful rotary pump (Welch 1397 B) maintains the gas pressure in the reaction chamber in the range 1-10 Torr for a variety of flow rates. The high-vacuum chamber is evacuated to about 3×10^{-5} Torr by a fast oil diffusion pump (700 liter sec^{-1}).

Care was taken to keep gases pure, and the use of a flow system was advantageous in this respect. The negative ion spectrum was found to be a good indicator of impurities. Negative ions were not detectable when the gases were quite pure.

The ions entering the high-vacuum system through the sampling aperture are subjected to a small, axial, accelerating field which directs their motion down the axis of a quadrupole spectrometer. The axial ion energy is four volts. Neutral molecules which effuse freely into the vacuum are pumped away. There is no differential pumping.

*This may well be a new manifestation of an old phenomenon.⁵

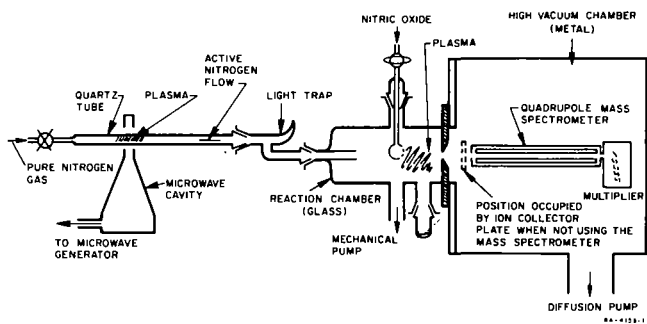


Fig. 1 A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SETUP

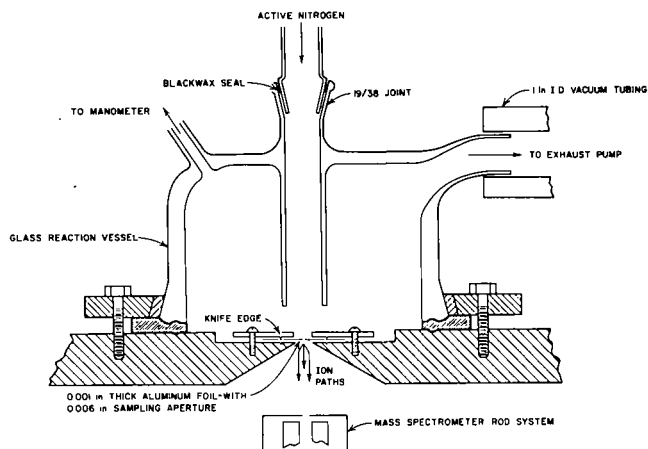


FIG. 2 A REACTION VESSEL USED FOR SAMPLING ACTIVE NITROGEN PLASMAS

Some details of the quadrupole rod system are:

The rod diameter is 0.63 cm. The rod centers are located at the corners of a square 0.87 cm on a side. The rod length is 25.4 cm and the deviation from straightness over this length is less than 0.003 cm. The entrance aperture is about 0.08 cm in diameter

Voltage sweep was used on the rods. D-C potentials were 0-100 volts and the RF frequency was 3.28 Mc/sec. RF and D-C signals were locked to a 90 sec/cycle sawtooth from a modified Tektronix waveform generator No. 162. The ion transmission efficiency of the rod system is no less than 80% of the low resolution value when the mass peaks 29 and 30 are well separated (as in Fig. 3b). The apparent poor resolution at lower mass numbers in this figure is due largely to the use of a D-C amplifier with a slow time response.

The mass spectrometer has been used with both a Faraday cup and with a photomultiplier. The "satelliting" shown in the upper spectrogram of Fig. 3a and evident in the "52" peak of the lower mass spectrum of Fig. 3a is probably due to inefficient ion collection by the Faraday cup.

Results

When care was taken to use "pure" nitrogen, only the mass 30 ion, NO^+ , was detectable in the mass spectrum of ions sampled from normal active nitrogen. Clearly, under these conditions, the last trace of oxygen had not been removed from our nitrogen. With a trace of moisture present, mass peaks at 18 and 35 showed up (NH_4^+ or H_2O^+ and N_2H_7^+ or H_3O_2^+) as well as the ever-present NO^+ .

Negative ions were present when nitric oxide was added to the active nitrogen through Tygon (vinyl acetate-vinyl chloride polymer) tube. We found that the negative ions maximized in concentration when the nitric oxide addition rate was adjusted to give the maximum positive ion concentration. (The very detection of negative ions probably indicates that plasma potential barrier effects at the walls of the system were not very serious).

Four negative ion peaks were detected at mass numbers 26, 35, 37, and 42 or 43. The sensitivity of the detection system was too low to allow us to resolve the fourth peak. The peaks at 35 and 37 may be assigned to Cl^- since they were in about the right ratio. Mass 26 may well be CN^- . Possible assignments for the fourth peak are CNO^- , CNOH^- , N_3^- , or HN_3^- . O_2^- and O^- ions were not detected, and these would have been seen had they represented 1/8 the total negative ion concentration. Atomic oxygen formed from the reaction between NO and N would have been a major constituent.⁹

With fast gas flow rates (5-20 m sec⁻¹) and using pure nitrogen we have been able to produce the pink afterglow in the flow system. Using a 60 kc/s RF excitation it has been possible to quench the light from the pink glow. Figure 4 shows the experimental arrangement for this. One electrode is external to the system. When "quenched," the pink glow radiation is reduced about tenfold.

The mass spectrum of ions collected is shown in Fig. 3d. The upper spectrum is of the unquenched glow and the lower spectrum for the quenched case. The ions present are at masses 28, 30, 42, and 56. The assignments are N_2^+ , NO^+ , N_3^+ , and N_4^+ since these seem to be the most reasonable ones. The ions N_2^+ , N_3^+ , and N_4^+ are detected whenever the pink glow is present in the system upstream of the mass spectrometer sampling aperture. The balance between N_2^+ , N_3^+ , and N_4^+ is similar to that illustrated for pressures in the range 1-10 Torr although further downstream from the pink glow the relative level of NO^+ becomes much greater. In addition to the nitrogen molecular ions, a mass peak at 14 (presumably N^+) has been detected downstream from the pink glow. This mass peak was below the noise level in the spectra shown. NO^+ normally decreases when the pink glow is in the system. The yellow-glowing gases upstream of the pink glow show only NO^+ ions.

With moisture impurity present in the system, mass peaks at 17, 18, 19, and 29 are added to the mass spectrum; assignments are NH_3^+ or OH^+ , NH_4^+ or H_2O^+ , H_3O^+ , and N_2H^+ . Admission of a trace of lab air into the active

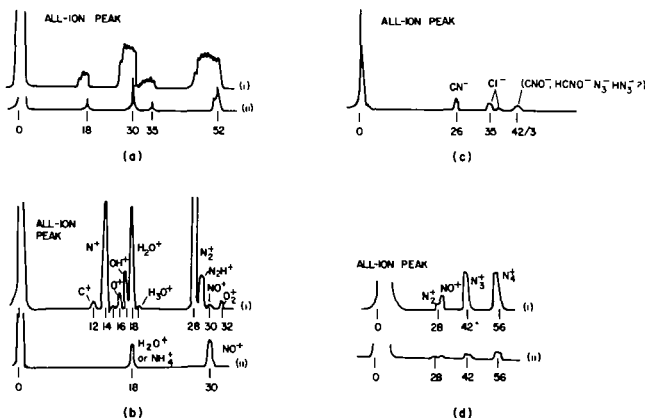


FIG 3 ION SPECTRA

- (a) (i) Active nitrogen slow flow rate 5 torr pressure, no pink showing. Moisture present. Low resolution. Sensitivity: Mass peak 30 corresponds to 2×10^{-10} A. (The ion multiplier tube was used).
(ii) As (i) but with higher resolution. The NO^+ mass peak corresponds to about 5×10^{-11} A.
- (b) (i) Ions passing through a hole in the cathode glow of a DC discharge in N_2 (impurities were present). H_2O^+ peak corresponds to a current of 1.5×10^{-9} A.
(ii) Mass spectrum of active nitrogen at the same dispersion. The mass 18 peak now corresponds to 10^{-10} A.
- (c) Negative ion mass spectrum of active nitrogen (impure NO was added to maximize the negative ion currents.) CN^- current was 5×10^{-13} A. (In this case, no ion multiplier was used.)
- (d) (i) Normal and (ii) Quenched pink glow mass spectra (see Fig. 4). N_3^+ current was 5×10^{-13} A. Again an ion multiplier was used.

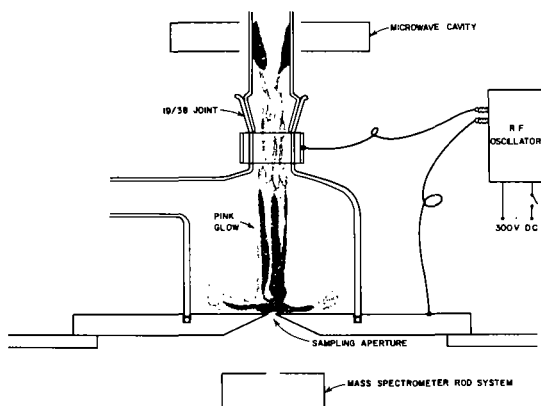


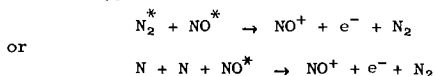
Fig. 4 EXPERIMENTAL SETUP FOR STUDYING
PINK GLOW QUENCHING

nitrogen gives rise to many more peaks up to and probably above mass 109. As far as could be judged some of these peaks correlated with $(\text{H}_2\text{O})_n\text{H}_3\text{O}^+$, where n takes on the values 3, 4, and 5.

Discussion

Nitrogen activated by an electrical discharge shows two distinct levels of activity. The first may be explained on the assumption that the active ingredient is ground state atomic nitrogen. This kind of activity is exhibited by the well-known yellow or Lewis-Rayleigh afterglow of nitrogen. The second kind of activity is found under certain conditions in association with the fast flowing active nitrogen showing the pink afterglow. Here the level of activity is much higher and can give rise to excited ionized nitrogen molecules.

That the chief ion in atomic nitrogen is nitric oxide comes as no surprise. The work of Kunkel and Gardner and of Gatz, Smith, and Wise⁸ has indicated a correlation between ion concentration and amount of added oxygen or nitric oxide. The latter group has given evidence for reactions of the type



Our general results agree with the assignation of the produced ion as NO^+ , although impurity ions will swamp the NO^+ if the gases are contaminated.

The negative ion spectrum showed CN^- and Cl^- and an ion at mass 42 or 43 when nitric oxide was introduced through Tygon tubing. CN and Cl radicals are presumably products of a reaction between vapors from the Tygon tubing and atomic nitrogen. The high electron affinity of CN and Cl ensures their stability. The peak at 42 or 43 may not be assigned with any confidence.

Whenever the pink glow was observed in the flowing gases, nitrogen ions N_2^+ , N_3^+ , N_4^+ , and nitric oxide ions were present in the mass spectrum of ions sampled up to one or two decimeters downstream from the pink glow. Upstream of the pink glow and beyond the quoted distance, only NO^+ ions were detectable (in the absence of moisture or other impurities).

The inference from this observation is that ionized nitrogen molecules and the pink glow are intimately related. The nitrogen ions are presumably created in the glow since they don't seem to be a normal product of the discharge.

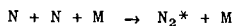
The following set of reactions is able to account energetically for the molecular ionic and atomic spectral emissions observed in the pink glow:

1. $\text{N}_3^+ + \text{e}^- \rightarrow \text{N}_2^* + \text{N}^* + 14.5 \text{ eV.}$
- 2.[†] $\text{N}_4^+ + \text{e}^- \rightarrow \text{N}_2^* + \text{N}_2^* + 15.46 \text{ eV.}$
3. $\text{N}_4^+ + \text{e}^- \rightarrow \text{N}_2^* + \text{N}^* + \text{N}^* + 5.70 \text{ eV.}$
4. $\text{N}_3^+ + \text{N} \rightarrow \text{N}_2^{+*} + \text{N}_2^* + 10 \text{ eV.}$
5. $\text{N}_2^+ + \text{e}^- \rightarrow \text{N}^* + \text{N}^* + 15.6 \text{ eV.}$

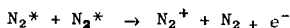
It is not possible at this stage to assess the full merits of these reactions since there is very little quantitative data on either the spectral radiance or the nature of the excited products of these reactions. The suggestion of Innes and Oldenberg¹⁰ that a hypothetical metastable nitrogen atom in a sextet S state carries the required energy from the discharge is not, at this time, discarded since there is some difficulty in accounting for the first formed ion. R. A. Young¹¹ has been unable to find evidence for such a species using ESR techniques.

[†]According to Kovar, Beatty, and Varney⁹ the dissociation energy of N_4^+ to N_2 and N_2^+ is 0.14 eV.

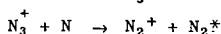
A possible mechanism for the initial step in ion formation may involve paths such as metastable neutral molecule formation by three-body recombination



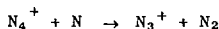
followed by



The first formed ions are then able to step up the metastable production rate by catalyzed nitrogen atom recombination



and at the same time



The quenching of the radiation would follow from the above mechanisms if the metastable molecules were deactivated, for example, by an RF field.

The vessel walls may play a part in pink glow mechanisms by enhancing metastable nitrogen molecule formation.

The effect of moisture on the mass spectra was quite pronounced. Comment on this is deferred to a future date.

Conclusion

A qualitative analysis has been made of the ions present in active nitrogen in the pressure range 1-10 Torr. We have found that the NO^+ ion is the chief ion in "normal" active nitrogen prepared by passing pure nitrogen gas through an electrical discharge. Clearly the gas is not extremely pure--just quite pure.

When the pink afterglow is present in the system, we have found that the ions N^+ , N_2^+ , N_3^+ , N_4^+ , and again NO^+ appear in the mass spectrum. There is enough energy available from the nitrogen ions to account for the observed spectral emissions. A mechanism of creation of nitrogen ions is suggested.

References

1. K. R. Jennings and J. W. Linnett, *Quarterly Reviews (London)* 12, 116 (1958).
2. R. J. Strutt, *Proc. Roy. Soc.* 85A, 219 (1911); 87A, 179 (1912); P. A. Constantinides, *Phys. Rev.* 30, 95 (1927).
3. W. B. Kunkel and A. L. Gardner, *J. Chem. Phys.* 37, 1785 (1962).
4. G. E. Beale, Jr. and H. P. Broida, *J. Chem. Phys.* 31, 1030 (1959).
5. J. Kaplan, *Phys. Rev.* 45, 671 (1934); R. Herman, *Compt. Rend.* 220 593 (1945).
6. H. P. Broida and I. Tanaka, *J. Chem. Phys.* 36, 236 (1962).
7. R. A. Young, *J. Chem. Phys.* 36, 2854 (1962).
8. C. Gatz, F. T. Smith, and H. Wise, Submitted for publication to *J. Chem. Phys.*
9. F. R. Kovar, E. C. Beatty, and R. N. Varney, *Phys. Rev.* 107, 1490 (1957).
10. F. R. Innes and O. Oldenberg, *J. Chem. Phys.* 37, 2427 (1962).
11. R. A. Young, Private communication.

MOLECULAR BEAM STUDIES OF THERMAL AND PHOTOLYTIC DEGRADATION PRODUCTS
OF ISOTOPICALLY LABELED METASTABLE INORGANIC COMPOUNDS

Amos J. Coleman and Donald P. Easter
Basic Research Group
U. S. Army Engineer Research and Development Laboratories
Fort Belvoir, Virginia

Manuscript Withdrawn

COMPARISON OF MASS SPECTROMETRIC AND GAS CHROMATOGRAPHIC
ANALYSES OF HIGH-BOILING OILS FROM COAL

by

A. G. Sharkey, Jr.,^{a/} J. L. Shultz,^{b/} and R. A. Friedel^{c/}

ABSTRACT

Naphthalene and anthracene oils from coal were analyzed by high-temperature mass spectrometry. These samples had been analyzed previously by gas chromatography at 13 European laboratories as part of a cooperative test program investigating analysis of high-boiling oils from coal. Carbon number distribution data were obtained by mass spectrometry for components containing up to 24 carbon atoms. For the majority of the structural types, good agreement was shown between gas chromatographic and mass spectrometric results.

INTRODUCTION

New mass spectrometric methods are being developed at the Pittsburgh Coal Research Center of the Federal Bureau of Mines to extend the molecular weight range of determinations for components in coal hydrogenation oils, coal extracts, and high-boiling liquid fractions from tars. Mass spectral techniques commonly applied in the laboratory include low-ionizing-voltage methods to establish the molecular weight range of components (1) and type-analysis methods to determine the total quantity of each structural type (2, 3). In most instances, adequate synthetic blends cannot be prepared to evaluate these methods because of the lack of pure compounds and the complexity of these high-boiling mixtures. Determinations on samples previously analyzed by other techniques are, therefore, helpful in evaluating these methods.

In 1958 F. Dupire and G. Botquin described the use of gas chromatographic techniques to analyze high-boiling oils from coal (4). The highest molecular weight alkyl derivative reported for any structural type had only dimethyl substituents. Mass spectrometric analyses of similar oils had shown the same structural types as reported in the above gas chromatographic analysis; however, the mass spectra indicated derivatives containing at least 10 carbon atoms in the alkyl substituents (5). It was therefore of interest to extend the characterization of these high-boiling fractions and compare mass spectrometric and gas chromatographic determinations made on the same oils.

Samples of naphthalene and anthracene oils previously analyzed by 13 European laboratories as part of a test program to evaluate analytical methods were obtained from Dr. A. Boyer of the CERCHAR Laboratory, Verneuil, France. The samples were from an industrial coke plant in Germany. The specific purpose of the cooperative study was to evaluate gas chromatographic methods for the analysis of this untreated, liquid product.

ACKNOWLEDGMENTS

The cooperation of Dr. A. Boyer of the CERCHAR Laboratory, Verneuil, France, is gratefully acknowledged for supplying the samples and results of the cooperative study and for helping to resolve

- a. Supervisory Physicist.
- b. Mathematician.
- c. Supervisory Chemist.

All authors are with the Pittsburgh Coal Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa.

Table 1.- Mass spectrometric analysis of naphthalene oil.

		Carbon numbers ^a												Total
		8	9	10	11	12	13	14	15	16	17	18	19	
Benzenes	Mol. wt.	106	120	134	148	162	176							31.3
	Vol. %	1.8	9.0	16.7	2.9	0.7	0.2							
Indenes	Mol. wt.		116	130	144									4.6
	Vol. %		3.1	1.2	0.3									
Indans	Mol. wt.		118	132	146	160	174							8.3
	Vol. %		3.5	2.3	2.2	0.3	0.04							
Naphthalenes	Mol. wt.		128	142	156	170	184	198	212	226				46.7
	Vol. %		35.3	9.7	1.2	0.2	0.2	0.05	0.01	0.01				
Biphenyls; Acenaphthenes	Mol. wt.				154	168	182	196	210	224	238			2.6
	Vol. %				1.0	0.3 ^b	0.4	0.2	0.05	0.03	0.02			
Acenaphthylenes; Fluorenes	Mol. wt.				152	166	180	194	208	222	236	250		1.2
	Vol. %				0.1	0.7	0.2	0.03	0.03	0.03	0.06	0.05		
Anthracenes; Phenanthrenes	Mol. wt.						178	192	206	220	234	248		1.9
	Vol. %						1.4	0.2	0.06	0.03	0.10 ^c	0.06		
Methylene- phenanthrenes ^d	Mol. wt.							190	204	218	232	246		0.3
	Vol. %							0.07	0.07	0.06	0.09	0.05		
4-rings pyri- condensed ^e	Mol. wt.			129	143									0.4
	Vol. %			0.4	0.3									
4-rings cata- condensed ^e	Mol. wt.								202	216	230	244		0.1
	Vol. %								0.2	0.1	0.1	0.02		
Indoles	Mol. wt.	117									228	242		0.1
	Vol. %	0.2									0.07	0.03		
Quinolines	Mol. wt.													0.2
	Vol. %													
Carbazoles	Mol. wt.													0.7
	Vol. %													
Phenols and Dihydrophenols ^f	Mol. wt.						167							0.3
	Vol. %						0.3							

^a/ Carbon number based on structural types indicated.

^b/ Also dibenzofuran.

^c/ Also benzidiphenylene sulfide; identified by CERCHAR in anthracene oil.

^d/ Identified in similar material by Allied Chemical Corporation.

^e/ Suggested compound types based on molecular weight.

^f/ Not included in gas chromatographic analyses.

differences in the analyses.

MASS SPECTROMETER ANALYSES

Experimental Technique

Mass spectrometric determinations were made on the samples without further separation or treatment in line with the purpose of the cooperative study and for comparison of results. Low-ionizing voltage techniques described previously were used (1). Spectra were obtained at 70 and approximately 10.5 electron volts using a Consolidated Electrodynamics Model 21-103C mass spectrometer. The inlet system was operated at 290° C and was equipped with a heated gallium disc.

Results

Naphthalene oil. (~bp 200°-230°C) Carbon number distribution data for the 14 structural types indicated in the mass spectrum are shown in table 1. Characteristics of the carbon number distribution data are illustrated by the data for the naphthalenes shown in figure 1. In most instances, the first member of the homologous series showed the highest percentage. Alkyl derivatives corresponding to the addition of 7 carbon atoms were found for the naphthalenes. Data shown in table 2 for the following structural types, including alkyl derivatives, are grouped as reported in the gas chromatographic analysis: Benzenes, indenenes, indans, naphthalenes, acenaphthylenes and/or fluorenes, acenaphthenes and/or biphenyls, phenanthrenes and/or anthracenes and pyrenes. Benzenes and naphthalenes account for about 31 and 47 percent of the sample, respectively. Over 50 percent of the sample is comprised of structures having 10 carbon atoms, primarily naphthalene and alkyl derivatives of benzene.

Anthracene oil. (~bp 300°-360°C) Components with molecular weights ranging from 120 to 300, for aromatic structures having from 1- to 5-ring systems, were found in the anthracene oil. Twelve structural types and their alkyl derivatives were determined as indicated in table 3. These data were also grouped to facilitate a direct comparison with gas chromatograph data (table 4). Anthracene and/or phenanthrene and their alkyl derivatives account for about 26 percent of the sample. Because of the complexity of the spectrum of this higher boiling oil, alkyl series beginning above mass 200 were assigned on the basis of 4- and 5-ring peri- or cata-condensed systems, rather than to specific structures.

GAS CHROMATOGRAPHIC ANALYSES

Experimental Technique

The gas chromatographic columns used by the 13 laboratories had silicone oil as the stationary phase and were operated at 200°-310°C.

Results

Gas chromatographic results were reported on the basis of eight groupings for the naphthalene oil and nine for the anthracene oil as shown in tables 2 and 4. Aromatic systems having from 1- to 4-rings were reported for the naphthalene oil and from 2-rings to a classification designated as > 4-rings for the anthracene oil.

COMPARISON OF RESULTS

Gas chromatographic results from the various European laboratories showed a wide range for both samples (last column of tables 2 and 4). As the CERCHAR Laboratory is monitoring the cooperative investigation and has

Table 3.- Mass spectrometric analysis of anthracene oil.

		9	10	11	12	13	14	15	16	17	18 ^a	19	20	21	22	23	24	Total
Benzenes	Mol. wt.	120	134	148	162	176												0.9
	Vol. %	0.04	0.3	0.2	0.2	0.2												
Naphthalenes	Mol. wt.	128	142	156	170	184	198	212	226									7.4
	Vol. %	1.6	1.0	1.0	1.0	0.8	0.6	0.4										
Biphenyls;	Mol. wt.																	10.8
	Vol. %																	
Acenaphthenes	Mol. wt.	154	168	182	196	210	224	238										10.2
	Vol. %	1.8	3.0 ^b	2.7	1.9	0.9	0.4	0.1										
Acenaphthylenes;	Mol. wt.																	10.2
	Vol. %																	
Fluorenes	Mol. wt.	166	180	194	208	222	236	250	264									25.9
	Vol. %																	
Anthracenes;	Mol. wt.																	15.3
	Vol. %																	
Phenanthrenes	Mol. wt.																	4.2
	Vol. %																	
4-rings peri-	Mol. wt.																	10.2
	Vol. %																	
condensed	Mol. wt.																	3.1
	Vol. %																	
4-rings cata-	Mol. wt.																	5.7
	Vol. %																	
condensed	Mol. wt.																	3.1
	Vol. %																	
Methylene-	Mol. wt.																	5.1
	Vol. %																	
phenanthrene ^d /	Mol. wt.																	5.7
	Vol. %																	
5-rings peri-	Mol. wt.																	3.1
	Vol. %																	
condensed ^e /	Mol. wt.																	5.1
	Vol. %																	
5-rings cata-	Mol. wt.																	5.7
	Vol. %																	
condensed ^e /	Mol. wt.																	3.1
	Vol. %																	
Diphenyls ^f	Mol. wt.																	5.1
	Vol. %																	
sulfoxides ^g /	Mol. wt.																	5.7
	Vol. %																	
Carbazoles ^h /	Mol. wt.																	3.1
	Vol. %																	
Estimated total of unidentified aromatic compound types, including nitrogen heterocycles, Vol. %																		5.7

^a/ Carbon number based on structural types indicated.

^b/ Also dibenzofuran.

^c/ Also benzidiphenylene sulfide; identified by CERQAR

^d/ Identified in similar material by Allied Chemical Corporation.

^e/ Suggested compound types based on molecular weights.

^f/ Identified by CERQAR.

made an intensive study of these samples, the mass spectrometric results were compared with results obtained by this laboratory. Considering the complexity of these gross samples and the lack of standards, mass spectrometric and gas chromatographic determinations for the major components (>10%) compare favorably.

For the naphthalene oil, large deviations are shown in determinations for the indenenes and indans by the two techniques (table 2). However, the total indene plus indan values show reasonable agreement (G.C.-16.2; M.S.-13.5). Perhaps there is some confusion in assigning these components. Mass spectrometric and gas chromatographic results for naphthalene and fluorenes in the anthracene oil differ by about a factor of two. However, both are minor components (<8%).

CONCLUSIONS

While it is difficult to judge the accuracy of determinations by M.S. and G.C. for components in high-boiling oils, data obtained after extensive studies by both techniques show at least semi-quantitative agreement. However, the diversity of results obtained for these samples by several of the major laboratories in Europe (in most instances a spread of a factor of two or more) indicates a need for developing methods for routinely determining the composition of some of the higher-boiling oils from coal.

REFERENCES

1. Sharkey, A. G., Jr. Low Ionizing Voltage Analysis of Complex Organic Mixtures. Ch. in Encyclopedia of Spectroscopy, ed. by G. L. Clark, Reinhold Publishing Corp., New York, 1960, pp. 609-613.
2. Clerc, R. J., Hood, A., and O'Neal, M. J. Mass Spectrometric Analysis of High Molecular Weight, Saturated Hydrocarbons. Anal. Chem. v. 27, 1955, pp. 868-875.
3. Crable, G. F., and Coggeshall, N. D. Application of Total Ionization Principles to Mass Spectrometric Analysis. Anal. Chem. v. 30, 1958, pp. 310-313.
4. Dupire, F., and Botquin, G. L'Analyse Qualitative et Quantitative des Huiles Lourdes de Goudron par Chromatographie Gazeuse. (The Qualitative and Quantitative Analysis of Heavy Oils from Coal Tar by Gas Chromatography). Anal. Chem. Acta, v. 18, 1958, pp. 282-290.
5. Sharkey, A. G. Jr., Shultz, Janet L., and Friedel, R. A. Application of Low-Ionizing Voltage Mass Spectrometry to Oils Derived from Coal. Fuel, London, v. 41, 1962, pp. 359-371.

TABLE 2. - Comparison of mass spectrometric and gas chromatographic analyses of naphthalene oil

Compound types, including alkyl derivatives ^{a/}	Volume percent		
	G.C. CERCHAR	M.S. Bureau of Mines ^{b/}	Range ^{c/}
Benzenes	25.6	32.4 ^{d/}	12.4 - 35.0
Indenes	10.7	4.8	8.0 - 17.8
Indans	5.5	8.7	5.5 - 12.2
Naphthalenes	54.0 ^{d/}	48.1	41.9 - 70.1
Acenaphthylenes; Fluorenes	0.9	1.0	0.5 - 1.3
Acenaphthenes; Biphenyls; Diphenylene oxide	2.4	2.6	1.4 - 6.4
Anthracenes; Phenanthrenes	0.9	2.0	0.9 - 1.9
Pyrenes	--	0.4	0 - 0.6

a/ Compound types and groups as reported by gas chromatography.

b/ Mass spectrometric analysis has been renormalized to eliminate nitrogen heterocyclics not included in gas chromatographic analysis.

c/ Range of G.C. results from the cooperative program.

d/ Thionaphthenes are included in the naphthalene summation in the G.C. data and in the benzene summation in the M.S. data.

TABLE 4. - Comparison of mass spectrometric and gas chromatographic analyses of anthracene oil

Compound types ^{a/}	Volume percent		
	G.C. CERCHAR	M.S. Bureau of Mines ^{b/}	Range ^{c/}
Below Naphthalene	0.6	1.0	0.4 - 1.6
Naphthalene	5.3	2.0	2.9 - 5.3
Σ Naphthalene homologs	6.1	6.6	2.8 - 7.4
Acenaphthenes ^{d/}	10.8	12.4	5.6 - 10.8
Fluorene	7.2	4.7	4.3 - 10.2
Phenanthrene; Anthracene	15.0	17.4	12.4 - 21.1
Σ Fluorene, Phenanthrene, and Methylenepheneanthrene homologs	29.0	31.0	10.1 - 29.3
Σ Pyrene; Fluoranthene	15.5	11.1	6.5 - 24.6
> 4-ring ^{e/}	10.5	13.8	3.5 - 10.5
	100.	100.	

a/ Compound types and groups as reported by gas chromatography.

b/ Mass spectrometric analysis has been renormalized to eliminate nitrogen and sulfur ring systems not included in gas chromatographic analysis.

c/ Range of G.C. results from the cooperative program.

d/ Includes acenaphthene homologs, diphenyl, and dibenzofuran; the two latter compounds were determined separately by gas chromatography.

e/ Also includes 4-ring cata-condensed aromatics not identified by gas chromatography.

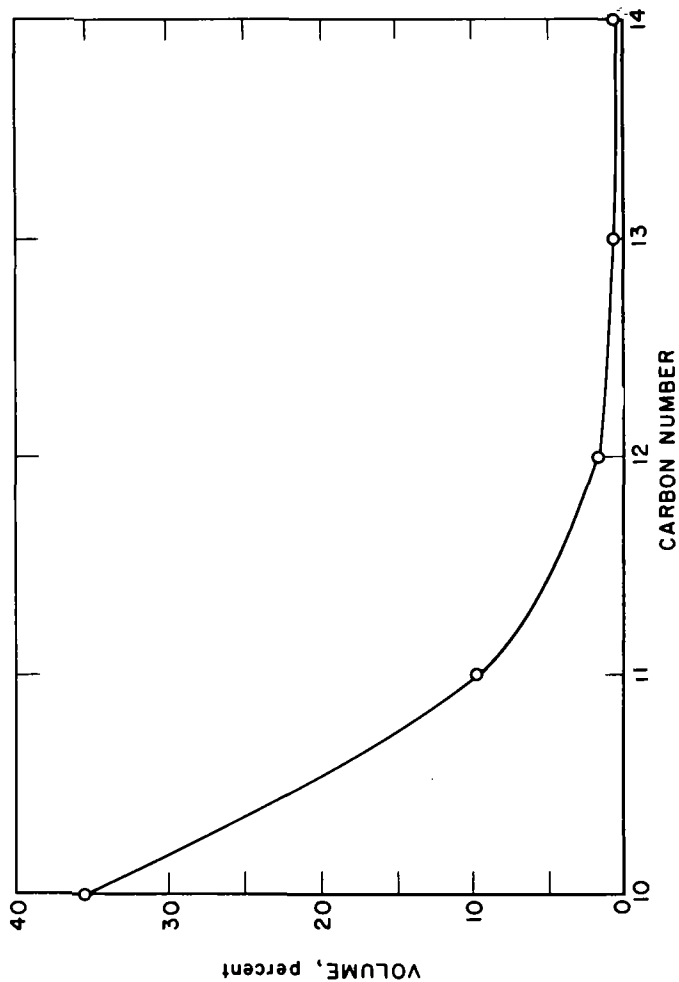


Figure 1.- Carbon number distribution for naphthalenes in naphthalene oil.

3-13-63 L-7964

MASS SPECTROMETER SYSTEM FOR BEAM SURFACE INTERACTION STUDIES

David Lichtman

Honeywell Research Center

Hopkins, Minnesota

A program has been underway to study the physics of high and ultra-high vacuum systems. Major emphasis is presently aimed at the detailed study of the interaction of various kinds of beams with surfaces in high and ultra-high vacuum environment. The parameters of interest include

- I (a) Target material
(b) Material preparation
(c) Target material temperature
- II Photon beam bombardment
(a) Photon density
(b) Photon energy
- III Electron beam bombardment
(a) Electron energy
(b) Total beam power
- IV Ion beam bombardment
(a) Type of ion
(b) Ion energy
- V Neutral particle bombardment
(a) Low energy evaporation
(b) High energy charge exchange

The analytical tool decided upon for this study is a 6" radius, 60° sector mass spectrometer system. The system is shown in Fig. 1. Except for the sapphire windows to enable photon injection, the entire system is constructed of metal and ceramic. Vacuum is achieved and maintained with the use of an activated charcoal in liquid nitrogen forepump and three 8-liter/second ion pumps. The target is mounted on the back plate and is provided with suitable heaters, thermocouples, etc. Six ports are equally spaced around the interaction chamber and aimed at the center of the target. The ionization chamber in front of the target is of standard construction and contains an ionization box with open grid construction to permit transmission of neutrals, condensibles, and ions.

Several interesting methods for the detection and display of spectra have been worked out. The conventional mode of operation utilizes a vibrating reed electrometer and recorder output. With this system it is theoretically possible to detect partial pressures of 10^{-16} Torr or lower. A typical spectrum indicating detectability at low partial pressures is shown in Fig. 2. The limiting noise level of the system is determined by the total system pressure and it is difficult to observe partial pressures much smaller than one part in 10^6 of the total pressure with the system set for maximum sensitivity. The main component in the system when this spectrum was taken is hydrogen at 3×10^{-9} Torr. The peak at mass 1 is due to H^+ and that at mass 3 is due to HD . This is a good check on the system since the deuterium isotope concentration is well known. The ratio of HD to H_2 observed agrees very well with published isotope concentrations.

The peak at mass 4 is due to helium. The sensitivity has been changed throughout the run to permit presentation on a single sheet of 5 decades of partial pressure. The peak at mass 6 is due to C^{++} , while that at mass 7 and the double peak at mass 8 are probably due to one or more doubly ionized components such as N^{++} , CH_4^{++} , CH_2^{++} , O^{++} , etc.

The multiplier enables one to work with extremely small ionization currents and still obtain considerable output signal. For example, one may use ionizing currents at 1 micro ampere and less and obtain spectra of partial pressures of 10^{-9} Torr and lower which are many orders of magnitude above the noise level. A typical spectrum taken this way is shown in Fig. 3.

Simple switching of polarity of the magnetic field and several of the applied potentials permits the negative ion spectrum to be scanned.

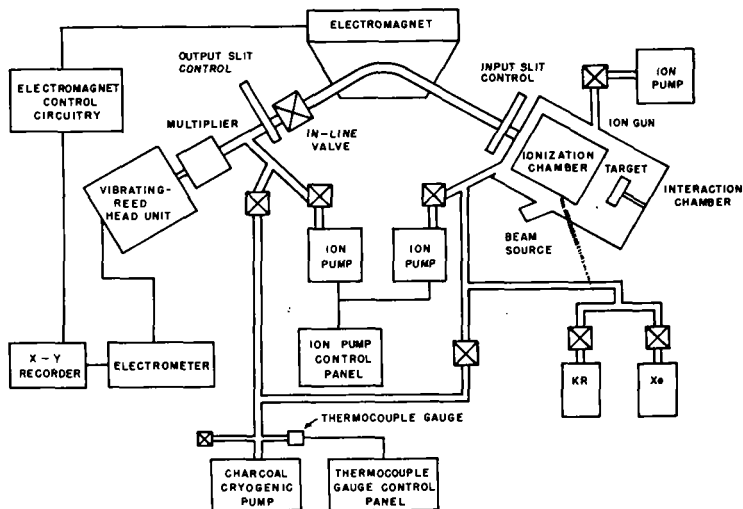


Fig. 1 Schematic of experimental ultra-high vacuum mass spectrometer system

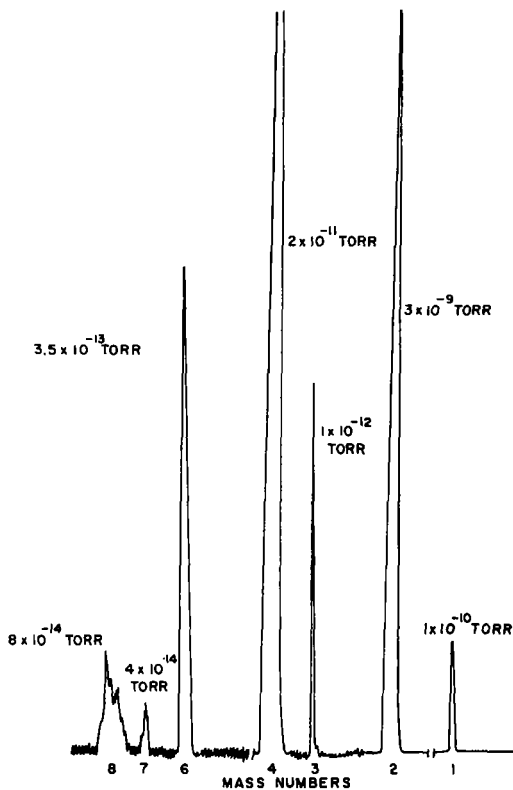


Fig. 2 Scan of mass range 1-8 a.m.u. The scale has been randomly changed throughout the run to permit display of 5 decades of partial pressure.

A second method of presentation utilizes oscilloscope display. In this mode of operation the magnetic field is maintained constant and the ion accelerating voltage consists of a DC level of about 500 V plus a saw-tooth voltage of variable magnitude and duration. Typically a 500 V saw-tooth of 200 millisecond duration is used. The output of the multiplier goes directly to the very sensitive (type 502 Tektronix) oscilloscope or through an AC amplifier and then to a conventional oscilloscope. Some typical spectra are shown in Figs. 4 and 5. By varying the DC level of the magnetic field different portions of the mass range can be displayed on the oscilloscope. Partial pressure as low as 10^{-11} Torr can be easily seen at a repetition rate which, when coupled with a long persistence screen, permits essentially a constant view of the mass spectrum. The limit in this type of display is reached when individual pulses due to single atoms arriving at the collector are observed. When the signals are of this low a magnitude, all peaks are approximately the same height since they are composed of a small number of single pulses of approximately the same magnitude. It is interesting to note the occurrence of single pulses arriving at random positions due to scatter in the mass spectrometer. The effect is very clear when viewing a scope presentation. Random background pulses appear at all positions but are more heavily concentrated near major peaks as one would expect.

A third method of detection utilizes the generation of pulses produced by the arrival of single atoms to the collector. In this case the output of the multiplier is again fed through an AC amplifier and then into a pulse height analyzer followed by a counter or rate meter. This method of detection is most useful when one is interested in working with very low partial pressures (in the order of 10^{-14} to 10^{-18} Torr) or when working with moderate pressures (10^{-7} to 10^{-10} Torr) and using extremely low ionizing currents, i.e. much less than one microamp. Scanning in this mode of operation is by conventional magnetic field variation. Many standard rate meters have provision for driving recorders. The typical output obtained with this detection system is shown in Fig. 6. In this case the output of the multiplier went through an AC amplifier, a pulse height analyzer and into a rate meter, the output of the rate meter driving the recorder. One can see the individual random pulses appearing between the main peaks.

Experiments have been started with the system while the various gun structures are in process of construction. A pulse type ruby laser was available and was used to bombard the target through the sapphire window. A sample of anodized beryllium was used as the target in this experiment. The laser provided approximately one joule of energy per pulse with a pulse width of about 1 millisecond. The system was baked out at 350°C and achieved a total background pressure of less than 1×10^{-9} Torr. The output of the laser was focused by a simple lens on to the target. After the application of several pulses the system was contaminated with hydrocarbon components. These components were eventually identified as ethylene diamine tetra-acetic acid which is the basic solution used in the anodizing process. This material is apparently thoroughly enmeshed in the anodized surface. After several repeated bursts from the laser beam the evolution from a single spot decreased until repeated laser beam bombardment produced no detectable gas evolution. Moving the laser spot to a new position on the target started the outgassing as before. Thus approximately 5 or 6 bursts from the laser beam would permanently outgas the spot in question. In this case the laser beam caused considerable heating to some depth, producing essentially a localized vacuum firing of the part. Careful observation of the target after the experiments were completed revealed no evidence of beryllium material removal.

One major aspect of interest in this study is to determine the surface condition of various kinds of material when they exist under ultra-high vacuum environment. At any value of ultra-high vacuum there are always several components in the system and we are interested in determining the manner in which these components reside on the surfaces. Thus, the scope display was used to observe desorption when a molybdenum ribbon was flash-heated for several seconds after various lengths of time at room temperature. Typical data obtained are shown in Fig. 7. The background components corresponding to partial pressures in the neighborhood of 10^{-10} Torr are shown in the lower portion of the figure. With the application of a low-power heat pulse one can see the rapid increase of the

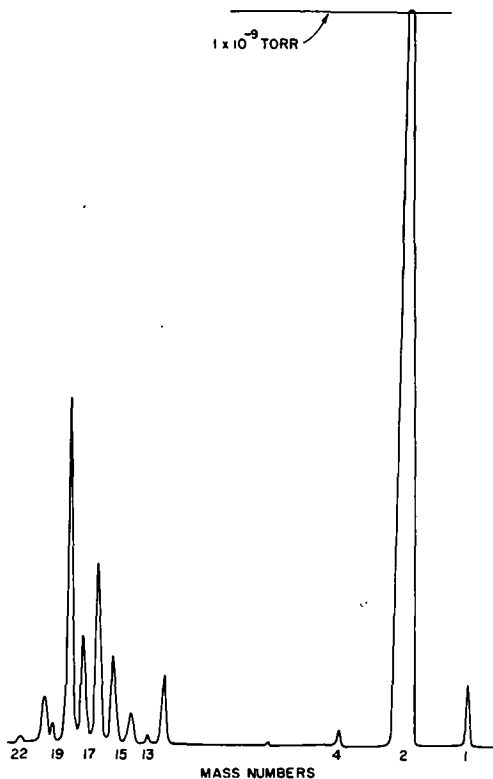


Fig. 3 Scan of mass range 1-22 a.m.u. Total pressure is about 1.5×10^{-9} Torr. An ionizing electron beam of one μ amp at

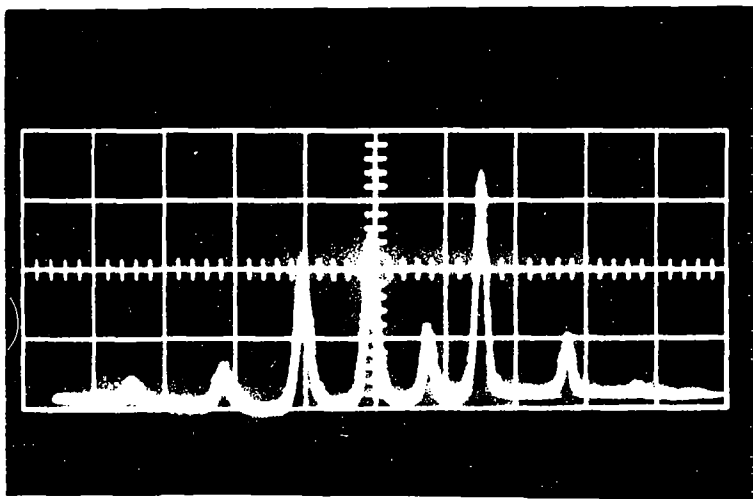


Fig. 4 Typical spectrum seen by oscilloscope display. Mass peaks (from left to right) correspond to 13, 14, 15, 16, (methane); 17, 18 (water vapor); 20 and 22 (neon). Full scale deflection corresponds to 4×10^{-9} Torr.

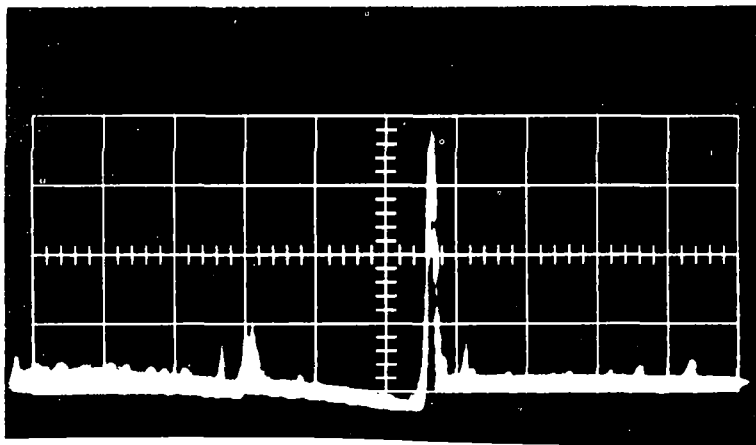


Fig. 5 Oscilloscope display at high sensitivity. Major peak is helium at mass 4. The smaller peak to the left is HD at mass 3. Full scale deflection is 4×10^{-11} Torr. Single pulses at random positions due to single scattered ions are easily seen.

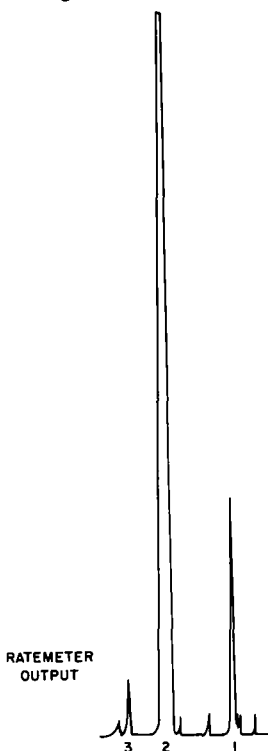


Fig. 6 Spectrum of hydrogen showing peaks due to H, H_2 , and HD. Output of the multiplier is fed through pulse height analyzer and ratemeter, the output of which feeds the recorder. Single pulses due to single scattered ions are clearly evident. The hydrogen partial pressure is about 2×10^{-9} Torr and the ionizing current is .1 μ amps.

methane peaks. At the higher power application the evolution of a carbon monoxide burst was detected. Of all the components in the system the one which shows virtually no desorption pulse is water vapor. The water vapor either does not stick to the moly or dissociates and does not desorb as H_2O .

Data were taken on the hydrogen desorption since it was the major component in the system with a partial pressure of about 1×10^{-9} Torr. The adsorption of hydrogen as a function of time shows a curve which seems to indicate conventional exponential adsorption for the first several hours indicating an approximate sticking coefficient of about .03 to .04. A total adsorbed quantity corresponding to about .01 monolayer is indicated. The curve then continues to rise slowly for at least 65 hours following what appears to be a logarithmic type adsorption. It is possible that the hydrogen is adhering to first monolayers of the other components such as methane or CO or building up a second monolayer on itself or responding to a decreasing sticking coefficient with increasing coverage according to the Elovitch equation. Further studies are needed to clarify the situation.

The additional bombarding beam gun structures are being added to the system and experiments will continue to determine the reactions that occur at the beam surface interface in the ultra-high vacuum environment.

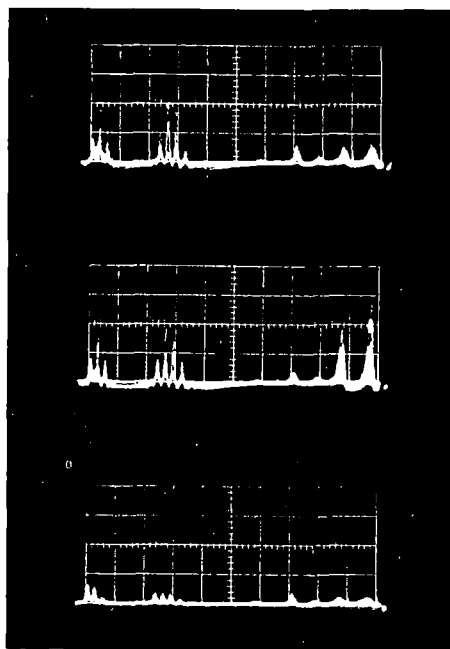


Fig. 7 Scope display of mass range 15-56 a.m.u. The lower figure is the background with full scale deflection of 4×10^{-9} Torr. Reading from right to left mass 15 and 16 (methane) and 17, 18 (water vapor) occupy the first 3 divisions. Peaks 26-29 occupy the 7th and 8th divisions. The extreme left peaks are 39, 41, and 43. The middle figure shows effect of low power heat pulse to the target. The upper figure was taken five minutes later with a higher power heat pulse through the target. Partial pressure gas desorption pulses in the 10^{-9} Torr range over a period of a few seconds are easily detectable.

A MASS SPECTROMETER FOR THE STUDY OF SPUTTERING

A. J. Smith, D. J. Marshall, L. A. Cambey and E. J. Michael
Nuclide Corporation
State College, Pennsylvania

Abstract

A single focusing mass spectrometer system has been built to study sputtering of metal surfaces by ion bombardment. Bombarding ions are formed in an oscillating electron source.

Sputtered ions are analyzed directly. Sputtered neutrals have been detected by ionizing them in a second electron bombardment ion source. The bombarding ion beam was pulsed, and a synchronous detector was used to improve the signal to noise ratio for the sputtered neutrals.

Bombarding argon ion currents of 10^{-6} ampere produce sputtered ion currents at the multiplier input of 10^{-15} to 10^{-12} ampere for a copper target. Energy spreads greater than 350 eV have been observed for sputtered ions.

Introduction

The application of mass spectrometry to the direct analysis of particles sputtered from a surface by ion bombardment is a useful technique for studying target composition and many types of surface phenomena.^{1, 2} To be most useful in such work, a mass spectrometer must meet several important requirements.

It is important that the system be capable of maintaining an ultra-high vacuum to prevent contamination of the target surface by background gases. The bombarding ion beam intensity should be such that the target surface can be kept clean of the contaminating gases that remain in the system. Overflow of gas into the target region from the source which supplies the bombarding beam should be low enough that back diffusion of sputtered particles to the target is negligible.

In addition to the standard Faraday cup ion collector the instrument must also have an electron multiplier detector in order that small currents of sputtered species might be recorded.

It must be capable of analyzing both sputtered ions and sputtered neutrals because the many studies which lend themselves to ion bombardment techniques are best carried out by recording either or both types of sputtered particles. Detection of the sputtered neutrals is particularly important because their relative intensities are apparently much more representative of sample composition than are sputtered ion intensities. The detection of neutrals, however, is complicated by the fact that residual background gases are ionized simultaneously with the neutrals and, therefore, the signal to noise ratio is, in practice, very low for neutral species.

The authors would like to report here on a mass spectrometer built for sputtering studies which meets these requirements.

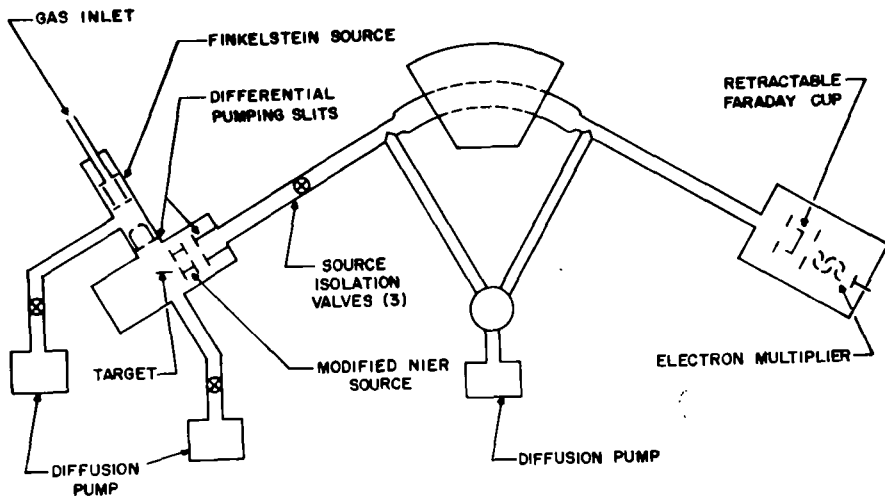


Fig. 1: Schematic diagram of the mass spectrometer

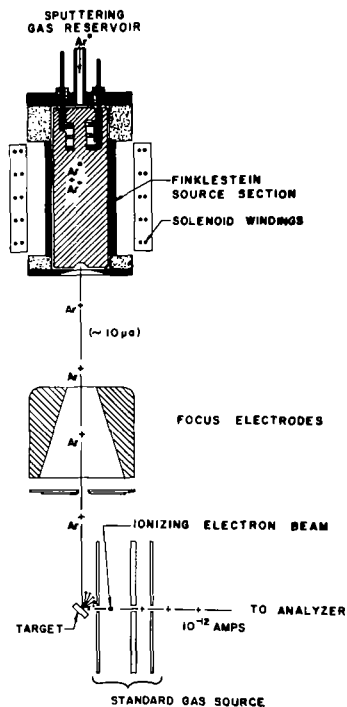


Fig. 2: Diagram showing the source geometry of the mass spectrometer. Ions and neutrals sputtered from the target flow through the standard gas source where residual background gases and some of the sputtered neutrals are ionized in the electron beam. The resulting ion beam is then mass analyzed in the magnetic sector field.

Description

A schematic diagram of the instrument is shown in Fig. 1.

The instrument is a 60° deflection, 6" radius magnetic sector field spectrometer with an all-metal bakeable vacuum enclosure.

The two source regions and the analyzer region are housed separately and are separated from each other by the ion beam collimating slits. Separate diffusion pumps are used on each of the housings, providing three stages of differential pumping. A system of all-metal valves isolates the source regions from the rest of the system whenever vacuum is broken to change targets.

The collector consists of a retractable Faraday cup and a 20-stage, pie-type electron multiplier. A vibrating reed electrometer and strip chart recorder can be switched to record the output from either detector.

The ion sources for the instrument are shown schematically in Fig. 2. The source which supplies the bombarding beam uses the oscillating electron arrangement described by Finkelstein.³ The detailed source geometry chosen by the authors is similar to that described by Almén and Nielsen.⁴ The ion beam is extracted from the source in the direction of the axis along which the electrons oscillate. The bombarding ion beam energy is variable from 200 eV to 5 keV. The second source is a modified Nier⁵ electron bombardment type which is used to ionize sputtered neutrals as well as residual background gases whenever the instrument is to be operated as a standard gas spectrometer. A slit cut into the rear of the ionization box allows sputtered particles to pass through the electron beam, where some of the neutrals are ionized. Sputtered ions pass through essentially undisturbed. The angle between the bombarding beam and the beam leaving the Nier source is fixed at 90° by the placement of the ion sources. The target mounts on the Nier source, directly behind the ionization region, in a holder which allows the angle between the normal to the target and the bombarding beam to be adjusted from 0° - 90° from outside the vacuum. Provision is made for measuring the bombarding current and for heating the target up to 600°C by electron bombardment.

The background pressures obtainable in the instrument are in the 10⁻⁹ Torr range and the principal background species are CO and CO₂.

Bombarding ion currents of 1-3 μ A at a current density of 3-10 μ A/cm² could be obtained for 0.1 μ argon gas pressure in the Finkelstein source. Under these conditions the target region pressure rises to about 1 x 10⁻⁶ Torr because of overflow of the un-ionized argon gas into this region.

Results

OFHC copper targets were used in the preliminary tests. These targets were given no special treatment except a mechanical polishing to remove the oxide layer, followed by a thorough degreasing with methanol and rinsing with distilled water.

It was found that the secondary Cu⁺ ion yield varied greatly from one target to the next, although the targets were obtained from the same source and received similar preparatory treatments before sputtering. The maximum initial sputtered Cu⁺ ion currents ranged from 1 x 10⁻¹²A to 5 x 10⁻¹⁵A for the group of targets used. Typically, currents of 10⁻¹³A to 10⁻¹⁴A were obtained from a new target. It was observed that the sputtered ion current intensity always decreased gradually by about 25% from its maximum initial value to a steady value after the first 5 - 10 minutes of sputtering.

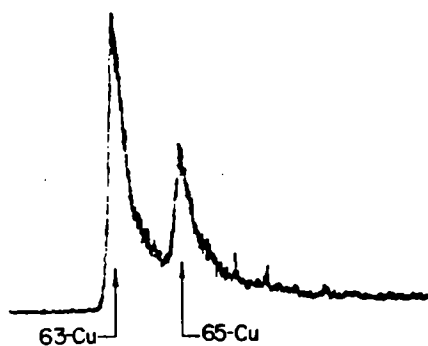


Fig. 3: Mass spectrum showing the sputtered ion peaks and part of their high energy tails. Argon ion energy 1000 eV. Magnetic scanning used with Nier source accelerating potential of 1200 V.

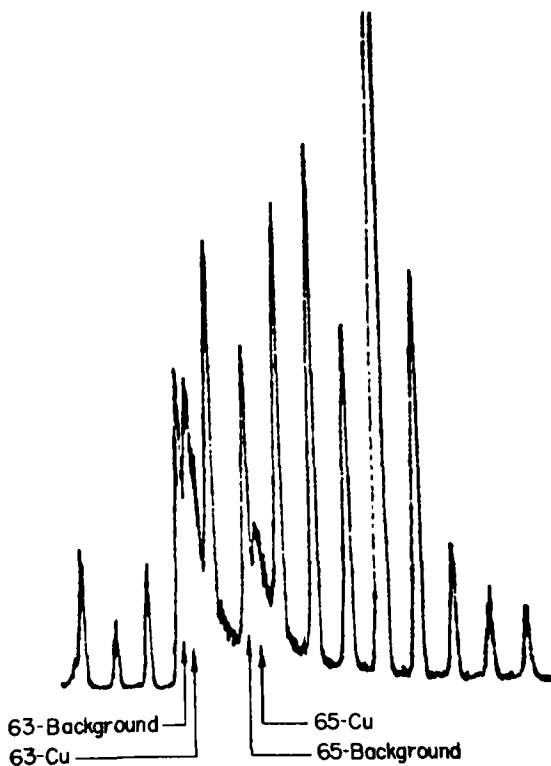


Fig. 4: Mass spectrum showing sputtered copper ion peaks along with background peaks originating from residual gases ionized in the Nier source. Experimental conditions same as for Fig. 3 except with electron beam on in Nier source.

Figure 3 shows the sputtered copper ion peaks obtained when the target was bombarded with 1 keV argon ions. The long up-mass tails indicate that the ions have a large initial energy spread, while the sharp low mass side of the peaks indicate that the ions had a definite minimum initial energy. Both by measuring the peak width and by placing a retarding potential on the target it was found that over 1% of the sputtered Cu^+ ions had initial energies in excess of 350 eV. Similar results were obtained for Be^+ and Cu^+ sputtered from a CuBe target.

By next switching the ionizing electron beam on in the Nier source a spectrum as shown in Fig. 4 results. Here the peaks originating from background gases and sputtered neutrals ionized in the Nier source are superimposed on the sputtered Cu^+ ion peak spectrum shown in Fig. 3. The sputtered neutrals, however, are obscured by the larger background peaks. The separation between the copper peaks and the background peaks. The separation between the copper peaks and the background peaks of the same m/e value indicates that the most probable initial energy of the Cu^+ ions was about 9 eV.

In order to increase the current of the ionized sputtered neutrals the electron emission current in the Nier source was increased to 30 ma. Under these conditions the residual background currents were greater than 10^{-14}A ; but, by using a synchronous source-detector system to suppress the residual background peaks the ion currents due to the ionized sputtered neutrals could be readily detected.

The working of the synchronous detector system is best explained by referring to Fig. 5 which shows the current waveforms in different sections of the instrument. The first waveform is that of the bombarding ion beam current which is pulsed by turning the Finkelstein source on and off with an electrical chopper.

The Nier source is on continually so the analyzed ion beam current measured at the collector or multiplier output has a steady dc component due to the background and an ac component due to the ionized sputtered neutrals as shown in the second waveform. This modulated current is put into an ac amplifier where the dc component is removed. The resulting output current of the ac amplifier as shown in the third waveform is rectified with another chopper synchronized with the first and is then recorded.

Figure 6 shows a sputtered neutral spectrum obtained with this system from a copper target bombarded by 2 keV argon ions. The sputtered ions were suppressed with a retarding target potential. The Cu^{63} peak current is $2 \times 10^{-15}\text{A}$, almost 2 orders of magnitude smaller than the background peak of the same m/e value, yet easily detectable as shown here. In addition the spectrum contains sputtered neutral species apparently originating on the inconel target holder.

There is no appreciable energy spread displayed in the sputtered neutral spectrum. This, however, is not conclusive evidence that an energy spread does not exist,⁶ for the higher energy neutrals pass through the ionizing region more rapidly and consequently have a smaller probability of ionization. Thus, the high energy tail, if it exists, is effectively filtered out by the electron bombardment ionization process.

The preliminary results obtained with this system indicate that sputtered neutrals can be accurately measured even in the presence of background species several orders of magnitude larger. Consequently, with the use of this technique, the application of mass spectrometry to sputtering studies should be extended. One application may be the use of a sputtering source for quantitative compositional analyses.

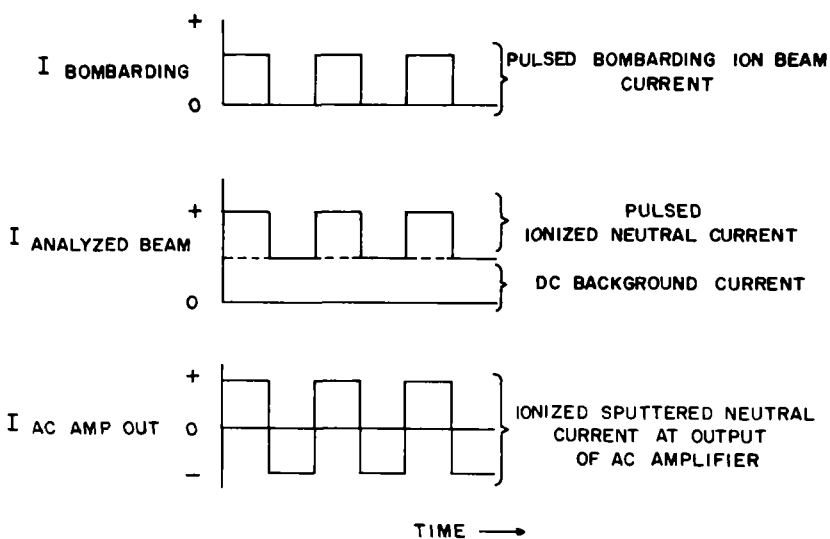


Fig. 5: Sketch of current waveforms in different sections of the instrument when synchronous source-detector system is in use.

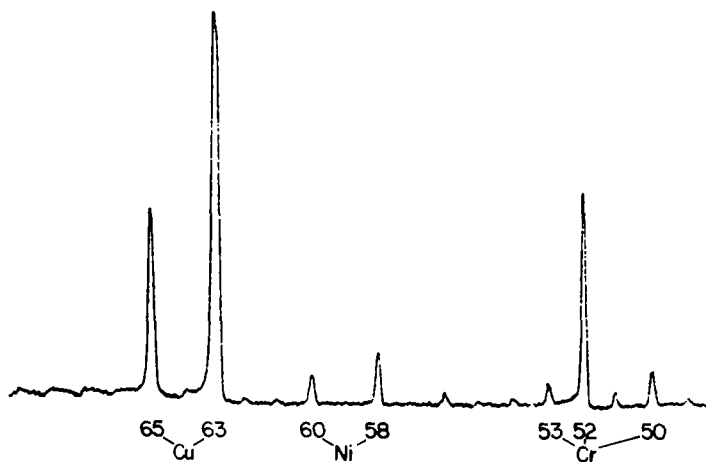


Fig. 6: Mass spectrum of neutrals sputtered from copper target and inconel target holder by a $1.5 \mu\text{A}$ beam of argon ions at 2000 eV energy. Mass spectrum obtained by magnetic scanning at Nier source accelerating potential of 3000 V.

References

1. R. E. Honig, J. Appl. Phys. 29, 549 (1958)
R. E. Honig, Advances in Mass Spectrometry, Vol. 2, p 25,
Pergamon Press, New York, 1963
2. R. C. Bradley, J. Appl. Phys. 30, 1 (1959)
R. C. Bradley, A. Arking and D. S. Beers, J. Chem. Phys. 33,
764 (1960)
R. C. Bradley and E. Ruedi, J. Appl. Phys. 33, 880 (1962)
3. A. Theodore Finkelstein, Rev. Sci. Inst. 11, 94 (1940)
4. O. Almén and K. O. Nielsen, Nucl. Inst. 1, 302 (1957)
5. A. O. C. Nier, Rev. Sci. Inst. 18, 398 (1947)
6. R. V. Stuart and G. K. Wehner, 1962 Vacuum Symposium Transactions,
p. 160, MacMillan Company, New York, 1962
K. Kopitski and H. E. Stier, Z. Naturf. 17a, 346 (1962)

ION SOURCE FOR SOLID MATERIALS

Helmut J. Liebl and Richard F. K. Herzog

Geophysics Corporation of America
Bedford, Massachusetts

The first ion source for solids, based on the sputtering phenomenon, as far as is known, was built by Herzog and Viehboeck¹ fourteen years ago. (Figure 1). In their experiment, the ion beam from a canal-ray tube struck the sample and the secondary ions released from the surface were accelerated into the mass spectrometer.

Our new design is basically similar (Figure 2). An arc-type discharge is maintained in the duoplasmatron in an argon atmosphere of about 20 microns. The anode has a central hole of 0.008-inch diameter, through which the argon ions are extracted and accelerated by the conical electrode, up to an energy of 15 kilovolts.

An ion current up to several milliamperes can be extracted from this small opening. The energy spread of the extracted ions is of the order of 10 volts. The ion beam is focussed by the einzel lens and deflected in a transverse electric field by 30°. It strikes the target at a 30° angle and the bombarded area is a circular spot of about 3 mm diameter. The current density is about 10 ma per cm². The secondary ions released from the surface are accelerated and focussed by an immersion lens arrangement onto the slit of the mass spectrometer.

The whole arrangement is mounted on the pumping port of a 4 inch oil diffusion pump station, which, during operation, keeps the ambient pressure of the target below 10⁻⁵ torr.

The target is mounted on a water cooled copper disc, which can be rotated from outside. In this way, up to six different samples can be mounted simultaneously and brought into the beam one after the other without breaking the vacuum or even turning off the primary beam.

Secondary ion currents of the order of 10⁻⁸ to 10⁻¹⁰ amp, depending on the sample material, are released from the sample surface; these currents are very stable and are therefore suitable for conventional mass analysis by sweeping the magnetic field of the analyzer or the acceleration voltage. The currents are measured with a Vibrating Reed Electrometer; permanent records are obtained with an X-Y recorder. Figure 3 shows a retarding field measurement, which was made with secondary aluminum ions produced by an 8 kv primary beam of argon ions. The derivative of the measured curve gives the energy distribution, showing a maximum at about 23 volts and a half-width of 26 volts.

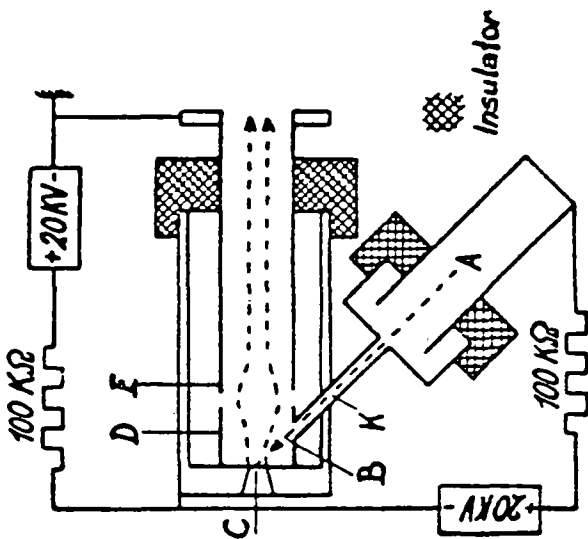
Secondary ion spectra from metals are very easy to obtain. The number of secondary ions per incident ion depends on the ionization potential of the element and range between 10⁻⁴ to 10⁻¹.

Figure 4 shows the secondary ion spectrum from a zinc sample, which is among the metals with the highest ionization potentials. Beside the zinc-peaks, one can see peaks in the same intensity ratio about one-tenth as high, but shifted by one mass unit, which can only be ZnH⁺.

We have also tried insulator samples and did not encounter any problems from a charge up effect. Figure 5 shows spectra obtained from rock samples. The pieces had the shape of a 1/4 by 1/4-inch and 1/16-inch thick wafer, which were clamped onto the target plate. A remarkable feature is the low peak at mass 40 in the lower spectrum, which suggests that the large 40-peak in the upper spectrum is Calcium rather than Argon.

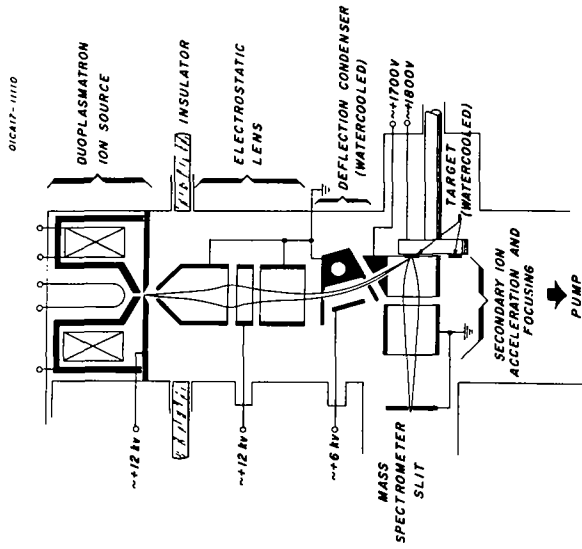
One of the most obvious questions is the applicability of this method for quantitative analysis. In this regard we can only give very preliminary results, since work about the problems involved in a quantitative analysis has only started quite recently. However, the following remarks will, roughly, characterize the situation.

¹ R. F. K. Herzog and R. P. Viehboeck, Phys. Rev. 76, 855 (1949).



OICA17-1130

Slide 1



SPUTTERING ION SOURCE

Slide 2

According to a widely accepted theory, the emission of secondary ions, by sputtering can be described in a manner similar to surface ionization, by a Langmuir-Saha equation:

$$\frac{n^+}{n^0} = \exp \frac{e(W-I)}{kT} = \exp 11606 \frac{W-I}{T} \quad (1)$$

n^+ = Number of sputtered ions

n^0 = Number of sputtered neutrals

W = Work function of surface (ev)

I = Ionization potential of element (ev)

T = "Apparent Temperature" ($^{\circ}\text{K}$)

The so-called "apparent temperature" T is a function mainly of the mass and energy of the bombarding ions. Application of this formula is restricted, since, in general, the number of sputtered neutrals and also the work function of the surface is unknown. However, this difficulty can be overcome by comparing two components of an alloy.

If one starts bombarding an alloy which consists of two components with different sputtering yields, then at the beginning, the component with the higher sputtering yield ratio is removed at a preferential rate from the surface, so that the surface concentration of the other component with the lower sputtering yield increases until an equilibrium is reached where the relative number of sputtered particles becomes equal to their relative concentrations. We now apply Equation (1) to the two components and take the ratio of the two expressions:

$$\frac{n_1^+}{n_1^0} = \exp 11606 \frac{W-I_1}{T} \quad (2)$$

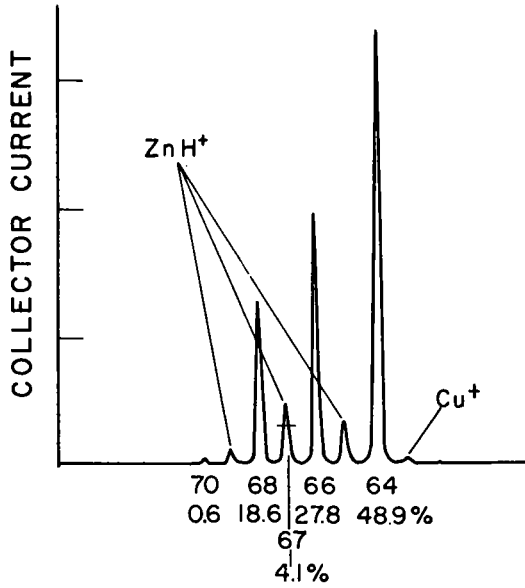
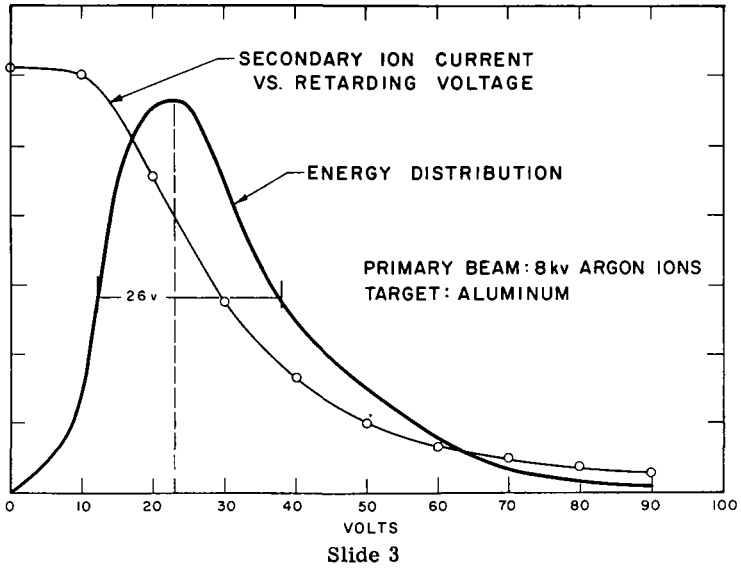
$$\frac{n_2^+}{n_2^0} = \exp 11606 \frac{W-I_2}{T} \quad (3)$$

$$\frac{n_1^+}{n_2^+} = \frac{n_1^0}{n_2^0} \exp \frac{I_2-I_1}{T} \quad (4)$$

The ratio of the ion currents, n_1^+/n_2^+ , equals the actual abundance ratio n_1^0/n_2^0 times a discrimination factor, $\exp(I_2-I_1)/T$, which has in the exponent the difference between the ionization potentials of the two elements divided by the "apparent temperature" T . The work function of the surface for the two components has been assumed to be equal and cancels out. As an example, the difference between the ionization potentials of iron and chromium is $I(\text{Fe})-I(\text{Cr}) = 7.90-6.76 = 1.14$ ev. Table 1 shows how the discrimination factor of iron against chromium decreases with increasing "apparent temperature".

$T(^{\circ}\text{K})$	5,000	10,000	20,000
$\exp 11606 \frac{1.14}{T}$	14	3.75	1.94

TABLE 1

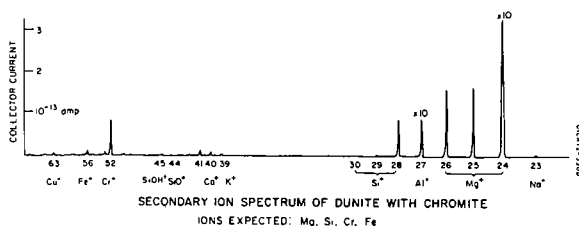
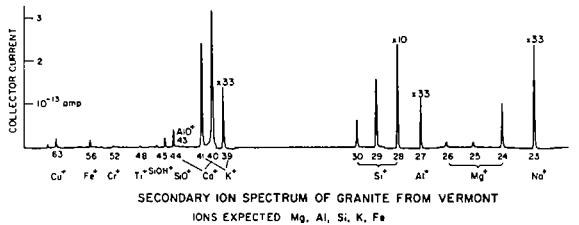


Zn^+ - SPECTRUM

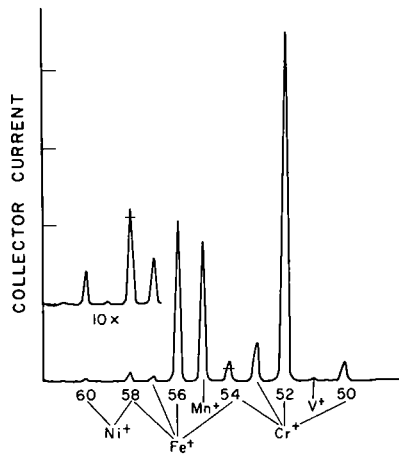
Slide 4

In order to find the "apparent temperature", we took the spectrum of a 304 Stainless Steel sample (Figure 6), the composition of which is fairly well known.

The chromium peaks are about eight times higher than one might expect from the actual abundance ratio of 1 to 4 of chromium to iron. Using this discrimination factor of eight, the "apparent temperature" turns out to be 6500°K under these conditions. In order to reduce the discrimination; we hope, that we can increase the "apparent temperature" by use of heavier bombarding ions and a higher energy. But even under present conditions, we feel that one can perform useful quantitative analysis by calibrating the instrument with samples of known composition containing the same components as the sample to be analyzed. We expect that this ion source will become a very useful tool for the analysis of solids especially since the ion currents are very stable, which permits direct electrometric measurement of the intensities. Compared with the conventional photographic plate method, the electrometric method is more accurate, faster and much more convenient.



Slide 5



SECONDARY ION SPECTRUM OF 304 STAINLESS STEEL

Slide 6

SOME PRELIMINARY DATA ON THE DETECTION OF IONS SPUTTERED FROM GLASS SURFACES

John T. Kerr
Corning Glass Works
Research & Development Laboratory
Corning, New York

ABSTRACT

Some commercial glasses have been bombarded in the source of a trochoidal mass spectrometer with beams of rare gas ions. Sputtered positive and negative ions of the major glass constituents have been detected using ion bombardment energies up to 3400 eV.

A short description of the instrument and data on a borosilicate, soda-lime and phosphate glass are given.

INTRODUCTION

Glass is used extensively in the construction of electrical gas discharge devices for commercial and experimental applications. No investigation seems to have been made of the ions sputtered from glass surfaces under the ion bombardment which must take place at various energies in such devices. A method, currently in use in the Corning Research Laboratory, is reported here which permits the detection and identification of positive and negative ions sputtered from glass surfaces by incident positive, rare gas ions with energies up to approximately 3000 eV. In principle, the method is similar to that used by other experimenters in the identification of ions sputtered from metals (1), (2).

APPARATUS

Samples of glass are bombarded in the source of a trochoidal orbit mass spectrometer similar in design to that described by Mariner & Bleakney (3) some years ago. In this design, mass separation takes place by the action of mutually perpendicular magnetic and electric fields. Perfect focussing and higher resolution than that available from 180° instruments of comparable magnetic field size are attractive features of this combination of fields.

The magnetic field used here is provided in a 3-1/8 inch wide gap by an electromagnet with 16-inch diameter pole pieces. The maximum field strength is about 11 kilogauss. The electric field is formed by a series of 20 picture-frame plates spaced 1 cm apart, and connected to a potential divider system outside the vacuum chamber. The object to image slit distance is 19.1 cm thereby giving a resolving power of 3800 with 0.0025mm. slit widths. No attempt has been made, so far, to achieve this resolving power. Because high sensitivity is required, the slits have been opened up so that the resolving power is about 120.

The instrument is constructed of metal with precautions taken to achieve ultimate background pressures in the low 10^{-8} torr range. It is designed to take copper shear-seal gasketing and is bakeable to 450°C. In these preliminary experiments, Teflon gasketing has been used and a base pressure below 5×10^{-8} torr is routinely attained. The vacuum chamber is suspended vertically in the magnet gap. The magnet is rolled away during bakeouts. Access to the source and sample is gained through two ports.

The vacuum is maintained by a 2" ultra-high vacuum, mercury system pumping the bombardment source region and a similar 6" system pumping the main vacuum chamber in which the sample is located. Since the only connection between these two regions is the exit slit in the bombardment ion source, differential pumping is maintained.

FIGURE 1
MASS SPECTROMETER SOURCE

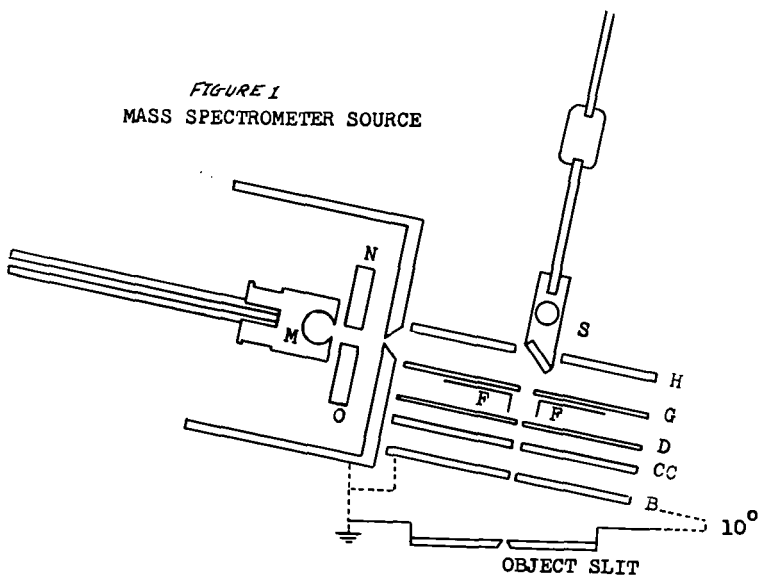


FIGURE 2
MASS SPECTRA OF IONS
SPUTTERED FROM A
SODA LIME GLASS
Bombarding ion— A^+
Current— 1×10^{-7} amps.

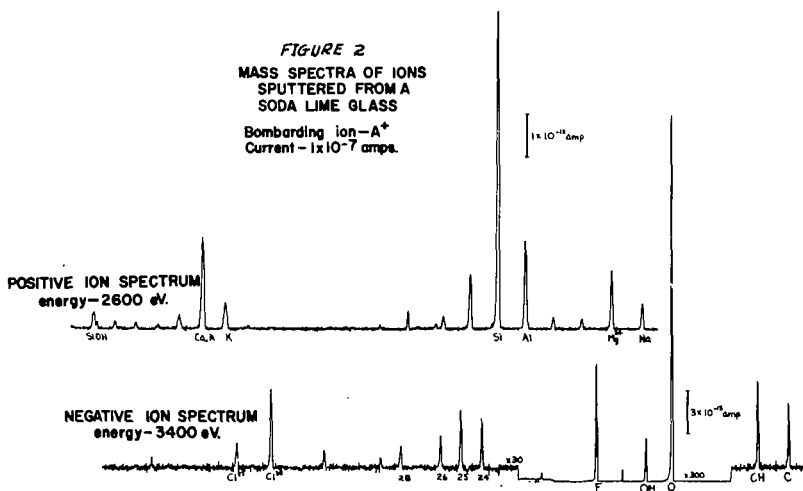


Figure 2 shows the sputtered positive and negative ion spectra from the polished surface of the soda-lime glass. Before bombarding, the glass was washed ultrasonically in a detergent, rinsed, and immersed in a boiling 3% (volume) H_2O_2 solution for 20-30 minutes. Then the glass was rinsed in tap water and finally in distilled water. Before running the negative spectrum, the glass was immersed in a 4% (Volume) HF solution for three minutes, rinsed in distilled water and dried at $100^\circ C$ after the aforementioned washing treatment.

The sodium peak in the positive spectrum was larger than the Si^{28} peak at the beginning of bombardment. Both the sodium and potassium peak decrease with time indicating, perhaps, a selective sputtering action or an electrolytic effect in which alkali ions in the glass are moved away from the surface because of a field induced across the sample by the arrival of positive charge at the surface. Without the HF rinse, the fluorine peak is much less than the OH peak.

Since actual recorder traces are duplicated in Figure 2, one can gain an impression of how well the instrument is performing in this application. Although the bombarding ion is argon, the mass 40 is not particularly large in these scans and hence does not interfere with surrounding peaks.

Figure 3 is a table of the sputtered positive ion peaks detected from the phosphate and borosilicate glasses. The phosphate glass was given a H_2O_2 wash as mentioned above while the thin borosilicate sample was used in its "as blown" state. A thin sample was used to compensate for its bulk resistivity which is higher than for the other two.

It is observed that the peak heights are not indicative of the glass composition. Of particular interest is the very small peak of phosphorus. Using the ideas presented by Honig(2) regarding the efficiency of ion production and ionization potential (IP), one would expect to see phosphorus as a negative ion. Indeed, it is seen as a negative ion in Figure 4, but combined with oxygen.

Figure 4 shows a table of the negative ions observed from the phosphate and borosilicate glass. In the case of the borosilicate, the only peaks clearly distinguishable down to about 7×10^{-16} amps are the four identified. However, a large array of peaks is obtained from the phosphate glass including the unexpected groups PO , PO_2 and PO_3 .

CONCLUSIONS

It has been demonstrated that positive and negative ions sputtered from three different glasses can be detected and identified. The next step is to look more carefully for sputtered neutrals.

REFERENCES

- (1) Early work cited in Massey and Burhop ELECTRONIC AND IONIC IMPACT PHENOMENA, Chapter 9, Oxford at Clarendon Press (1952).
- (2) Honig, RE., ADVANCES IN MASS SPECTROMETRY, Vol. 2, Ed. R.M. Elliott, Pergamon Press, Oxford, 1963, P. 25 (a number of applicable references cited).
- (3) Mariner, Thomas and Bleakney, Walker, Rev. Sci. Instruments, 20, 297, (1949).

FIGURE 3
SPUTTERED POSITIVE IONS FROM A
PHOSPHATE AND A BOROSILICATE GLASS

Mass		Phosphate		Borosilicate		IP ev.	
		Pk. Ht.	Comp.	Pk. Ht.	Comp.		
10	B		2.8	1.0	5.0	8.3	Bombarding energy- 2600 ev. Current- 1×10^{-7} amps. Argon ⁺
11	B			4.3			
23	Na	2.0	16.0	36.0	2.7	5.1	
24	Mg	0.5				7.6	
27	Al	114.0	8.9	6.8	.05	6.0	
28	Si			50.0	27.5	8.1	
29	Si						
	SiH			5.0			
30	Si			1.3			
31	P	1.0	8.0			11.0	
39	K	10.0				4.3	
40	A						
	Ca	11.5				6.1	
41	K	1.0	7.7				
	Zn		3.6				

1 div. = 10^{-14} amps. Comp. - Mole%

FIGURE 4
SPUTTERED NEGATIVE IONS FROM A
PHOSPHATE AND A BOROSILICATE GLASS

Phosphate				Borosilicate						
Mass		Pk. Ht.		Mass		Pk. Ht.		Mass		Pk. Ht.
12	C	13.8		43	AlO	43.0		12	C	2.0
13	CH	17.7		47	PO	12.0		13	CH	1.5
16	O	1000.0		48	C ₄	2.0		16	O	55.0
17	OH	67.0		59	AlO ₂	12.0		17	OH	3.0
19	F	31.0		63	PO ₂	288.0		1 div.=1x10 ⁻¹⁴ amps.		
24	C ₂	16.0		79	PO ₃	96.0				
25	C ₂ H	15.7								
26	C ₂ H ₂	6.3								
27	C ₂ H ₃	7.3								
31	P	11.5								
32	PH	23.0								
35	Cl	42.0								
36	C ₃	2.0								
37	Cl	11.3								
42		10.0								

Bombarding Energy - 3400 ev.

Current - 1x10⁻⁷amps.

Argon⁺

1 div.=3x10⁻¹⁵amps.

1 div. = 3×10^{-15} amps.

The ion detector is a vibrating reed electrometer generally operated to give a noise level of 3×10^{-15} amps peak-to-peak and less than 1 second response time.

Figure 1 shows a schematic of the source of the instrument which is immersed in the same magnetic field used for mass analysis. Bombarding ion energies between 300 and 3000 eV can be obtained.

Gas is leaked into the region M and is ionized by an oscillating electron beam. The positive ions so formed are accelerated between deflector plates O and N toward an exit slit in the shield. Upon passing through the slit, the ions travel between plates H and G to the sample mounted on the sample block S. The voltage difference between H and G is adjusted to compensate for deflection in the magnetic field. S can be set at any voltage between H and G. Ions emitted from the sample surface are accelerated between deflector plates FF', through D, CC' and B and are focussed on the object slit at the entrance to the analysing fields. The source structure is rotated 10° with respect to the object slit plane to compensate for deflection in the magnetic field. An electron beam, designed to ionize neutrals from the surface of the sample and residual gas, passes between F and F' perpendicular to the plane of the paper. So far, no neutrals have been detected.

The sample block holds a sample with maximum dimension $7/16 \times 1/4 \times 0.020$ inches and can be heated to over 400°C . Temperature is monitored with a copper-constantan thermocouple. The area of the sample bombarded seems to be $(4 \times 4) \text{ mm}^2$. The total current to the sample is generally 1×10^{-7} amps and this is obtained when the pressure in M is about 7×10^{-6} torr. The pressure in the analysing region, i.e., around the sample is estimated to be 30 to 50 times less.

RESULTS

Before attempting to run glass samples, a number of metals were bombarded with argon ions and their sputtered positive ion spectra were observed.

The bombarding current was about 10^{-7} amps and the energy was 2600 eV. Detected ion currents of the major constituents of the bulk metals are as follows:-

<u>Material</u>	<u>Major Constituents Pk.</u>	<u>Ion Current Observed (amps)</u>
Mg metal	Mg^{24}	2.2×10^{-12}
Al metal	Al^{27}	8×10^{-12}
Cu metal	Cu^{63}	2×10^{-13}
Stainless Steel (300 series)	Fe^{56}	5×10^{-13}

The surface cleaning of these samples was neither rigorous nor standardized. Generally, it consisted of polishing, ultrasonic washing in a detergent and distilled water, rinsing in distilled, over-flowing water and drying in an oven at slightly over 100°C .

The results of bombarding three glasses, a soda-lime glass (Corning Code 0081), a phosphate glass (Corning Code 7295) and a borosilicate (Corning Code 7740) are shown in Figures 2, 3 and 4. The soda-lime and phosphate glasses were 0.5 mm thick while the borosilicate was 20μ thick. All were heated to about 200°C to maintain some conductivity and reduce surface charging.

H.D.Beckey, Institut für Physikalische Chemie der Universität Bonn, Germany
and
G.Wagner, Gaswaerme-Institut Essen, Germany,
now ATLAS Mess- und Analysentechnik GmbH (MAT) Bremen, Germany

"Analytical applications of a mass spectrometer equipped with field emission ion source".

Abstract: Work was recently carried out with an ATLAS model CH4 mass spectrometer fitted with a field emission ion source. This source permits almost fractionless molecule ion spectra of hydrocarbon compounds to be obtained with resolution and pressure characteristic similar to those obtained with the normal electron bombardment ion source. The detection limit with this equipment is $1 : 10^6$. By using a Wollaston wire instead of a field emission tip, H.D.Beckey further increased the ion yield by a factor of 1000 and improved the stability of the ion currents to 0.7 %. These performance data indicate that the field emission ion source is suitable for chemical analysis applications. The following is a discussion of some of the advantages of this field emission ion source over the electron bombardment ion source in the field of hydrocarbon analysis.

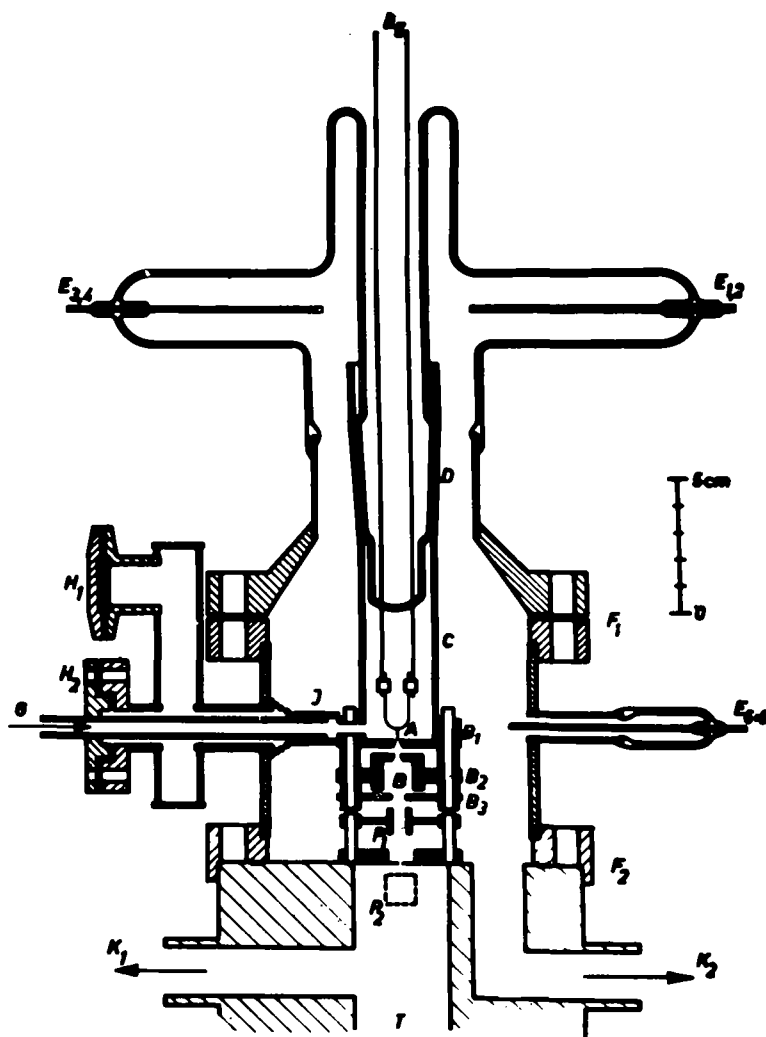
References have been made to the theoretical advantages of using a field emission ion source for the mass spectrometrical analysis of organic compounds by I n g h r a m and G o m e r [1] and by B e c k e y [2, 3, 4, 5]. The following experiments were conducted with a conventional ATLAS model CH4 mass spectrometer with magnetic 60° sector field and 20 cm mean ion path radius. The instrument was fitted with a field emission ion source (slide No.1) and a secondary electron multiplier [6].

Our field ion source was developed by B e c k e y [7]. The emission system of this source incorporates a fine platinum spike anode A (the radius of the spike tip is 10^{-5} to 10^{-4} cm) situated 2 mm from a cathode diaphragm B, with a central aperture. The same tip could be used for a series of experiments over a period of several months. The platinum tip has an accurately stabilized positive potential of 3000 volts and the diaphragm is at a negative potential, variable from 0 to - 15000 volts. This potential differences give electric fields in the vicinity of the tip of about 10^8 to 10^9 volts/cm.

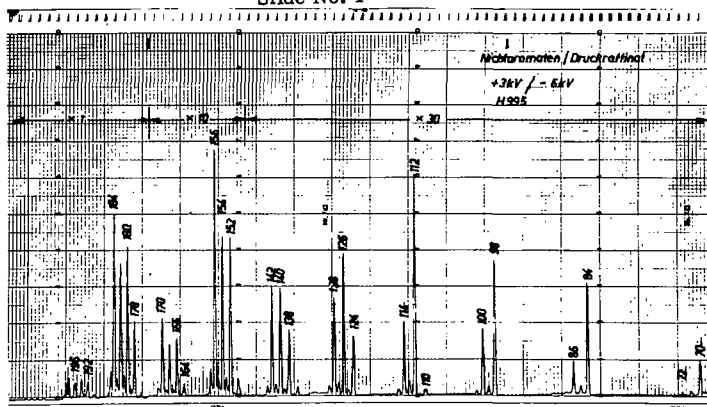
This strong electrical field distorts the internal field equilibria of gas molecules approaching the anode. Under these conditions electrons of the molecular ground state leave the gas molecules (quantum mechanical "tunnel effect") and collect on anode spike. The positive ions generated are accelerated to the cathode of the emission system. The theory of field ionization, developed by K i r c h n e r [8], M u e l l e r [9] and G o m e r [10] can not be outlined here. Ions that pass through the cathode 2 mm diameter aperture B, are focussed on the entrance slit of mass spectrometer by electrostatic lenses B₂, B₃ and deflection plates P₁. This ion beam is then analyzed by scanning the magnetic field of the mass spectrometer.

During the field ionization no electronic excitation energy is transferred to the molecules. But close to the anode surface ions will fragment if they are subjected to the strong electric field for a time in excess of 10^{-14} sec as B e c k e y [11] showed. This may almost be avoided by using a larger diameter tip on the spike anode (radius about $5 \cdot 10^{-5}$ cm) and a smaller potential difference (8 to 10 kV) between the anode and cathode of the emission system. With this system almost fractionless molecule ion currents in the order of 10^{-8} amps were produced and ion currents up to 10^{-11} amps reached the first dynode of the electron multiplier.

In recent investigations B e c k e y [12] replaced the anode spike with a thin platinum wire ($2.5 \cdot 10^{-4}$ cm diameter) placed parallel to the plane of the cathode. This anode was produced by etching a Wollaston wire. Using this emission system the emitting area is increased by a factor of about 10000, the effective increase of ion currents at wires is of a factor of about 100 compared with tips. With typical operation conditions the field strengths at tips are somewhat higher than at 2.5μ wires. But all organic molecules can be field ionized also at the wire anode (the ionization



Slide No. 1



Slide No. 2

probability being small only for the light hydrocarbons up to C_4). Besides the better stability of ion currents, there are two more advantages in using wire anodes for field ionization: the ion intensities are increased such that a Faraday collector may be used; second, the fragmentation is further reduced because of the low value of electric field [12].

The two field sources were examined for stability, pressure proportionality and reproducibility of their ion currents. Short term deviations of ion currents of about + 5 % were obtained with the platinum anode spike and of about + 0.7 % with the wire anode. The ion currents remained linear with sample pressure in the ion source over a wide range. Mass spectra were reproduced with the two anodes with a variation in the order of the short term deviations of the ion currents [6, 12]. A constant potential difference at the ionization system is necessary for these stabilities.

For the molecule ion currents of a number of hydrocarbon compounds the comparative field ion mass spectrometric sensitivities were determined and their dependence of ionizing field observed. Increasing the ionizing field caused fragmentation to occur. Some simple rules for the fieldinduced and metastable fragmentation of organic molecule ions were apparent [7]. Publications of further results will be given after a short time. Because of these rules the field ion mass spectrometer promises advantages in structure analysis of organic molecules [6].

For brevity we now only can report some work with a field ion source in mass spectrometric analysis of hydrocarbon mixtures.

Next slide shows the field ion mass spectrum of a mixture of saturated hydrocarbons, fractionated from a pressure-hydrated coke-oven-plant benzene by using a chromatographic technique. This fraction contains the saturated non aromatic compounds, previously tested by a gas chromatographic analysis *).

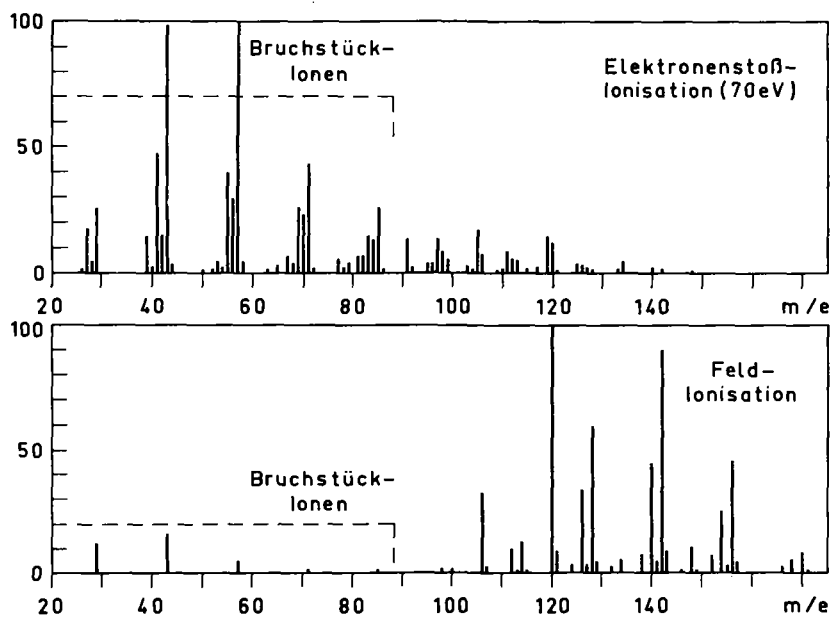
You may observe ten distinct groups of molecule ion peaks. In every group the peak of highest mass number is attached to the paraffine hydrocarbon $C_{n+2}H_{2n+2}$. This spectrum shows all the paraffines from pentane and its isomers (mass number 72) up to tetradecane and isomeres (mass number 198). Two, four, six or eight mass numbers below the paraffine mass in every group appear the peaks of mono- and corresponding poly-cyclic saturated hydrocarbons. Involving the foregoing determinations of comparative field ion mass spectrometric sensitivities, we obtain without expense of identification and computation a quantitative analysis of the mixture. This method will not detect different isomeres.

Comparison of electron impact and field ion mass spectra of a gasoline shows the advantageous application of field ion source. The mass spectra are schematically presented (slide 3). In both the mass spectra the mass lines are referred to the most intensive peak. You may notice the distinctive and important difference: The intensive peaks appear in different ranges of the mass scale.

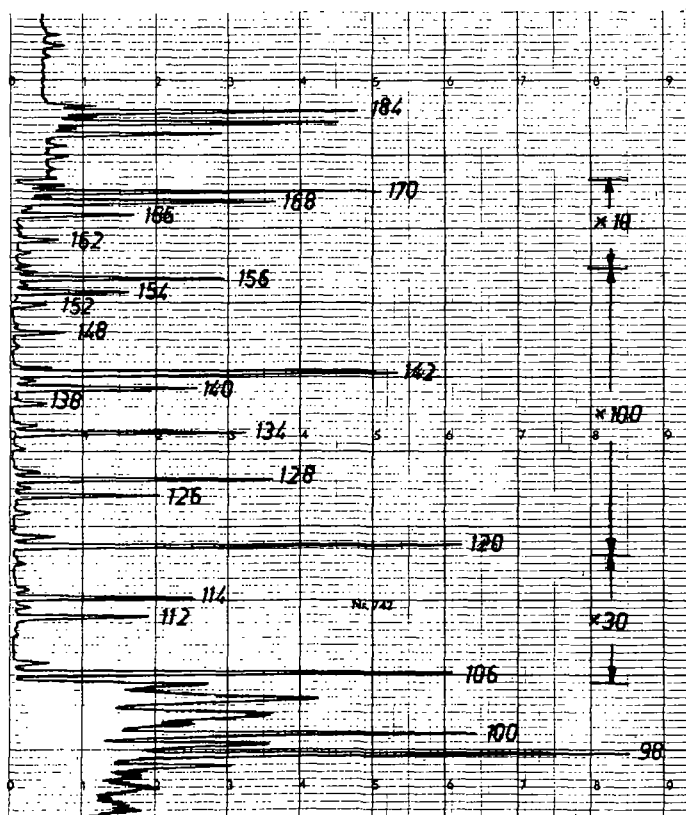
Electron impact mass spectrum with 70 eVolts of ionizing electron beam energy gives a lot of intensive fragment ion peaks at the lower mass number range. The field ion mass spectrum however shows only fragment ion peaks of masses 29 (ethyl-), 43(propyl-), 57 (butyl-), 71 (pentyl-) and 85 (hexyl-radical-ions) in mentionable intensities. In this way the field ion mass spectrum shows quickly that the gasoline contains large quantities of paraffines and paraffine-substituted alicyclic and aromatic hydrocarbons. These compounds are fieldinduced fragmented only in C-C-single bonds and almost not in C-H-bonds, as analysis of pure substances confirm. Fieldinduced fragmentation of benzene rings of aromatic compounds was never observed. These aromatic hydrocarbons are to some extent doubly ionized. They lose two electrons and are detected at half mass number at low ionization fields with about 0.1 to 1 % intensity of single ionized aromatic molecules.

Consider now the ranges of mass spectra upward from mass number 90. The electron impact spectrum shows here low intensity peaks. The groups 91/92, 105/106, 119/120 and 133/134 signify an amount of substituted benzenes in the mixture. More exact analytical informations require the use of "low voltage" techniques and computation expense.

*) For preparation of this sample we thank Dr. Franz T r e f n y, Gelsenkirchen



Slide No. 3



Slide No. 4

In this range of mass scale the field ion mass spectrum of the gasoline has only molecule ion peaks. You may recognize in the original spectrum (slide 4) again the groups of non aromatic saturated hydrocarbons, already observed in the first field ion mass spectrum (slide 2). But now in the areas, where in the first showed spectrum no peaks were detected, appear with large intensities the peaks of substituted benzenes and polycyclic hydrocarbons. You may also recognize the different recording sensitivities of this mass spectrum.

Also here we get an analysis of compounds of different chemical formula and mass number (slide 5) and no information about amounts of different isomers in one peak. But for a lot of peaks the number of probable isomers is small. To obtain the volume percentage of the different compounds, a small computation is necessary involving the different field ion mass spectrometric sensitivities of different substances or groups. These sensitivities vary between 1.0 and 2.5 for aromatics and between 0.50 and 0.66 for paraffines, mono- and polycyclic saturated hydrocarbons in comparison to benzene for a field strength, where n-pentane field ion mass spectrum shows aethyl-fragment (mass number 29) of 2 %.

Two spectra here were selected from a large number of analyses using the field ion source with tip anode, which affords 5 % stability of ion currents.

Closing this report the results of field ion mass spectrometric analysis of a seven component hydrocarbon mixture by application a wire anode field ion source is given (slides 6 and 7). The composition of the mixture was determined also by gas chromatographic analysis. The upper portion of the picture shows the molecule peaks and the lower part the fragment peaks of field ion mass spectrum. Fragment peaks are marked by typical tailing, caused by field induced fragmentation of molecule ions over a distance during their acceleration. These tails may be used to determine the mean reaction times of field induced fragmentation in the order of 10^{-11} sec. [11]. The analysis deviations conform to the values obtained with normal electron impact ion sources. But much time is saved by this method because only one calibrating spectrum is required for analysis of n-component mixtures, whereas using an electron impact ion source n calibrating spectra must be measured.

The next slide (slide 8) shows the reproduction of n-heptane spectrum, using a wire anode. You will notice distinct "metastable" mass lines. These were also obtained with relatively high intensity (up to 1 %) in spectra of other paraffines and amines [6]. They offer information on "metastable" fragmentation of field ionized organic molecules (reaction times in the order of 10^{-9} sec) and to their identification in mixtures. For normal analysis the metastable ions may be repressed by a retardation potential near the ion collector, as shown in the last n-heptane spectrum (slide 9).

- [1] M.G.Inghram and R.Gomer: Z.f.Naturforschung 10a, 863/72, 1955
- [2] H.D.Beckey: Z.f.Naturforschung 14a, 712/21, 1959
- [3] H.D.Beckey: Z.f.analyt.Chemie 170, 359/64, 1959
- [4] H.D.Beckey: "Feldionisations-Massenspektrometrie", paper at Physikertagung Bad Nauheim, Germany 1961
- [5] H.D.Beckey: "Field Ionization Mass Spectroscopy", Symposium on Mass Spectrometry Oxford, 1961
- [6] G.Wagner: Thesis, Technische Hochschule Aachen, Germany, 1963
- [7] H.D.Beckey: Z.f.Naturforschung 17a, 1103/11, 1962
- [8] F.Kirchner: Naturwiss. 41, 136, 1954
- [9] E.W.Mueller and K.Bahadur: Phys.Rev. 102, 624, 1956
- [10] R.Gomer: "Field Emission and Field Ionization", Harvard University Press 1961
- [11] H.D.Beckey: Z.f.Naturforschung 16a, 505/10, 1961
- [12] H.D.Beckey: Z.f.Instrumentenkunde 71, 51/54, 1963

M/e		Anteil am Gesamt-Ionenstrom in %	
92	C ₇ H ₈	0,034	
98	C ₇ H ₁₄	0,039	
100	C ₈ H ₁₆	0,046	
106	C ₈ H ₁₀	5,772	
110	C ₈ H ₁₄	0,068	
112	C ₈ H ₁₆	1,732	
114	C ₈ H ₁₈	2,367	
118			
120	C ₉ H ₁₀	0,144	
124	C ₉ H ₁₂	17,637	
126	C ₉ H ₁₆	0,637	
128	C ₉ H ₁₈	5,985	
132	C ₁₀ H ₁₂	10,526	
134	C ₁₀ H ₁₄	0,467	
138	C ₁₀ H ₁₈	9,270	
140	C ₁₀ H ₂₀	1,477	
142	C ₁₀ H ₂₂	7,895	
146	C ₁₁ H ₁₄	16,019	
148	C ₁₁ H ₁₆	0,255	
152	C ₁₁ H ₂₀	1,986	
154	C ₁₁ H ₂₂	1,330	
156	C ₁₁ H ₂₄	4,406	
160	C ₁₂ H ₁₆	8,132	
162	C ₁₂ H ₁₈	0,051	
164	C ₁₂ H ₂₀	0,178	
166	C ₁₂ H ₂₂	0,025	
168	C ₁₂ H ₂₄	0,458	
170	C ₁₂ H ₂₆	1,019	
174	C ₁₃ H ₁₈	1,452	
176	C ₁₃ H ₂₀	0,003	
178	C ₁₃ H ₂₂	0,008	
180	C ₁₃ H ₂₄	0,061	
182	C ₁₃ H ₂₆	0,112	
184	C ₁₃ H ₂₈	0,122	
194	C ₁₄ H ₂₆	0,004	
196	C ₁₄ H ₂₈	0,007	
198	C ₁₄ H ₃₀	0,005	

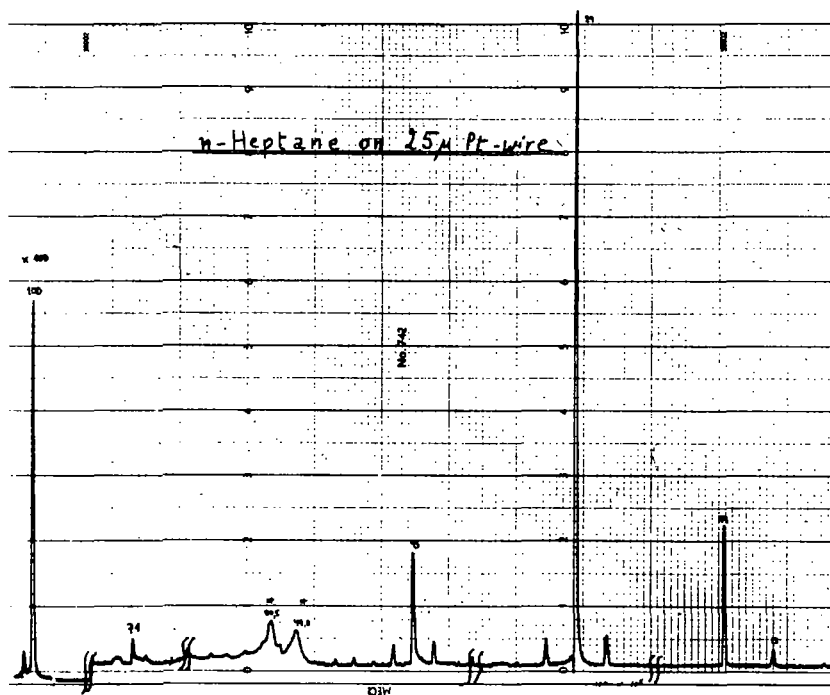
Slide No. 5

Slide No. 6

Analysis of a mixture of seven hydrocarbons
by means of a field ion mass spectrometer (F.I.M.S.)

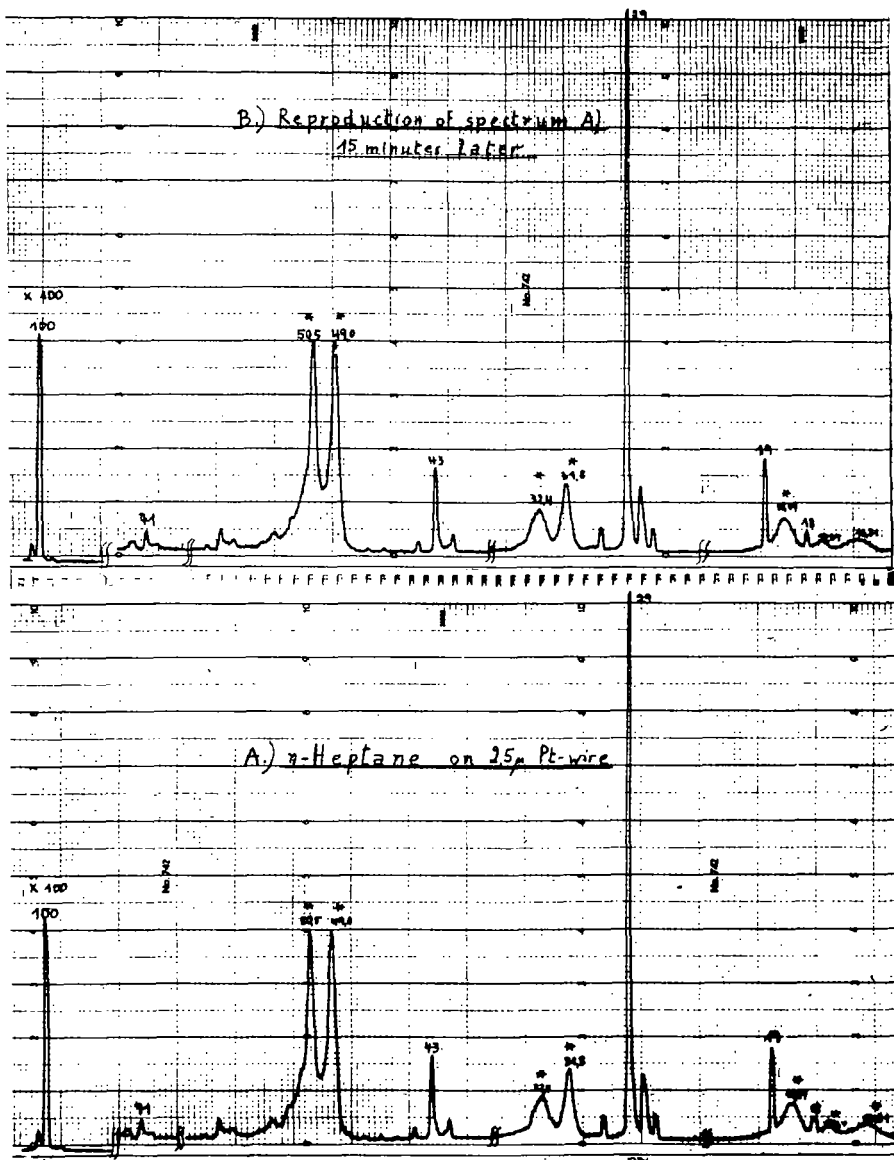
Substance	Mass Number	Mole %	Analysis (F.I.M.S.) Mole %	Deviation Mole %
Benzene	78	31,6	32,8	+ 1,2
Cyclohexane	84	4,3	4,1	- 0,2
Hexane	86	26,8	27,1	+ 0,3
Toluene	92	11,0	11,5	+ 0,5
Heptane	100	12,7	12,5	- 0,2
Octane	114	7,1	7,1	0,0
Nonane	128	6,6	6,0	- 0,6

Slide No. 7



Suppression of metastable ions by a retarding potential
in front of the ion collector

Slide No. 9



Slide No. 8

PERFORMANCE OF A HIGH RESOLUTION MASS SPECTROMETER
By: C. M. Judson, C. G. Blanchard, & D. J. Comaford
Consolidated Electrodynamics Corporation
Pasadena, California

The 21-110 mass spectrometer manufactured by Consolidated Electrodynamics Corporation is a double focussing instrument designed for use with both spark and electron bombardment sources. The version using the spark source has been described on several occasions and its performance has been reported. The version with an electron bombardment source, developed to obtain high resolution spectra of organic compounds has been mentioned in connection with descriptions of the spark instrument, but its performance has not been described publicly in any detail prior to this meeting. Since commercial models have now been in use for over three years and since rather extensive modifications have been made over the last three years, and particularly during the last year, it seems appropriate to describe the performance of the instrument in its present form.

Biemann reported this morning¹ on his experience using a version of this instrument having a combined photoplate and electrical collector detection system in which he used the photoplate method of obtaining spectra. The work we are reporting this afternoon will be concerned mainly with the electrical collector methods, and will, we hope, complement the results presented by Biemann using the photoplate method.

The data presented represent the performance of one instrument of recent production, and do not necessarily represent sales specifications.

The instrument uses the design of Mattauch and Herzog² in the form described by Robinson³. The analysing system consists of a 25 inch radius electrostatic sector followed by a 12 inch radius magnetic sector. An accelerating voltage of 8 KV is used with an electron bombardment source similar to that used in the Consolidated 180° analytical mass spectrometer (model 21-103) with addition of a source magnet to collimate the electron beam. The standard introduction system is a 350° C. glass inlet system with glass ball valves, but a 150°C. metal inlet system with micromanometer is also available. These systems use a molecular leak but provision can also be made for direct introduction to the source, by-passing the leak.

The instrument was originally offered with a choice of detectors, either a photoplate system, or an electrometer system consisting of a collector, amplifier and recording oscillograph. We have since provided an electron multiplier for use with the electrical collector system and, more recently, a combination detector in which the photoplate, electrometer, and multiplier are all installed together so that the method of detection can be changed at will. In order to permit effective use of the speed available with the electron multiplier, we have developed a wide range continuously adjustable control for the magnet scan speed and an amplifier-oscillograph system with considerably increased speed.

Control of resolution is provided by means of adjustable slits in the source and collector and by use of an offset voltage in the electric sector. It has been reported previously in connection with a coincident field instrument developed by Consolidated⁴, that an offset voltage in the electric sector, used so that the geometric center is not at ground potential, has an effect on the focus of a double focussing instrument. Optimum resolution is generally obtained in the present instrument with an offset not more than 15 volts with a total electric sector voltage of 750. The offset voltage is not critical within a few volts but the resolution is significantly reduced when the offset voltage is varied by larger amounts.

Adjustment of the source and collector slits is used to provide a compromise between resolution and sensitivity. Measurements of sensitivity as a function of resolution are shown in Figure 1. Measuring resolution from the peak width at 10% of the peak height, a limit is reached at about 10,000. Over a range from the lowest resolution (a few hundred) to a value close to the maximum (9000) the loss in sensitivity is only a factor of ten. These measurements were obtained by adjustment of source and collector slits only. As pointed out in the paper by Berry this morning⁵, ultimate sensitivity for any particular resolution requires adjustment of the alpha and beta stops as well as the source and collector slits, and will lead to a curve becoming asymptotic at either high resolution or high sensitivity permitting higher resolution at one end and

higher sensitivity at the other end compared to the results in Fig. 1. We are in the process of making relatively minor modifications which we believe will permit us to obtain significant improvement in resolution over that shown in Fig. 1.

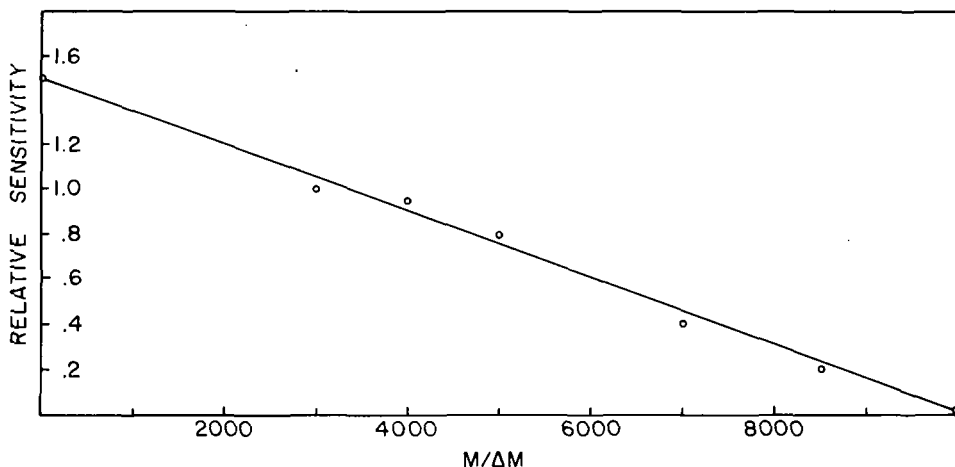


FIG. 1

The practicality of obtaining spectra by scanning over a range of masses with electrical recording is dependent on the response speed of the amplifier and recorder used. This limitation is particularly severe in high resolution spectra because of the very narrow peaks which must be passed over quickly. Table I shows the maximum scan speeds for various recording systems at which one just begins to lose resolution at a resolution of 3000.

TABLE I
Maximum Scan Speeds

<u>Detector</u>	<u>Recorder</u>	<u>Scan Speed</u> <u>(Octaves/min.)</u>
multiplier	200 c oscill.	> 2
mult. or electr.	30 c oscill.	0.3
mult. or electr.	10 c oscill.	0.1
mult. or electrs.	1/2 sec. rec.	< 0.03

Using a multiplier and providing a faster amplifier and oscillograph response has permitted us to increase the speed quite substantially over that originally available with a 10 cycle oscillograph system. With the 200 cycle oscillograph the maximum speed is actually limited by the magnet scan speed which, even in the new faster version, has a maximum average value over the mass range 12-400 of 1.5 octaves/min. This limitation is, however, readily overcome.

The slow speeds required with a chart recorder are useful only for scanning a single peak or multiplet and are attained by scanning the electric sector and accelerating voltages (which have a common control).

Our ability to detect small signals is dependent on the noise of the detection system which depends on the response speed we require and on the current gain required in the amplifier, that is on whether or not we use a multiplier. Table II shows the noise observed for 1 cycle, 30 cycle, and 200 cycle systems, first with an electrometer with 5×10^{11} ohms input to the amplifier, then with

a multiplier with a gain of 10^8 and an amplifier input of 10^7 ohms. The last column shows the statistical noise, the smallest average current which we can be 90% certain will produce at least one ion in a peak.

TABLE II
Noise Measurement

Bandwidth	Noise (Amps)		
	Electr.	Multipl.	Statist.
1 c	2×10^{-15}	$< 3 \times 10^{-17}$	6×10^{-19}
30 c	2×10^{-14}	$< 3 \times 10^{-17}$	2×10^{-17}
200 c	-----	$< 3 \times 10^{-17}$	1×10^{-16}

Use of a multiplier not only permits faster scanning, but permits this to be accomplished with about two orders of magnitude less noise. A limit of detection can be calculated from the noise and sensitivity. Arbitrarily using the sensitivity of n-butane at mass 58 which is about 2×10^{-14} amps/micron (based on pressure in the inlet reservoir) as a standard, the limit of detection calculated from the noise at the fastest speed (1×10^{-16} A) is 0.005 microns. At slower speeds the limit of detection is still smaller.

The most important property of a high resolution mass spectrometer is its ability to provide exact mass measurements for each peak. While this measurement is made most conveniently from a photographic plate, we have studied the accuracy obtainable with electrical collection methods. Table III shows accuracy obtained in measuring mass of one line in a doublet at mass 105 by comparison with the other line with a mass difference of 35 millimass units.

TABLE III
Mass Accuracy

Scan	Recorder	Speed oct./min.	Accuracy ppm
magnetic	oscill.	0.04	6
magnetic	oscill.	0.4	19
magnetic	10 mv.	0.01	25
electric	X-Y	manual	0.4
electric	control	manual	1.4

With magnetic scan accuracy of a few ppm can be obtained at moderate scan speeds, becoming somewhat less accurate at higher or slower speeds. Higher accuracy, of the order of 1 ppm can be obtained using electric scan and measuring the voltage on an X-Y recorder or measuring the dial reading on the duodial control.

The focus and repeller adjustments in this instrument are mass dependent. Conditions in the source are constant during scanning and no compensation for mass discrimination due to the source magnet is made in the scanning process. Patterns measured after focussing at different masses indicate, however, that over a range of 3 octaves (2 below the point of focus and one above) the sensitivity at a particular mass does not vary by more than a factor of 2 from the optimum. On the other hand to reproduce a pattern accurately it is necessary to focus the instrument in a specified way at a specified mass.

As an approach to consideration of use of this instrument for analysis of mixtures, measurements of reproducibility of the 43/58 pattern ratio in n-butane were made with resolution adjusted to about 1000. Successive scans were reproducible to 1%. Slightly larger differences were observed over longer periods (1 hour) which were attributed to lack of temperature control. Refocus of the instrument (readjustment of slits and of focus and repeller controls) did not appear to adversely affect the pattern reproducibility. Provision for temperature control to improve pattern reproducibility will be provided on future instruments.

In conclusion the performance described for electrical collection methods should be compared with that expected using photoplate detection. (1.) Ultimate resolution should be somewhat but not greatly higher with the photoplate. (2.) At speeds of the order of a few minutes per spectrum, the two methods are comparable in sensitivity. The photoplate, however, offers a more straight-

forward compromise between speed and sensitivity with advantages at very high or very slow speeds. (3.) In the present state of the art, at least, the measurement of exact masses for an entire spectrum is carried out more conveniently by photoplate detection. (4.) Finally intensity measurements are made more conveniently and more accurately by electrical detection.

References:

1. K. Biemann, The use of high resolution mass spectrography in the determination of the structure of organic compounds, ASTM Mass Spectrometry Conference, 1963.
2. Mattauach & Herzog, Zeit. fur Physik, 89, 786, 1934.
3. Robinson, Rev. Sci. Instr. 28, 777, 1957.
4. Voorhies, Robinson, Hall, Brubaker, & Berry, in Waldron, Advances in Mass Spectrometry, p. 44, 1959.
5. Berry, Remarks on high resolution mass spectrometry, ASTM Mass Spectrometry Conference, 1963.

SPARK SOURCE MASS SPECTROSCOPY FOR MICROANALYSIS OF SOLIDS

W. M. Hickam and G. G. Sweeney
Westinghouse Research Laboratories
Pittsburgh 35, Pennsylvania

The application of the radio frequency vacuum spark source mass spectrograph to the analysis of bulk impurities in high purity solids has provided a stimulus for the interest and growth of this type instrumentation in the last few years. Their introduction into the laboratory has brought about the recognition of numerous other applications. An example, to be presented in this paper, is the use of the instrument as a microprobe. In this application, it is desirable to have high sensitivity while moderate resolution is acceptable for much of the work.

About three years ago, we completed construction of a spark source mass spectrograph⁽¹⁾, similar to that described by Hannay⁽²⁾ and Goto⁽³⁾, having an electrostatic analyzer of 15 cm radius and a resolution of the order of 500. The instrument has been used primarily to study the composition of microsamples and examples of this will be given. The technique has been referred to by Dr. A. Ahearn in an earlier paper on the program. In general, an attempt is made to draw a single spark between an optically aligned point-to-plane configuration in which the portion of the plane directly opposite the point represents the sample under investigation. In this type sampling one is working with short exposure times and relatively high concentrations.

In obtaining a spectrum within this short time interval it is difficult to utilize the procedure of racking the photographic plate normally used in analyzing bulk impurities. Early in this work, it was recognized that a means of extending the effective range of the photographic plate was desirable. This was achieved to some degree by making the ion monitor, located at the exit of the electrostatic analyzer, with an opening in the form of a step slit similar to that used in emission spectroscopy. In the mass spectra to be shown, the influence of the step slit can be seen where the height of the line is an indication of the ion intensity.

In a stationary point-to-plane configuration and in attempting a single spark we achieve craters having a diameter of 25-40 microns and a depth of 3-5 microns. In samples of this type, we normally detect concentrations as low as 0.1 - 0.01 atom percent. At times it is desirable to achieve small physical dimensions and a lower concentration limit. Lower concentrations are obtained by extending the sparking time.

An example of this is in diffusion couple investigation, where two elements, yttrium and molybdenum were heated in contact at elevated temperatures for an extended period of time. In Figure 1 is shown a series of three craters made on the molybdenum surface in approaching the interface. The three craters were made starting from the right and in order going to the left. Each sampling required the shut down of the instrument, removal of the head, realigning the point-to-plane under a microscope and reloading the head. The craters are approximately 100 microns in diameter and 10 microns deep. In craters of this magnitude we expect to reach the detectable limit of 1 ppm. Yttrium was detected on the surface but not in the bulk. The perimeter of the closest crater being within 100 microns of the interface.

In many applications the concentration gradient exists in dimensions small, compared with the 100 microns. Since the depth of sampling is one tenth the diameter, it is possible to take advantage of this resolution by orientating the point perpendicular to the interface instead of parallel to it as in the example just given.

Figure 2 illustrates the technique in sampling silicon which was doped to a depth of 3 microns with .02 atom percent antimony as determined by electrical measurements. The crater is 40 microns in diameter and 4 microns deep. A portion of the spectrum is shown in Figure 3. The singly charged 121-123 antimony ions are easily detected. The gold is the counter electrode used. Concentrations measured vary over a range of .016 - .04 atom percent, where the number of silicon atoms sampled is of the order of 10^{16} atoms and the detectable limit of the order 10^{11} atoms.

Figure 4 is an example of the spectrum obtained using the microprobe to study a film of niobium of the order of 250 Å thickness deposited on high purity silicon. The same high purity silicon was used as a counter electrode. The depth of the crater was of the order of 3 microns or 30,000 Å. The 29 and 30 silicon isotopes at the 4% abundance would be equivalent to a film of 1000 Å. The niobium line is less than these and suggest the niobium film to be a few hundred angstroms. The doubly charged niobium line is clearly evident suggesting a detectable limit more than a factor of 5 lower.



Fig. 1 - Three craters (100 μ diameter) made on molybdenum surface in approaching yttrium-molybdenum interface of diffusion couple.

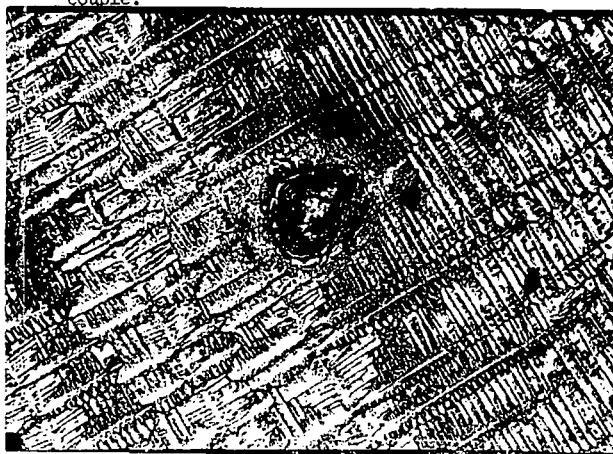


Fig. 2 - Crater (40 μ diameter and 4 μ deep) made in sampling doped silicon layer.

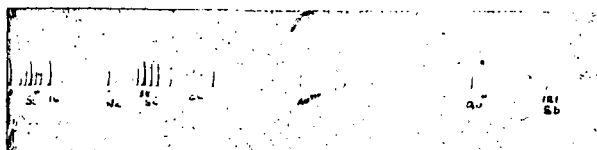


Fig. 3 - Mass spectrum obtained in sampling silicon doped with antimony. Gold was used as counter electrode.

The high concentrations of carbon and oxygen in the film have been confirmed to some degree by electron diffraction experiments.

In the course of obtaining several hundred mass spectra using short sparking times, a number of spectra have been obtained in which only the carbon and oxygen ions are observed. The material sparked involved copper, silicon, iron, gold, silver and tin. These samples were sparked at a gauge pressure of 10^{-7} TORR, and since an attempt was being made to draw a single spark while simultaneously observing the sample it is certain that a spark was drawn. If the carbon and oxygen lines observed are associated with a diameter of 25-40 microns, the intensity of the lines would suggest a film of several hundred angstroms. The exact source of the carbon and oxygen is not understood but it might suggest that the sampling area for material on the surface is appreciably larger than the area associated with the crater or that the detectable limit is lower than the generally quoted 10^{11} atoms. A detailed understanding of these carbon and oxygen spectra might enhance appreciably the usefulness of the instrument for analyzing carbon and oxygen in solids.

In the examples cited thus far, we have used a stationary point-to-plane configuration as is represented schematically in Figure 5. Vernier adjustments are made on the sample position and simultaneously observed under the microscope. One can visualize numerous areas where this technique could provide useful compositional information. It is obvious that a slow translation of the plane with respect to the point will allow the coverage of a larger area and the simultaneous integrating of the ion signal on the photographic plate. This manual translation technique enhances the detection limit for segregation on the surface whereby the detection of an equivalent average coverage of a monolayer is observable. This technique has been useful in examining surfaces associated with stress corrosion failure of metal, brittle and ductile fracture and the examination of residues left by certain cleaning techniques.

References

1. Accepted for publication in Review of Scientific Instruments.
2. Hannay, N. B., Rev. Sci. Instr. 25, 644 (1954).
3. Goto, M. and Kai, J., Mitsubishi Denki Lab. Report, Vol. 1, No. 1, Jan. 1960.

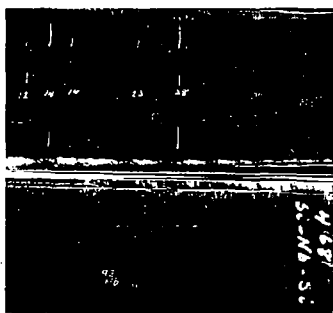


Fig. 4 - Mass spectrum obtained in sampling 250 Å niobium film on silicon.

DWG 2958139

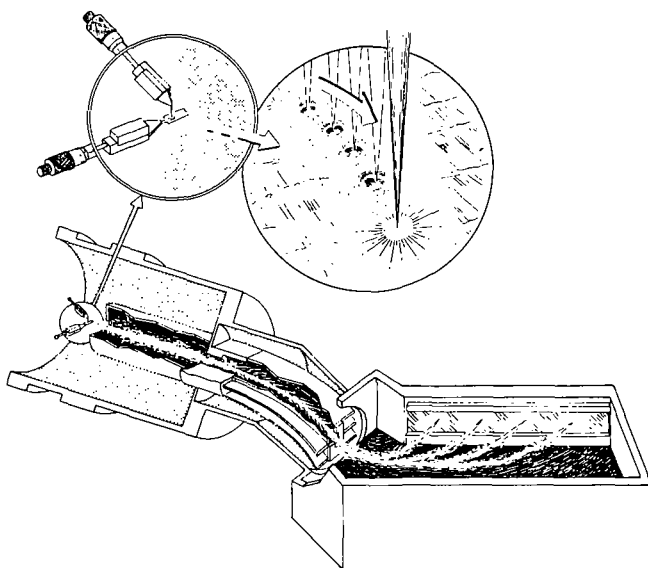


Fig. 5 - Mass spectrographic microprobe schematic.

COMPOSITION OF SULFUR VAPOR*

J. Berkowitz, J. R. Marquart and W. A. Chupka
Argonne National Laboratory
Argonne, Illinois

ABSTRACT

The equilibrium composition of sulfur vapor has been deduced by studying its mass spectrum and also the mass spectra of a number of metal sulfides which decompose upon heating. The latter provide a source of sulfur vapor below saturation, which is essential to the elucidation of the fragmentation pattern. The results clearly point to S_8 , S_7 , and S_6 as the major sulfur species in the saturated vapor from room temperature to the boiling point of sulfur. Heats of formation of the various S_n species ($n = 1, 2, \dots, 10$) have been measured.

The kinetics of vaporization of various sulfur allotropes has also been studied. It reveals marked variations, characteristic of the structure of the condensed phase.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

SOME NEW EXPERIMENTS IN HIGH-TEMPERATURE MASS-SPECTROMETRY

Alfred Büchler
A. D. Little Inc.
Cambridge, Massachusetts

ABSTRACT

High-temperature mass spectrometry has so far been mainly concerned with the identification of gaseous species in thermodynamic equilibrium with condensed species, and with the determination of their heats of formation. In this report, some applications of mass spectrometry in the kinetics of high-temperature solid-gas reactions and to problems of molecular structure will be discussed. The oxidation of molybdenum and tungsten at oxygen pressures near 1 μ was studied over a temperature range of 1100°-1700°C for Mo and 1400°-2100°C for W. In each case the products of the reaction were found to differ significantly from those expected from equilibrium thermodynamics, the principal gaseous species formed at high temperatures being the dioxides MoO₂ and WO₂. As to molecular structure determination, an electric quadrupole focussing field interposed between a molecular beam oven and the mass spectrometer ion source has been used to discriminate between polar and non-polar molecules effusing from the oven. For lithium fluoride vapor, the results obtained are in agreement with a planar symmetric structure for the dimer Li₂F₂.

THE DISSOCIATION AND POLYMERIZATION ENERGIES OF GROUP IV-GROUP VI MOLECULES(*)

J. Drowart and R. Colin
Laboratoire de Chimie Physique Moléculaire
Université Libre de Bruxelles, Brussels, Belgium.

The diatomic molecules of the group IV-group VI elements have been known for a long time from optical spectroscopy, which made it possible to obtain accurate dissociation energies for a number of these molecules⁽¹⁾. The condensed compounds of this group, either MeX or MeX₂ are in general also known. Most have been studied thermochemically and total vapor pressures and heats of formation have been measured⁽²⁾.

Mass spectrometric investigations of the composition of the gas phase which concerned SiO₂⁽³⁾, PbSe⁽⁴⁾, PbTe⁽⁴⁾, SnS⁽⁵⁾ and PbS⁽⁵⁾ have been extended systematically during the last two years in this laboratory to the remaining compounds⁽⁶⁾. These studies made it possible to identify in the gas phase a number of (MeX)_n polymeric molecules and MeX₂ molecules and to determine quite accurate values for the dissociation energies of the gaseous MeX molecules. A summary of the results is given in the present paper.

1. EXPERIMENTAL.

The mass spectrometer used is a 60°, 20 cm radius of curvature, single focussing instrument, adapted⁽⁷⁾ for the study of high temperature inorganic processes, and equipped⁽⁸⁾ with a secondary electron multiplier. The samples were placed in Knudsen cells heated by radiation from a tungsten loop and when necessary by electron bombardment. In the studies reported here, the latter were mainly quartz cells. Their temperature was measured either with an optical pyrometer or with a Pt-PtRh 10% thermocouple. A molecular beam originating from the cells was collimated and directed into the ion source of the mass spectrometer where the atomic and molecular species were ionized by electron bombardment and then mass analyzed.

The identification of the species was made in the usual way⁽⁹⁾ from the mass, appearance potential and isotopic distribution of the ions and the intensity distribution in the molecular beam.

2. EVALUATION OF THERMODYNAMIC DATA.

The pressures are in general the total pressures given in the literature, corrected, when necessary, for the presence of polymeric species. A number of quantitative vaporization experiments were also carried out to confirm the literature values of the pressure or to complete these. For most of the diatomic molecules the thermodynamic functions are given in the literature^(10,11); whenever not, they were calculated from statistical mechanical formulae using the known molecular parameters⁽¹⁾. Since no information is available for the dimeric species, free energy functions were estimated. Very little is known about the structure of these molecules except that one may think that they are analogous to those of the isoelectronic P₄, As₄ and Sb₄ molecules. It was therefore assumed that the free energy function could be estimated by analogy with these isoelectronic molecules⁽¹²⁾, which implies that a decrease in the symmetry number is compensated by an increase in the vibration frequency. For the higher polymers the free energy functions were estimated by analogy with those of a number of molecules of comparable molecular weight, containing the same total number of atoms⁽¹³⁾. For the MeX₂ molecules which are of the same type as the well known CO₂ and CS₂ molecules, free energy functions were calculated assuming these molecules to be similar in structure and in nature of the electronic states to the

(*) This work was sponsored in part by the Wright Air Division of the Aeronautical Systems Division A.F.S.C., U.S. Air Force, through its European Office.

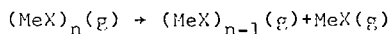
TABLE I. Comparison of Spectroscopic (D_0'') and Thermochemical (D_0°) Values of the Dissociation Energies of Group IV-Group VI Molecules (in eV.)

Molecule	Convergence Limit E state	D_0'' *	D_0°
CO		11.111±0.06	
CS			7.53±0.15 ⁽¹⁷⁾
CSe			6.00±0.15
(CTe)			(4.8 ±0.4)**
SiO			8.32±0.15
SiS	6.44±0.06 ⁽¹⁸⁾	6.38±0.06	
SiSe	5.66±0.15 ⁽¹⁹⁾	5.40±0.15	
SiTe	(4.70±0.25) ⁽¹⁹⁾	(4.11±0.25)	
GeO			6.82±0.13
GeS	5.79±0.03 ⁽²⁰⁾	5.67±0.03	5.78±0.15
GeSe	5.25±0.03 ⁽²⁰⁾	4.93±0.03	
GeTe	4.49±0.30 ⁽²⁰⁾ -0.10	3.84±0.30 -0.10	4.04±0.15
SnO	5.66±0.05 ⁽²¹⁾	5.45±0.05	5.53±0.13
SnS	5.06±0.10 ⁽²²⁾	4.80±0.10	4.78±0.12
SnSe	4.54±0.06 ⁽²³⁾	4.08±0.06	4.12±0.17
SnTe	(4.07) ⁽²³⁾	(3.28)	3.46±0.17
PbO	>4.86 ⁽²⁴⁾	>3.87	4.00±0.13
PbS	4.55±0.20 ⁽²⁴⁾	3.53±0.20	3.42±0.12
PbSe	>4.32 ⁽²⁴⁾	>3.10	3.08±0.12 ⁽²⁵⁾
PbTe			2.30±0.17 ⁽⁴⁾

* Values based on Birge-Sponer extrapolations have not been included

** Estimated.

TABLE II. Enthalpies of Polymerization of Group IV-Group VI Molecules MeX (in kcal/mole).



Molecule	n=2	n=3	n=4	n=∞ (solid)
SiO	53.5			85.5*
SiS				64.3
SiSe				
SiTe				
GeO	49.4	47.7		53.1
GeS				38.7
GeSe				
GeTe	<33			45.3
SnO	69.7	68.9	70.6	73.6
SnS	48.7			52.6
SnSe	46.5			51.0
SnTe	46.8			52.1
PbO	57.3	57.2	62.0	67.3
PbS	44.8			55.7
PbSe	44.4			53.9
PbTe				53.8

* for $1/2\text{SiO}_2 + 1/2\text{Si}$

latter molecules. Thermodynamic functions of the condensed phase were taken from the literature whenever available or estimated by methods discussed by Latimer⁽¹⁴⁾ and Kubaschewski and Evans⁽²⁾.

3. RESULTS

a) Dissociation energies.

Table I gives the dissociation energies from thermochemical cycles based on the heat of sublimation of the molecule from the condensed phase, the heat of formation of the latter⁽²⁾, and the heats of sublimation of the elements⁽¹²⁾. The thermochemically determined dissociation energies can now be compared to the convergence limits for the electronically excited states observed spectroscopically. Amongst these the best known is that of the E state. It has already been shown previously from rotational analyses that at least for PbO⁽¹⁵⁾ and PbS⁽¹⁶⁾ this state correlates most probably with the atoms in their $^3P_1 + ^3P_1$ state. On the basis of the agreement between spectroscopic and thermochemical values for the dissociation energies of SnS and PbS it has also been shown^(5,6) that the most probable correlation is with the 3P_1 state of the group IV element and the 3P_1 or 3P_0 state of the group VI element (the small difference between the two mentioned sublevels of the group VI elements makes it difficult to distinguish between them). Table I also gives a comparison between the thermochemically determined dissociation energy and that derived from the electronically excited E state wherever this state is known.

b) Polymerization energies.

The polymerization energies measured to day are summarized in Table II. This table shows that the complexity of the polymers observed is highest for SnO and PbO. It further shows a regular decrease of the dimerization energies from oxides to tellurides. The heat of abstraction of one MeX molecule from a given polymer is also compared with the heat of sublimation of monomeric MeX. This heat of sublimation is that of the MeX compound or of the mixture $\text{MeX}_2 + \text{Me}$. In those instances where the MeX compound is metastable the heat of the reaction $1/2\text{MeX}_2(\text{s}) + \text{Me}(\text{s}) \rightarrow \text{MeX}(\text{s})$ was taken into account. When it is not known it has been assumed equal to zero. From Table II it can be seen that for several molecules the dimerization energy is of the same order of magnitude as the heat of sublimation of the monomer and that the energy required to detach a MeX group from the dimers and more complex polymers is also of the same order of magnitude and tends to show an alternation from even to odd species.

c) MeX₂ molecules.

In addition to the diatomic and polymeric species a number of MeX₂ molecules were observed in these systems. These are analogous to the well known CO₂ and CS₂ molecules to which one analogue was already known, SiO₂⁽³⁾. Until now the further molecules of this type observed are SiS₂, SiSe₂, SiTe₂, GeTe₂ and SnTe₂. The atomization energies for these MeX₂ molecules are summarized in Table III. It is to be noted that for these molecules the ratio of the atomization energy to the dissociation energy of the MeX molecule is quite constant.

REFERENCES

1. G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co, Inc. Princeton, N.J. (1945).
2. O. Kubaschewski and L.L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York (1958).
3. R.F. Porter, W.A. Chupka and M.G. Inghram, J.Chem.Phys., 23, 216(1955)
4. R.F. Porter, J.Chem.Phys., 34, 583 (1961).
5. R. Colin and J. Drowart, J.Chem.Phys., 37, 1120 (1962)
6. R. Colin and J. Drowart, Technical Note 10, AF 61(052)-225, 28 Feb. 1963.
7. J. Drowart and R.E. Honig, J.Phys.Chem., 61, 980 (1957).
8. J. Drowart and P. Goldfinger, J.Chim.phys., 55, 721 (1958).
9. M. Ackerman, F.E. Stafford and J. Drowart, J.Chem.Phys., 33, 1734 (1960).
10. M.G. Inghram and J. Drowart, in "High Temperature Technology", McGraw Hill Book Co, Inc., New York (1960).
11. K.K. Kelley, U.S. Bureau of Mines. Bull. 584, (1960).
12. K.K. Kelley and E.G. King, U.S. Bureau of Mines Bull. 592 (1961).
13. D.R. Stull and G.C. Sinke, Advances in Chem. Ser. 18 (1956).
14. JANAF Thermochemical Tables, The Dow Chemical Co, Midland, Michigan.
15. W.M. Latimer, J.Am.Chem.Soc., 73, 1480 (1951).
16. R.F. Barrow, J.L. Deutsch and D.N. Travis, Nature, 191, 374 (1961)
17. R.F. Barrow, P.W. Fry and R.C. Le Bergy, Proc.Phys.Soc., 81, 697 (1963).
18. H. Schaefer and H. Wiedemeier, Z.anorg.allgem.Chem., 296, 241(1958)
19. S.J.Q. Robinson and R.F. Barrow, Proc.Phys.Soc., 67A, 95 (1954).
20. E.E. Vago and R.F. Barrow, Proc.Phys.Soc., 58, 538 (1946).
21. G. Drummond and R.F. Barrow, Proc.Phys.Soc., 65A, 277 (1952).
22. R.F. Barrow and H.C. Rowlinson, Proc.Roy.Soc. London, A224, 374 (1954).
23. R.F. Barrow, G. Drummond and H.C. Rowlinson, Proc.Phys.Soc., 66A, 885 (1953).
24. E.E. Vago and R.F. Barrow, Proc.Phys.Soc., 58, 707 (1946).
25. E.E. Vago and R.F. Barrow, Proc.Phys.Soc., 59, 449 (1947).
26. recalculated from ref.4, using $D_0^{\circ}(\text{Se}_2) = 75 \pm 2$ kcal/mole.

TABLE III. Stability of Group IV-Group VI MeX_2 Molecules (in kcal/mole)

Molecule	$\Delta H_{0,\text{at}}^{\circ}(\text{MeX}_2)$	$D_0^{\circ}(\text{MeX})$	$\Delta H_{0,\text{at}}^{\circ}(\text{MeX}_2)/D_0^{\circ}(\text{MeX})$
CO_2/CO	381.5	256.2	1.49
CS_2/CS	272.0	173.6	1.57
SiO_2/SiO	302.8	191.9	1.58
SiS_2/SiS	230.4	147.0	1.57
$\text{SiSe}_2/\text{SiSe}$	185.1	124.5	1.49
$\text{SiTe}_2/\text{SiTe}$	140.9	94.7	1.50
$\text{GeTe}_2/\text{GeTe}$	137.1	92.7	1.48
$\text{SnTe}_2/\text{SnTe}$	123.2	79.8	1.55

THERMOCHEMICAL STUDY OF THE HOMONUCLEAR DIATOMIC MOLECULES AND OF SOME GASEOUS OXIDES OF SCANDIUM YTTRIUM AND LANTHANUM AND OF THE MOLECULE ScC_2^* .

by J. Drowart, G. Verhaegen and S. Smoes
Laboratoire de Chimie Physique Moléculaire
Université Libre de Bruxelles Brussels Belgium

INTRODUCTION

Classical chemistry and optical spectroscopy⁽¹⁾ have identified about 30 diatomic homonuclear molecules and determined their dissociation energies^(1,2) with a varying degree of accuracy. Mass spectrometry applied to the study of chemical equilibria at high temperatures⁽³⁾ added until now 5 molecules, Al_2 ⁽⁴⁾, Ga_2 ⁽⁴⁾, In_2 ⁽⁵⁾, Ge_2 ^(6,7) and Sn_2 ⁽⁶⁾ to this number and made it possible to determine with good accuracy the dissociation energy of 15 molecules, B_2 ⁽⁸⁾, Al_2 ⁽⁴⁾, Ga_2 ⁽⁴⁾, In_2 ⁽⁵⁾, C_2 ⁽⁹⁾, Si_2 ^(10,11), Ge_2 ⁽¹⁰⁾, Sn_2 ⁽¹⁰⁾, Pb_2 ⁽¹⁰⁾, S_2 ⁽¹²⁾, Se_2 ⁽¹³⁾, Te_2 ⁽¹⁴⁾, Cu_2 , Ag_2 and Au_2 ^(15,16). Most of these molecules are for the principal elements and except for copper, silver and gold, zinc, cadmium and mercury none have been identified for the transition elements, although a search was already made for some of these, Mn_2 ⁽¹⁷⁾, Cr_2 ^(17,18), Ni_2 ⁽¹⁷⁾ and Pd_2 ⁽¹⁸⁾.

The dissociation energies of the known homonuclear molecules were recently correlated with the heat of sublimation of the elements⁽¹⁹⁾. This correlation suggested that the homonuclear diatomic molecules of the elements scandium, yttrium and lanthanum would be relatively easier to observe than those of other transition elements. The vapors of these metals were therefore studied and the corresponding molecules indeed observed. This investigation further led to the determination of the dissociation energy of the ScO molecule and to the observation and determination of the atomization energies of the molecules ScC_2 , Sc_2O , Y_2O , La_2O , Y_2O_2 and La_2O_2 .

EXPERIMENTAL

The mass spectrometer is a 60°. 20 centimeter radius of curvature, single focussing instrument, adapted^(10,20) for the study of high temperature inorganic processes. It is equipped with a secondary electron multiplier⁽¹⁶⁾ and differential pumping between the Knudsen cell compartment and the ion source. The Knudsen cells, made of tungsten, tantalum, molybdenum or graphite, the latter wrapped in tantalum sheets, were heated by electron bombardment. In general no liners were used. Tantalum, molybdenum and tungsten cells were found acceptable for yttrium and lanthanum and mixtures of these. None of the materials was found entirely adequate for scandium. Temperatures were measured with an optical pyrometer calibrated both against the melting point of gold and a standard lamp. The yttrium and lanthanum were commercial samples, while the scandium was kindly made available by the Union Carbide Company. In all instances low energy ionizing electrons were used to avoid fragmentation and charge exchange reactions of the type $\text{Me}^{++} \rightarrow \text{Me}^+$ which, when occurring in the region between the entrance slit and the magnetic field, give rise to peaks at an apparent mass 2 Me^+ . It was further estimated that ion-molecule reactions $\text{Me}^{++} + \text{Me} \rightarrow \text{Me}_2^+$ possibly occurring in two or three body collisions in the source are unlikely to affect the measured Me_2^+ intensities. Appearance

(*) This work was supported in part by the Wright Air Division of the Aeronautical Systems Division A.F.S.C., U.S. Air Force, through its European Office.

TABLE 1. Dissociation Energy of the Molecules Sc_2 , Y_2 , La_2 and YLa

Equilibrium	T°K	$\log I_1/I_2(a)$	logK	ΔH°_0 kcal/mole	D°_0 kcal/mole
$\text{Sc}_2(g) \rightarrow 2\text{Sc}(g)$	2097	4.94	2.66	25.4	25.9±5
	2152	5.04	2.90	23.7	
	2165	4.92	2.67	26.2	
	2000	4.67	2.39	26.6	
	2001	4.68	2.50	25.6	
	1999	4.56	2.25	27.8	
$\text{Y}_2(g) \rightarrow \text{Y}(g) + \text{Y}(g)$	2300	4.82	4.82	-60.9	37.3±5
	2266	4.69	4.69	-59.3	
	2304	4.58	4.58	-58.5	
	2315	4.80	4.80	-61.0	
	2248	4.99	4.99	-61.6	
	2271	4.84	4.84	-60.5	
$\text{La}_2(g) \rightarrow \text{La}(g) + \text{La}(g)$	1998	4.14	4.19	-47.3	57.6±5
	2065	3.80	3.85	-45.3	
	2091	3.79	3.84	-45.5	
	2185	3.62	3.67	-45.3	
	2274	3.66	3.71	-47.1	
	2307	3.65	3.71	-47.4	
$\text{YLa}(g) + \text{La}(g) \rightarrow \text{La}_2(g) + \text{Y}(g)$	2307		0.46	-10.2	48.0
	2311		0.30	- 8.5	
	2220		0.49	-10.1	
$\text{YLa}(g) + \text{Y}(g) \rightarrow \text{Y}_2(g) + \text{La}(g)$	2262		-0.91	8.6	45.6
	2248		-0.85	8.1	
	2190		-0.89	8.3	
$2\text{YLa}(g) + \text{Y}_2(g) \rightarrow \text{La}_2(g)$	2158		-0.47	-0.9	47.0
				mean	47.3±5

(a) $P_1/P_2 = (I_1/I_2)(\sigma_{Y_1}/\sigma_{Y_2}) : \sigma_2/\sigma_1 = 1.6$ = ratio of relative ionization cross sections of dimer and monomer, γ_2/γ_1 = ratio of secondary electron multiplier yields.

TABLE 2. Relative Intensities of M_2O^+ and M_2O_2^+ Ions.

M	T°K	$\log I_{\text{M}}^+$	$\log I_{\text{M}_2\text{O}}^+$	$\log I_{\text{M}_2\text{O}}^+$	$\log I_{\text{M}_2\text{O}_2}^+$
Sc	1733	6.10	2.78	(2.04)	-
Y	2323	6.53	4.79	3.43	(2.11)
La	2232	6.08	6.40	3.12	3.20

potentials were difficult to measure because of the very low intensity of most of the molecular ions. They appear however to be of the same magnitude as those of the corresponding metal atoms or slightly lower.

1. Sc₂, Y₂, La₂ and YLa.

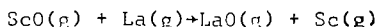
The experimental data and dissociation energies for these molecules are summarized in Table I. The dissociation energies were derived by the absolute entropy method. To calculate the free energy functions, vibration frequencies of 230 cm⁻¹ were estimated for all three molecules by analogy with the frequencies of homonuclear molecules of comparable stability and molecular weight. The interatomic distances, 2.70, 2.80 and 2.80 for Sc₂, Y₂ and La₂ respectively, were obtained subsequently from Badger's rule²⁽²¹⁾. The electronic contribution was based on a quantum weight 5. Values (in cal.deg.⁻¹ mole⁻¹) of 68.3, 72.3 and 74.1 at 2000°K and 69.6, 73.6 and 75.4 at 2300°K were so calculated for Sc₂, Y₂ and La₂ respectively. For YLa, the values for Y₂ and La₂ were averaged and corrected for the absence of symmetry. The values of the free energy functions for gaseous Sc, Y and La⁽²²⁾ were taken from Stull and Sinke's compilation⁽²²⁾. For consistency, those for condensed Y and La were taken from the same source as the heats of sublimation⁽²³⁾.

For Y₂ and La₂, the dissociation energy was derived from the pressure independent reaction M₂(g) + M(s, l) + M(g) and the literature values for the heats of sublimation, ΔH⁰(Y) = 97.6⁽²³⁾ and ΔH⁰(La) = 104.1⁽²³⁾ kcal/mole. This was not possible in the case of the Sc₂ molecule since at the temperatures of the experiments pronounced alloy formation took place between scandium metal and the crucible materials. Pressures under the conditions of the experiments were therefore derived by relating time-integrated intensities and weight losses⁽³⁾. Alloy formation between scandium and the crucible material occurring below the reported melting point of scandium could further explain the discrepancy between second and third law results⁽²³⁾ for the heat of sublimation of this element. Several measurements made by the present authors using the mass spectrometrically monitored weight loss method⁽³⁾, both for small (≈5 mg) and large (≈100 mg) samples, carried out at temperatures between 1180 and 1740°K in Mo, W and graphite crucibles lead to the value ΔH⁰₂₉₈(Sc) = 85.3 kcal/mole calculated with the free energy functions given in the literature^(22, 24).

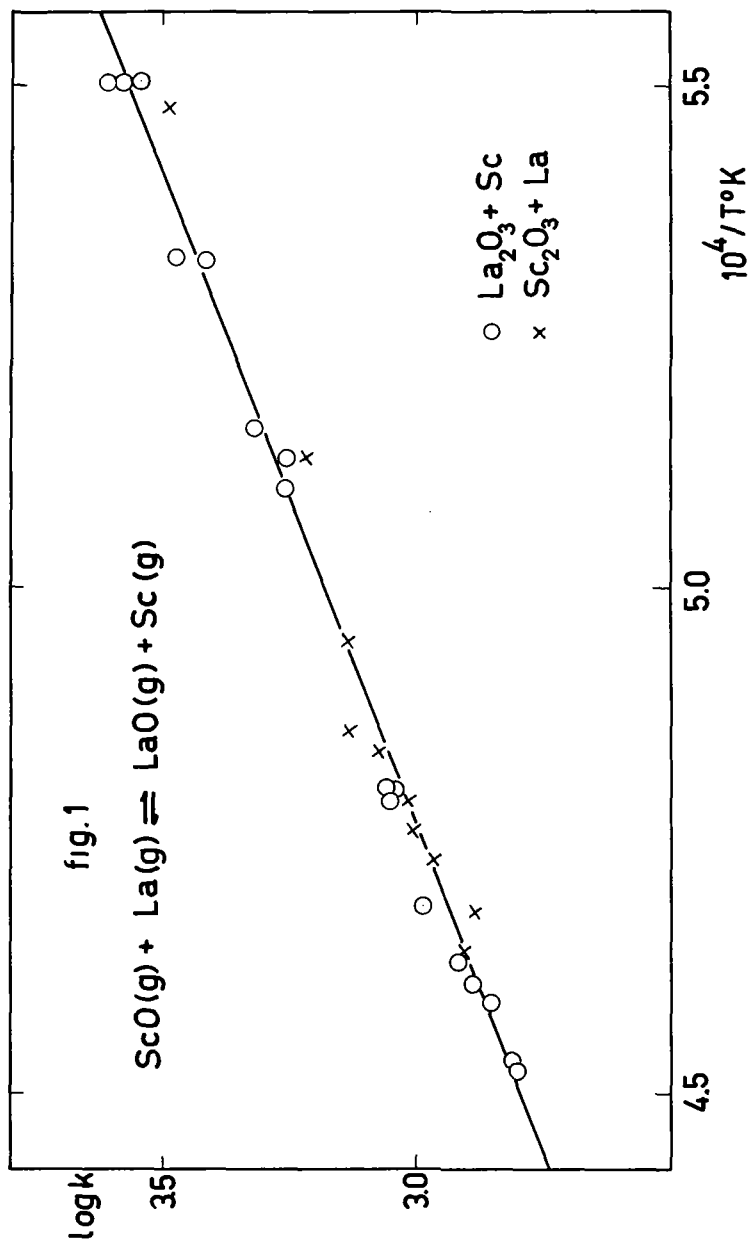
The dissociation energies of Sc₂, Y₂ and La₂ are of the same order of magnitude as those of Cu₂, Ag₂ and Au₂, 45.5, 37.6 and 51.5 kcal/mole respectively, and seems as for these molecules, to be related to the availability of low-lying excited states of the atoms.

2. ScO.

The dissociation energy of this molecule was derived from the iso-molecular exchange reaction



for which the equilibrium constant (figure 1) was measured both for initial samples of scandium oxide and lanthanum metal and of lanthanum oxide and scandium metal. The reaction enthalpy, calculated by a least square treatment is ΔH⁰₂₀₀₀ = - 35.1 kcal/mole. The uncertainty, including possible systematic errors is estimated to be ±3 kcal/mole. Considering only the known electronic states (Σ) of both ScO and LaO, ΔH⁰ = - 31.8 ± 3 kcal/mole was calculated. A third law treatment of the same data, assuming mutual compensation of relative ionization cross sections (σ) and secondary electron multiplier yields, and considering again only the known electronic states of ScO and LaO in the evaluation of the thermodynamic functions, gives ΔH⁰ = -28.7 ± 2 kcal/mole. The average, ΔH⁰ = - 30.0 together with D⁰(LaO) = 188.8 ± 5 kcal/mole yields D⁰(ScO) = 158.8 ± 5.0 kcal/mole. The value D⁰(LaO) = 188.8 ± 4.5 kcal/mole is the average of the third law values determined by Chupka, Inghram and Porter⁽²⁶⁾, recalculated with a ratio σ_{ScO}/σ_{LaO} = 1, a heat of sublimation ΔH⁰(La) = 104.1⁽²³⁾ and a heat of formation ΔH⁰₂₉₈(La₂O₃) = - 428.6⁽²⁸⁾ giving 187.1 kcal/mole, and by White, Walsh,



Ames and Goldstein⁽²⁷⁾, $D^0(\text{LaO}) = 190.4$, both values being based on a $4f$ ground state. $D^0(\text{ScO}) = 158.8 \pm 5.0$ can be compared with the value $D^0(\text{ScO}) = 170 \text{ kcal/mol}$ ⁽¹⁾ obtained from a linear Birge-Sponer extrapolation.

3. ScC_2 .

In the measurements of the scandium vapor pressure referred to above, this element reacted with graphite around 1500°K , with the subsequent and stepwise formation of three different carbides in the condensed phase, presumably Sc_2C , Sc_4C_3 and ScC ⁽²⁸⁾ with approximate heats of formation (obtained by taking $\Delta C_P = \Delta H_{298}^0$) of -12 , -19 and $-26 \text{ kcal/gatom of Sc respectively}$.

Between 2015 and 2111°K the ScC_2 gaseous molecule was also observed. Relative intensities $\text{Sc}^+/\text{ScC}_2^+$ were 6.8×10^2 and 3.7×10^2 and the relative pressures $P_{\text{Sc}}/P_{\text{ScC}_2} = 9 \times 10^2$ and 5×10^2 at the same temperatures

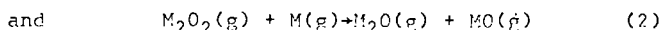
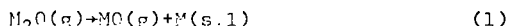
With free energy functions calculated for a linear Sc-C-C molecule by analogy with those for other similar gaseous carbides^(4,11,30) the enthalpy of the reaction $\text{ScC}_2(\text{g}) + \text{Sc}(\text{g}) + 2\text{C}(\text{graphite})$ was calculated: $\Delta H^0 = -49.2 \pm 5 \text{ kcal/mole}$, whence the Sc-C₂ bond strength $D^0(\text{Sc-C}_2) = 146.3 \pm 5$ and the atomization energy of ScC_2 , $D_{\text{O.at}}^0(\text{ScC}_2) = 290.0 \pm 5 \text{ kcal/mole}$.

4. Sc_2O , Y_2O , La_2O , Y_2O_2 and La_2O_2 .

Oxide impurities present in the yttrium and lanthanum samples in low concentration led to the observation of the YO , Y_2O , Y_2O_2 , LaO , La_2O_2 molecules. The concentration of the suboxides and dimeric monoxides in the gas phase was well below the upper limits previously given^(26,27). In a search for the corresponding oxides of scandium, a mixture of Sc_2O_3 and Sc was studied. The Sc_2O molecule was tentatively identified, while the Sc_2O_2 molecule could not be observed.

Typical relative intensities are given in table 2.

Thermochemical data for these molecules were determined by the absolute entropy method from pressure independent reactions of the type



The free energy functions of the suboxides were estimated following a bent symmetrical model, using interatomic distances and force constants identical to those in the corresponding monoxides⁽²⁵⁾. For the dimeric monoxides closed structures were considered.

The enthalpies of reactions 1 and 2 are summarized in Table 3 together with the atomization energies.

ACKNOWLEDGEMENTS.

The authors wish to acknowledge the incentive to perform these experiments and the interest of Professor P. Goldfinger. They thank Mr. F. Degève for his assistance in the experiments and calculations, and the Union Carbide Company for pure scandium metal.

TABLE 3. Atomization Energies of Gaseous Suboxides and Dimeric Monoxides of Sc, Y and La (kcal/mole).

M	$\Delta H(1)$	$\Delta H(2)$	$\Delta H_{at}^O(M_2O)$	$\Delta H_{at}^O(M_2O_2)$
Sc	(-1.0)	-	(245)	-
Y	-6.0	(+29.0)	262	(460)
La	-29.0	+22.2	265	475

REFERENCES

1. G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., Inc., Princeton, N.J. (1950).
2. A.G. Gaydon, "Dissociation Energies", 2nd Ed., Chapman and Hall, Ltd., London (1953).
3. M.G. Inghram and J. Drowart, in "High Temperature Technology", McGraw Hill Book Co., New York (1960).
4. W.A. Chupka, J. Berkowitz, C.F. Giese and M.G. Inghram, J.Phys. Chem., 62, 611 (1958).
5. G. De Maria, J. Drowart and M.G. Inghram, J.Chem.Phys., 31, 1076 (1959).
6. R.E. Honig, J.Chem.Phys., 21, 573 (1953) ; 22, 1610 (1954).
7. G. Koehl, Z. Naturforschg., 9a, 913 (1954).
8. W.A. Chupka, Argonne National Lab. Rept. 5667, p.75 (1957) ; also quoted in ref.3. ; G. Verhaegen and J. Drowart, J.Chem.Phys., 37, 1367 (1962).
9. M.G. Inghram and W.A. Chupka, J.Chem.Phys., 21, 371 (1953). R.E. Honig, J.Chem.Phys., 22, 126 (1954) ; W.A. Chupka and M.G. Inghram, J.Phys.Chem., 59, 100 (1955) ; J. Drowart, R.P. Burns, G. De Maria and M.G. Inghram, J.Chem.Phys., 31, 1131 (1959).
10. J. Drowart and R.E. Honig, J.Phys.Chem., 61, 980 (1957).
11. J. Drowart, G. De Maria and M.G. Inghram, J.Chem.Phys., 29, 1015 (1958).
12. R.Colin, P.Goldfinger and M. Jeunehomme, Nature, 187, 408 (1960).
13. M.Jeunehomme, Thesis, University of Brussels (1962).
14. R. Colin, Ind.Chim.Belf., 26, 51 (1961) ; R.F. Porter, J. Chem. Phys., 34, 583 (1961).
15. J. Drowart and R.E. Honig, J.Chem.Phys., 25, 581 (1956) ; P. Schissel, J.Chem.Phys., 26, 1276 (1957).
16. M. Ackerman, F.E. Stafford and J. Drowart, J.Chem.Phys., 33, 1784 (1960).
17. J. Drowart, Thesis, University of Brussels (1957).
18. M.Ackerman, F.E. Stafford and G. Verhaegen, J.Chem.Phys., 36, 1560 (1962).

References (continued).

19. G.Verhaegen, F.E. Stafford, P.Goldfinger and M. Ackerman, Trans Faraday Soc., 58, 1926 (1962).
20. J. Drowart and P.Goldfinger. J.Chim.phys., 55, 721 (1958).
21. P.M. Badger. J.Chem.Phys., 3, 710 (1935).
22. D.R. Stull and G.C. Sinke. "Thermodynamic Properties of the Elements". Advances in Chemistry Series (American Chemical Society. Washington D.C., 1956). Vol. 18.
23. R.J. Ackermann and E.G. Rauh. J.Chem.Phys., 36, 448 (1962).
24. W.W. Weller and K.K. Kelley. Bureau of Mines, Rept. of invest; , 5984, (1962).
25. L. Åkerlind, Ark.Fys., 22, 41 and 65 (1962).
26. W.A. Chupka, M.G. Inghram and R.F. Porter, J.Chem.Phys., 24, 792 (1956).
27. D. White, P.W. Walsh, L.L. Ames and H.W. Goldstein, in "Thermodynamics of Nuclear Materials", p.417, I.A.E.C., Vienna 1962.
28. E.J. Huber Jr. and C.E. Holley Jr., J.Am.Chem.Soc., 75, 3594 (1953).
29. M. Hansen and K. Anderko, "Constitution of Binary Alloys", (McGraw Hill Book Co., 1958) 2nd Ed.
30. G. Verhaegen, F.E. Stafford and J. Drowart. Technical Note No 13, Contract AF 61(052)-225. 25 June 1963.

MASS SPECTROMETRIC STUDIES OF NEW HIGH MOLECULAR WEIGHT BORON SULFIDES

Frank T. Greene and Paul W. Gilles
Department of Chemistry
University of Kansas
Lawrence, Kansas

ABSTRACT

The new, high molecular weight boron sulfides that were recently reported¹ have been investigated by mass spectrometric techniques with samples enriched in B¹⁰. Specimens of B₂S₃ containing excess sulfur were prepared by passing H₂S over the B¹⁰-enriched elemental boron in silica tubing at temperatures at about 700-800°C forming HBS₂ which was thermally decomposed to B₂S₃. After being heated in a graphite crucible in low vacuum for about one-half hour at about 300° to discharge some of the excess sulfur, the sample and crucible were heated in a 12-inch, 60° magnetic field mass spectrometer. The mass scale was established by actual counting of individual peaks, and the observed and calculated intensities were compared.

Three groups of molecules have been observed. The identities of more than thirty high molecular weight boron sulfide molecules that were previously reported have been confirmed. The Group II substances that were originally suggested to be boron sulfur hydroxides contain one fewer boron atom than proposed originally and have been shown to contain boron, sulfur, and additional elements whose atoms total either 28 or 60 mass units. The third group containing boron, sulfur, and an unknown radical has been discovered in B¹⁰ enriched samples.

1 F. T. Greene and Paul W. Gilles, J. Am. Chem. Soc. **84**, 3598 (1962).

MASS SPECTROMETRIC STUDY OF THE REACTION
OF WATER VAPOR WITH BERYLLIUM OXIDE*

Lowell P. Theard and Donald L. Hildenbrand
Research Laboratory,
Aeronutronic Division of Ford Motor Company
Newport Beach, California

Abstract

The reaction of water vapor with beryllium oxide under Knudsen conditions has been studied using a high temperature mass spectrometer. Results yield lower limits of -25 kcal/mole and -156 kcal/mole for the heats of formation (298°K) of BeOH(g) and $\text{Be(OH)}_2\text{(g)}$, respectively.

Mass spectral evidence for the presence of $\text{Be}_2\text{O(g)}$ in the equilibrium vapor above beryllium oxide at high temperatures is presented. The heat of formation of $\text{Be}_2\text{O(g)}$ at 298°K is calculated to be -7 ± 10 kcal/mole.

Introduction

Atmospheric pressure transpiration experiments have shown that water vapor reacts with beryllium oxide at high temperatures to form volatile products.¹⁻⁴ The principal reaction product present under these conditions has been assumed to be a gaseous beryllium hydroxide, Be(OH)_2 . In an effort to observe the products directly we have studied the reaction under Knudsen conditions in the mass spectrometer, and while the results obtained have not allowed complete analysis of the reaction products, we have inferred from the data limiting values for the heats of formation of the gaseous dihydroxide, Be(OH)_2 , and subhydroxide, BeOH .

In the course of these studies we have also investigated the direct vaporization of beryllium oxide. Our efforts in this area, for the most part, have been directed toward establishing the existence of $\text{Be}_2\text{O(g)}$ in the equilibrium vapor at temperatures above 2300°K and determining its heat of formation.

Experimental

The mass spectrometer is a Nuclide Analysis Associates Model HT 12-60, a single focusing 60°, 12" radius of curvature, high temperature instrument, which is similar in design to the one described by Chupka, Berkowitz, and Giese.⁵ A gas handling system for use in studying heterogeneous reactions was constructed external to the mass spectrometer. The reactant gas or vapor can be placed in a 3-liter reservoir bulb and allowed to leak into the Knudsen cell compartment of the mass spectrometer at rates that can be closely controlled with a Granville-Phillips variable viscous leak.

The Knudsen cell assembly used for the $\text{H}_2\text{O-BeO}$ reaction is shown schematically in Figure 1. A cold-pressed beryllia cell liner and water vapor inlet tube, fabricated by National Beryllia Corp., were used. Preliminary experiments had shown that metallic parts could not be used in the hot zone because of extensive reaction with water vapor.

By cementing all joints along the inlet line the background pressure of water vapor was kept low enough to permit detection of the effusing water vapor molecules by shutter effects. In Figure 2 the shutter profile for H_2O^+ from $\text{H}_2\text{O(g)}$ obtained with the present cell assembly is shown together with that for Be^+ from Be(g) measured during a study of the vaporization of beryllium metal. Heights of the peaks have been normalized for comparison. Although the H_2O^+ peak is small relative to the total H_2O^+ intensity, its position and half-width are nearly equivalent to those of Be^+ . The tailing-off of the H_2O^+ intensity toward the ends of the shutter slit travel apparently results from a reduction of H_2O background pressure in the ion source due to reduced transmission of water molecules from the Knudsen cell chamber to the ion source.

* Work supported by the Advanced Research Projects Agency and the Air Force Systems Command under contract AF 04(611)-8523.

KNUDSEN CELL ASSEMBLY FOR H_2O - BeO REACTION

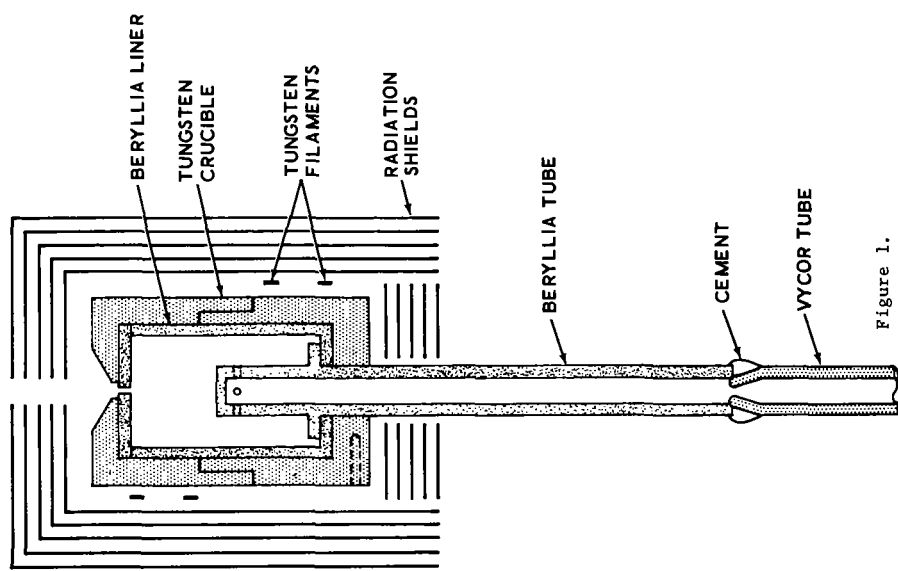


Figure 1.

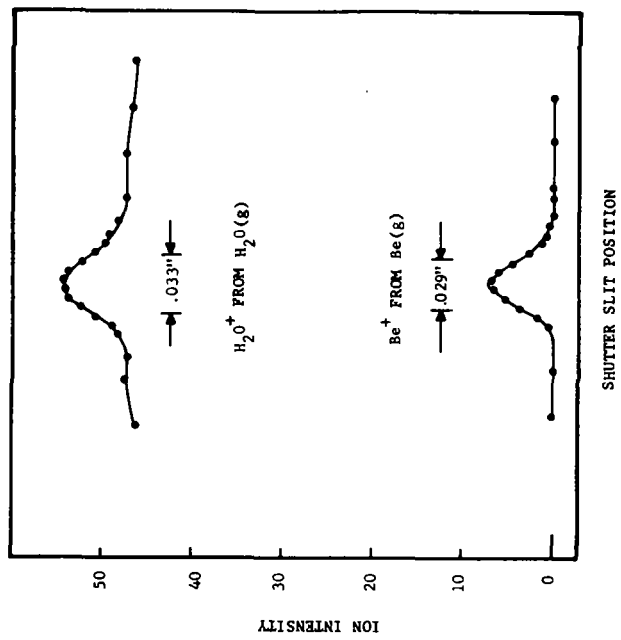


Figure 2. - Shutter profiles for H_2O^+ from $\text{H}_2\text{O}(\text{g})$ and Be^+ from $\text{Be}(\text{g})$.

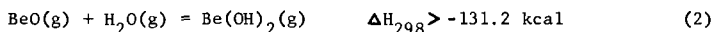
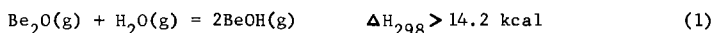
The proper "shutter-check" intensity is the difference between the peak intensity and the height of the plateau just off the sides of the peak.

Both tungsten and beryllia Knudsen cells were used for studying the vaporization of beryllium oxide. Mass spectra obtained with beryllia cells differed significantly from those obtained with tungsten only as regards the presence of tungsten-containing ions.

Reaction of Water Vapor With Beryllium Oxide

Using cell pressures of water vapor on the order of 10^{-6} atm and temperatures in the range 1900 to 2400°K, the mass spectrum was examined for shutter-dependent ion signals. In addition to the ions formed from beryllium oxide vapor species and from water vapor, small shutter-dependent ion signals were observed at the mass numbers which correspond to the ions BeOH^+ and $\text{Be}(\text{OH})_2^+$. The latter peaks were too small, however, to permit appearance potential and temperature dependence measurements. Several experiments that were attempted with higher temperatures and/or greater pressures of water vapor were unsuccessful because of electrical breakdown and structural failure brought about by reactions involving residual water vapor in the region of the oven.

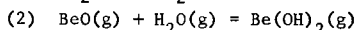
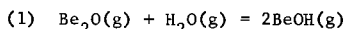
If the m/e 26 and 43 ion currents, measured at 2327°K with 1.3×10^{-6} atm $\text{H}_2\text{O}(\text{g})$ in the cell, are taken as upper limits of the BeOH^+ and $\text{Be}(\text{OH})_2^+$ intensities for simple ionization of the corresponding neutral vapor species, then limiting third-law heats can be calculated as follows:



Pertinent data are given in Table I.

Table I

Calculations for the reactions



<u>Vapor species</u>	<u>Ion intensity, arbitrary units</u>	<u>Estimated relative cross section</u>	<u>Corrected intensity</u>	<u>Pressure, atm T = 2327°K</u>
BeO	8.3	1.0	8.3	3.1×10^{-8}
Be ₂ O	0.77	1.3	0.59	2.2×10^{-9}
H ₂ O	278	0.8	348	1.3×10^{-6}
BeOH	< 7.5	1.0	< 7.5	$< 2.8 \times 10^{-8}$
Be(OH) ₂	< 4.8	1.3	< 3.7	$< 1.4 \times 10^{-8}$

<u>Reaction</u>	<u>T(°K)</u>	<u>K_{eq}</u>	<u>$\Delta F^\circ/T$ cal/deg</u>	<u>$-\Delta\left(\frac{F^\circ - H_{298}^\circ}{T}\right)$ cal/deg</u>	<u>ΔH_{298}° kcal</u>
1	2327	< 0.26	> 2.6	3.5	> 14.2
2	2327	$< 3.5 \times 10^5 \text{ atm}^{-1}$	> -25.4	-31.0	> -131.2
		$\Delta H_{298}^\circ \text{ BeOH}(\text{g})$	> 1/2 (14.2 - 7 - 57.8)		
			> -25.3 ± 10 kcal/mole		
		$\Delta H_{298}^\circ \text{ Be}(\text{OH})_2(\text{g})$	> -131.2 + 32.5 - 57.8		
			> -156.5 ± 10 kcal/mole		

$\text{Be}_2\text{O}(\text{g})$, which is the subject of the next section, and $\text{BeO}(\text{g})$ are components of the equilibrium vapor above $\text{BeO}(\text{c})$. In calculating the heat of reaction 1 ion currents were used directly without pressure calibration since the equilibrium constant is dimensionless. For reaction 2 pressures were cali-

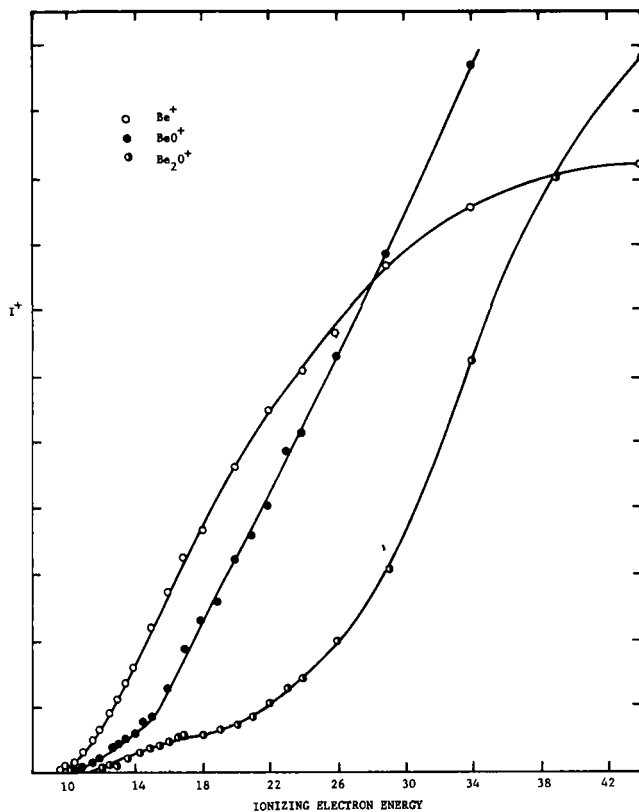


Figure 3. - Ionization efficiency curves for Be^+ , BeO^+ , and Be_2O^+ from beryllium oxide vapor.

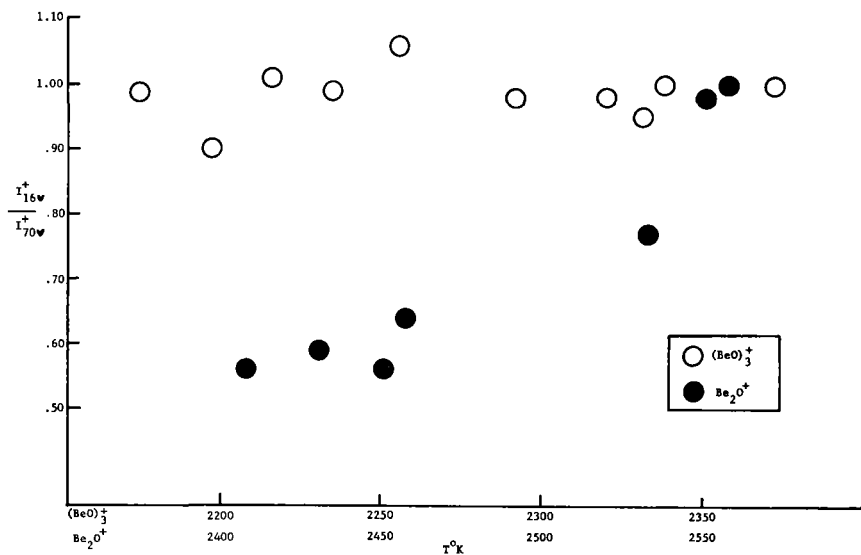


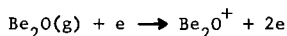
Figure 4. - Temperature dependence of intensity ratios for Be_2O^+ and $(\text{BeO})_3^+$ ions from beryllium oxide vapor.

brated with the aid of the BeO(g) partial pressure calculated from data given in reference 5. Relative ionization cross sections and free energy functions were estimated. Low ionizing electron energies were used to avoid fragmentation effects.

When combined with known heats of formation, the above results yield (1) $\Delta H_{298}^0 > -25$ kcal/mole (less negative) for BeOH(g), and (2) $\Delta H_{298}^0 > -156$ kcal/mole (less negative) for Be(OH)₂(g). Uncertainties of ± 10 kcal/mole are assigned to both heats. The data for BeOH are believed to be more reliable than those for Be(OH)₂, since the free-energy functions can be estimated with greater accuracy. The limiting heat for BeOH, when combined with O-H bond energies taken from H₂O and OH, leads to a Be-O bond energy which is less than 105 to 113 kcal. This is consistent with the Be-O bond energies derived from beryllium oxide vapor species.⁵ The JANAF Tables⁶ list the standard heat of formation of BeO(g) as -41 kcal/mole, which now appears to be somewhat too large negatively.

Vaporization of Beryllium Oxide: Heat of Formation of Be₂O(g)

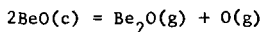
In addition to the large number of ions previously observed in the mass spectrum of beryllium oxide vapor,⁵ we detected small intensities of the ions Be_nO_{n-1}⁺, where n = 2 through 5, at temperatures above 2300°K. The ionization efficiency curve for Be₂O⁺ is shown in Figure 3 together with those for Be⁺ and BeO⁺. The form of the Be₂O⁺ curve, like that for BeO⁺, suggests the existence of at least two important modes of ion formation. The magnitude of the appearance potential suggests that in the low energy region Be₂O⁺ ions are formed by simple ionization of Be₂O(g) molecules, i.e.



Starting in the vicinity of 17 volts, additional Be₂O⁺ ions are produced by a second process which is presumably fragmentation of a larger neutral molecule. The effect of temperature on the relative importance of the two processes is shown in Figure 4, where the ratio of the Be₂O⁺ intensity for 16 ev electrons to the intensity for 70 ev electrons is plotted against cell temperature. Data for (BeO)₃⁺ ions are plotted in a similar fashion. The curves have been normalized by assigning the value 1.00 to the intensity ratio obtained with the highest temperature used for each of the two ions. Relatively little variation is observed with (BeO)₃⁺, the ionization efficiency curve for which has no sharp breaks beyond the threshold. On the other hand, with Be₂O⁺ a significant trend is seen. As the temperature increases the low energy process becomes relatively more important.

Third-law calculations for three equilibria involving Be₂O(g) are given in Table II. In order to avoid fragmentation contributions, intensities of the appropriate atomic and molecular ions were measured using ionizing electron energies four volts above the appearance potentials. Pressure calibration, where needed, was provided by the Be⁺ and O⁺ intensities, as the product of the Be(g) and O(g) partial pressures could be calculated from known thermodynamic data. Free energy functions for Be₂O(g) were calculated using molecular constants which were estimated by analogy with Li₂O(g).⁷ The resulting third-law heats, when combined with available heats of formation, give for the heat of formation of Be₂O(g) at 298°K the values -7.4, -6.2, and -6.6 kcal/mole. A weighted average of -7 kcal/mole is indicated and the uncertainty is estimated to be ± 10 kcal/mole. This leads to 222 kcal for the heat of dissociation of Be₂O(g) to the gaseous atoms and an average Be-O bond energy of 111 kcal for the Be₂O(g) molecule. By comparison, thermochemical data for BeO(g) and its gaseous polymers⁵ (assuming ring structures) yield Be-O bond energies ranging from 106 to 120 kcal.

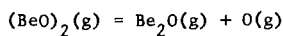
TABLE II

Calculations for reactions involving $\text{Be}_2\text{O}(\text{g})$.

$T(^{\circ}\text{K})$	$K \times 10^{13},$ atm ²	$\Delta F^{\circ}/T$ cal/deg	$-\Delta \left(\frac{F^{\circ} - H_{298}^{\circ}}{T} \right)$ cal/deg	ΔH_{298}° kcal
2380	1.0	59.5	84.4	342.5
2345	0.46	61.0	84.4	341.0
2368	1.3	59.0	84.4	339.6
2450	14.0	54.3	84.2	339.3
2497	60.0	51.4	84.1	338.3

$$\Delta H_{298}^{\circ} = 340 \pm 2 \text{ kcal}$$

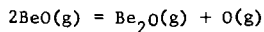
$$\Delta H_{298}^{\circ} [\text{Be}_2\text{O}(\text{g})] = 340 - 59.6 - 2(143.1) = -6.2 \pm 10 \text{ kcal/mole}$$



$T(^{\circ}\text{K})$	$K \times 10^6,$ atm	$\Delta F^{\circ}/T$ cal/deg	$-\Delta \left(\frac{F^{\circ} - H_{298}^{\circ}}{T} \right)$ cal/deg	ΔH_{298}° kcal
2380	1.5	26.6	38.3	154.4
2345	1.4	26.8	38.3	152.6
2368	2.3	25.8	38.3	151.8
2450	5.3	24.2	38.3	153.1
2497	11.1	22.6	38.4	152.1

$$\Delta H_{298}^{\circ} = 153 \pm 1 \text{ kcal}$$

$$\Delta H_{298}^{\circ} [\text{Be}_2\text{O}(\text{g})] = 153 - 59.6 - 100 = -6.6 \pm 10 \text{ kcal/mole}$$



$T(^{\circ}\text{K})$	K	$\Delta F^{\circ}/T$ cal/deg	$-\Delta \left(\frac{F^{\circ} - H_{298}^{\circ}}{T} \right)$ cal/deg	ΔH_{298}° kcal
2380	19.3	-5.9	2.3	-8.6

$$\Delta H_{298}^{\circ} [\text{Be}_2\text{O}(\text{g})] = -8.6 - 59.6 + 2(30.4) = -7.4 \pm 10 \text{ kcal/mole}$$

REFERENCES

1. C. A. Hutchison, Jr. and J. G. Malm, J. Am. Chem. Soc., 71, 1338(1949).
2. L. Grossweiner and R. L. Seifert, Ibid., 74, 2701 (1952).
3. G. R. B. Elliott, UCRL Report No. 1831, June 1952.
4. W. A. Young, J. Phys. Chem., 64, 1003 (1960).
5. W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys., 30, 827(1959).
6. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, December 31, 1960.
7. D. White, private communication.

MASS SPECTROMETRIC STUDIES OF INORGANIC FLUORIDES

G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave
Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Gaseous mono- and difluorides of four of the alkaline earth metals and of silicon have been studied mass spectrometrically and their thermodynamic properties derived from both absolute pressure and temperature dependence measurements. Data for the reduced states were obtained by adding Al or Si to an alkaline earth difluoride and by observing various homogeneous and heterogeneous equilibria. The monofluorides of Mg, Ca, Sr, and Ba were found to be much more stable than was previously supposed and the results tend to support an ionic model for these molecules. The data for the difluorides and SiF are in general agreement with literature values. A heat of formation of gaseous aluminum trifluoride has also been obtained.

In the sublimation studies^{1,2} the MF₂ salts (where M = Ca, Sr, Ba)

1. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. 67, 877 (1963).
2. J. W. Green, Ph. D. Thesis, University of Wisconsin (1963).

were vaporized from a tantalum Knudsen cell and the intensities of the MF⁺ ions resulting from dissociative ionization of MF₂ gaseous molecules were measured as a function of temperature. Second Law heats of sublimation were obtained from the slopes of log I⁺T vs 1/T plots with suitable enthalpy corrections³ to 298°K.

3. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).

Third Law heats of sublimation were obtained by combining the free energy function changes³ with absolute pressures derived either from an internal calibration of the mass spectrometer or from comparison with the results of Langmuir studies employing a vacuum microbalance.^{1,4} The results of the mass

4. R. G. Bautista, Private Communication.

spectrometric studies are shown in Table I together with the Langmuir studies,^{1,4} the earlier results of Ruff and LeBoucher,⁵ and the recent work on CaF₂ by

5. O. Ruff and L. LeBoucher, Z. anorg. u. allgem. Chem. 219, 376 (1934).

Schulz and Searcy.⁶

6. D. A. Schulz and A. W. Searcy, J. Phys. Chem. 67, 103 (1963).

The stabilities of the gaseous alkaline earth monofluorides⁷ were determined

7. G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, Bull. Am. Phys. Soc. 8, 112 (1963).

by utilizing the mass spectrometer to analyze the vapors effusing from a heated tantalum Knudsen cell which contained an alkaline earth difluoride salt with aluminum present as a reducing agent.^{1,8,9} Ionization efficiency curves for the

8. G. D. Blue, Ph. D. Thesis, University of Wisconsin (1963).
9. T. C. Ehlert, Ph. D. Thesis, University of Wisconsin (1963).

systems Al-SrF₂ and Al-BaF₂ are presented in Figures I and II. Temperature dependence studies were made to determine the molecular precursors of the ions observed, and fragmentation effects were then minimized by working at suitable

low ionizing electron energies. The ion currents were used to form the equilibrium constants for the various homogeneous and heterogeneous equilibria by using the usual relation, $P = kI^+T$. These constants were combined with free energy function changes^{3,10,11,12} to obtain the Third Law heats of reaction shown in Table II.

10. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., Advances in Chemistry Series, No. 18, (1956).
11. JANAF Interim Thermochemical Tables, Edited by D. R. Stull, The Dow Chemical Company, Midland, Michigan (1960).
12. K. K. Kelley, U. S. Bureau of Mines Bulletin 584, (1960).

Second Law heats were used to check these values whenever possible and showed good agreement. The dissociation energies, $D(MF)$, were obtained by combining the heats of the homogeneous reactions with $D(AlF)^{11,13}$ or $D(MgF_2)^{14}$. Values for

13. W. P. Witt and R. F. Barrow, Trans. Faraday Soc. 55, 730, (1959).
14. W. N. Hubbard, Private Communication, $\Delta H_{1298}^\circ [MgF_2(s)] = -264.4 \pm 0.6$ kcal/mole.

$D(MF)$ were obtained through a thermochemical cycle from the heats of the heterogeneous reactions and the known heats of formation of $M(g)$,¹⁰ $F(g)$,¹¹ and $MF_2(s)$.^{3,14} The results are shown in the first two rows of Table III, together with a thermochemical value for $D(BeF)^{15}$.

15. M. A. Greenbaum, R. E. Yates, M. L. Arin, M. Arshadi, J. Weiher, and M. Farber, J. Phys. Chem. 67, 703, (1963).

The electron impact limits on $D(MF)$ shown in the third row of Table III were obtained from the values for $AP(MF^+/MF)$ and $AP(MF^+/MF_2)$ derived from the ionization efficiency curves^{2,8,9} and the values for the heats of atomization of $MF_2(g)$ calculated from the sublimation data. Rittner's¹⁸ ionic model using

16. E. S. Rittner, J. Chem. Phys. 19, 1030, (1951).

estimated^{17,18} values of 0.84, 2.2, 6.0, 8.6, and 11.3A³ for the polarizabilities

17. L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," (McGraw-Hill, New York, 1935), p. 204 ff.
18. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," (John Wiley and Sons, Inc., New York, 1954), p. 955.

of Be^+ through Ba^+ was used to calculate the values of $D(MF)$ in the fourth row. Skinner's Valence State Hypothesis¹⁹ predicts the $D(MF)$ values in the fifth

19. H. A. Skinner, Trans. Faraday Soc. 45, 20, (1949).

row of the table. A comparison of our measured values of $D(MF)$ with the atomization energies of the difluorides shown in row six yields an average value of $D(MF)/D(MF_2) = 0.46$. Finally, the values recommended by Gaydon²⁰ and

20. A. G. Gaydon, "Dissociation Energies," (Chapman and Hall, Ltd., London, 1953).

based on the study of band spectra are presented in the last row of Table III.

Figures III and IV show the ionization efficiency curves for the important ionic species obtained when silicon was used to reduce calcium fluoride. The appearance potentials of Si^+ , Ca^+ , and SiF^+ are 8.1 ± 0.3 , 5.9 ± 0.3 , and 7.5 ± 0.4 eV, respectively. These agree well with the spectroscopic ionization potentials of Si , Ca , and SiF which are 8.15, 6.11, and 7.26 eV,²¹ respectively. The CaF^+ curve

21. (a) C. Moore, Vol. I, NBS Circular 467, (1949).
- (b) J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. 71A, 476, (1958).

is similar to that obtained from the aluminum-reduced system¹ with the low energy foot beginning at 6.1 ± 0.5 ev and a second process occurring above 12.5 ev. The precursors of these processes are believed to be CaF(g) and $\text{CaF}_2\text{(g)}$. Finally, the appearance potential of SiF_2^+ , 11.0 ± 0.5 ev, is close to the ionization potential of CF_2 ,²² indicating that its precursor is $\text{SiF}_2\text{(g)}$.

22. W. C. Price, Private Communication.

The Second and Third Law heats for the reactions shown in Table IV were calculated from ion currents obtained with low energy electrons. The JANAF¹¹ free energy functions for SiF(g) and $\text{SiF}_2\text{(g)}$ were used along with $\Delta H_{\text{subl},298}^\circ[\text{Ca}]$,¹⁰ $\Delta H_{\text{subl},298}^\circ[\text{Si}]$,²³ $\Delta H_{\text{f},298}^\circ[\text{CaF(g)}]$,⁷ and $\Delta H_{\text{f},298}^\circ[\text{CaF}_2\text{(s)}]$ and $\Delta H_{\text{f},298}^\circ[\text{CaF}_2\text{(g)}]$.^{2,24}

23. R. E. Honig, RCA Review 23, 567, (1962).

24. F. Rossini, D. Wagman, E. Evans, and I. Jaffee, NBS Circular 500, (1952).

The heat of formation of $\text{SiF}_2\text{(g)}$ so obtained was used to establish $\Delta H_{\text{f},298}^\circ$ of SiF(g) as -3.0 ± 4.7 kcal/mole and D_{298}° of SiF as 5.60 ± 0.12 ev. This latter value agrees with the spectroscopic value, 5.4 ± 0.4 ev.^{21b} The lower limit set by the ionization efficiency data is $\geq 5.5 \pm 0.1$ ev.

The heat of formation of $\text{SiF}_2\text{(g)}$, -138.7 ± 2.0 kcal/mole, is somewhat less negative than the estimate of Margrave, Kanaan, and Pease,²⁵ -148 ± 4 kcal/mole.

25. J. L. Margrave, A. S. Kanaan, and D. C. Pease, J. Phys. Chem. 66, 1200, (1962).

This discrepancy appears to be real and Kanaan and Margrave²⁶ have suggested the

26. (a) A. S. Kanaan, Ph. D. Thesis, University of Wisconsin, (1962).

(b) A. S. Kanaan and J. L. Margrave, to be published, 1963.

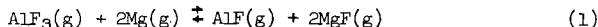
possibility of $(\text{SiF}_2)_2\text{(g)}$ as a significant species at low temperatures (800-1200°K) when silicon or silicides are heated in the presence of SiF_4 . The atomization energy of SiF_2 , 12.31 ± 0.17 ev, is almost exactly half that of SiF_4 , 24.7 ev.²⁷

27. S. S. Wise, W. N. Hubbard, H. Feder, and J. L. Margrave, J. Phys. Chem. 67, 815, (1963).

Considerable AlF_2^+ ion was produced from molecules over the heated mixture of aluminum and magnesium fluoride. The appearance potential, 15.5 ± 0.4 ev, agrees with that found by Porter²⁸ for AlF_2^+ from AlF_3 . It was then assumed

28. R. F. Porter, Cornell University, Private Communication.

that AlF_3 was the only precursor of the AlF_2^+ ion observed and the equilibrium



was used to establish the reaction heat as -50.1 ± 1.3 kcal/mole at 298°K. With the same supplementary data previously cited, one then calculates $\Delta H_{\text{f},298}^\circ[\text{AlF}_3\text{(g)}] = -284.3 \pm 2.7$ kcal/mole by the Third Law method. Previously, $\Delta H_{\text{f},298}^\circ[\text{AlF}_3\text{(g)}] = -285.4 \pm 5$ kcal/mole was obtained¹¹ from the heat of formation of the solid, -356.3 ± 5.0 kcal/mole²⁹ and the heat of sublimation calculated from the data

29. P. Gross, C. Hayman, and D. L. Levi, Bull. Chem. Thermodynamics 2, 29, (1959).

of Ruff and LeBoucher.⁵

If one uses a newer value for $\Delta H_{\text{subl},298}^\circ[\text{AlF}_3]$, 72.6 kcal/mole,^{30,31} and the

30. R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858, (1960).

31. W. P. Witt and R. F. Barrow, Trans. Faraday Soc. 55, 730, (1959).

$\Delta H_{\text{f},298}^\circ[\text{AlF}_3\text{(g)}]$ reported here, he finds $\Delta H_{\text{f},298}^\circ[\text{AlF}_3\text{(s)}] = -356.9 \pm 2.7$ kcal/mole which is in good agreement with the data of Gross, et al.²⁹

Table I

Heats of Sublimation at 298°K (kcal/mole)

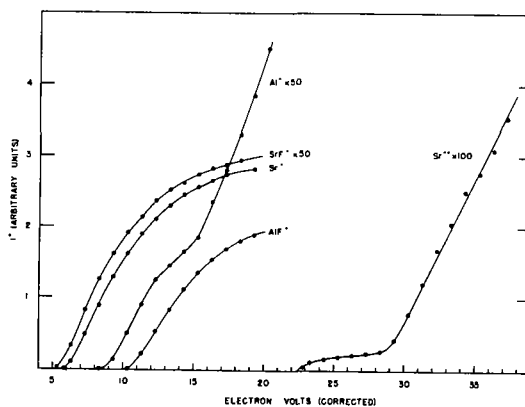
Method	CaF ₂	SrF ₂	BaF ₂
Mass Spectrometer			
Second Law	103.6	106.8	93.8
Third Law	103.3	103.7	92.3
Vacuum Microbalance			
Second Law	98.3	104.8	94.4
Third Law	103.3	104.0	92.4
Ruff and LeBoucher	102.3	101.6	87.6
Schulz and Searcy	101.3		

Table II

Heats of Various Reactions for the Al-MF₂ Systems

Reaction	ΔH_{298}° (kcal/mole) for M =			
	Mg	Ca	Sr	Ba
$M(g) + AlF(g) = Al(g) + MF(g)$	(≥ 45.2)	32.7 ± 0.2	33.1 ± 0.3	23.9 ± 0.2
$M(g) + MF_2(s) = 2MF(g)$	128.2 ± 0.8	120.7 ± 0.8	116.0 ± 0.8	97.9 ± 0.4
$Mg(g) + MgF_2(g) = 2MgF(g)$	37.8 ± 1.0	-----	-----	-----

Figure I

Ionization Efficiency Curves for Species in the Al + SrF₂ SystemAcknowledgments

This work was supported financially by the National Science Foundation, the United States Atomic Energy Commission, and the Advanced Research Projects Agency, under ARPA Order Number 40, and monitored by the Army Research Office (Durham).

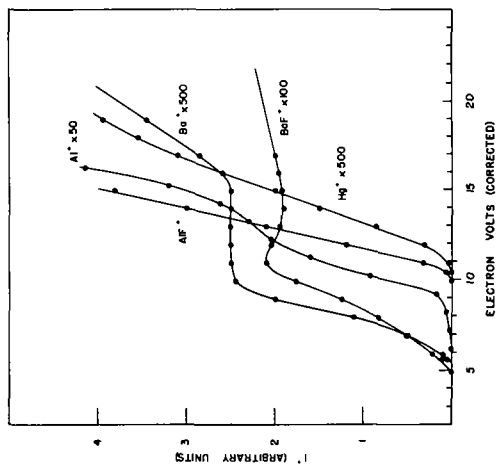
Table III
Dissociation Energies of MF Molecules by Various Methods

Method	$D_{298}^0(\text{MF})$ in electron-volts for M =				
	Be	Mg	Ca	Sr	Ba
Homogeneous Reaction	-----	4.60 $\pm$ 0.06	5.44 $\pm$ 0.10	5.45 $\pm$ 0.10	5.80 $\pm$ 0.09
Heterogeneous Reaction	6.25	4.50 $\pm$ 0.04	5.41 $\pm$ 0.12	5.45 $\pm$ 0.10	5.82 $\pm$ 0.10
Electron Impact	-----	4.6 $\pm$ 0.6	4.9 $\pm$ 0.9	5.1 $\pm$ 0.9	5.7 $\pm$ 0.9
Ionic Model	5.20	4.31	5.24	5.46	5.84
Valence State Hypothesis	4.81	3.92	4.73	4.73	5.16
1/2 $\Delta H_A(\text{MF}_2)$	6.50	5.50	5.81	5.75	6.05
Gaydon	4.0 $\pm$ 1.0	3.2 $\pm$ 0.7	3.2	2.7 $\pm$ 1.0	3.0 $\pm$ 1.0

Table IV
Heat of Various Reactions for the Ca-Si-F System

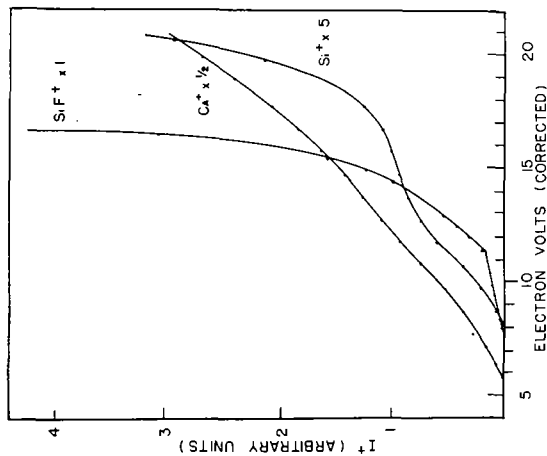
Reaction	ΔH_{298} (kcal/mole)	$\Delta H_{298}^0[\text{SiF}_2(\text{g})]$ (kcal/mole)	Method
$\text{CaF}_2(\text{g}) + \text{Si}(\text{g}) \rightleftharpoons \text{Ca}(\text{g}) + \text{SiF}_2(\text{g})$	-11.5 $\pm$ 12.0 -16.7 $\pm$ 1.5	-131.5 $\pm$ 12.0 -138.5 $\pm$ 6.5	Second Law Third Law
$2\text{CaF}(\text{g}) + \text{Si}(\text{g}) \rightleftharpoons 2\text{Ca}(\text{g}) + \text{SiF}_2(\text{g})$	-39.5 $\pm$ 20.0 -34.7 $\pm$ 0.9	-143.9 $\pm$ 24.0 -139.1 $\pm$ 4.7	Second Law Third Law
$\text{CaF}_2(\text{s}) + \text{Si}(\text{g}) \rightleftharpoons \text{Ca}(\text{g}) + \text{SiF}_2(\text{g})$	88.0 $\pm$ 9.0 86.7 $\pm$ 1.5	-137.1 $\pm$ 12.0 -138.4 $\pm$ 4.5	Second Law Third Law
$\text{Si}(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{SiF}_2(\text{g})$	----- ----- -----	-137.5 -138.7 -138.7 $\pm$ 2.0	Average, Second Law Average, Third Law "Best" Value
$\Delta H_{f,298}^0[\text{SiF}(\text{g})]$			
$\text{Si}(\text{g}) + \text{SiF}_2(\text{g}) \rightleftharpoons 2\text{SiF}(\text{g})$	25.3 $\pm$ 1.4	- 3.0 $\pm$ 4.7	Third Law
D_{298}^0			
$\text{SiF}_2(\text{g}) \rightleftharpoons \text{Si}(\text{g}) + 2\text{F}(\text{g})$	-----	283.7 $\pm$ 4.0 (12.31 $\pm$ 0.17 eV)	
$\text{SiF}(\text{g}) \rightleftharpoons \text{Si}(\text{g}) + \text{F}(\text{g})$	-----	129.2 $\pm$ 2.7 (5.60 $\pm$ 0.12 eV)	
$\text{SiF}(\text{g}) \rightleftharpoons \text{Si}(\text{g}) + \text{F}(\text{g})$	-----	$\geq$ 5.5 $\pm$ 1.0 eV	Ionization Efficiency Curve

Figure II



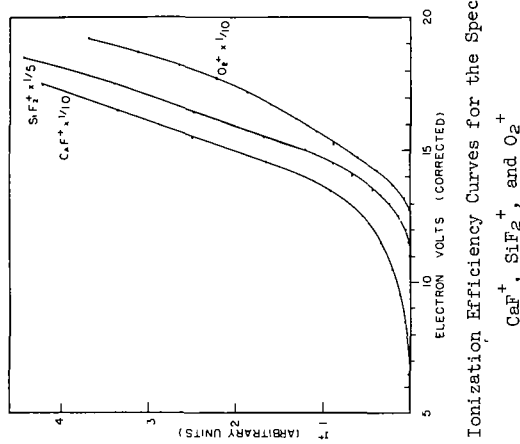
Ionization Efficiency Curves for Species
in the Al + BaF₂ System

Figure III



Ionization Efficiency Curves for the Species
Si⁺, Ca⁺, and SiF⁺

Figure IV



Ionization Efficiency Curves for the Species
CaF⁺, SiF₂⁺, and O₂⁺

A STUDY OF DIFFERENT DESIGNS OF COLD ELECTRON SOURCES CAPABLE OF
MASS SPECTROMETRIC APPLICATIONS

M. K. Testerman, R. W. Raible, G. W. Grimes, J. R. Williams, B. E. Gilliland

Department of Electronics and Instrumentation
University of Arkansas Graduate Institute of Technology
Little Rock, Arkansas

A well collimated, homogeneous beam of low energy electrons is the most dependable agent known for producing nearly monoenergetic ions from a neutral gas. Ordinarily an incandescent filament generates the electrons for this beam. However, it is sometimes necessary, and almost always preferable, to eschew the presence of any heating element in the ionization region; that is to say, to use a "cold" source of electrons. One such source was described previously in a paper presented at the Eighth Annual ASTM E-14 Meeting, Atlantic City, New Jersey, 1960. The results of subsequent investigations into cold electron sources form the basis of this report.

In all mass spectrometric applications, the heating effect of the thermionic electron emitter is a disadvantage. In the special environment of space flight, where electric power is severely limited, the several watts of power required to heat the filament precludes its use as a source of electrons. Our studies have shown that a cold electron source can eliminate all heating elements, use only microwatts of power, and still be compact, light-weight, and highly efficient.

Our first cold source of electrons¹ consisted of a photocathode excited by ultraviolet radiation and an electron multiplier which amplified the photoelectron current and directed it into the ionization region of a mass spectrometer. Figure 1 illustrates this electron source used in an RF mass spectrometer tube. The photocathode was tantalum irradiated by a hydrogen arc lamp outside the vacuum system. The electron multiplier had ten silver--magnesium bucket dynodes of the type used in the DuMont 6291 electron photomultiplier tube. This electron source could produce an ionizing current of 20-40 microamps from an input of several nanoamps. The power consumed in producing one microamp of ionizing current was 160 microwatts, which may be contrasted to the 5.76 watts of power required by a thermionic emitter of comparable output current. A mass spectrum of n-butane obtained using the cold source is shown in Figure 2. There is no significant loss in resolution due to the use of the cold electron source.

Studies of the electron multiplier in continuous action indicated a rapid drop in secondary emission coefficient during the first few hours of operation after which the rate of reduction leveled off and gradually approached zero (see Figure 3). Thus the secondary emission coefficient approached a constant value.

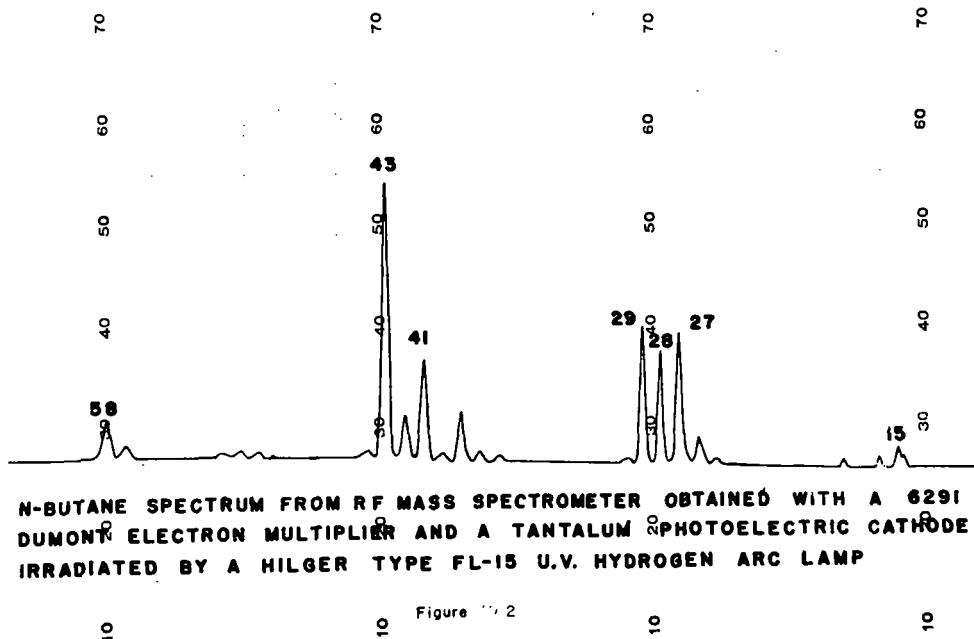
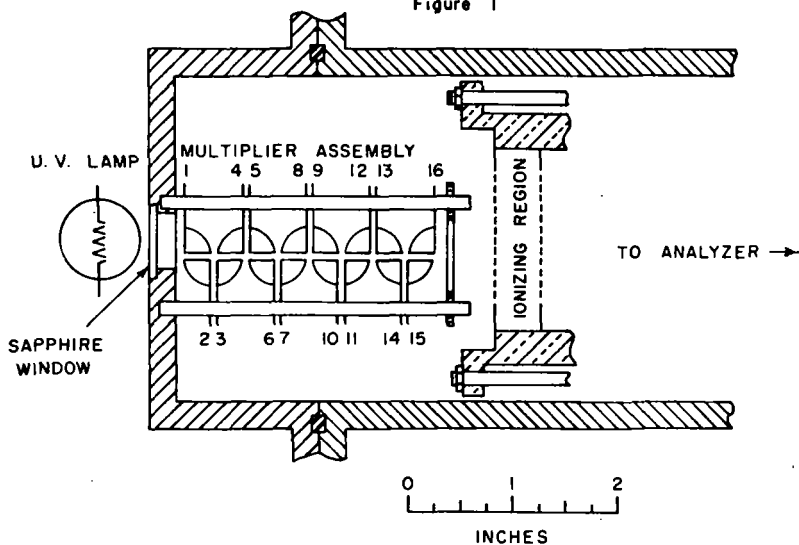
Figure 4 shows the effect of different gases on the secondary emission yield of the dynodes. The silver-magnesium proved remarkably resistant to poisoning. There was no detectable change in the relative energy distribution of the electrons leaving the multiplier as the dynodes were deliberately poisoned. This constant energy distribution assures a constant cracking pattern even though gain may vary.

Subsequent work has been devoted to evaluating various types of electron multipliers and primary electron sources capable of sustained operation in a mass spectrometer ion source.

Three types of electron multipliers have been designed and constructed at this laboratory. Two are of the resistance strip type and are based on a design originally developed by the Bendix Corporation² for use as an ion

USE OF ELECTRON MULTIPLIER WITH R.F. MASS SPECTROMETER TUBE.

Figure 1



N-BUTANE SPECTRUM FROM RF MASS SPECTROMETER OBTAINED WITH A 6291 DUMONT ELECTRON MULTIPLIER AND A TANTALUM PHOTOELECTRIC CATHODE IRRADIATED BY A HILGER TYPE FL-15 U.V. HYDROGEN ARC LAMP

detector. Of these two multipliers, one uses an electromagnet to create its magnetic field, while the other has permanent magnets. The third multiplier is a ten-stage venetian blind type.

The basic resistance strip multiplier, shown schematically in Figure 5, consists of two plane-parallel, resistive surfaces. These surfaces are ordinarily made up of a semiconducting coating applied to an insulating base, but may be a wholly insulating material with the proper volume resistivity. Equal potential gradients are established along each surface by applying equal potential differences across their long dimensions. The true potential of one surface (field strip) is maintained more positive than that of the other surface (dynode strip). Thus the equipotential lines are parallel to each other and slanted in the direction shown in the diagram. The entire structure is placed in a uniform magnetic field normal to the electrostatic field. An electron released from the dynode strip at any point will describe a cycloidal path whose initial direction is determined by the equipotential at its point of origin. It will return to the dynode strip with an impact energy corresponding to the difference in potential between its points of origin and impact. In a properly designed multiplier this energy will be large enough to give a secondary emission ratio greater than unity. Thus this electron will release more electrons at its point of impact, which will continue along the strip in a similar fashion. The total gain in electron current along the strip will be a function of the field strengths and the length of the dynode.

An approximate analysis can be made of the path of an electron in the resistance strip multiplier by assuming the electron trajectory to be trochoidal and the initial electron energy to be negligible. The radius of curvature of the electron path is given by:

$$R = \sqrt{\frac{2mV}{eB^2}} \quad (1)$$

where R = path radius, cm
 m = mass of charged particle, gm
 e = electronic charge, abcoulombs
 B = magnetic field intensity, gauss
 V = accelerating potential, abvolts

However, the accelerating potential is determined by the length of the jump of the electron and the electric field strength E along the dynode, or:

$$V = 2 RE \quad (2)$$

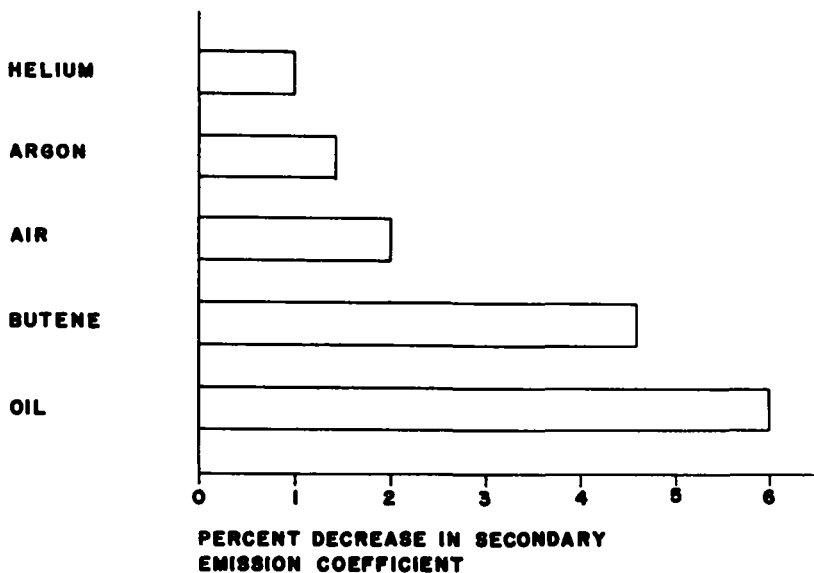
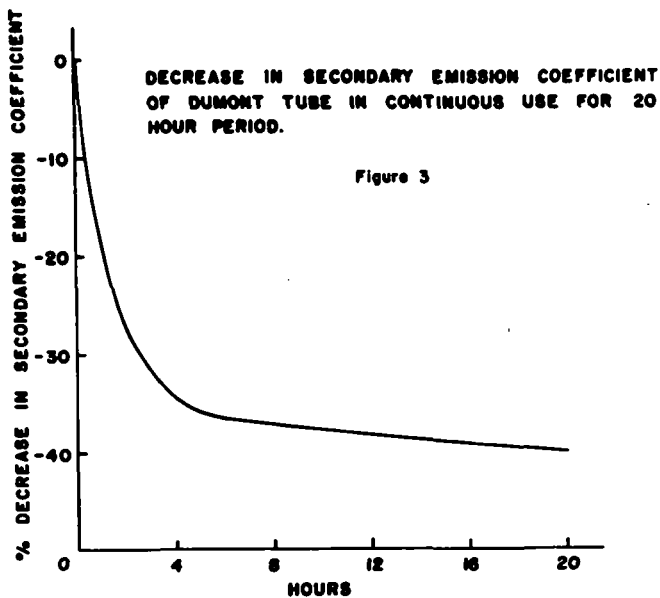
Substituting equation (2) into equation (1) gives:

$$R = \frac{4mE}{eB^2} \quad (3)$$

The total effective number of stages is given by dividing the dynode length by the diameter of the individual jumps. This number can be altered by adjusting either the magnetic field intensity or the potential gradient along the dynode. There is, however, a maximum gain reached at a particular value for each combination of parameters. The working parameters are chosen as the best compromise in performance between many low-gain stages and only a few high-gain stages. The electromagnet multiplier has been used to study combinations of electrostatic and magnetic field strengths. These studies indicated an optimum magnetic field strength of 180 gauss in combination with electrostatic fields created by the application of 1000 - 1400 volts across the dynode, for our particular multiplier configuration.

The parameters of the permanent magnet multiplier were chosen from the results of the electromagnetic multiplier tests. The use of permanent magnets greatly reduces the over-all size of the multiplier, requires no power for operation as does the electromagnet, and does not generate heat.

The resistance strip multipliers utilize thin films of tin oxide for dynode surfaces. These films, and films of tin in combination with other



POISONING AGENTS ON DUMONT DYNODES **Figure 4**

metals, have shown stability, ruggedness, high secondary emission ratios, and good resistivity to poisoning by atmospheric contaminants. The dynode strips have clean glass microscope slides as their substrates. Preliminary preparation of a slide includes evaporating a thin film of titanium onto the surface and oxidizing it until its measured resistance is one megohm. Finally, a thin film of tin is evaporated over the titanium oxide and activated (oxidized) by heating in air at an appropriate temperature until the resistance of the slide returns to that of the titanium oxide. The incorporation of the titanium oxide film between the glass substrate and the secondary emissive surface has improved dynode performance over the case where the final film was applied directly to the glass, in the following ways; bonding of the film to the substrate is much better; the resistance of the dynode remains constant during prolonged exposure to the atmosphere; a more uniform resistivity is obtained; and arcing over the electrical contacts has been eliminated.

Electrical contact was made by soldering leads onto evaporated gold or silver-manganese contacts using indium solder. The silver-manganese contacts as described by Gould and Finnegan³ have proven to be superior to gold contacts in adhesiveness, ruggedness, and ease of soldering.

The secondary emission yield obtained with tin oxide activated in air below 500°C was 3.50 for 180 volt primary electrons, while tin oxide activated at 500°C to 600°C showed a yield of approximately 8.0 for 180 volt primary electrons. This marked increase in yield indicates either that a change in crystal structure occurred at the higher temperatures or that the tin was not completely oxidized at the lower temperatures. The films did not exhibit the Malter effect, but field enhanced emission cannot be discounted completely in explaining the higher gain obtained when the tin oxide was activated at higher temperatures.

Tin oxide surfaces were selected because of their longer lifetime under electron bombardment along with their high gain. Other films investigated included beryllium-copper, beryllium, beryllium-silver, aluminum-magnesium and silver-magnesium. Several of these films exhibited higher yields than tin oxide but none even approached the lifetime of tin oxide under continuous electron bombardment. The secondary emission yield of evaporated tin oxide films is unaffected by long exposures to the atmosphere.

The venetian blind multiplier consists of ten stages, each stage containing five individual emissive surfaces of copper-beryllium. Dies were constructed to punch individual pieces so that there would be no line-of-sight path through the successive stages. The blinds are electropolished, heated to 600°C under fore-vacuum of 10-25 microns, and maintained at that temperature during a two step activation process which consists of exposure to water vapor for 20 minutes followed by exposure to dry oxygen for 10 minutes. The yields for individual stages range up to a maximum of 8.0 with the average falling between 4.0 and 5.0. This type of multiplier would be useful in applications where the magnetic field of the resistance strip multiplier would be intolerable.

Both the resistance strip multiplier and the venetian blind multiplier are physically small, being only 2 1/2 to 3 inches in length, 1 1/2 inches wide and 1 1/2 inches high. Their small size would facilitate installation in a mass spectrometer ion source.

Sources of activating electrons have been studied from two points of view; use of photoelectrons and use of beta-emitting radioactive materials. A tantalum photocathode, under ultraviolet irradiation by a hydrogen lamp, was used as a source of photoelectrons. Even the relatively low ultraviolet intensity of this lamp provided sufficient energy for good secondary electron emission. Such a photocathode excited by sunlight in space should be even more effective. Of the soft beta-emitting materials investigated, promethium 147 was chosen for study because it produces no gamma rays, has a half-life of 2.6 years, a beta ray energy of 0.223 Mev, radio-chemical purity exceeding 99 percent, and it is relatively inexpensive. Because promethium 147 emits only betas it is fairly easy to shield. One curie of promethium 147 yields 3.7×10^{10} disintegrations per second or a total electron current of 5.925 nanoamps

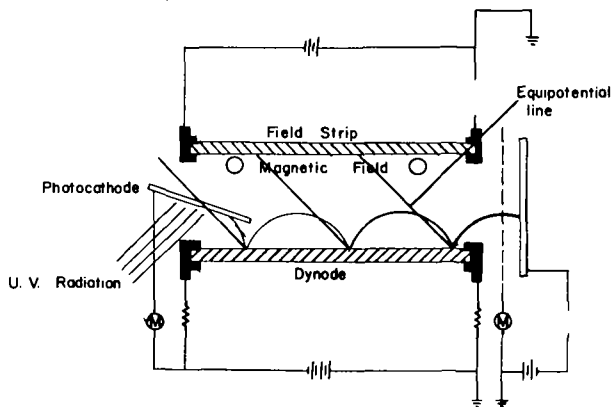


Figure 5
SCHEMATIC OF MULTIPLIER

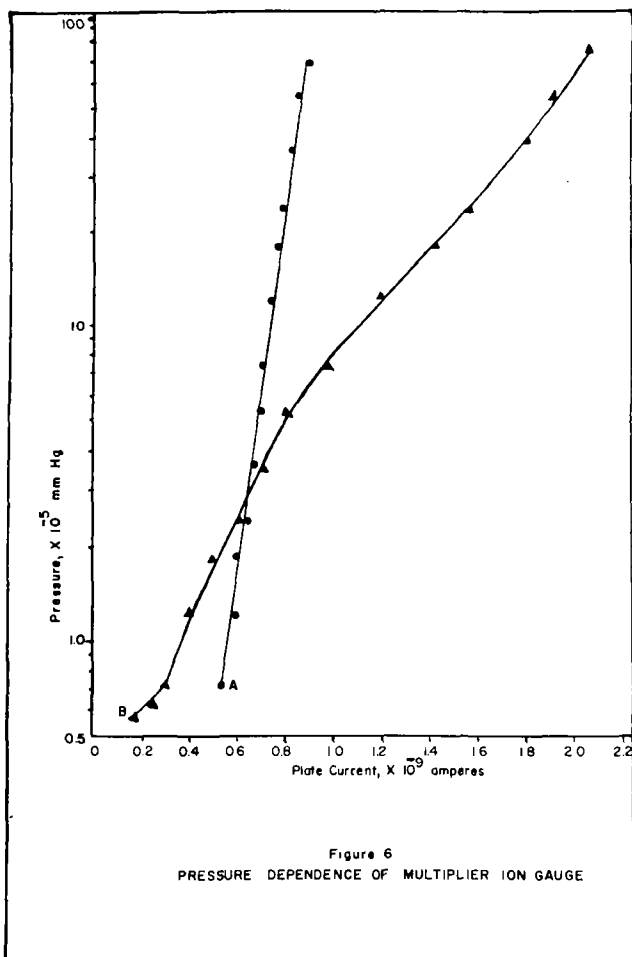


Figure 6
PRESSURE DEPENDENCE OF MULTIPLIER ION GAUGE

per second. This is more than enough, when used with any multiplier having a total gain of at least 10^4 , to furnish sufficient current for ionizing gas molecules, either in a mass spectrometer or in an ionization gauge.

The electron multipliers were employed as ion gauges to test their sensitivity, response, and stability. The use of an electron multiplier as an ion gauge was initially described by Riemersma, Fox and Lange⁴. The operation of electron multipliers as ionization gauges serves to show their feasibility as cold electron sources. Hydrogen lamps supplied ultraviolet radiation. A resistance strip multiplier incorporating an electromagnet was assembled using a 500 megohm, titanium dioxide field strip and a one megohm, tin oxide dynode. The tin oxide dynode had been activated at 190°C and showed a maximum yield of 3.5 for 180 volt primary electrons when evaluated on a secondary emission test stand. The multiplier showed gains of up to 3500 for an applied potential of 1000 volts across the dynode and a magnetic field of 180 gauss. The effective number of stages or jumps was calculated to be 18, with a gain per jump of 1.58⁵.

Figure 6 illustrates the pressure dependence of the ion gauge. For these measurements, the grid was connected through a meter to ground and a collector bias maintained at a value negative with respect to the exit potential of the multiplier⁵. At a grid current of 0.136 microamps, the linearity is quite good, although a slight curvature may be noted at a collector ion current of 0.85 nanoamps. At a grid current of 0.3 microamp this curvature, at the same value of plate current, indicates a considerable increase in sensitivity of the ion gauge. This sensitivity increase may be the result of an ion cloud created between the grid and the plate which increases the efficiency of the impinging electron toward ionization. Continuing this reasoning, as the ion cloud enlarges with increasing grid current, a sufficient potential is created between the plate and grid to allow the grid to collect some of the ions as well as the electrons. The resultant grid current will then decrease. Therefore, it is difficult to maintain a constant grid current above 0.3 microamps with increasing pressure⁵.

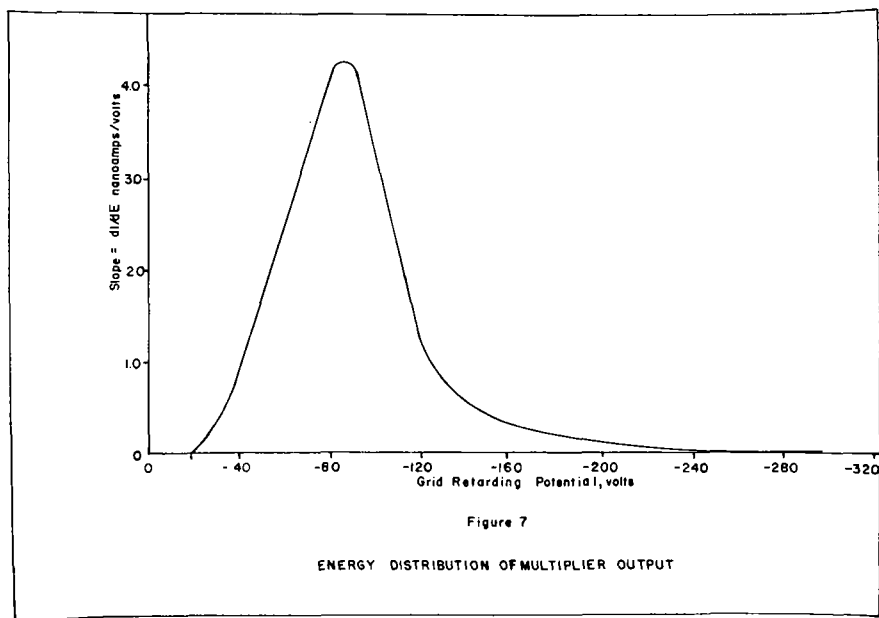
The maximum sensitivity of this gauge was 4.5 microamps/micron/milliamp of grid current, compared with 10 microamps/micron/milliamp of grid current for the RCA 1949 ionization gauge⁵.

The energy of the electrons emerging from the multiplier, as illustrated in Figure 7, is approximately equal to the energy gained by the electrons during individual jumps in the multiplier. The broadness of the curve indicates that the points at which the electrons finally departed from the dynodes were not all the same potential, but rather distributed along the last two millimeters of the active surface of the dynode. Reflected primary electrons caused the high energy tailing of this curve⁵.

The stability of the output current was good, providing the system pressure was maintained below 2×10^{-5} torr. In this pressure region, only slight reductions, on the order of a few percent, could be observed after thirty minutes of operation. Much of this decrease could be traced to a reduction in the magnetic intensity due to heating of the electromagnet. This multiplier was capable of a sustained output in excess of 2 microamps and of sufficient energy to ionize the residual atmosphere of the vacuum⁵.

Work is continuing on optimizing the design of the resistance strip and the venetian blind multipliers. Gains of 10,000 to 20,000 are considered sufficient. Long life is a primary consideration, as is constant output energy distribution. The construction of a Pm^{147} source is presently in progress. About 0.5 curie of Pm^{147} is being electroplated onto the end of a 0.030 inch diameter platinum wire embedded in epoxy. The Pm^{147} coated wire will then be incased in a stainless steel tube, the open end of which will be directed into the electron multiplier.

In summary, an electron multiplier, activated by photoelectrons or beta particles from a radioactive material, can be used as a source of ionizing electrons. Such a source is characterized by low temperature operation, high ionization efficiency, and an electron energy distribution that does not change with multiplier gain variations. Advantages of such a source over a thermionic emitter, for space applications, include: (1) appreciable decrease



in power consumption; (2) reduced outgassing; (3) no getter effect; (4) more rugged construction; (5) high frequency modulation capability of the electron beam; and (6) considerably less emission fluctuation. Previous tests have shown such a source to be highly efficient, to give good resolution and to eliminate many of the ambiguities directly attributable to extra heating in the mass spectrometer.

This study constitutes an interim report. Work is continuing on development of a mass spectrometric ion generation sources using electron multipliers in conjunction with both beta-emitting radioactive materials and photoelectrons.

ACKNOWLEDGMENT: This work was supported in part by the National Aeronautics and Space Administration, Goddard Space Flight Center, Grant NSG 153-61.

REFERENCES

1. U. S. At. Energy Comm. ORO-299, 36 pp. (1959)
2. Goodrich, G. W. and Wiley, W. C., Rev. Sci. Instr., 32, 846 (1961)
3. Gould, P. R. and Finnegan, J. J., Rev. Sci. Instr., 33, 767 (1962)
4. Riemersina, H., Fox, R. E. and Lange, W. J., Rev. Sci. Instr., 32, 218 (1961)
5. Semiannual Progress Report, The National Aeronautics and Space Administration Research Grant NSG 153-61, 1 July 1961 to 31 December 1961.

THE COINCIDENCE MASS SPECTROMETER*

M. L. Vestal, M. Krause**, A. L. Wahrhaftig[†] and W. H. Johnston
William H. Johnston Laboratories, Inc.
Baltimore 15, Maryland

ABSTRACT

A mass spectrometer utilizing the detection in delayed coincidence of secondary electrons and positive ions is described. Relative travel times are such that the time interval between collection of a secondary electron and its coincident positive ion is an accurate measure of the mass-to-charge ratio of the ion. Noise level reduction due to the coincidence technique results in an absolute sensitivity that is several orders of magnitude higher than that of conventional mass spectrometers.

INTRODUCTION

In the conventional mass spectrometer only the positive ions produced in the ion source are collected and analyzed while the secondary electrons are ignored. Recently Rosenstock (1) described the coincidence mass spectrometer in which both the secondary electron and the positive ion produced by an ionizing collision are collected. If the travel time of the electron to its detector is constant (actually, small compared to the travel time of the positive ion) the time interval between collection of an electron and the positive ion produced by a single ionization event is an accurate measure of the mass-to-charge ratio of the ion. The present paper describes the successful design, construction and operation of an electron impact coincidence mass spectrometer. Another model of the coincidence mass spectrometer has also been built and successfully used in mass spectrometric studies of x-ray ionization (2). Proper application of this coincidence principle results in an increase in signal-to-noise ratio amounting to several orders of magnitude over that obtained with similar detectors not operating in coincidence.

The coincidence principle has been employed for several years in studies of nuclear phenomena (3) and in measuring the time-of-flight of high energy particles (4). However, the coincidence mass spectrometer is the first application of this principle to studies on the molecular scale. The important advantages derived from application of the coincidence principle to mass spectrometry include the following:

1. High absolute sensitivity due to the significant improvement in signal-to-noise ratio. This allows operation at much lower ionizing rates than has heretofore been feasible in a mass spectrometer.
2. Source of ions is localized. Ions due to wall reactions are excluded.
3. Additional data is available through the collection of the secondary electrons. Distributions of electron energy and/or angle of ejection may be measured and correlated with the simultaneously measured mass spectra.

*This work was supported by the U. S. Atomic Energy Commission, Division of Isotopes Development, under Contracts AT(11-1)-650, Section 8 and AT(30-1)-2901.

[†]Johnston Laboratories and University of Utah, Salt Lake City, Utah.

**Present address, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

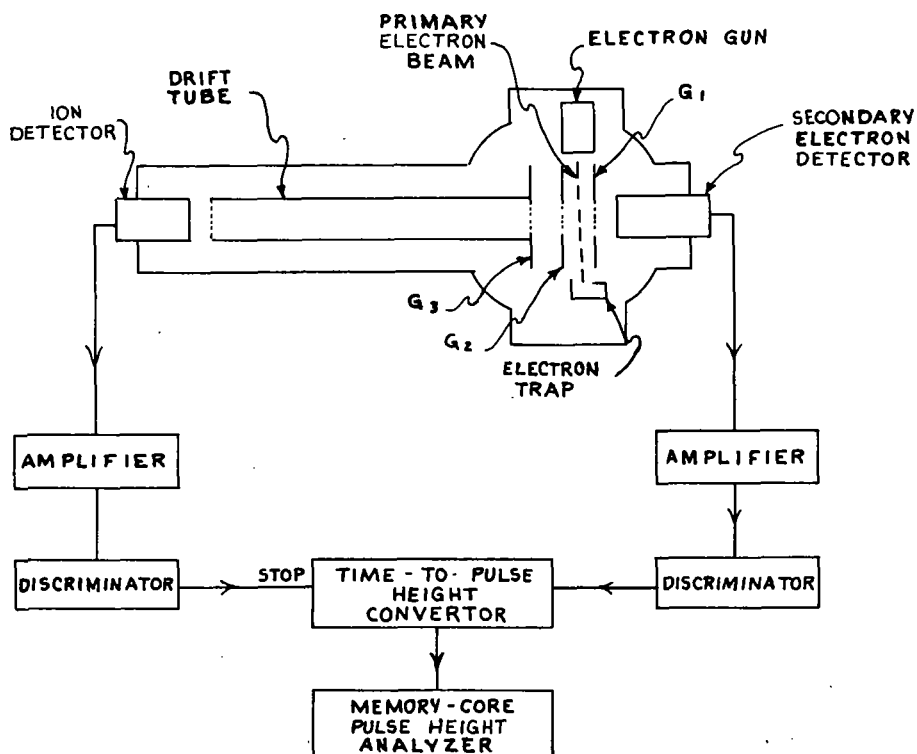


Figure 1. Schematic Diagram of the Coincidence Mass Spectrometer.

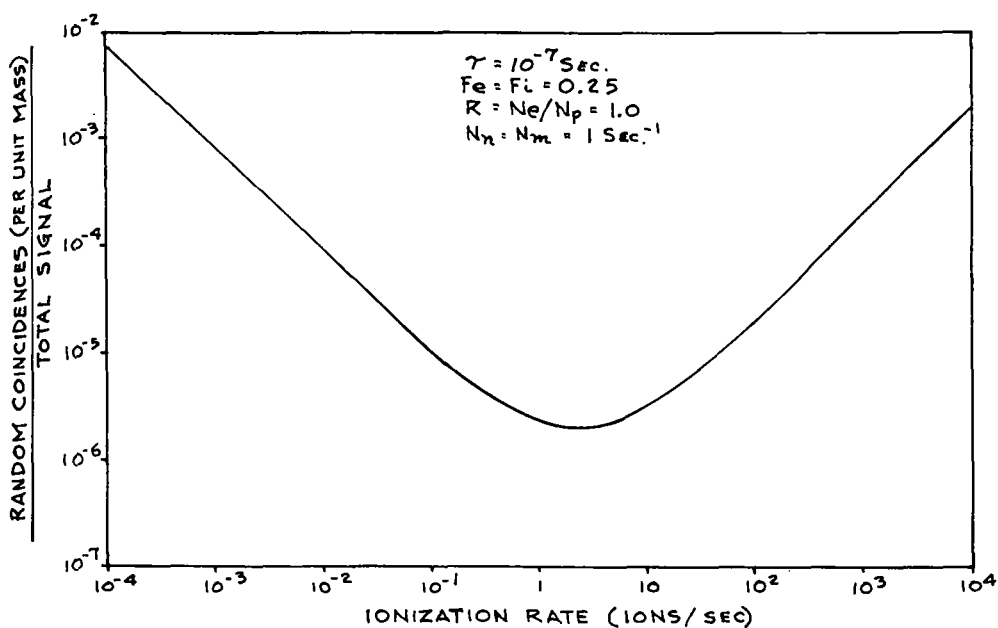


Figure 2. Plot of the ratio of random coincidence per unit unit mass to total signal as a function of ionization rate as given by equation (6). The parameter values used in the calculation are shown in the figure.

GENERAL DESCRIPTION

In the coincidence mass spectrometer each ionization event is observed separately. This is accomplished by collecting both the secondary electron and the ion resulting from an ionizing collision. The collection of a secondary electron signals that an ionization has occurred. The flight time of the ion, accelerated through appropriate electric fields, then allows its mass-to-charge ratio to be determined.

A schematic diagram of the coincidence mass spectrometer is shown in Figure 1. The ionizing beam traverses the center of the region between grids G1 and G2 and is detected at the beam trap. The constant electric field, E_1 , in this region causes the ions formed to be accelerated in the direction of the ion detector while the secondary electrons are accelerated toward the electron detector. Normally, the electron detector is located very close to G1 to minimize the travel time of the electrons. The ions are given an additional acceleration by the electric field E_2 in the region between grids G2 and G3 and are then allowed to drift through a field-free region to the ion detector. Additional grids and fields may be employed to focus the ions and secondary electrons onto their respective detectors.

With this arrangement the travel time for the secondary electrons is negligibly small compared to the ion travel time; hence the time between detection of the secondary electron and the corresponding ion is proportional to the square root of the mass-to-charge ratio of the ion.

Thus the primary data obtained for each ionization observed is the time interval between detection of the secondary electron and detection of the corresponding ion. Several systems have been used in the course of developing the coincidence mass spectrometer for measuring and recording this data. The most satisfactory method, and the one currently used, employs a time-to-pulse-height converter which feeds a conventional memory-core pulse height analyzer. This system allows simultaneous accumulation of all, or any selected part, of the mass spectrum, visual display of the spectrum as it accumulates, and fast, convenient recording of the data.

SENSITIVITY

The most important unique feature of the coincidence mass spectrometer is the high absolute sensitivity possible due to the reduction in the noise level produced by application of the coincidence principle. In most mass spectrometers there exists an essentially constant noise level which sets the limit of maximum sensitivity. In the coincidence instrument, on the other hand, the related noise varies with signal while the coincidence requirement greatly reduces the absolute noise.

If the number of ionization events which occur per second in the region from which ions are collected is N_p , and a fraction of the secondary electrons, F_e , is collected, then the number of true secondary electrons arriving per second at the electron detector is

$$N_s = F_e N_p \quad (1)$$

In addition to the true secondaries, N_e electrons per second may be detected from other sources, including gas ionization in regions other than that from which ions are detected and secondary electrons from metal surfaces struck by the primary beam. Also, the electron multiplier detectors may produce a number N_n of purely random noise pulses from such sources as cosmic rays. Under these conditions, the total number of pulses per second from the electron detector is given by

$$N_t = F_e N_p + N_e + N_n \quad (2)$$

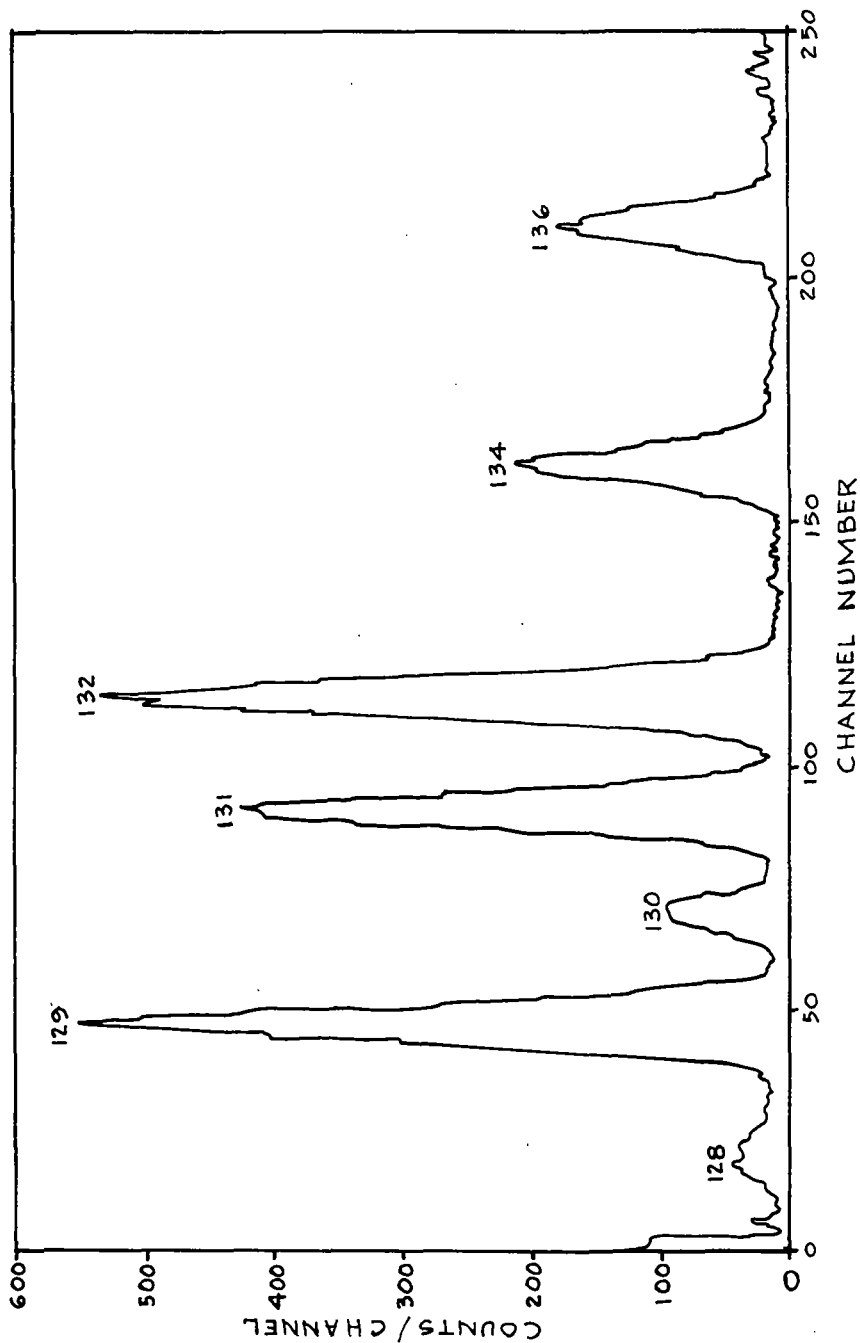


Figure 3. The mass spectrum of the xenon isotopes 128, 129, 130, 131, 132, 134, and 136 measured in the coincidence mass spectrometer.

Since in general no source of stray ions is present, the corresponding number of pulses at the ion detector is

$$N_i = F_i N_p + N_m \quad (3)$$

where F_i is the fraction of the ions formed in the ionization region which are collected, and N_m is the number per second of noise pulses from the ion collector multiplier.

An ion is detected in the proper delayed coincidence with the electron only if both the secondary electron and the ion from an ionization event are collected. The number of such coincidences per second is

$$N_c = F_e F_i N_p \quad (4)$$

During operation of the Coincidence Mass Spectrometer, the circuit for measuring ion arrival times is active only for a short time, τ , after detection of an electron pulse. Obviously, $N_i \tau$ must be less than unity; for proper operation, one should have $F_e N_p \tau \ll 1$. The number of pulses at the ion multiplier which are not in the correct time coincidence with an electron pulse is just the difference between the total number of pulses at the ion detector, N_i , given by equation (3), and the number of pulses in the correct delayed coincidence with electron pulses, N_c , given by equation (4). The number of coincidences per second due to uncorrelated pulses at the electron and ion multipliers is given by the total number of uncorrelated ion pulses per second times the fractional "live time" of the ion detector, or

$$\begin{aligned} N_R &= (N_i - N_c) \tau N_e \\ &= \tau [(1 - F_e) F_i N_p + N_m] (F_e N_p + N_e + N_n) \end{aligned} \quad (5)$$

The signal independent part is seen to be $\tau N_m (N_e + N_n)$. The usual pulsed time-of-flight instrument would have a signal independent noise of $\tau N_m P$, where P is the instrument repetition rate in pulses per second.

The ratio of random coincidence or "background" counts to the true coincidence rate is

$$B = \frac{N_R}{N_c} = \frac{N_p \tau (F_e + N_e / N_p + N_n / N_p) [(1 - F_e) F_i + N_m / N_p]}{F_e F_i} \quad (6)$$

If in equation (6) τ is taken as the total time scanned each time the electron detector gives a trigger pulse, then the noise-to-signal ratio given by equation (6) refers to the ratio of total noise to total signal. The noise is, of course, distributed uniformly throughout the time interval while the signal accumulates in particular mass peaks. A more meaningful measure of the noise-to-signal ratio is obtained by taking τ as the time interval corresponding to the width of a single mass peak. Equation (6) then gives the ratio of noise per mass peak to total signal and determines the dynamic range of the instrument.

Only in case the signal independent noise level becomes much larger than signal level does one reach the conditions in which the absolute noise level is independent of signal level. It must be re-emphasized that the noise level and signal level are independent for all signal levels in non-coincidence mass spectrometers. Furthermore, as long as the effective duty cycle $N_n \tau$ is less than unity a net improvement in the signal-to-noise ratio is obtained by coincidence operation as compared with non-coincidence operation.

The variation of noise-to-signal ratio (with ionization rate, N_p ,) as given by equation (6) is shown in Figure 2 for parameter values appropriate to an experimental coincidence mass spectrometer now operating in the laboratory.

RESOLUTION

In the coincidence mass spectrometer, as in the conventional time-of-flight mass spectrometer, the principle difficulties in obtaining high resolution arise as a result of variation in total travel time due to variations in initial position and kinetic energy of the ions formed in the source. In the time-of-flight instrument described by Wiley and McLaren (5), resolution was obtained by using a two-field ion acceleration followed by a relatively long field-free drift space. As is shown by these authors, the variation in travel time due to wide variations in initial position can be minimized by an appropriate choice of field strengths and distances.

In the coincidence mass spectrometer resolution is obtained by using a very narrow, well-collimated electron beam. As a result, there is no need to attempt to minimize variations in travel time due to variations in initial position. Thus a single-field ion accelerating system gives good resolution and, in addition, no rigid restrictions are placed on the relation between field strengths and geometry required to obtain satisfactory resolution.

For an ion formed with a velocity component in the direction of the axis of the drift tube corresponding to a kinetic energy V_0 , the total travel time in microseconds is given by

$$T(S, V_0) = 1.44(m)^{1/2} \left\{ \frac{(V_0 + ES)^{1/2} \pm (V_0)^{1/2}}{E} + \frac{D}{2(V_0 + ES)^{1/2}} \right\} \quad (7)$$

where m is the mass of the ion in amu, V_0 is the kinetic energy in e.v., E the accelerating field in volts/cm, S the distance in cm the ion travels through the field E , and D the length of the drift space in cm. The plus and minus signs on V_0 in equation (7) correspond to the ion being initially directed away from the ion detector or toward the ion detector, respectively. If the ion is formed with no kinetic energy, then equation (7) reduces to

$$T(S, 0) = 1.44 m^{1/2} \left\{ \left(\frac{S}{E} \right)^{1/2} + \frac{D}{2(ES)^{1/2}} \right\} \quad (8)$$

If the potential zero is taken at the nominal or mean position of ionization, then the nominal travel time of an ion of mass m is given by

$$T(S_0, 0) = 1.44 \left(\frac{m}{V_1} \right)^{1/2} \left\{ S_0 + \frac{D}{2} \right\} \quad (9)$$

where $V_1 = ES_0$ is the total accelerating potential.

The actual travel time of an ion of given mass and charge will fluctuate about the nominal time due to variations in kinetic energy and due to variations in initial position.

Under most normal operating conditions the total fluctuation in ion flight time for an initial kinetic energy V_0 is given by the time required for an ion of kinetic energy V_0 directed away from the ion detector to return to its original position. This "turn-around" time is given

$$\Delta T_1(V_0) = \frac{2.88}{E} (mV_0)^{1/2} \quad (10)$$

However, under some conditions an ion initially directed away from the ion detector with a kinetic energy V_0 may arrive before an ion with no initial kinetic energy. In this case, the total flight time fluctuation will be between the flight time required for an ion with kinetic energy V_0 directed toward the ion detector and that for an ion of no kinetic energy. This fluctuation may be expressed as the difference between $T(S, V_0)$ given by equation (7), taking the negative sign on the V_0 term, and $T(S, 0)$ given by equation (8). Since for all cases of interest $V_0 \ll ES$, it is a satisfactory approximation to expand the radicals in equation (7) and retain only first order terms in V_0 . This time difference can then be expressed as

$\frac{V_0}{ES}$

$$\Delta T_2(V_0) = 1.44(m)^{1/2} \left\{ \frac{V_0^{1/2}}{E} + \frac{V_0}{(ES)^{3/2}} \left(\frac{D}{4} - \frac{S}{2} \right) \right\} \quad (11)$$

Under any given conditions the total time fluctuation due to kinetic energy will be given by the larger of ΔT_1 or ΔT_2 . Comparing equations (10) and (11), it is apparent that the conditions under which equation (10) gives the correct travel time fluctuation due to kinetic energy are determined by the inequality

$$\left(\frac{V_0}{ES} \right)^{1/2} \left(\frac{D}{4S} - \frac{1}{2} \right) \leq 1 \quad (12)$$

If the inequality is in the opposite direction, then equation (11) is applicable.

If, on the other hand, the ions are formed with no kinetic energy but over a region ΔS in width, then the variation in travel time due to the variations in initial position is given by

$$\Delta T(\Delta S) = 1.44 \left(\frac{m}{V_i} \right)^{1/2} \Delta S \quad (13)$$

In order to define the mass resolution, an explicit expression for the travel time difference between ions of adjacent masses is required. The difference in nominal travel time between an ion of mass $m + 1$ and one of mass m is given by

$$\Delta T_m = 1.44 \left(\frac{m}{V_i} \right)^{1/2} \left(S + \frac{D}{2} \right) \left[\left(1 + \frac{1}{m} \right)^{1/2} - 1 \right] \approx \frac{0.72}{(mV_i)^{1/2}} \left(S + \frac{D}{2} \right) = \frac{T_m}{2m} \quad (14)$$

The limiting mass resolution due to kinetic energy effects can be found by equating the time fluctuation due to kinetic energy given by equation (10) with the time difference between adjacent masses given by equation (14). This gives the maximum resolvable mass as

$$m(V_0) = \frac{1}{4} \left(\frac{V_i}{V_0} \right)^{1/2} \left(1 + \frac{D}{2S} \right) \quad (15)$$

Similarly, the limit on mass resolution due to variation in initial positions is given by

$$m(\Delta S) = \frac{1}{2} \frac{(S + D/2)}{\Delta S} \quad (16)$$

For the experimental electron impact instrument presently in operation, the maximum resolvable mass is determined primarily by the fluctuations due to initial kinetic energy. The calculated value of approximately 400 amu for the maximum resolvable mass is somewhat higher than is actually attained in the experimental Coincidence Mass Spectrometer. The experimental resolution is illustrated by the measured mass spectrum of the xenon isotopes. Extrapolation of this result indicates that the maximum useable resolution of the present instruments extends to about 350 amu. The additional loss of resolution is due to fluctuations in travel time through the electron multiplier and pulse amplifiers and to the limited resolution of the timing circuitry.

CONCLUSION

Three experimental coincidence mass spectrometers have been built and tested. Two of these are currently in operation in our laboratory. These instruments are being used in studies of multiple ionization, fast metastable decomposition of excited polyatomic molecule-ions, x-ray ionization and fragmentation, and secondary electron energy spectra. The detailed results of these investigations will be published elsewhere.

REFERENCES

1. H. M. Rosenstock, U. S. Patent 2,999,157, assigned to Wm. H. Johnston Laboratories, Inc., Baltimore, Maryland.
2. The x-ray ionization studies using the coincidence mass spectrometer were supported by the U. S. Air Force under Contract No. AF 33(616) - 7678.
- 3a. T. D. Newton, Phys. Rev. 78, 490 (1950).
- b. R. E. Bell, R. L. Graham, and H. E. Petch, Canad. J. Phys. 30, 35 (1952).
- 4a. D. P. James and P. B. Treacy, Proc. Phys. Soc. (London) A64, 847 (L) (1951).
- b. G. K. O'Neill, Phys. Rev. 95, 1235 (1954).
- c. L. E. Beghian, R. A. Allen, J. M. Calvert, and H. Halbon, Phys. Rev. 86, 1044 (L) (1952).
- d. G. C. Neilson and D. B. James, Rev. Sci. Instr. 26, 1018, (1955).
5. W. C. Wiley and I. H. McLaren, Rev. Sci. Instr. 26, 1150, (1955).

INVERTED MAGNETRON TYPE MASS SPECTROMETER

Richard F. Herzog and Walter P. Poschenrieder

Geophysics Corporation of America
Bedford, Massachusetts

The instrument which I am going to describe is characterized by its simplicity and by its very low power consumption which would be of advantage for space probes to analyze planetary atmospheres. For this reason, a brief study* was made to investigate the performance and limitations of the instrument. It turned out that within the present extremely stringent weight limitations, the resolution is too low to separate oxygen from nitrogen — one of the main objectives of such a planetary probe. However, it is likely that at some later date the weight limitations will be relaxed. At this time, it might become worthwhile to consider the instrument again, and for this reason, I am going to describe our experience with it.

It is well known that the original standard ion source¹ for gases — originally developed by Bleakney and later refined by Nier — uses a magnetic field normal to the electric accelerating field in order to maintain a narrow electron beam across the whole ionization chamber. This magnetic field must be kept rather weak to avoid deflection of the ion beam, which would result in preselection and discrimination of different masses. This effect, which is very undesirable for any analytical work, was recently thoroughly investigated by Coggeshall.² The discrimination effect raised the question in my mind whether it might be possible to utilize this effect for a mass analysis by increasing the magnetic field strength, in order that ions of different masses should leave the ion source in different directions, thus eliminating the need of a separate mass analyzer.

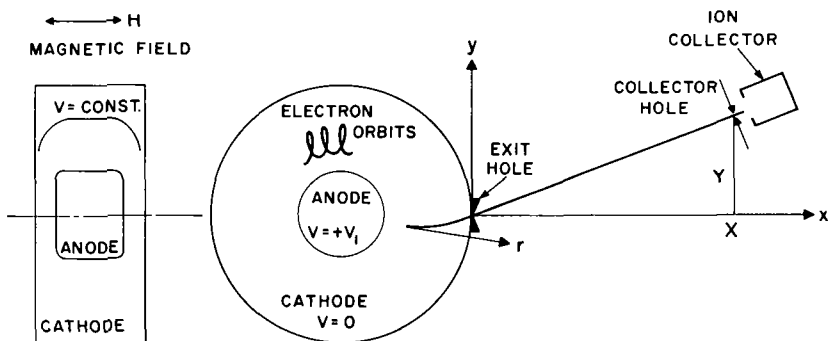
Slide (1) shows the typical arrangement of the electrodes. The anode is mounted in the center of a grounded cylinder which acts as the cathode. A magnetic field of about one thousand gauss is applied in the direction of the axis. This field arrangement is a simplified version of the original Redhead³ inverted magnetron vacuum gauge. A discharge is initiated on application of a few kilovolts to the anode. The electrons are trapped axially in a potential well, and radially by the magnetic field. The orbits of the electrons are approximately cycloidal around the anode with superimposed axial oscillations. The electrons collide with neutral gas molecules and produce a large number of ions and new electrons. The ions are accelerated initially in a radial direction and then deflected slightly under the influence of the magnetic field. One does not need any calculation to appreciate that the angle of azimuthal deflection depends on the mass of the ion, being larger for lighter masses. However, the angle of deflection also depends on the location where the ion is formed, being almost zero for an ion formed near the cathode and becoming larger, in general, if the ion is formed nearer the anode. A detailed computation shows that the angle of deflection can have a maximum for a certain location of ionization and decreases again if the ionization takes place closer to the anode. This is shown in the next slide (2) which has been computed under the assumption of an electric field between coaxial cylinders and a homogeneous magnetic field inside the cathode. The ordinate is proportional to the magnetic deflection of the ions and the abscissa is proportional to the deflection of ions in an electrostatic energy analyzer. The

* This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, Sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

¹A. O. Nier, Phys. Rev. 52, 933 (1937).

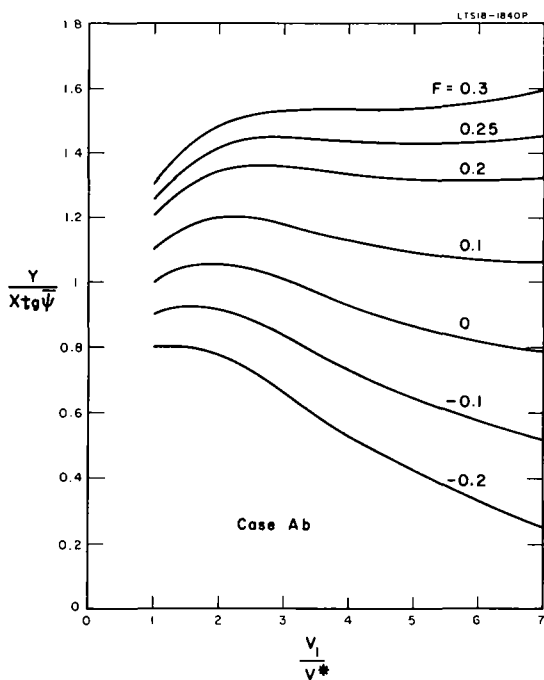
²N. D. Coggeshall, Advances in Mass Spectrometry, Ed. by R. M. Elliott, Vol. 2, p. 51, Pergamon Press, 1963.

³P. A. Redhead, Can. J. Phys. 36, 255 (1958).



INVERTED MAGNETRON TYPE MASS SPECTROMETER

Slide No. 1



Fringe field effect (homogeneous magnetic field)

Slide No. 2

abscissa is therefore a function of the location where the ion is formed. The value of l corresponds to an ion formed at the anode which has gained the highest energy V_1 ; the higher values V_1/V^* correspond to ions formed nearer to the cathode. The parameter F is a measure of the magnetic fringe field outside the cathode. Let us first look at the curve for $F=0$ corresponding to a case where the fringe field has no effect. This curve has a flat maximum for ions having about one-half of the highest energy. This maximum can be shifted towards the cathode or anode by a weak magnetic fringe field of equal or opposite direction as the main field, or by a different radial distribution of the electric and magnetic field.

The fact that these curves do have maxima is the real key that permits the use of the inverted magnetron structure as a mass spectrometer. In practice, ionization takes place only in a limited region between the electrodes; therefore, the deflection is essentially independent of the location of ionization. We may call this effect energy focusing since particles of widely different energy are deflected by the same amount. However, this type of energy focusing does not include focusing of ions originally produced with different initial energies resulting from the thermal energy of the gas molecules and from the ionization process itself.

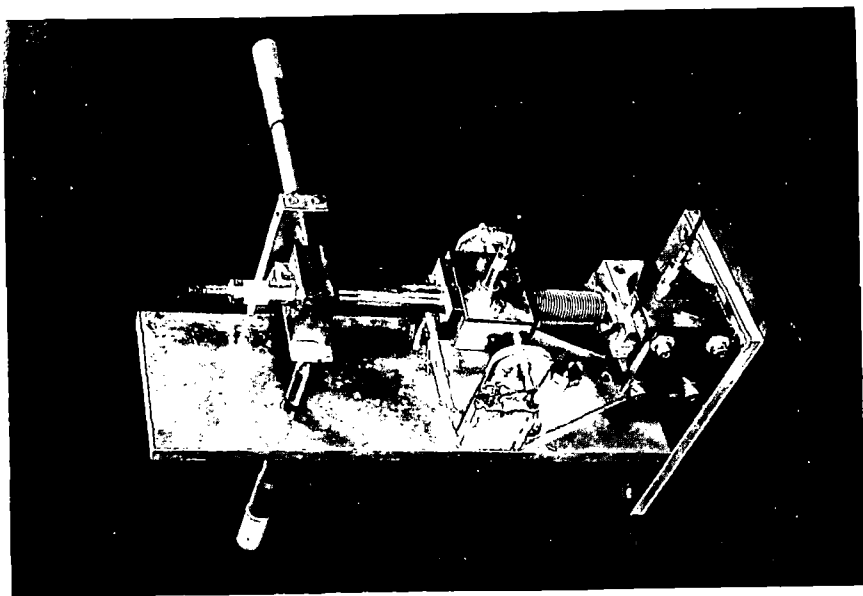
The next slide (3) shows a photograph of the test model. You will recognize the housing of the inverted magnetron together with the small magnet and the feedthrough connector for the anode. The ion collector is movable by two micrometer screws. The box in the center contains an electric deflecting field, which would not be needed in a final instrument, but was incorporated here to permit a thorough investigation of the focusing properties.

The next slide (4) shows the results of some actual measurements on the helium peak. The coordinates in this slide are again electric and magnetic deflection, similar to the theoretical diagram which I showed before. You see that good energy focusing can really be achieved over a very wide energy range: the magnetic deflection is essentially constant for ions within the energy range from 1 to 0.4. The behavior of particles with lower energies is not important since their intensity is negligible.

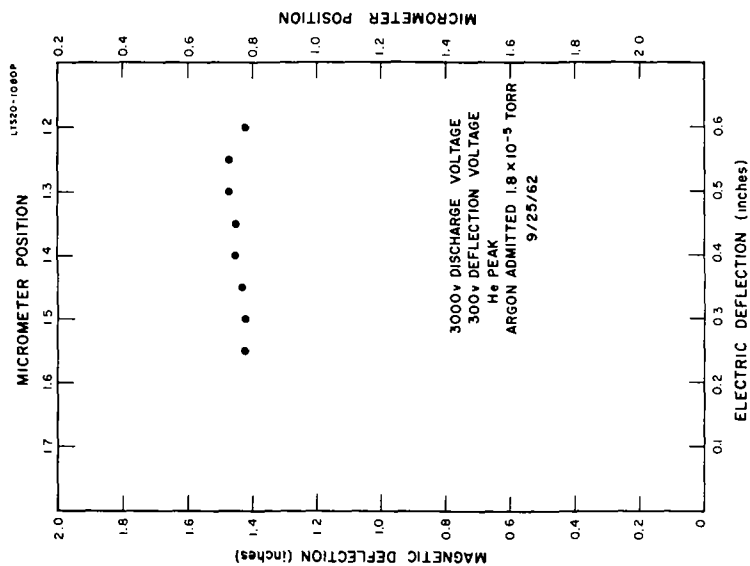
The next slide (5) shows a typical mass spectrum from a mixture of air, helium and mercury. The undeflected beam would be on the right near the mercury peak and the deflection is directed towards the left. Since the deflection is proportional to $1/\sqrt{m}$, the dispersion is much larger for the lighter masses. The peak width is essentially independent of the mass, and as a result of this, the resolution is mass dependent and decreasing rapidly with higher masses. Therefore, no characteristic figure for the resolution of this instrument can be given. The light masses, hydrogen and helium, are always well separated. Separation of the nitrogen molecule from water vapor is still fairly good. However, the resolution is not good enough to separate nitrogen from oxygen.

This result leads directly to the basic question: What does actually limit the resolution and how can the resolution be improved? Reduction of the geometric beam-spread by use of a smaller exit hole was initially successful. However, further reduction did not result in any further improvement. In this case, the beam-spread was determined by the initial thermal velocity of the ions. The only way to increase the resolution is to increase the magnet size and field strength which would require a considerable increase in weight, since the weight is roughly proportional to the third power of the resolution.

Another result of the tests was that electric scanning can only be used for a very narrow mass range because of the disturbing effect of the strong electric field generated by the electron cloud. In general, the scanning has to be done by mechanical movement of either the collector or the exit hole. Another possibility is to provide a separate collector for each mass of interest around a common anode and cathode and to scan electrically by switching from one collector to the next, or to measure all collector currents simultaneously.



Slide No. 3

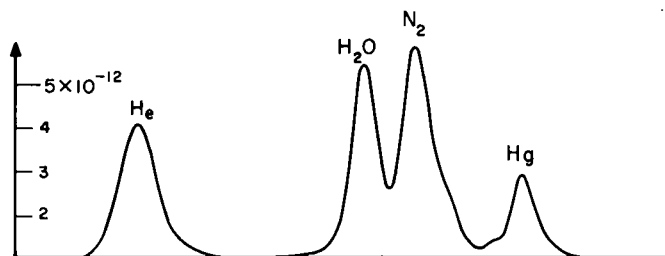


Experimental energy dependence of magnetic deflection for Test Model 1. Demonstration of velocity focusing.

Slide No. 4

The application of this instrument will always be restricted to light masses due to the limited resolution which can be achieved with a magnet of reasonable size. The main attractive features of the inverted magnetron type mass spectrometer are its simplicity; the very low power consumption of the ion source - about 40 milliwatts or less; and finally, its reliability based on the fact that it does not contain a filament that may break or burn out.

LTS22-210P



DISCHARGE: 750 VOLTS 48 MICROAMPS.
MIXTURE OF AIR, HELIUM AND MERCURY.
TOTAL PRESSURE ABOUT 1.4×10^{-5} TORR.

Slide No. 5

THE INFLUENCE OF ION ENTRANCE APERTURE SIZE AND EXCITATION FREQUENCY
ON THE PERFORMANCE OF A SATELLITE QUADRUPOLE MASS FILTER

by

Wilson M. Brubaker and Johannes Tuul
Bell & Howell Research Center, Pasadena, California

ABSTRACT

The transmission efficiency and the resolving power of a quadrupole mass filter have been investigated as functions of entrance aperture size and frequency of excitation. The aperture size was varied from 10% to 40% of the rod diameter. Larger transmitted ion currents at lower transmission efficiencies are observed with the larger aperture sizes. High resolution is obtained more readily with smaller apertures and higher frequencies.

INTRODUCTION

The quadrupole mass filter¹, shown schematically in Figure 1, is a recently-introduced device which transmits only those ions whose mass-to-charge ratio lies within a band of easily-varied width. The sensitivity increases and the resolution decreases as the width of the pass band is increased. This ready control of these parameters adds desirable flexibility to this true m/e analyzer.

The quadrupole mass filter is particularly well suited for upper atmosphere research because it combines the following characteristics: high sensitivity, small size, light weight, low power requirements, no magnet and consequently no stray magnetic field which might interfere with adjacent apparatus. It accepts ions within a cone of 30° half-angle, is uniquely tolerant to a spread in the energy of the incoming ions, and it operates with good resolution at higher pressures than other mass analyzers.

The theory of the quadrupole mass filter was outlined by Paul *et al.*^{1,2,3}, and further developed by Brubaker⁴. The equations of motion of the ions in the quadrupole mass filter are given by solutions of the Mathieu equation, which are quite cumbersome. However, Brubaker has developed the theory of operation without recourse to the Mathieu equation. This solution is based on Newton's laws, and gives a physical insight into the motions of the ions as they traverse the mass filter. It is approximate, but of satisfactory accuracy. The trajectories of the ions and the operating parameters are expressed as functions of the dimensionless variables a and q .

$$a = 8eV_{dc}/mr_0^2\omega^2 \text{ and } q = 4eV_{ac}/mr_0^2\omega^2;$$

e is the electronic charge, V_{dc} the dc potential and V_{ac} the peak ac potential on the rods, ω the angular excitation frequency, m the mass of the ion, $2r_0$ the distance between opposing rods. The trajectories are stable, i.e., of bounded amplitude, for limited values of a and q as shown in Figure 2.

In this study the resolution and the ion transmission efficiencies are studied as functions of a number of variables. These include: the size of the entrance aperture, the frequency of the ac excitation, and the ratio of the dc

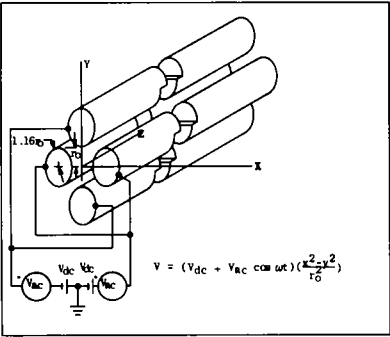


FIGURE 1

Quadrupole Mass Filter

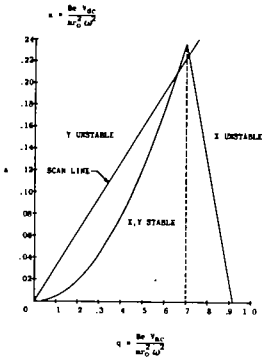


FIGURE 2

Stability Diagram

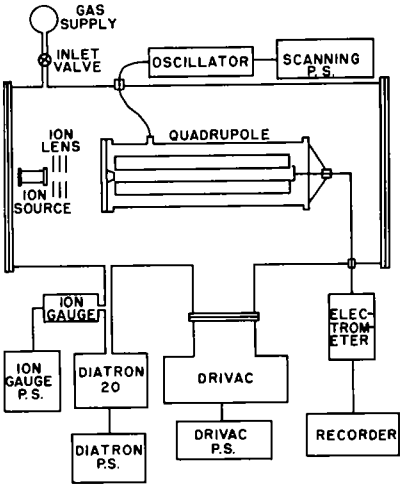


FIGURE 3

SCHEMATIC DIAGRAM OF THE APPARATUS

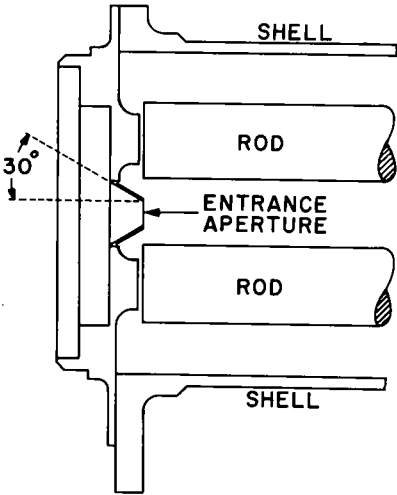


FIGURE 4

ENTRANCE GEOMETRY

to the ac potentials (resolution setting). Emphasis is given to the use of the instrument for the analysis of the earth's upper atmosphere.

APPARATUS

The experiments were carried out on a quadrupole mass filter which is suitable for use in earth satellites. The rods are 0.600 inch in diameter and 10 inches in length. The inner diameter of the containing envelope is 2.5 inches, and the total weight of the mass filter (exclusive of electronics) is 3.75 pounds. The quadrupole was energized by a controllable amplitude oscillator which provided ac excitation at a constant frequency in the neighborhood of 0.87, 1.2, or 1.7 Mc/s. The corresponding ratios of power dissipation in the oscillator coil are 1:5:25.

The mass filter was mounted in a 30-liter metal vacuum envelope as indicated in Figure 3. The system was rough-pumped with a zeolite adsorption pump, and fine-pumped with a 30-liter/second DriVac* ion pump. This method eliminates the danger of hydrocarbon contamination which is always present when conventional pumps are used. The total residual pressure in the system was usually in the neighborhood of 2×10^{-7} torr as indicated by an ionization gauge. Partial pressures were observed with a Diatron 20* (one-cm radius, 180° magnetic) mass spectrometer.

The ion beam was produced by an electron impact source, and electrostatically focused onto the entrance aperture of the mass filter. The entrance geometry is shown in greater detail in Figure 4.

PROCEDURE

Although the observations were made over the whole range of masses from 1 to 50, most evaluations were based on measurements of mass 28 peak, and only the characteristic results are reported. The reasons for choosing the mass 28 peak as the representative one, are the following. It is the dominant peak when working with residual gases as well as with air, carbon monoxide, and carbon dioxide. It appears near the middle of the mass range which is of primary interest in upper atmosphere research. Interferences from its neighboring peaks, which would complicate resolving power measurements, can be minimized by proper choice of the measuring gas.

The transmission efficiency is defined as the ratio of the current transmitted to the collector to that which enters the quadrupole. The total current was found by observing the incremental current due to mass 28 as the mass scan was made with zero dc potential on the rods. In this mode the filter exhibits strong focusing characteristics for ions of all masses above a critical value. The intensity of the mass 28 peak was monitored by the Diatron 20 mass spectrometer. These data were used to normalize the mass 28 peak given by the quadrupole.

Resolution is defined as $m/\Delta m$, where m is the mass number and Δm the peak width in mass units, which in the present paper is measured at 10% of the

*Registered Trade Mark.

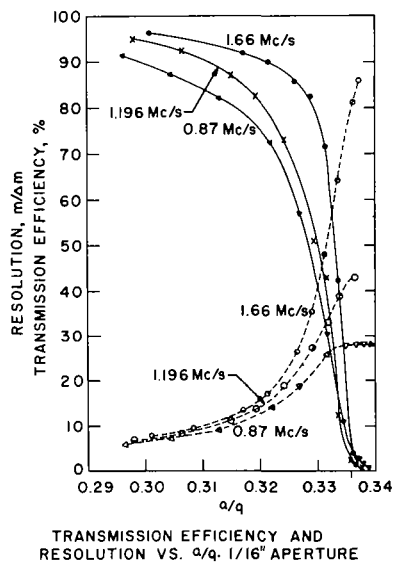


FIGURE 5

Transmission Efficiency and Resolution for Mass 28 as Functions of (a/q) with 1/16" Diameter Entrance Aperture. Ion Injection Energy 9.5 eV.

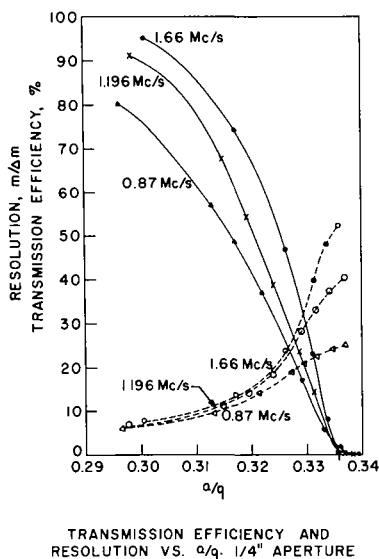


FIGURE 6

Transmission Efficiency and Resolution for Mass 28 as Functions of (a/q) with 1/4" Diameter Entrance Aperture. Ion Injection Energy 9.5 eV.

peak height. Unit resolution is defined as that at which the peak width is equal to the distance between masses separated by one mass unit. The mass scale is determined by observing the distance between two nearby peaks. In case of the mass 28 peak this determination is made by measuring the distance between mass 28 peak and mass 32 peak.

A satellite, orbiting near the earth, has a velocity of approximately 8 kilometers per second. Ions, therefore, enter an uncharged satellite with this velocity. Usually the mass spectrometer is at vehicle potential, because this simplifies the telemetry of the ion current signal. From $mv^2/2 = Ve$, one obtains for this particular velocity.

$$V = mv^2/2e = (M \times 1.67 \times 10^{-27} \times 8^2 \times 10^6)/(2 \times 1.6 \times 10^{-19})$$

$$= 0.34 M,$$

where V is the ion's kinetic energy in electron volts, v its velocity, m the mass and M the molecular weight of the ion, and e the electronic charge. To simulate these conditions in the laboratory, the ion accelerating potentials were scanned with the mass of the transmitted ions to give energy equal to $0.34M$ electron volts.

Because the ac potentials cannot readily be measured with precision at the frequencies used, the apex of the stability diagram is best found by observing the transmission efficiency as the ratio of (a/q) is varied. In the ideal case the transmission falls to zero as this ratio is increased to its apex value of 0.336. Experimentally, the ratio of the applied dc and ac voltages at which the extrapolated curve of transmission efficiency becomes zero has a weak dependence upon the frequency of excitation. In this work the intersection of the extrapolated transmission efficiency curve (obtained with 9.5 eV ion injection energy) with the (a/q) -axis has been assigned the value $(a/q) = 0.336$.

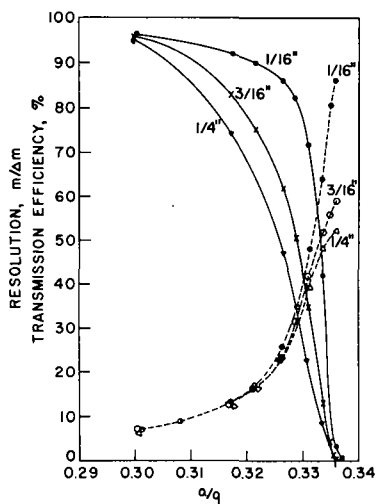
To simulate uniform illumination of even the largest apertures used, the ion beam was swept back and forth across the entrance aperture 600 times per second by means of a sawtooth voltage.

RESULTS

The transmission efficiency and resolving power are presented as functions of (a/q) in Figures 5 and 6. These data were obtained with 1/16" and 1/4" diameter apertures, respectively. The injection energy of mass 28 ions was 9.5 eV. Higher excitation frequency results in increased resolving power and higher transmission efficiency, particularly at the higher resolution settings. The ultimate obtainable resolving power is 2 to 3 times higher with 1.66 Mc/s than with 0.87 Mc/s excitation.

The dependence of the transmission efficiency and resolving power on the entrance aperture size is shown in Figure 7 for 1.66 Mc/s excitation. The highest transmission efficiency and resolving power are always obtained with the smallest entrance aperture. This effect, although considerable, is smaller than the influence of the ac excitation frequency. Aperture size influences the transmission efficiency more than it does the resolving power.

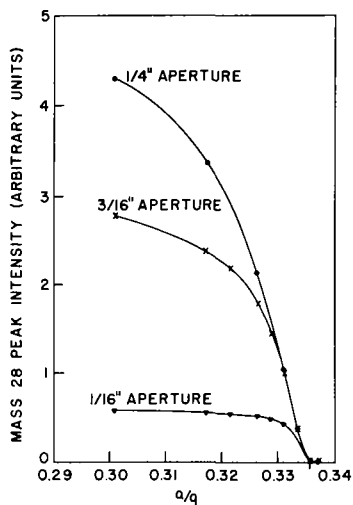
The transmission efficiency is high at low resolution. In the ideal case it drops abruptly to zero as the resolution is increased to its limiting value. The data of Figure 7 show that this ideal is more nearly realized with the smaller apertures than with the larger ones.



TRANSMISSION EFFICIENCY AND
RESOLUTION VS. a/q AT 1.66 Mc/s

FIGURE 7

Transmission Efficiency and Resolution for Mass 28 as Functions of (a/q) with 1.66 Mc/s ac Excitation. Ion Injection Energy 9.5 eV.



MASS 28 PEAK INTENSITY VS.
 a/q AT 1.66 Mc/s EXCITATION

FIGURE 8

Transmitted Mass 28 Peak Current in Arbitrary Units as a Function of (a/q) . Frequency of ac Excitation 1.66 Mc/s. Ion Injection Energy 9.5 eV.

Table I illustrates the interdependence of the transmission efficiency, ac excitation frequency, and entrance aperture size for a specific case, viz., mass 28 at unit resolution.

TABLE I

Transmission Efficiency (E) and Relative Total Ion Current (I) (Arbitrary Units) for Mass 28 at Unit Resolution. Ion Injection Energy 9.5 eV

Frequency Mc/s	1/16" Aperture		3/16" Aperture		1/4" Aperture	
	E	I	E	I	E	I
0.87	4%	0.006	0%	0.00	0%	0.00
1.196	52%	0.08	33%	0.45	24%	0.62
1.66	85%	0.14	62%	0.90	39%	1.00

Figure 8 shows mass 28 peak intensities for three different aperture sizes as functions of (a/q) . For (a/q) less than 0.33 the larger apertures yield considerably higher intensities, but on approaching the limiting value of (a/q) , these differences become gradually smaller. For (a/q) larger than 0.332, about the same intensities are obtained with the 3/16" as with the 1/4" aperture.

DISCUSSION

The sensitivity of the quadrupole mass filter is not determined solely by the transmission efficiency, but it is proportional to the product of transmission efficiency and entrance aperture area. It is seen from Table I that higher ion currents (sensitivities) are obtained with larger apertures in spite of decrease in transmission efficiency with increase in aperture. For instance, with 1.66 Mc/s excitation and unit resolution at mass 28 the sensitivity is about 7 times higher with the 1/4" aperture than with the 1/16" aperture. From Figures 5 to 8, one can find the best combination of the entrance aperture size and the ac excitation frequency for this particular instrument, consistent with the imposed requirements with regard to resolving power.

This investigation has shown the important role played by the excitation frequency. Theory⁵ shows the restoring force which accelerates the ions toward the axis of the instrument to be proportional to the square of the frequency: $y = F(a,q)\omega^2 y$. It is not surprising, therefore, that the frequency of excitation is such an important factor.

CONCLUSIONS

The most important single factor affecting the resolving power of the quadrupole mass spectrometer is the frequency of ac excitation. Further, higher transmission efficiencies are obtained with higher frequencies.

The investigation of the influence of the entrance aperture size has shown that higher transmission efficiencies and higher resolving power at smaller collected ion currents are obtained with smaller apertures. Larger apertures, up to 40% of rod diameter, result in higher sensitivity at the same resolving power, particularly at higher excitation frequencies. The combination of a large entrance aperture and high frequency of ac excitation gives the best results.

REFERENCES

1. Paul, W., and Steinwedel, H., Z. Naturforschung 8a, 448 (1953).
2. Paul, W., and Raether, M., Z. Physik 140, 262 (1955).
3. Paul, W., Reinhard, H. P., and von Zahn, U., Z. Physik 152, 143 (1958).
4. Brubaker, W. M., Proc. Fifth International Instruments and Measurements Conference, Stockholm, 1960, p. 305 (1961).
5. Brubaker, W. M., Paper presented to the American Physical Society, February 3, 1961, (Bull. Am. Phys. Soc. 6, 45 (1961).

ION BEAM PROFILES IN THREE-DIMENSIONAL MAGNETIC FIELDS

by A. C. Lilly, Jr. and T. J. Weismann
Gulf Research & Development Company
P. O. Drawer 2038, Pittsburgh 30, Pennsylvania

INTRODUCTION

Recently, calculations of the focal properties of ion trajectories in the nonhomogeneous magnetic fields of an electromagnet and permanent magnet, made from extensive measurements of the z-component of the magnetic fields in the median plane of the magnets, were reported.⁽¹⁾ In the present paper, these measurements have now been extended to the x and y components of the field both on and off the median plane, and calculations of beam shape and the effects of z-focusing have been made using an IBM 7094 computer.⁽²⁾

EXPERIMENTAL

The two magnets measured were a permanent magnet with an apparent 60° magnetic sector fabricated from magnetron magnets using soft iron pole pieces and a 60° electromagnet built by Nuclide Analysis Associates. Measurements were made at spacings of 0.1 cm for the permanent magnet and 0.1 inch for the electromagnet. In general, there were no measurable x and y components of the field on the median plane. The measurements were made with a Radio Frequency Laboratory Model 1295A gaussmeter equipped with an indium arsenide probe which was mounted on the carriage of a stepping device, permitting the desired interval for measurement to be selected arbitrarily. The coordinate system used for the measurements is shown in Figure 1. An alternate coordinate system could have been chosen with the y-axis perpendicular to the entrance face of the pole pieces and the x-axis parallel to this face. In this latter coordinate system, if the pole pieces are long compared with their gap width, only B_y will be detected. However, in the coordinate system adopted for the present measurements, measurable components of both B_x and B_y are expected.

In making the measurements, the probe was first placed parallel to the x-axis and the z-component of the field (B_z), the angle through which the probe was rotated to read the maximum field and the maximum field were measured. The probe was then placed parallel to the y-axis and the same procedure followed. Figure 2 shows the orientation of the Hall crystal probe in the magnetic field and illustrates the manner in which these measurements permit the calculation of B.

In order to have some idea of the absolute accuracy of the field measurements, the Hall crystal was calibrated against the same field measured by a proton resonance gaussmeter which was accurate to 0.1 gauss. The calibration curve is shown in Figure 3. The coincidence of the Hall effect measurement and that from proton resonance at 1000 gauss reflects the accuracy of the standard magnet used in calibration of the Hall crystal.

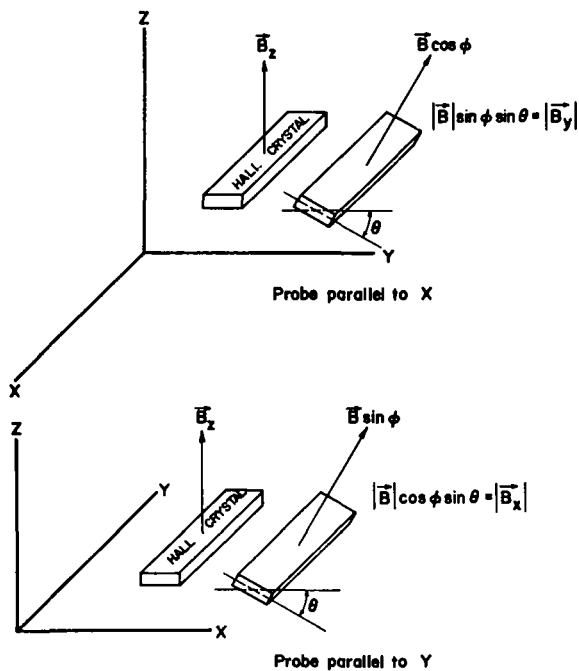
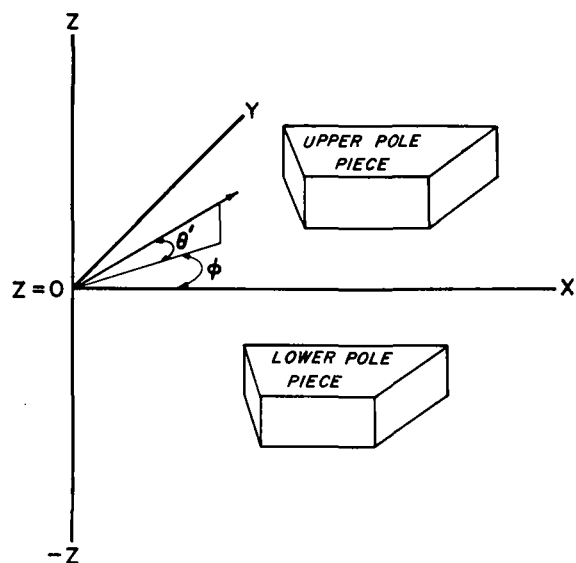
The procedure for making the calculations is as follows:

One begins with the Lorentz force equation in the absence of electric fields:

$$F = \frac{e}{c} (\mathbf{v} \times \mathbf{B}) \quad (1)$$

(1) Lilly, A. C., Weismann, T. J., and Lowitz, D. A., J. Appl. Phys. 34, 631 (1963).

(2) The program is available from the authors.



Expansion of the vector cross-product gives:

$$\frac{e}{c} \mathbf{v} \times \mathbf{B} = \frac{e}{c} \left[\begin{aligned} i (\dot{y} B_z - \dot{z} B_y) + j (\dot{z} B_x - \dot{x} B_z) \\ + k (\dot{x} B_y - \dot{y} B_x) \end{aligned} \right] \quad (2)$$

which yields the following coupled differential equations:

$$\begin{aligned} \ddot{x} &= \frac{e}{mc} \left[\dot{y} B_z - \dot{z} B_y \right] \\ \ddot{y} &= \frac{e}{mc} \left[\dot{z} B_x - \dot{x} B_z \right] \\ \ddot{z} &= \frac{e}{mc} \left[\dot{x} B_y - \dot{y} B_x \right] \end{aligned} \quad (3)$$

Taking the first integral of the three equations above, the velocity expressions in terms of integrals of the fields are:

$$\begin{aligned} \dot{x} &= \frac{e}{mc} \left[\int B_z dy - \int B_y dz \right] + \dot{x}_0 \\ \dot{y} &= \frac{e}{mc} \left[\int B_x dz - \int B_z dx \right] + \dot{y}_0 \\ \dot{z} &= \frac{e}{mc} \left[\int B_y dx - \int B_x dy \right] + \dot{z}_0 \end{aligned} \quad (4)$$

These integrals can be evaluated numerically since $B(x', y', z')$ are known, measured quantities. Therefore, the summation expressions for the velocity components may be written:

$$\begin{aligned} \dot{x}_k &= \frac{e}{mc} \sum_{n=1}^k \left[B_{zn}(x', y', z') (y'_n - y'_{n-1}) - B_{yn}(x', y', z') (z'_n - z'_{n-1}) \right] + \dot{x}_0 \\ \dot{y}_k &= \frac{e}{mc} \sum_{n=1}^k \left[B_{xn}(x', y', z') (z'_n - z'_{n-1}) - B_{zn}(x', y', z') (x'_n - x'_{n-1}) \right] + \dot{y}_0 \\ \dot{z}_k &= \frac{e}{mc} \sum_{n=1}^k \left[B_{yn}(x', y', z') (x'_n - x'_{n-1}) - B_{xn}(x', y', z') (y'_n - y'_{n-1}) \right] + \dot{z}_0 \end{aligned} \quad (5)$$

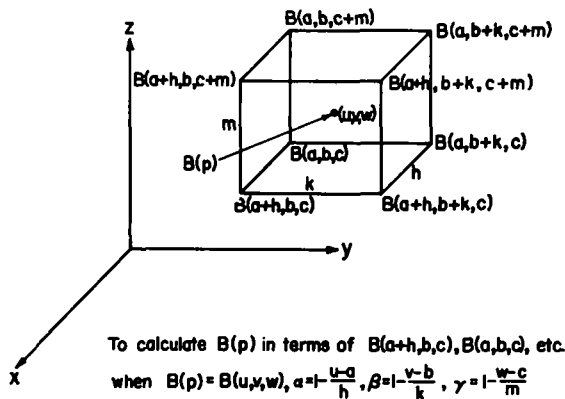
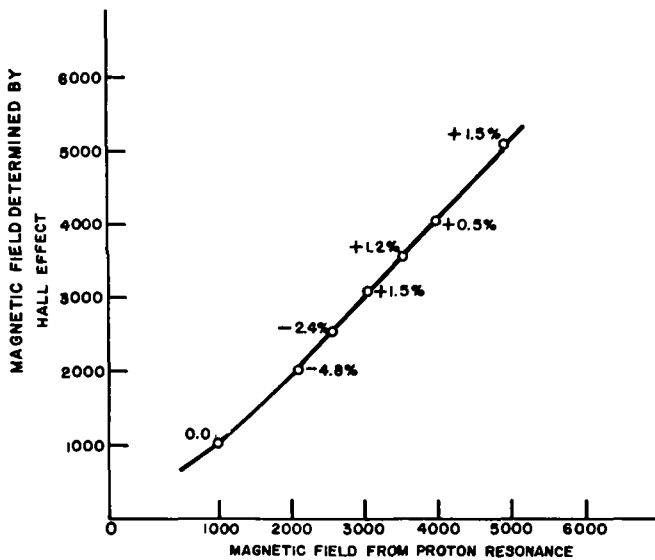
Here $B_n(x', y', z')$ is the interpolated field at step n , for adequately small stepping intervals (.001 cm intervals were used in these calculations), this is a good approximation to the true average field between step (n) and step $(n-1)$. It is convenient in making the calculation to employ one constant step interval as follows:

$$\text{If } x_n - x_{n-1} = L = .001 \text{ cm.}$$

$$\text{then } x_{n-1} (\Delta t)_{n-1} = x_n - x_{n-1} = L, \quad (6)$$

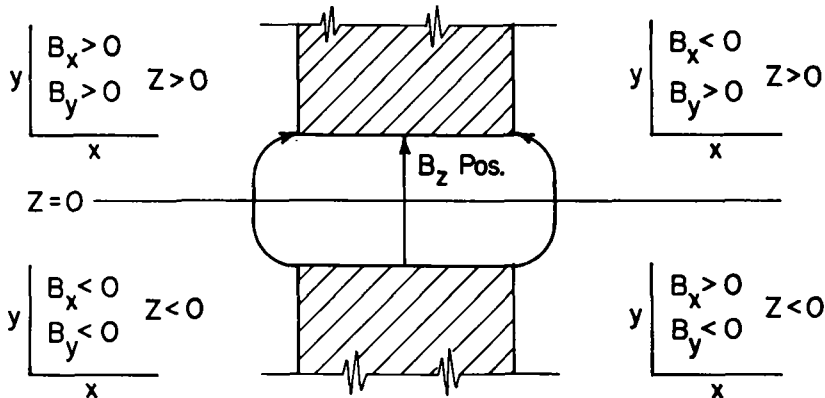
$$y_n = y_{n-1} + \dot{y}_{n-1} \left(\frac{L}{x_{n-1}} \right),$$

$$\text{and } z_n = z_{n-1} + \dot{z}_{n-1} \left(\frac{L}{x_{n-1}} \right)$$



First approximation for $B(u, v, w)$ is:

$$\begin{aligned}
 B(u, v, w) = & \alpha\beta\gamma B(a, b, c) + \alpha\beta(1-\gamma) B(a, b, c+m) + \alpha(1-\beta)\gamma B(a, b+k, c) \\
 & + \alpha(1-\beta)(1-\gamma) B(a, b+k, c+m) + (1-\alpha)\beta\gamma B(a+h, b, c) \\
 & + (1-\alpha)\beta(1-\gamma) B(a+h, b, c+m) + (1-\alpha)(1-\beta)\gamma B(a+h, b+k, c) \\
 & + (1-\alpha)(1-\beta)(1-\gamma) B(a+h, b+k, c+m)
 \end{aligned}$$



The only quantity needed in order to make the calculation is $B_n(x', y', z')$ which must be obtained from a three-dimensional interpolation, since the interval used in the integration is much smaller than that used in the measurements. Figure 4 shows the linear interpolation employed in the calculations taking into account only the values of nearest neighbor points.

Because the sign of B_z was always taken to be positive, the signs of B_x and B_y are dependent upon their position above or below the median plane and their lateral orientation with respect to the magnet pole pieces. Figure 5 shows the sign convention employed on B_x and B_y in order to satisfy the vector character of B .

RESULTS

Figure 6 shows the contours of B_z for the median plane and two planes above the median plane for the NAA 6" magnet. The field profiles are as expected. Figure 7 shows the contours of B_x for the same two planes above the median plane. $B_x=0$ on the median plane itself. The value of B_z as a function of z and x for three constant values of y is contoured in Figure 8. A consideration of the expected change in shape of a line source passing through the magnetic fringing fields typically encountered in laboratory magnets indicates that a qualitative dependence on the B_z profiles should be followed. This prediction is borne out on examination of the line shapes displayed in Figures 10 through 13.

Figure 9 shows the contours of B_z in the $z=0$ plane for the 3.25" permanent magnet. The B_x and B_y components for this magnet were very small as the gap width was only 5/16".

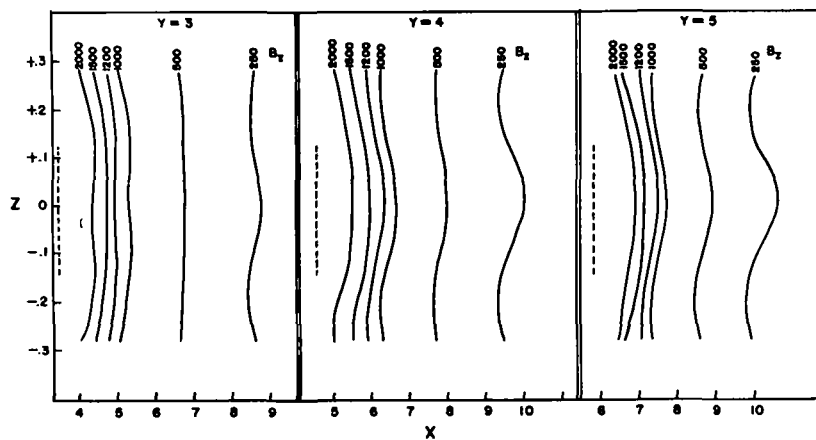
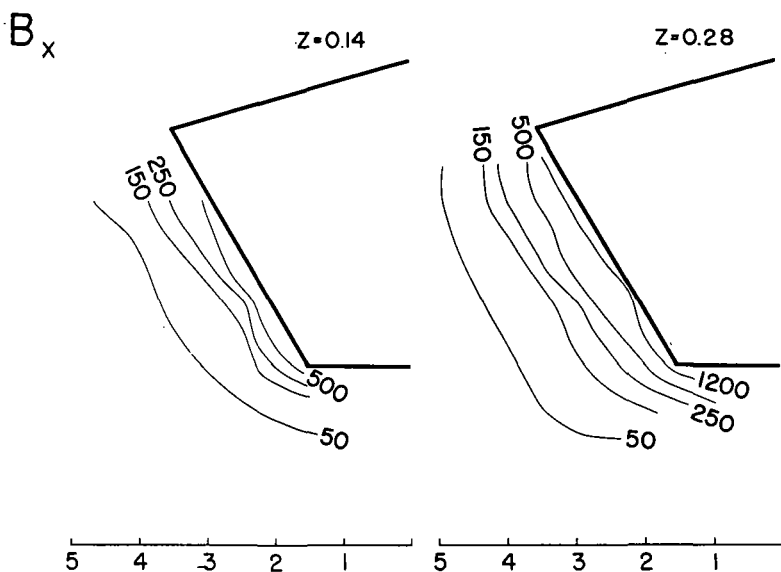
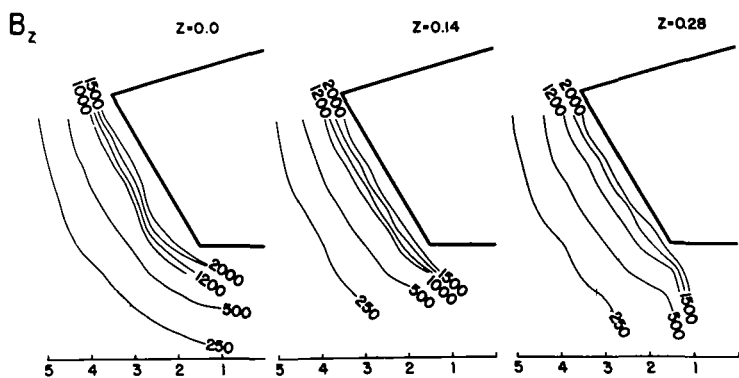
(3) Herzog⁽³⁾ and Camac⁽⁴⁾ have discussed in detail what is expected for z -focusing in sector magnetic fields. One defines ϵ'_1 as the angle between the entry ray to the magnet sector and the normal to the entrance sector pole face and assigns it negative if the ray is on the apex side of the normal and positive if it is on the other side of the normal. Also ϵ'_2 is defined as the angle between the normal to the exit sector pole face and the exit ray. Like the entrance ray, it is assigned negative on the apex side of the normal and positive on the other side. From Herzog's⁽³⁾ consideration, z -focusing is expected if ϵ'_2 is positive and z -defocusing when ϵ'_2 is negative. In this investigation, a plane wave line source at the object plane of the two magnets was adopted and z - x trajectory and beam shapes at the x - y turning points, and at x - y focal plane calculated. Figure 10 shows the beam profile in the z - x plane for $\epsilon'_2 = -10^\circ$ and the beam shapes at three values of x . The beam diverges as expected. Figure 11 shows the same beam for $\epsilon'_2 = -7.0^\circ$ with less divergence. Figure 12 shows the same beam with $\epsilon'_2 = -3.0^\circ$. Here there is a small convergence despite an expected divergence for the case of a magnet with an ideal fringing field. Figure 13 shows the same beam with $\epsilon'_2 = +1.0^\circ$. Convergence is expected; however, there still is a slight divergence. The range of ϵ'_2 used in the calculations for the NAA electromagnet are limited by the angular restrictions imposed by the physical dimensions of the mass spectrometer tube.

The one case of convergence (Figure 12) occurs for $\epsilon'_1 = -1.0^\circ$, which is capable of practical attainment with very reasonable operating conditions.

Figure 14 shows the effect on displacement in the z - x plane for three rays as calculated for the permanent magnet. The measured fringing field with this magnet⁽¹⁾ deviates but slightly from that predicted by

(3) Herzog, Richard F. K., Nation Bureau of Standard Circular 522, "Mass Spectroscopy in Physics Research", pp. 85-93, (1953).

(4) Camac, Morton, Rev. Sci. Inst., 22, 197, (1951).



Coggeshall⁽⁵⁾ and extends over but a small portion of the field normal to the entrance and exit pole faces. There is little effect from off-axis field components on the calculated beam profile in this case.

For a plane wave source with $z_0=0.15$, $\dot{z}_0=0$, and for the largest tolerable range of ϵ_1 , ϵ_2 does not deviate largely from 0.0° and, in all cases, there is small divergence in the beam.

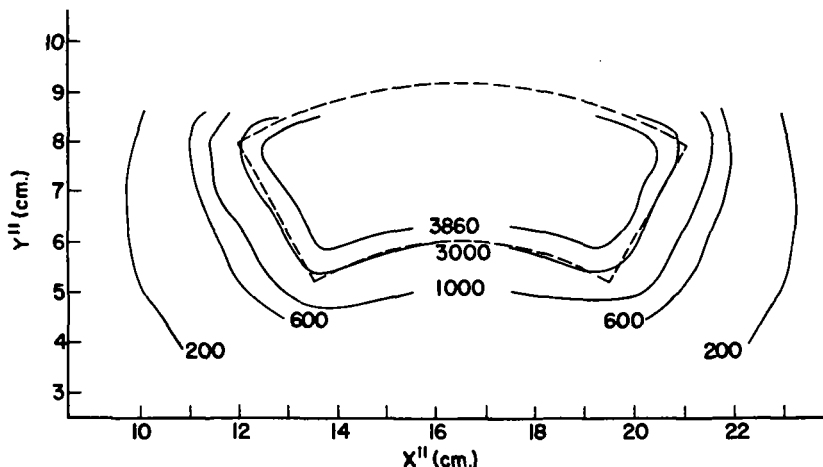
CONCLUSIONS

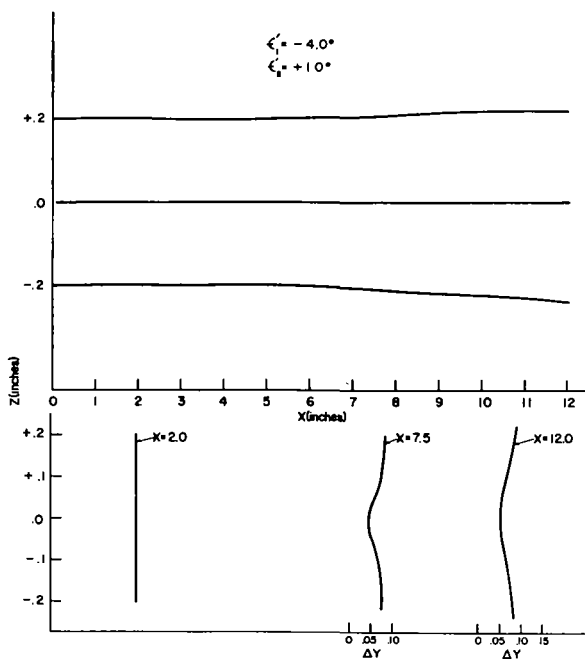
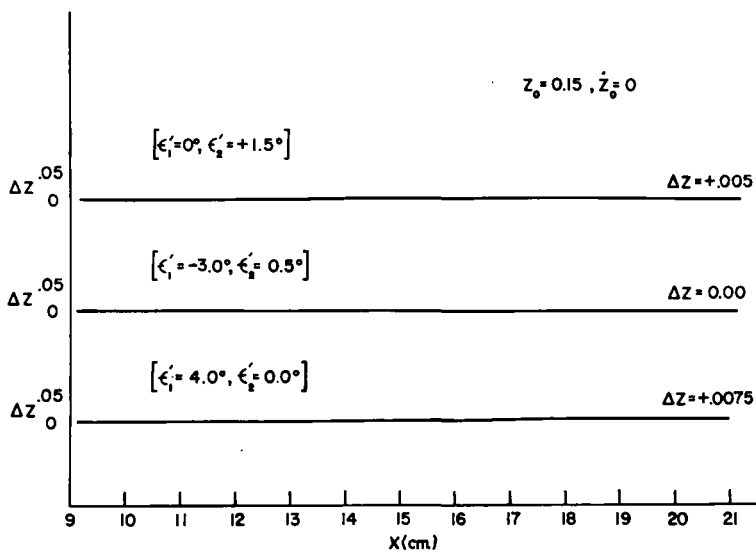
Using the measured values of the three-dimensional magnet field intensity, it is possible by numerical techniques, to calculate three-dimensional trajectories for charged particles in these fields. These trajectories (particularly those in the z - x plane) agree qualitatively with what is expected from ideal fringing fields at large values of $\pm \epsilon_2'$, however, as ϵ_2' approaches zero, deviations from the ideal field cause greater deviations from predictions of qualitative theories. Also, it is apparent that in the sector magnets normally used in mass spectrometry, there will be z -defocusing instead of z -focusing unless shaped pole pieces are employed to make ϵ_2' very much positive.

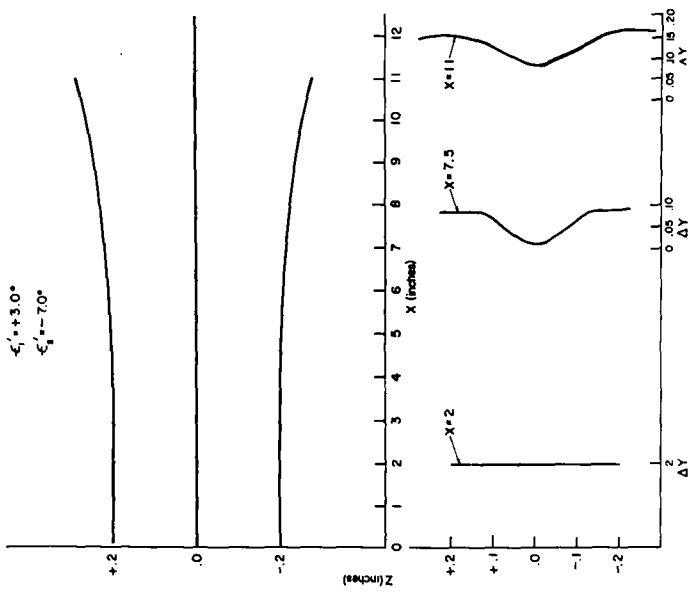
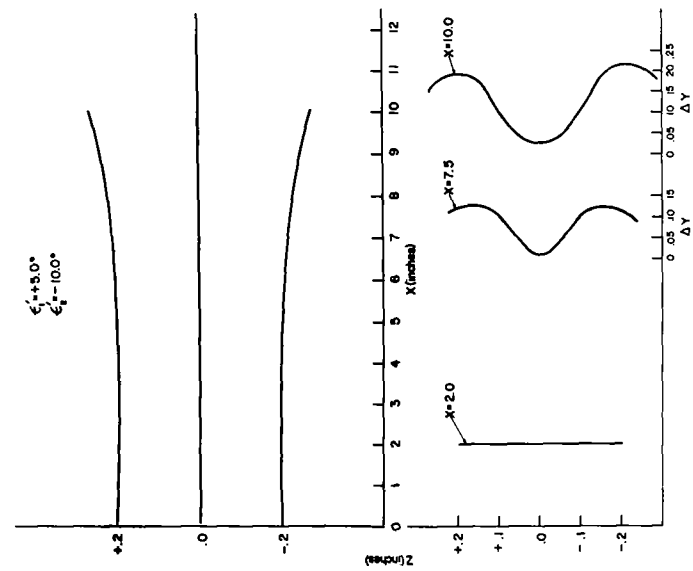
ACKNOWLEDGMENTS

The authors are indebted to Mr. and Mrs. R. Bothur for assistance in programming the force equations, to Dr. D. A. Lowitz for valuable discussions, and to Mr. E. B. Shutes for design of the angular mounting device for the Hall probe.

(5) Coggeshall, N. D., J. Appl. Phys. 18, 855 (1947).







THE ATLAS QUADRUPOLE MASS SPECTROMETER

by

C. Brunnée, L. Delgmann, K. Kronenberger

Atlas Mess- und Analysetechnik G.m.b.H., Bremen, Germany

Abstract

Construction and performance data of a new quadrupole mass spectrometer for the analyses of residual gases in high- and ultra high vacuum systems are given. The quadrupole tube with its length of 20 cm and weight of 7.3 lbs. is of all metal construction offering a simple and compact design. The tube is bakeable up to 450 °C. As the mass separation is performed via a high frequency field the use of a deflecting magnet is not necessary. The mass range is from 1 a.m.u. to 100 a.m.u. with a resolution of approx. $M/\Delta M$ 100. For 100% transmission the sensitivity amounts to approx. $2 \cdot 10^{-4}$ A/Torr; the smallest detectable partial pressure is in the region of 10^{-15} Torr.

1. Introduction

The following report concerns the construction and performance of a small quadrupole mass spectrometer according to the principle described by PAUL et al [1 - 3]. It is particularly intended for the analyses of residual gases in high- and ultra high vacuum systems.

Fig. 1 shows the basic design: The ionization is effected through an axial electron beam in a nude ion source. The ion beam of about 1 mm diameter travels through the quadrupole-field which is produced by four parallel cylindrical rods to which there is applied a d-c voltage U with superimposed high frequency voltage V.

As is well known, the trajectory of ions is described by equations of motion which can easily be transposed into MATHIEU'S differential equations. These show that the injected ions perform oscillations perpendicular to the axis Z which remain below a maximum amplitude only for a certain mass or mass range of ions. Only these ions can pass through the quadrupole-field. All other ions perform unstable oscillations with rapidly rising amplitudes so that they hit the rod electrodes.

2. Basic advantages of the quadrupole principle

The principle of mass separation by a quadrupole-field was chosen for this instrument since it offers several basic advantages for the

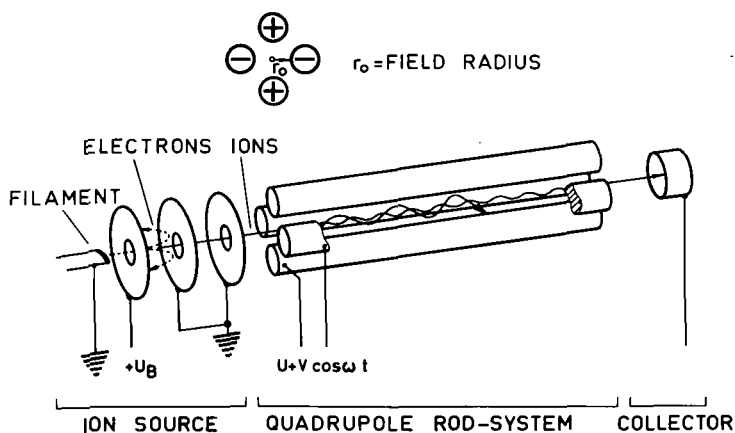


Fig. 1: Basic design of the quadrupole mass spectrometer

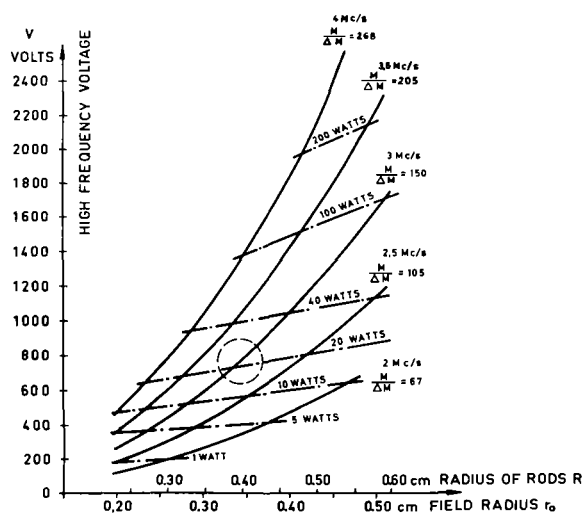


Fig. 2: Relationship between high frequency output, frequency, rod radius and resolution.

analyses of residual gases:

- a) There is no magnet used, therefore, the nude source design is simple, the analyser tube is light, and the proximity of magnetic materials (i.e., the magnetic walls of a vacuum chamber) does not affect operation.
- b) A high partial pressure sensitivity can be achieved.
- c) Total ion current and in turn total pressure can be measured.
- d) A secondary electron multiplier can be used.
- e) The entire mass range can be covered in one scan.
- f) Rapid scanning using oscilloscopic display is straightforward.
- g) A rather high resolution is obtained with only 25 cm tube length.

3. Dimensioning of the quadrupole tube

For partial pressure measurements the tube should cover a mass range from mass number 1 to approx. 100. To minimize the residual gas contribution the tube should not be longer than approx. 25 cm. Mass range, resolution, and sensitivity is determined by the parameters: radius and length of the rods, and frequency and amplitude of the high frequency voltage. For a mass setting of 100 with the given quadrupole rod's length of 20 cm and an ion accelerating voltage of 100 volts, the relation between radius of the rods and both high frequency voltage and output power is shown in Fig. 2 using resolution as a parameter. If one selects for instance the line which belongs to the resolution value of 150 and moves still further up along the line, then one can obtain high sensitivity since the field radius and in turn the ion beam cross section become also large. This, however, calls for an undesired increase of the corresponding high frequency amplitude. If one moves too far down the line the radius of the field becomes smaller, therefore, sensitivity is reduced. A reasonable compromise lies in the area which is marked by a dotted circle. We have selected the following design data: rod's diameter 8 ± 0.002 mm, length 200 mm. The entire rod-system is self aligning with an accuracy better than 0.01 mm. Maximum high frequency voltage V : 800 volts, maximum d-c voltage U : 120 volts. The high frequency generator could then be limited to a maximum power of 30 watts. Scanning from mass number 1 to 100 is achieved by varying the amplitudes of both the high frequency and d-c voltage at constant frequency.

4. Construction of the quadrupole tube

In Fig. 3 there is shown the all metal construction of the quadrupole tube which utilizes the best ultra high vacuum techniques. The tube

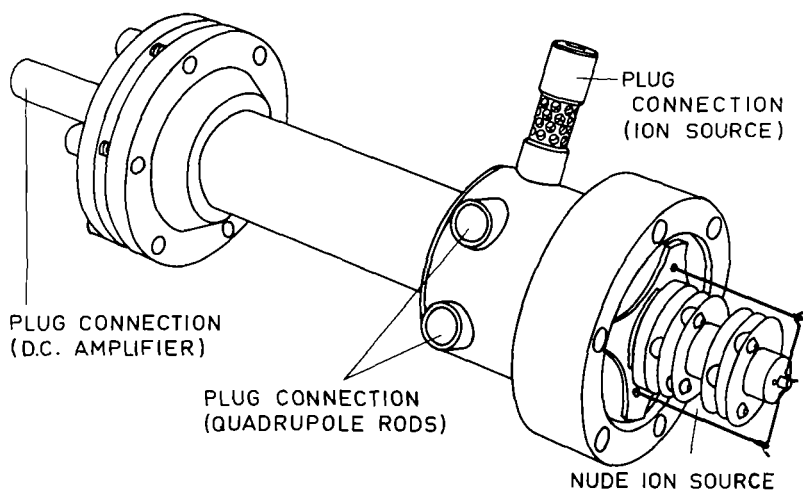


Fig. 3: Construction of the Atlas quadrupole tube type AMP 3.

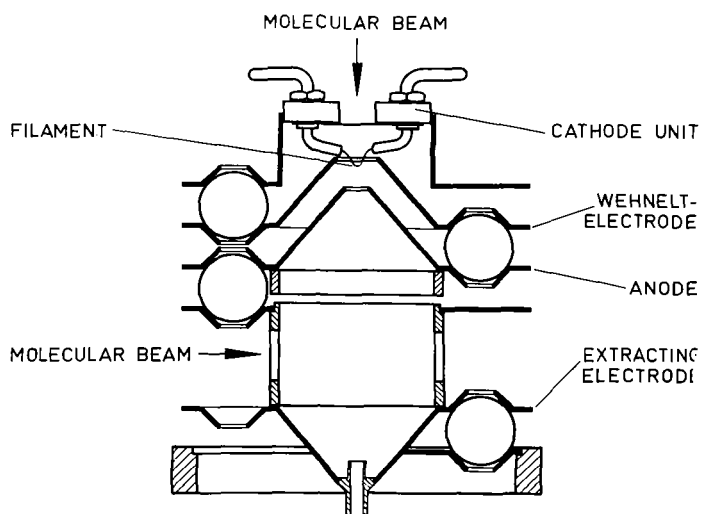


Fig. 4: Sectional view of the ion source.

can easily be flange connected to any evacuated vessel using a gold wire gasket. Since the ion source protrudes directly into the evacuated vessel errors caused in the measurement of partial pressures are greatly minimized. Such errors are noticable in the case when the ion source and evacuated vessel are interconnected via tubulation. The total length of the quadrupole tube with ion source and collector is 30 cm. The tube is bakeable up to 450 °C. The precise self alignment of the rods and the ion source is not affected by this temperature since all critical parts are spring-retained to maintain their exact positions.

Fig. 4 shows a sectional view of the nude ion source which is mounted on alumina-balls and which can very easily be disassembled. For eventual molecular beam studies the molecular beam can pass through the ion source either parallel or at right angles to the axis of the ion source.

For achieving very high sensitivity a 16 stage Allen type multiplier, with a detection limit of approx. 10^{-17} A may be used in addition to the normal Faraday ion collector. Changing from one detector to the other can be done rapidly without breaking vacuum.

5. Performance data

The significant performance data of the Atlas Quadrupole Mass Spectrometer Type AMP 3 are listed in Table 1.

Mass range:	1 - 100 a.m.u.
Max. scanning rate:	10 Spectra/sec
Resolution:	$(M/\Delta M)^*_{10\%} \approx 100$
Sensitivity (Argon):	
10% Transm. $M/\Delta M \approx 100$	$2 \cdot 10^{-5}$ A/Torr
100% Transm. $M/\Delta M \approx 35$	$2 \cdot 10^{-4}$ A/Torr
Max. pressure:	$2 \cdot 10^{-4}$ Torr
Smallest detectable partial pressure:	
with d-c amplifier	10^{-10} Torr
with multiplier	10^{-13} Torr (approx.)
	* 10% valley

Table 1: Performance data of AMP 3.

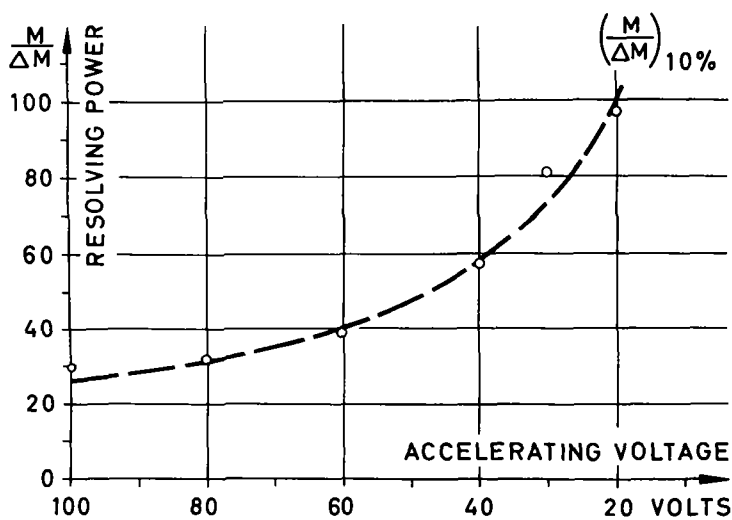


Fig. 5: Relationship between resolution and ion energy for the H_2O^+ ions.

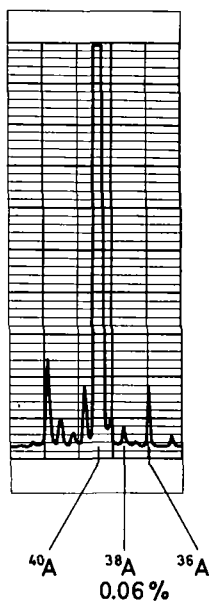


Fig. 6: Argon-spectrum, showing the abundance sensitivity.

In operation the transmission and resolution can be varied by varying the ratio U/V of the d-c and high frequency voltage. The resolution can be increased at the expense of transmission and vice versa. For 100% transmission the sensitivity amounts to approx. $2 \cdot 10^{-4}$ A/Torr.

To obtain a certain resolution it is necessary for the ions to perform a certain number of oscillations within the quadrupole-field. That means the longer the ions remain in the quadrupole-field, meaning that their injection energy is low, the higher the resolution will be. The dotted line in Fig. 5 represents the theoretical relationship - according to ZAHN [3] - between achievable maximum resolution and ion energy. As shown, the measured values for the H_2O^+ ions are plotted likewise. In order to achieve a maximum resolution the present design provides a retardation of the ions from 120 eV to approx. 30 eV at the entry of the quadrupole-field.

The abundance sensitivity can be recognized from a spectrum of argon. As shown in Fig. 6 the amount of the main peak's tail with respect to the adjacent peak is in the order of 10^{-4} .

It is desirable for the analyses of residual gases to obtain a mass independent sensitivity. When scanning the mass spectrum by varying the high frequency amplitude the ratio U/V of the d-c and high frequency voltages should remain constant, according to theory. For an exact constant ratio, however, one measures as the curves show in Fig. 7 a decrease in transmission with rising mass. For each of the plotted sensitivity curves the U/V ratio is constant with U/V ratio as parameter. The ratio of U/V and thereby the resolution increases and the transmission decreases from a) to f). The higher the resolution, the greater the mass-dependency. To obtain a mass-independent ion current one must vary the U/V ratio according to a certain functional relationship during mass scanning. A device for the functional variation of the U/V ratio during mass scanning is incorporated in the associated electronic control unit of the quadrupole mass spectrometer. By this means one can obtain an approximate mass-independency as proved by the comparisons of spectra being recorded by both the quadrupole spectrometer and an analytical sector field Atlas Mass Spectrometer Type CH4. The sector field instrument shows practically no mass discrimination so that the recorded spectra could be used as reference spectra. Fig. 8 shows the residual gas spectrum of a vacuum vessel recorded with the

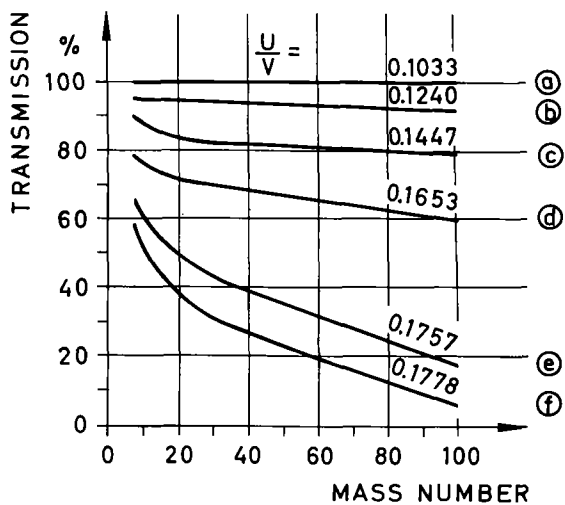


Fig. 7: Mass-dependency of transmission

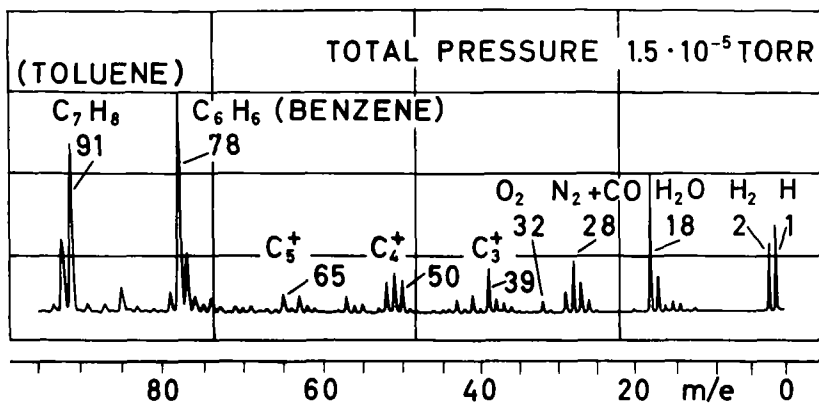


Fig. 8: Spectrum of residual gases

optimum functional relationship between high frequency and d-c voltage amplitudes.

The stability of the instrument can be seen from the data given in Table 2.

Ions	He ⁺	Ar ⁺⁺	Ar ⁺	CF ₂ ⁺	CF ₂ Cl ⁺	CFC1 ₂ ⁺
m/e	4	20	40	50	87	101
Peak heights (% of total current)	23.5	4.1	23.2	13.9	28.0	7.3
Std. Dev. of peak heights (40 runs in 8 hours)	1.2%	1.3%	1.1%	1.1%	1.0%	1.3%
Std. Dev. of total current	± 0.8%					

Table 2: Stability

Plotted are the mean values of the relative peak heights of a mixture comprising helium, argon and freon. The standard deviation of ± 1% of these peaks heights has been evaluated from 40 mass spectra recorded in 8 hours. The fluctuation of the total sensitivity amounts to approx. ± 0.8%.

One particular advantage of the quadrupole spectrometer when applied to the analyses of residual gases is that the separation of masses can be made ineffective by switching off the d-c voltage U. In this manner a measurement of total ion current and thereby total pressure can be performed. If one chooses a certain high frequency voltage one measures the total ion current of all masses greater than a certain cut off mass m. This cut off mass can be varied by changing the high frequency amplitude. At very low high frequency amplitudes all ions are collected. If the high frequency amplitude is increased the ion current drops stepwise. At the maximum high frequency amplitudes - mass setting to approx. mass number 100 - all ions with masses greater than 100 a.m.u. will be collected.

6. Electronics and auxiliary equipments

The design of the Quadrupole Mass Spectrometer Type AMP 3 incorporates modular construction. The various electronic stages are incorporated in a single control unit which is arranged on a chassis with standard front panel dimensions of 19 x 9 inches. The control unit comprises the high frequency generator, power supply for the ion source, amplifier including power supply for the multiplier and an additional Penning vacuum gauge. The control unit and quadrupole tube are interconnected with a cable of 2 metres length. A different version incorporates an oscilloscope and potentiometer recorder. For the analyses of gases under higher pressures, the measuring tube can be provided with pumps and various gas inlet systems.

References

- [1] PAUL and STEINWEDER: Z. Naturforschg. 8a, 448 (1953)
- [2] PAUL and RAETHER: Z. Phys. 140, 262 (1955)
- [3] PAUL, REINHARD and ZAHN: Z. Phys. 152, 143 (1958)

AN ION SOURCE USING A PARALLEL-PLATE ELECTRON-ENERGY SELECTOR*

Dwight A. Hutchison, Louis G. Pobo, and William K. Brookshier

Argonne National Laboratory, Argonne, Illinois

An ion source is described wherein an electron beam of low energy spread is employed. The energy selection and analysis is accomplished by passing the beam through an electric field determined by a potential placed across two plane-parallel plates. Electron-energy distributions have been measured for beams of energies from 20.0 to 7.5 volts. Beams of 3.5 volts energy have been used in studies of ionization in the rare gases. The ion source was used with a 12 in. radius 60°-sector type of direction-focusing mass spectrometer. Electronic circuitry for differentiation of ion-appearance-potential curves is described. Some experimental results and expected calculated results on krypton are presented.

Introduction

The efforts which have been made by various workers over the last 25-30 years to obtain low energy electron beams of narrow energy spread for use in studies of ionization processes are well known. Of the various methods employed, the one with which we're concerned is the electrostatic parallel-plate method.

A final test of an energy-selected beam for our purposes is the effectiveness with which a change in slope of an ion appearance potential (AP) curve may be revealed. Except in cases where energy levels of ions are separated by amounts of energy greatly in excess of the reported energy widths of beams used by various workers, the changes in slopes of AP curves are very difficult to observe. If graphical differentiation is used to reveal the slope changes, then most of the precision of the data is lost. We wish to describe briefly the parallel-plate method of electron-energy selection; the incorporation of the latter into a mass spectrometer ion source, our method of electronic differentiation of AP curves, the calculation of AP curves from measured electron-energy distributions and an assumed ionization threshold law, and finally, some experimental results on first ionization in krypton.

Principles of the Parallel-Plate Method

Referring to Fig. 1, suppose we have two plane-parallel conducting plates P_1 and P_2 spaced a distance d apart and with a potential V placed between them. If a beam of electrons enters slit S_1 at 45° to the P_1 plane and is opposed by the electric field, then the beam travels a parabolic path with range x and emerges from slit S_2 . The energy resolution R of the selected beam is given to good approximation by

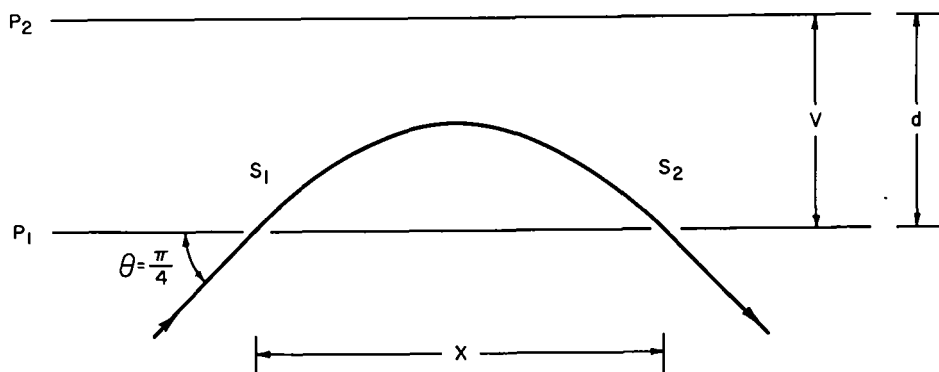
$$R = \frac{E}{\Delta E} = \frac{x}{s} \quad (1)$$

where E is the energy of the beam and s is the sum of the slit widths.

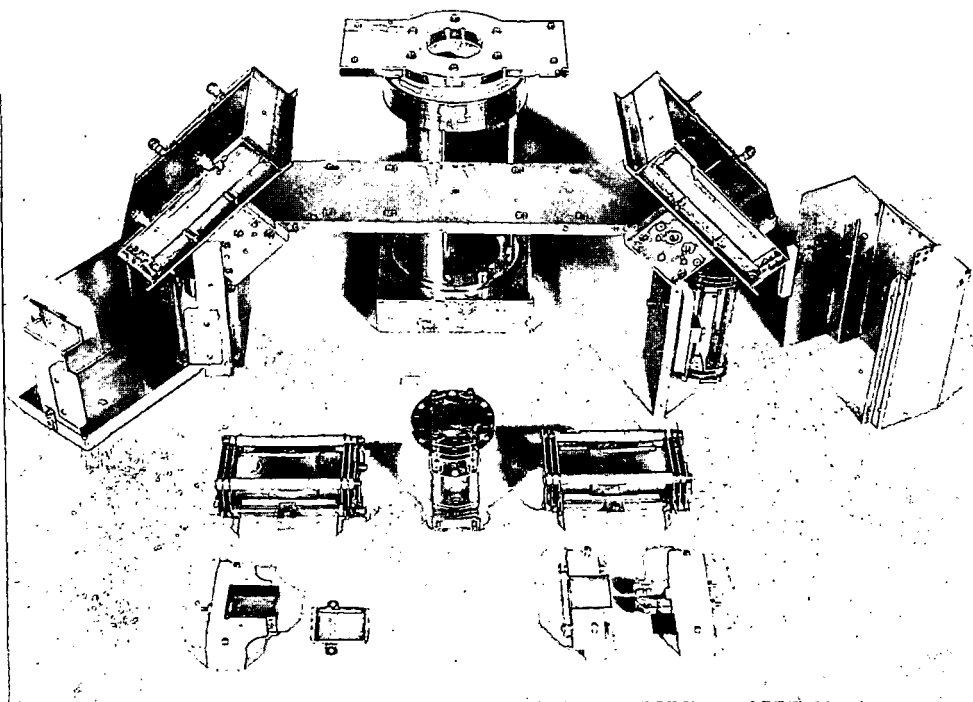
Description of the Instrumentation

The salient features of the parallel-plate ion-source are as follows: An electron beam is formed from a hot tungsten filament and is directed by a line-focus lens onto the entrance slit of the electron-energy selector. The emergent energy-selected beam is focused into the region of ionization. The undeflected beam passes to the entrance slit of a parallel-plate energy analyzer where the energy distribution of the selected beam is determined. An ion current is withdrawn from the ionization region for mass-to-charge separation in a 60°-sector magnetic-field mass spectrometer. The ion current may be collected on a vibrating-reed electrometer or on an 11-stage Ag-Mg electron multiplier with a gain

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.



1. Schematic of a parallel-plate energy selector.



2. Photograph of a double parallel-plate ion source before assembly.

of 4×10^6 for Ar^+ . Electronic differentiation is accomplished by superposing a 25 cps sine-wave voltage signal on the energy-selected electron beam. A 25 and 50 cps signal is thus transferred to the ion beam. Synchronous detectors are tuned to pass these signals. Amplitude measurements with energy of the 25 and 50 cps signals, which are proportional to the first and second derivatives of the AP curves, respectively, are recorded on a strip chart.

In Fig. 2 is shown a photograph of the ion source elements before final assembly. The box on the right is the electron-energy selector and that on the left is the energy analyzer with the top plates removed. Upper-middle is a stand on which the ion source is mounted in the vacuum housing. In the middle is the ionization assembly with accelerating plates. On either side of this are line-focus lenses arranged in sequence similar to that when mounted on the frame above. In the lower part is a thermal filament assembly for ionization of molecules electronically excited by the energy-selected beam.

Equations for Computation of Appearance Potential Curves

If the energy-distribution function $f(E-V)$ for an electron beam is known where V is a nominal energy and E is the energy of a given group of electrons, then one may calculate expected AP curves $i_+(V)$ for assumed ionization probability functions $P(E)$ according to the equation

$$i_+(V) = C \int_{E_1}^{E_2} f(E-V) P(E) dE \quad (2)$$

where E_1 and E_2 are the limits of the electron distribution and C is a constant including various parameters of the experiment. If the threshold law has the form of some power $n = 1$ of the excess energy over the critical energy E_c , then the first derivative AP curve is given by

$$\frac{di_+(V)}{dV} = C \int_{E_1}^{E_2} f(E)(E-E_c+V)^{n-1} dE \quad (3)$$

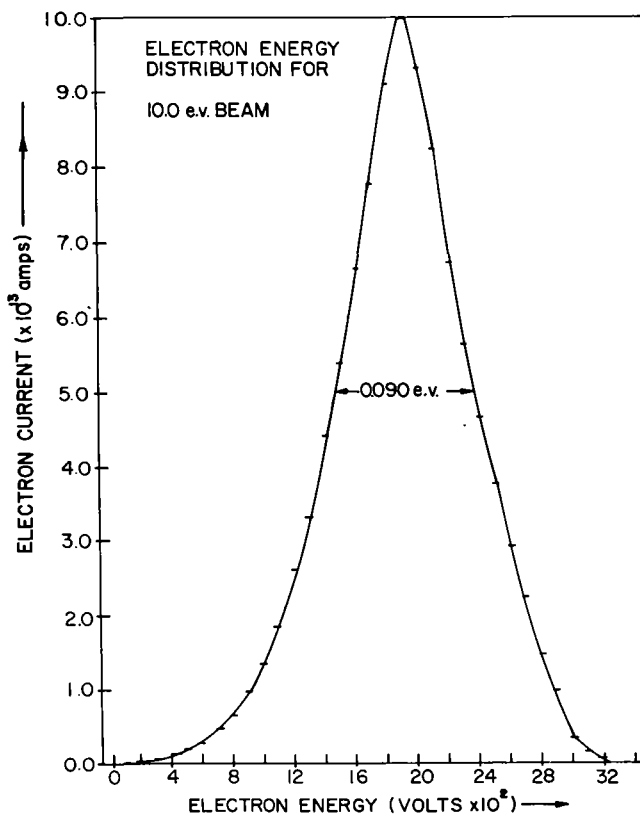
Eq.(3) was used for obtaining the computed curves. Integrations were made numerically using Simpson's rule and performed on an IBM 704 electronic computer.

Determination of the Electron Distribution Function

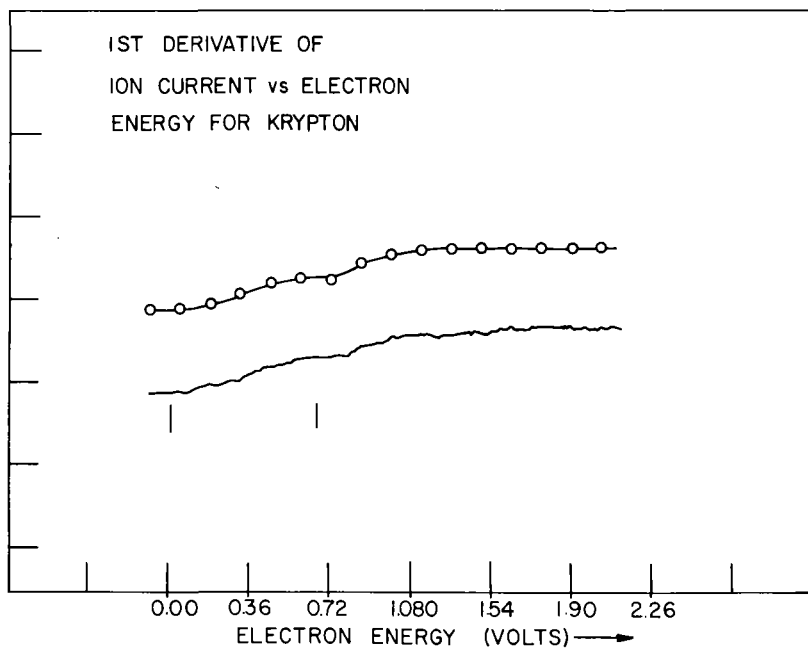
Measured electron-energy distributions were made at energies ranging from 7.5 to 20.0 volts for the selected beam. The distribution shown in Fig. 3 for a beam selected at 10.0 volts remained unchanged in form with energy of selection and with pressure changes of krypton by over a factor of 20 in the ionization region. The experimental conditions of our ionization experiments lie well within the ranges of the above experimental variables.

Experimental and Calculated Curves for Krypton

As an example of the efficiency of the double parallel-plate ion source, we show in Fig. 4 the first derivative data taken for formation of Kr^+ . The lower curve is a typical recorded curve taken with an electron beam selected at 3.5 volts. The circles of the upper curve are averages of twelve recorded tracings. The solid line is the curve computed from Eq.(3) using the electron distribution of Fig. 3. The agreement is good. The two step-functions can be seen as expected for the first derivative AP curve. The two steps are separated by about the expected 0.67 volt separation due to the $^2P_{3/2}$ and $^2P_{1/2}$ ground states. The agreements support a first order threshold law.



3. Electron-energy distribution for a beam selected at 10.0 volts.



4. First derivative appearance potential curves for formation of Kr^+ .

Conclusions

The procedure of many workers who draw straight lines through the experimental points of a curve of ion-current vs. electron-energy can be done with very little accuracy. The method of obtaining the first derivative AP curve and comparing it with the curve computed from a measured electron distribution allows us to obtain the ionization threshold law and to observe closely lying energy levels of ions.

MASS DISCRIMINATION IN ELECTRON MULTIPLIER ION DETECTORS
By: C. R. McKinney, Consolidated Electrodynamics Corporation &
D. Maynes, California Institute of Technology
Pasadena, California

For interlaboratory comparison of the isotopic composition of various elements and for precise absolute age determinations it is necessary to know the mass discrimination factor for each mass spectrometer. It is well known that most mass spectrometers exhibit some degree of discrimination and if an electron multiplier ion detector is used an additional discrimination results. The early work by Plock and Walcher, and the later verification and expansion by Inghram and Hayden, indicated that for low ion energies and high masses the number of secondary electrons emitted from a metal surface per incident positive ion varies inversely as the square root of the ion mass. Inghram and Hayden further concluded that an electron multiplier can never be considered an absolute collector; it must always be calibrated before use.

The mass spectrometer used for age determinations and for lead isotope studies at Cal Tech was constructed from a modified design of Inghram. The ion collector in this instrument was an electron multiplier using AgMg dynodes. The physical arrangement and materials of construction of the multiplier approximated the conditions and limitations of the studies reported by Inghram and Hayden. The one limitation which may not have been met was whether an ion energy of 7000 e.v. could be classed as "low energy."

In 1959 Chow and Patterson reported an investigation of the problem of multiplier discrimination in this instrument by analyzing mixtures of carefully prepared solutions of natural and enriched uranium. They concluded that a discrimination factor of 1.0136 ± 0.002 as given in Fig. 1 should be used for uranium when observed as the UO_2^+ ion and when the ratio is expressed as the heavy mass over the light mass.

This value is considerably greater than the value of 1.0056 one would expect on the basis of a square root of the mass ratio. Chow and Patterson have proposed that the 1.0136 factor is the product of two factors: One, the square root of the mass ratio and two, an additional factor proportional to the fractional change in the analyzer magnetic field.

In view of the large difference between the Chow-Patterson factor and the square root of the mass ratio, a series of experiments were performed to try to verify their factor. Four replicate runs were made over a period of several months of the same normal uranium sample used by Chow and Patterson. The samples were run in the same manner using a single Ta filament and observing the UO_2^+ ions. The average value for the four runs of the $U^{238} - U^{235}$ ratio was 137.2 ± 0.7 . The error is quoted as the 95% confidence interval. The ratio of the currently accepted value to the observed value of the isotope ratio of 1.0044 ± 0.006 is sufficiently different from the Chow-Patterson factor to warrant further investigation.

One question which immediately comes to mind is whether the discrimination factor has changed with time. To resolve this, a sample of a shelf standard lead which they also analyzed was re-run. When our observed isotope ratios were corrected by the same factors as used by Chow and Patterson, we obtained well within experimental error, the same values as they reported. It therefore seems reasonable to conclude that the discrimination factor has not changed with time. The actual value of the factor however still remains to be determined.

Recently, Shields, Craig, and Dibeler have reported the results of a study of the isotopic composition of silver. A sample of their standard silver nitrate was obtained and analyzed. The results of these analyses are given in Fig. 2. The accepted value of the Ag^{107}/Ag^{109} ratio of 1.075 ± 0.003 is the determination reported by Shields, Craig, and Dibeler. These authors determined the discrimination factor of their mass spectrometer which did not employ an electron multiplier by using mixtures of separated silver isotopes. Their instrument discrimination factor was reported as 0.99444 ± 0.00062 .

Work performed at the California Institute of Technology under USAEC Contract AT(11-1)-208.

Two sample preparations and methods of mass analysis were used. Since some background peaks were observed in the single filament runs, only the triple filament data was used to calculate the ratio of the accepted to the observed isotope ratios. Shields, Craig, and Dibeler used a triple filament for their runs. As can be seen, the accepted to observed ratio lies between the square root of the mass ratio and the calculated Chow-Patterson factor. While this tends to confirm the results of the uranium analyses, data at intermediate masses would add strength to the argument.

To this end a sample of thallium was analyzed. The results from these runs are given in Fig. 3. The sample was reagent grade thallous chloride which was precipitated and loaded as Tl_2O_3 . The sample was loaded on a tantalum filament without a fluxing agent. The accepted value of the Tl^{203}/Tl^{205} ratio of 0.4184 was calculated from data given by Bainbridge and Nier. The average observed value from four separate preparations and runs was found to be 0.4220 ± 0.0006 . The ratio of the accepted to the observed value is therefore 0.9915 ± 0.0015 . This is to be compared with the square root of the mass ratio of 0.9951 and the calculated Chow-Patterson factor of 0.9882. Once again the observed factor is less than the square root factor and greater than the Chow-Patterson factor.

The uranium, silver and thallium data are compared in Fig. 4. The value of the accepted to the observed ratio is plotted as R on the ordinate; mass on the abscissa. The triangles are the square root of the mass ratio (low mass over high mass) the open circles with the associated 90% confidence interval are the R values calculated from the data of Chow and Patterson. In the case of silver the uppermost open circle point is the discrimination factor observed by Shields, Craig, and Dibeler for their instrument. It is given here only for reference. The solid circles with their associated 95% confidence intervals are the data from the present study.

One can see that for the two elements, thallium and silver the values of R lie intermediate between the square root of the mass ratio factor and the Chow-Patterson factor. In the case of uranium, the value of R is essentially identical with the square root of the mass ratio.

In an attempt to add further evidence to the total picture the isotopic composition of the rhenium in the rhenium filaments was determined. The accepted value of the Re^{185}/Re^{187} ratio was calculated from the data of White and Cameron. We see that the value of R for Re falls well away from the expected value of about 0.990. There are several possible explanations for this aberrance which will be discussed later.

A thallium mixture experiment was performed using isotopically enriched thallium. A purification procedure was devised to provide spectroscopically pure Tl and at the same time have a high yield for thallium. Both the normal and enriched samples were purified by this procedure. Fig. 5 presents the data from the mixture experiments. The isotopic composition of each of the solutions was determined. The mixtures were roughly 3:1, 2:1, and 1:1 normal to enriched. The isotopic composition of these mixtures was determined and from these data the discrimination factor was calculated.

It can be shown that the discrimination factor R is given by

$$R = - \frac{N_A(R_A - R_C) + N_B(R_B - R_C)}{N_A R_B(R_A - R_C) + N_B R_A(R_B - R_C)}$$

where N_A = number of mols of normal Tl

N_B = number of moles of enriched Tl

R_A = the observed isotope ratio of the normal Tl

R_B = the observed isotope ratio of the enriched Tl

R_C = the observed isotope ratio of the mixture of N_A and N_B

The average value of 0.9971 which we feel is known to ± 0.0025 is greater than the square root of the mass ratio by 0.0020. If our error assignments are correct the discrimination factor from the mixture experiment and the square root of the mass ratio are almost indistinguishable.

We conclude, that for the mass range covered by these experiments and for the conditions of operation of the mass spectrometer the square root of the mass ratio appears to be a generally applicable correction. There is no known reason why the square root factor should not also be applicable to other sector mass spectrometers using a similar magnetically well shielded electron multiplier detector. Similarly there is no known reason why this factor should not also be applicable to multipliers using BeCu dynodes. It might well be, for the instrument used in these experiments, that a factor other than the square root should be used for very precise work particularly at the lower masses. There appears to be a significant difference in the discrimination factor determined by the isotope ratio method compared with the isotope mixture method.

We would like to point out that thallium would be an ideal inter-laboratory standard for those laboratories doing precise lead isotope ratio studies inasmuch as the problems of contamination normally encountered with lead are not present in the case of thallium.

As has been previously mentioned, the value of R for Re of 0.9760, differed considerably from the expected value of about 0.990. There are several possible explanations for this aberrance:

1. A large fractionation factor may exist for rhenium run by surface ionization from a rhenium filament.
2. There may be a discontinuity in the discrimination factor in the rhenium mass region.
3. The two samples of rhenium may have been isotopically fractionated during preparation.
4. There may be a variation of the isotopic composition in nature.
5. The presently accepted value for the isotopic composition may be in error.

Further work must be done before one can say which of these possibilities is correct. Using the observed ion current ratio of 0.6036 as given in Fig. 6 and assuming the discrimination factor to be the square root of the ion mass ratio one calculates the isotopic composition given in the lower part of the table. When compared with the data of White and Comerón, the Re^{185} is seen to be increased from 37.07 to 37.51 atom percent. The Re^{187} is decreased from 62.93 to 62.49 atom percent.

Uranium

Sample - Solution used by Chow and Patterson

Single Ta filament		UO_2^+ ions
Accepted value	$\frac{\text{U}^{238}}{\text{U}^{235}}$	$= 137.8 \pm 0.1$
Observed value	(4)	$= 137.2 \pm 0.7$
Ratio	$\frac{\text{Accepted}}{\text{Observed}}$	$= 1.0044 \pm 0.006$
	$\sqrt{\frac{270}{267}}$	$= 1.0056$
Chow and Patterson		$= 1.0136 \pm 0.002$

FIG. 1

Silver

Sample: NBS Isotope Ref. No. 13

Single Ta and triple Ta-Re		Ag ⁺ ions
Accepted value	$\text{Ag}^{107}/\text{Ag}^{109}$	= 1.075 ± 0.003
Observed: Single	(3)	= 1.094 ± 0.002
	Triple (4)	= 1.090 ± 0.002
Using triple filament data	$\frac{\text{Accepted}}{\text{Observed}}$	= .9862 ± 0.0026
	$\sqrt{\frac{107}{109}}$	= 0.9908
Chow - Patterson factor		= 0.9780 ± 0.002

FIG. 2

Thallium

Sample Reagent Tl Cl loaded as Tl₂O₃

Single Ta filament		Tl ⁺ ions
Accepted value	$\frac{\text{Tl}^{203}}{\text{Tl}^{205}}$	= 0.4184
Observed value	(4)	= 0.4220 ± 0.0006
Ratio	$\frac{\text{Accepted}}{\text{Observed}}$	= .9915 ± 0.0015
	$\sqrt{\frac{203}{205}}$	= .9951
Chow - Patterson		= .9882

FIG. 3

RHENIUM

Sample - Re metal as filament Observed Re⁺ ion

Accepted value	$\frac{\text{Re}^{185}}{\text{Re}^{187}}$	= 0.5891
Observed value (6 runs)		= 0.6036 ± 0.0006
Ratio	$\frac{\text{Accepted}}{\text{Observed}}$	= 0.9760 ± 0.001

$$\sqrt{\frac{185}{187}} = 0.9946$$

Atom %	White and Cameron	This work
Re ¹⁸⁵	37.07	37.51
Re ¹⁸⁷	62.93	62.49

FIG. 6

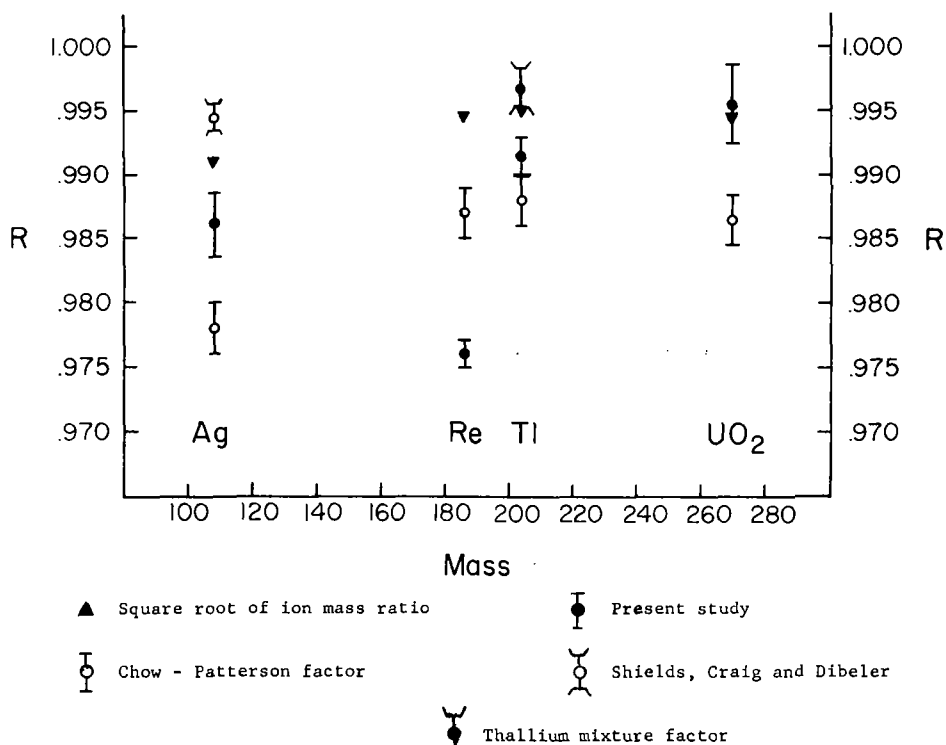


FIG. 4

THALLIUM MIXTURE EXPERIMENT

Solutions: Normal (A) 1.0338×10^{-6} Mol Tl per gram
 Enriched (B) 1.1866×10^{-6} Mol Tl per gram

Isotope Ratios: $R_A = 0.4219$ $R_B = 12.446$

Nominal Ratio	Mols Sol'n A $\times 10^6$	Mols Sol'n B $\times 10^6$	Observed Isotope Ratio Of Mixture	Discrimination Factor
3:1	3.1552	1.2042	0.8891	0.9973
2:1	2.0812	1.3500	1.1952	0.9968
1:1	1.0287	1.3633	1.9022	<u>0.9971</u>

Average 0.9971

FIG. 5

TANDEM MAGNETIC ANALYZER MASS SPECTROMETER SYSTEMS

By

E. J. Michael and D. J. Marshall
Nuclide Analysis Associates
State College, Pennsylvania

Abstract

Tandem mass spectrometer systems with twelve inch radius, ninety degree sector magnetic analyzers have been built for the precise analysis of low abundance isotopes of uranium and plutonium.

A triple filament ion source is used. Ions are detected either by a standard electrometer system or by an electron multiplier. System pressures of 1×10^{-8} Torr are achieved in the analyzer region.

The instruments have provision for collection of all or part of the ion beam at the intermediate focus. The abundance sensitivity of the "S" tandem is compared to that achieved in the first stage of the instrument.

Introduction

The abundance sensitivity of a mass analyzer system is a figure of merit which defines the contribution, due to a major spectrum peak, at a point one mass unit away from that peak.⁽¹⁾ A high abundance sensitivity (i.e., a low contribution) is clearly desirable when particular isotopes of very small abundance must be determined.

The contributions to the tail of the major peak may be due to the combined effects of elastic and inelastic gas scattering, initial energy spread, space charge defocusing, and scattering from solid parts of the instrument.

It has been shown that a tandem mass analyzer system provides a higher abundance sensitivity than does a conventional single stage instrument, even though the resolution may not be increased appreciably.⁽²⁾

The types of tandem analyzers which have been built include tandem magnetic sector, with and without an intermediate acceleration stage,^(3,4) and tandem magnetic sector - electrostatic sector configurations.⁽⁵⁾

In this paper we will discuss two tandem magnetic analyzer systems and present a comparison of the results of their performance in the uranium mass range, both with single stage instruments and with previously described tandem systems.

General Description

The tandem systems consist of two 12" radius 90° sector magnetic analyzers. A schematic layout of a system in the "S" configuration is shown in Figure 1. The geometry of the system is conventional, the image of the first analyzer being the object of the second.

The intermediate slit is externally adjustable both in width and lateral position and is insulated for use as a multiple detector, collecting all components of the beam within a 4% mass range, except that component passing through the defining slit. A retractable Faraday cup is located behind the intermediate slit to permit operation of the first stage as a conventional instrument. Electron suppressors are provided to reduce emission from the slit plate and cup.

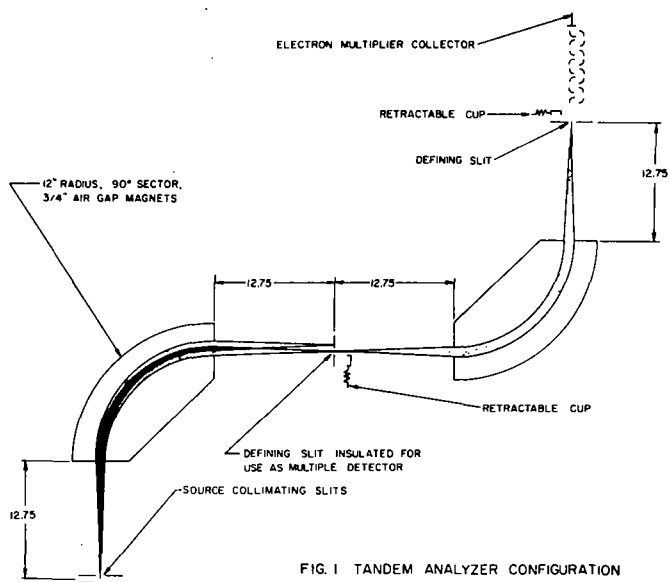


FIG. 1 TANDEM ANALYZER CONFIGURATION

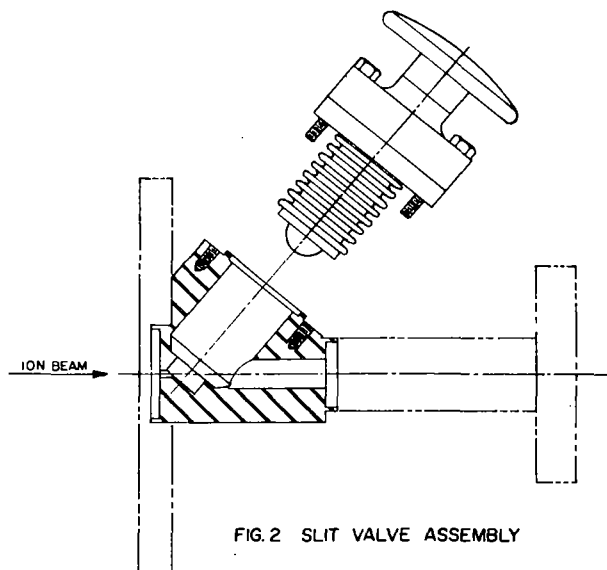


FIG. 2 SLIT VALVE ASSEMBLY

The final defining slit is also insulated from ground and is externally adjustable in width. A pie-type electron multiplier detector is located beyond the final defining slit and its suppressor and retractable Faraday cup. Provision is made for detaching the second analyzer and installing the electron multiplier at the first collector, if desired.

The general layout of the instrument is arranged so that the instrument can be readily converted between the "S" and "C" configurations.

Vacuum housings are fabricated from Inconel with all joints welded by the inert-gas shielded-arc process. Gold wire gasket flanges are used except on the ion pumps, which use copper shear-seal gaskets supplied by the pump manufacturer, Ultek Corporation.

Ion pumping is used throughout on the instruments. A 200 l/sec. ion pump is used on the source. Also, two 50 l/sec. ion pumps are used, one at the initial part of each analyzer tube.

Although a vacuum lock sample changer was not installed, sample changing is facilitated by the use of two high vacuum valves. One is a gate valve, using a Viton O-ring seal, located between the source region and its ion pump. The other is a specially designed all metal straight through valve, located in the ion beam path between the source and first analyzer. Two high vacuum roughing valves are provided for roughing source and analyzer regions independently. This valve arrangement permits one to vent only the source region while changing samples, thereby permitting retention of high vacuum in the analyzer at all times. This method also reduces the number of starts required on the source ion pump, thereby promoting longer pump life and a cleaner system.

Slit Valve

An overall view of the all metal slit valve is shown in Figure 2. Actual size is about 3" x 6" x 3 1/2" long including the handle but not mounting flanges. In use, the valve is flanged to the ion source housing and to the first analyzer tube. It is oriented so that only the valve seat and nose are exposed to air when the source is vented, thereby keeping the bellows-driver mechanism continuously at high vacuum. The driver housing is inclined with respect to the beam axis, so that withdrawal of the valve nose from the seat provides a straight through path with an aperture of 3/4" x 1/8".

The valve seat is a machined shoulder in the Inconel valve body. The replaceable valve nose is a polished 304 S.S. hemisphere. The entire bellows-driver assembly is flange mounted to provide ready accessibility to any internal part. When the valve is hand tightened, requiring a torque of about 12 ft. lbs., leakage is sufficiently small to permit maintaining vacua of 1 to 3 x 10⁻⁸ Torr in the analyzer region when the other side of the valve is vented to atmosphere.

Use of this valve system permits a sample changeover time, from venting to running the next sample, of from 30 to 45 minutes, of which approximately 15 minutes is required for actual pump down after sealing the end flange.

Magnet Assembly

The magnet support and motion system is designed to permit easy motion in any direction in the horizontal plane. This magnet motion is made possible by means of an air bearing technique. With the use of this air bearing it is comparatively easy for one person to move the large magnets about by hand.

A cutaway view of the magnet assembly and air bearing assembly is shown in Figure 3. The component parts include the air distribution plate, which serves as a manifold between the air inlet and exit ports; the brass bearing plate, which has numerous small holes drilled through it to provide air jets on the bottom side; and the aluminum base plate, which is the fixed bearing surface. With the application of a pressure of 20 psi of clean air, the magnet is lifted off the base plate

MASS POSITION	INSTRUMENT CONFIGURATION :		IMPROVEMENT FACTOR, SINGLE TO TANDEM
	SINGLE STAGE	TANDEM	
237	1.7×10^5	9.3×10^5	X 5
237.5	4.2×10^4	1.2×10^5	X 3
238.5	2.3×10^5	9.1×10^5	X 4
239	3.4×10^5	1.8×10^6	X 5

SPECTROMETER CONDITIONS :

SOURCE PRESSURE - 8×10^{-8} TORR

ANALYZER " - 1.4×10^{-8} TORR

ACCELERATING VOLTAGE - 10.5 KV

SLIT SETTINGS :

SOURCE - 6 MILS , 5 MILS

CENTER COLLECTOR - 14 MILS

FINAL COLLECTOR - 25 MILS

TABLE I ABUNDANCE SENSITIVITIES, SINGLE STAGE & TANDEM MASS SPECTROMETERS

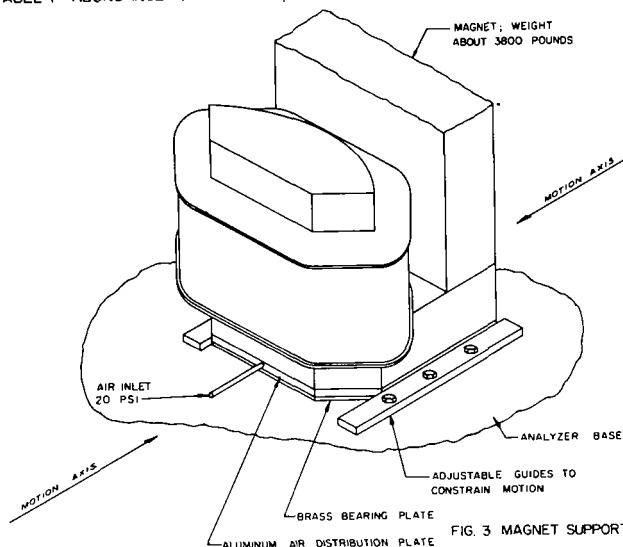


FIG. 3 MAGNET SUPPORT ASSEMBLY

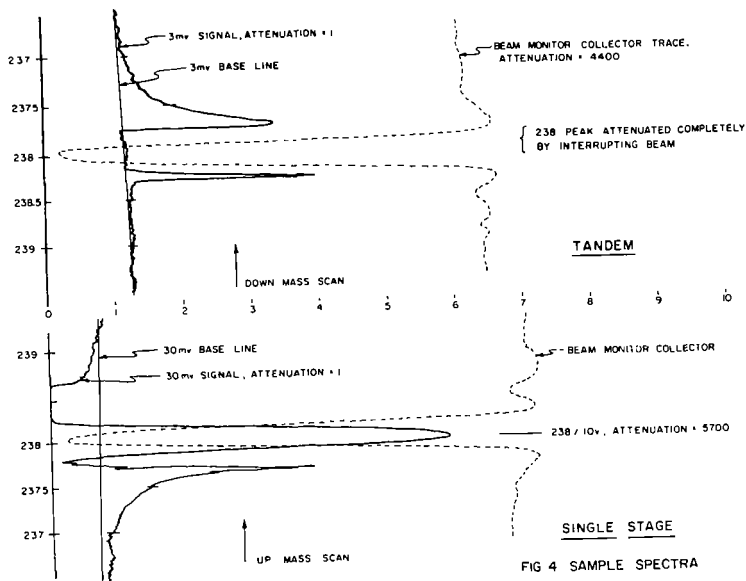


FIG 4 SAMPLE SPECTRA

less than 1/1000 inch, and one can make small adjustments in the magnet position while still observing the ion beam. Adjustable guides permit constraint of the motion along any desired horizontal axis, useful particularly for returning the magnet to position after system bakeout.

The two electromagnets each achieve field strengths of 10,000 gauss, sufficient to permit focusing the uranium-plutonium isotopes at the full accelerating voltage of 15 KV. Power dissipation is low enough that water cooling is not necessary. A balance circuit is provided to permit adjustment of magnet current, and therefore field strength, of the second magnet without altering the field in the first.

Harvey-Wells Corporation Model FC-502 nuclear magnetic resonance equipment is employed as part of the sensing circuit of the magnet regulator and direct regulation of the magnet field is thereby obtained. The NMR equipment also facilitates the matching of the fields of the two magnets, and provides, with its oscilloscope display, evidence of a "locked in" or matched condition. With the NMR field control, absolute field stability of $1/10^5$ is achieved.

Ion Source

Two ion sources have been used, both of the surface ionization type. One is the KAPL type single filament ion source as described by Dietz, et al,⁽⁶⁾ and the other is a triple filament source as described by Inghram and Chupka.⁽⁷⁾ The triple filament technique has been employed with both of these sources. Accelerating voltages up to 15 KV have been used with both.

Performance

We first measured the abundance sensitivity of the single stage instrument. To do this, the Faraday cup detector was inserted at the intermediate collector position. Ion currents were measured by a vibrating reed electrometer with a choice of two input resistors.

A natural uranium sample was loaded on the filaments and the ion beam intensity increased to approximately 10^{-10} amperes. Analyzer pressures of 1.4×10^{-8} Torr and source pressure of 5 to 8×10^{-8} Torr were measured after sample outgassing. The ion beam was scanned, switching resistors as the major peak came into the slit to prevent overloading of the amplifier. A scan in each direction was made to enable us to determine the tail height on both the up mass and down mass sides without any complication due to the switching of the electronics or to time constants in the electrometer circuit.

In Figure 4, part of the spectrum obtained in this manner is shown. The base line was determined by extrapolation from several mass units away. We also confirmed that there was no uniform background signal of any significance by closing the slit valve to completely turn off the ion beam. This measurement showed that the background signal a few mass units away was less than the noise level, which is to say 10^{-16} amperes or less in this trace.

Rather than use the attenuation factor introduced by resistor switching to compute the abundance sensitivity, we used the 235 peak height and the known abundance ratio of 238/235 in this sample to make the calculation.

The measurements of abundance sensitivity on the tandem arrangement were made in a similar manner except that the electron multiplier detector was used. In this case we used the Faraday cup to intercept the major peak to prevent overloading of the multiplier-detector system.

The trace obtained in the tandem instrument is shown in the upper section of Figure 4. As before, the base line was obtained by extrapolation and confirmed by use of the slit valve.

In Table 1 the results of these measurements are listed. We have listed these numbers for abundance sensitivity in the form of the ratio of the major peak height to the height of the tail contribution, as defined by White and Collins.⁽⁸⁾

First let us consider the results for a single stage instrument. The abundance sensitivity observed is a part in 170,000 on the low mass side of the 238 and a part in 340,000 on the high mass side. At the half mass positions, we observed abundance sensitivities of 42,000 and 230,000 on the low and high mass sides respectively. We believe that these figures for abundance sensitivity compare quite favorably with similar observations on other single stage instruments. They are better than we have typically observed on our 12" radius 60° sector instruments. The only apparent factor which may explain this is that the analyzer pressure is approximately a factor of 10 better in the ion pumped tandem systems.

The results for the tandem "S" configuration instrument are also listed. The abundance sensitivities observed are one part in 930,000 on the low mass side of the 238 peak and one part in 1,800,000 on the high mass side, both measured one mass unit away. The abundance sensitivities at the adjacent half-mass positions are one in 120,000 and one in 910,000 on the low and high mass sides respectively. These results compare well to the abundance sensitivities reported by others for tandem magnetic sector mass spectrometers. Knolls Atomic Power Laboratory reported 10^6 in the uranium range for a 12" instrument.⁽⁹⁾ Aldermaston reported 3 to 5×10^6 at the 239 mass position for their 15" radius tandem instrument,⁽¹⁰⁾ and a value of the order of 10^6 on the low mass side of the major peak, in this case at mass 236. Aldermaston's results indicate at least a factor of 5 improvement in the abundance sensitivity from the low mass side to the high mass side. In our instrument, the abundance sensitivity on the low mass side is only a factor of two poorer than that on the high mass side.

Perhaps one of the more striking results of our measurements is the observation that the factor of improvement of the tandem instrument over the single stage is considerably less than expected if one bases his prediction on a square law dependence. This improvement factor is indicated for reference in the right hand column of Table 1 and is seen to be of the order of five. Of course, an improvement of even this amount is quite important for some measurements.

We may be overly conservative in determining the base line on the tandem instrument, in which case the abundance sensitivity may be 2 to 3 times greater than that reported. The factor of improvement would then be correspondingly larger than that listed. When tests with pulse counting equipment are completed, we should have more accurate results for this measurement. Further studies are also planned at reduced ion beam current intensities in an attempt to determine the importance of this parameter.

References

- (1) White, F. A. and Collins, T. L., Applied Spectroscopy 8, 169 (1954)
- (2) Op cit
- (3) Inghram, M. G., Hayden, R. J., and Hess, D. C., AECU 2120, Mass Spectroscopy
- (4) Dietz, L. A., Pachucki, C. F., Sheffield, J. C., Hance, A. B. and Hanrahan, L. R., Anal. Chem. 32, 1276 (1960)
- (5) White, F. A., Rourke, F. M. and Sheffield, J. C., Applied Spectroscopy 12 (1958)
- (6) Op cit (4)
- (7) Inghram, M. G. and Chupka, W. A., Rev. Sci. Instrum. 24, 518 (1953)
- (8) Op cit (1)
- (9) Op cit (4)
- (10) Wilson, H. W. in Proceedings, Symposium on Mass Spectrometry, Oxford, 1961 (Pergamon Press, Oxford, 1963)

A Method for the Determination of Ion Source Pressures in
Mass Spectrometers Operated at Very High Pressures

F. H. Field
M. S. B. Munson
Humble Oil & Refining Company
Research and Development
Baytown, Texas

In recent years a number of laboratories have undertaken studies involving operation of mass spectrometers at very high ionization chamber pressures, that is up to 0.3-0.5 Torr. These studies generally are made to observe the ion-molecule reactions occurring, and it is oftentimes desirable to determine the rates at which various reactions proceed. To obtain accurate rate constants it is necessary to know accurately the pressures existing in the ionization chamber of the mass spectrometer, but the determination of these quantities presents difficult problems. We wish to describe in this paper a method of determining mass spectrometer ionization chamber pressures in the range 0.010-0.400 Torr and also to present results we have obtained concerning the flow behavior of gases entering the ionization chamber of our mass spectrometer.

Experimental

The experiments were performed using the Humble chemical physics mass spectrometer, which has been described previously.¹ A McLeod gauge is

¹ F. H. Field, J. Am. Chem. Soc. 83, 1523 (1961).

attached to the tube which conducts the gas into the ionization chamber at a point about 15 inches from the ionization chamber. The diameter of the tube varies between 7 mm. and 4 mm., and for about 5 inches it includes a co-axial thermocouple well (annular distance $\cong$ 2 mm.). The gas flows out of the ionization chamber partly through the electron entrance slit, which has the dimensions 3 x 0.5 mm., and partly through the ion exit slit, which has the dimensions 5 x 0.5 mm. This constitutes a fairly open ionization chamber, and consequently the gas flow through the system attains values as large as 200 micron-liters/second at the highest pressures used. Thus one might anticipate a considerable pressure drop from the McLeod gauge to the ionization chamber, which in fact is generally observed.

In our new method for determining source pressures a thermistor is used as the pressure sensing element. A 5/16" diameter blind hole was drilled in the ion source block at a distance about 1/4" from the ionization chamber. To allow gas flow between the two cavities, a channel with 4.0 mm.² cross-sectional area was fabricated in the wall between the two cavities. The top portion of the wall of the cavity thus fabricated is threaded, and a short (1/4") length of stainless steel tubing is screwed into the cavity. The mounting ring of the thermistor is silver soldered to the top of the short length of tubing, and an effort was made to make this closure at the top end of the thermistor cavity gas tight. Thus the thermistor cavity is a cul-de-sac connected only to the ionization chamber, and one can reasonably expect that the gas pressure in the thermistor cavity will be equal to the pressure in the ionization chamber. The thermistor used is a Type G 112 unit manufactured by Fenwal Electronics Company and is the thermistor used as a sensing element in the Perkin Elmer Model 154 vapor fractometer. A current manually maintained constant at 4.00 ma. was passed through the thermistor. The voltage drop across the thermistor comprises the output signal, and this quantity is measured with an appropriate milli-voltmeter.

A thermistor is a semi-conductor device with a large negative temperature coefficient of resistance, and its usefulness as a pressure measuring device results from the fact that the temperature of a thermistor heated somewhat above ambient temperature depends upon the amount (pressure) of gas conducting heat away from it. Thus for the thermistor to be used as a pressure sensor, the temperature of its surroundings must either be maintained constant, or else the effect of temperature changes must be taken into account. In our experiments with the mass spectrometer ion source it was easier to correct for changes in temperature. Thus the temperature coefficient of the thermistor was

Table 1
Flow Constants for Several Substances

<u>Compound</u>	<u>A</u>	<u>B</u>	<u>A/B</u>	<u>$\frac{A M^2}{\eta} \times 10^6$</u>	<u>$\frac{B M^2}{\eta} \times 10^6$</u>
H ₂	4,000	255	15.7	51	3.3
He	10,500	905	11.7	87	7.5
CH ₄	4,200	285	14.7	117	8.0
Ne	10,250	650	15.8	119	7.5
N ₂	5,500	330	15.2	119	7.9
C ₂ H ₄	4,000	371	10.8	156	14.4
Ar	6,600	521	12.7	145	11.4
n-C ₄ H ₁₀	2,100	213	9.9	134	13.6
Kr	4,500	237	19.0	124	6.6
Xe	4,100	290	14.1	153	10.9
AV.			14.0 ± 2.1	128 ± 17	9.8 ± 2.5
			14%	13%	26%
				H ₂ Value Omitted	

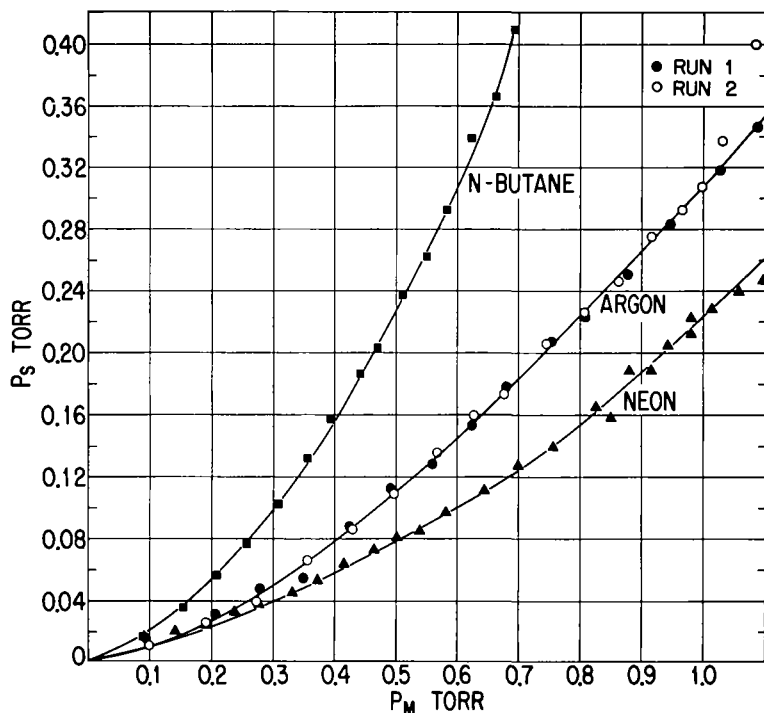


Fig. 1. PLOTS OF P_S vs. P_M .

determined by measuring the thermistor voltage drop as a function of the temperature of the ionization chamber block. This was measured with the chromel-alumel thermocouple comprising part of the mass spectrometer ion source assembly. It was established that the magnitude of the thermistor temperature coefficient depends upon the gas pressure in the system, and thus the temperature coefficient was determined at source pressures of about 0.010, 0.150, and 0.300 Torr. This encompasses the range of pressures with which we are generally concerned. The temperature coefficient increased as the gas pressure was increased, and the amount of increase varied from a factor of 1.5 to a factor of 2, depending upon the identity of the gas being studied. The temperature coefficients obtained at the various pressures were plotted, and these plots were used in connection with the pressure calibration of the thermistor.

To make the pressure calibration of the thermistor, the oil diffusion pumps of the mass spectrometer were turned off, and stopcocks placed in the lines leading from the diffusion pumps to the rotary forepumps were closed. Under these circumstances no gas flow through the mass spectrometer occurred, and thus no pressure differentials between one portion of the system and another were to be expected. The pressure measured with the McLeod gauge on the inlet line could be expected adequately to represent the pressure in the ionization chamber and the thermistor chamber. The pressure of gas in the system was adjusted by allowing an appropriate amount of gas to leak through the gold foil leaks of the mass spectrometer inlet system, and the output of the thermistor was determined as a function of pressure. The temperature of the ionization chamber block was simultaneously determined using the block thermocouple, and using the temperature coefficient graphs obtained previously, the thermistor output was corrected to a standard block temperature of 135°C. Standard thermistor outputs obtained in this way at different pressures were tabulated and plotted. Then to determine the ionization chamber pressure under flow conditions, the diffusion and forepumps were started, and the thermistor output was determined at different pressures as determined by the McLeod gauge. The block temperature was also determined, and the thermistor output corrected to 135°C was converted to pressure readings using the pressure calibration graph. The temperature corrections to the pressure calibrations were of the order of 10%.

A brief study was made of the source pressures obtained as a function of McLeod gauge pressure when the source was maintained at room temperature (25°C). To do this, all the mass spectrometer heaters were turned off and the procedure described above was repeated.

Results

The relationships between the manometer pressure, P_M , and the source pressure, P_S , were determined at a source temperature of 135°C for ten gases (He, Ne, Ar, Kr, Xe, N_2 , H_2 , CH_4 , C_2H_4 , and $n-C_4H_{10}$) and for three gases at room temperature (H_2 , Kr, CH_4). The number of gases investigated at the lower temperature was limited because in this study we were not primarily concerned with determining the temperature coefficients of the flow patterns in the mass spectrometer.

The relationships between P_M and P_S varied from one gas to another in rather surprising ways. Figure 1 shows the plots of P_S vs. P_M for neon, argon, and n-butane. The points represent the data, while the curves are calculated from the values of the constants given in Table I and eq. (10). The plots for these three compounds span the range of results obtained; the P_S value obtained for a given P_M value is smallest for neon, largest for n-butane, and argon is intermediate. At a manometer pressure of 0.700 Torr, the source pressure obtained with n-butane is about three times larger than that obtained with neon. As can also be seen from Figure 1, the argon graph includes two sets of data, namely, the data from an original run and also the data from a replicate run made two weeks later. The two sets of data are indistinguishable, and from this and from the scatter of the data obtained generally, we estimate that the precision of our measurements is on the order of 2-5%.

The experiments carried out on H_2 , Kr, and C_2H_4 with the mass spectrometer temperatures lowered to room temperature gave the results that the

flow pattern is unaffected by temperature (at least over the range investigated) for Kr and CH_4 , but for H_2 the source pressure for a given manometer pressure is about 20% lower at the lower temperature.

It is of interest to attempt to analyze the gas flow mathematically and to correlate the results obtained with the different substances. We represent the flow system by a model consisting of a chamber, M, connected by a tube with a chamber, S. Gas is assumed to flow continuously into chamber M, through the system, and out of chamber S through a small hole in the wall of the chamber. We assume (1) the existence of a steady state of pressure and flow rate, (2) that the flow through the tube connecting chambers M and S has both molecular and viscous components, and (3) that the gas passes out of chamber S by a molecular flow mechanism. For most of the gases with which we are concerned the mean free paths will be greater than the dimensions of the orifices out of the ionization chamber up to a pressure of about 0.20 Torr, and thus the approximation that only molecular effusion occurs will not be seriously in error even at the highest pressures studied (0.400 Torr).

Applying a steady state treatment, we write

$$\frac{dn_S}{dt} = k_M \left(\frac{n_M}{V_M} - \frac{n_S}{V_S} \right) - k_S \frac{n_S}{V_S} = 0 \quad (1)$$

where n_M/V_M = conc. of molecules in chamber M

k_M = flow constant for flow out of chamber M, and

n_S/V_S and k_S are defined equivalently.

From eq. (1) we get

$$\frac{n_S}{V_S} = \frac{k_M (n_M/V_M)}{k_S + k_M} \quad (2)$$

or, applying the gas law,

$$P_S/T_S = \frac{k_M P_M/T_M}{k_S + k_M} \quad (3)$$

In our experiment, except for the three temperature variation studies, a constant relationship is maintained between T_S and T_M , i.e. $qT_M = T_S$, and eq. (3) becomes

$$P_S = \frac{q k_M P_M}{(k_S + k_M)} \quad (4)$$

From the previously stated assumptions, k_M includes both a viscous flow term and a molecular flow term, but k_S contains only a molecular flow term. For viscous flow the flow constant is proportional to the pressure, and we write

$$k_M = \alpha \frac{(P_M + P_S)}{2} + \beta \quad (5)$$

$$k_S = \gamma \quad (6)$$

From Poiseuille's equation

$$\alpha = \frac{\pi a^4}{8\eta l} \quad (7)$$

$$\beta = K_p \left(\frac{T_M}{MW} \right)^{\frac{1}{2}} \quad (8)$$

$$\text{and} \quad \gamma = K_y \left(\frac{T_S}{MW} \right)^{\frac{1}{2}} \quad (9)$$

The terms in these equations have their usual significance except that MW is used for molecular weight. K_β and K_γ are structural factors referring to the flow system under consideration.

One substitutes eqs. (5) and (6) in eq. (4) and solves to obtain the relation

$$P_S = \frac{1}{2} \{ (q-1) P_M - A + (A^2 + [2(1-q)A + 4qB] P_M + [4q + (1-q)^2] P_M^2)^{\frac{1}{2}} \} \quad (10)$$

where

$$A = 2(\beta + \gamma)/\alpha, \quad B = 2\beta/\alpha, \quad \text{and } q = T_S/T_M. \quad (11)$$

The values of A and B which apply to the various substances investigated were obtained from eq. (10) by substituting the experimentally determined values of P_M and P_S . The solutions for A and B were obtained using an analog computer to get preliminary values and using these in a variation program in a digital computer to obtain values which would accurately represent the P_S - P_M relationship obtained experimentally. The values thus obtained are given in Table 1.

By combining eqs. (7), (8), (9), and (11) it may be seen that A/B , $A(MW)^{\frac{1}{2}}/\eta$, and $B(MW)^{\frac{1}{2}}/\eta$ should be invariant from one compound to another, that is,

$$A/B = 1 + \gamma/\beta = 1 + K_\gamma/K_\beta, \quad (12)$$

$$\frac{A(MW)^{\frac{1}{2}}}{\eta} = \frac{16g(K_\beta + K_\gamma)T_M^{\frac{1}{2}}}{\pi a^4}, \quad \frac{B(MW)^{\frac{1}{2}}}{\eta} = \frac{16gK_\beta T_M^{\frac{1}{2}}}{\pi a^4}$$

We include in Table 1 the values for these quantities for the several compounds investigated. The values of η are taken from Handbook of Chemistry and Physics². Except for H_2 and, to a lesser extent, He, the quantities A/B

² Handbook of Chemistry and Physics, 44th Ed., C. D. Hodgman, Ed., Chemical Rubber Publishing Company, Cleveland, Ohio (1962).

and $A(MW)^{\frac{1}{2}}/\eta$ are constant to about 15%, and $B(MW)^{\frac{1}{2}}/\eta$ is constant to about 25%. It is particularly gratifying to note that while the P_S - P_M relationships for Ne and $n\text{-C}_4\text{H}_{10}$ differ by a factor of 3, the values of $A(MW)^{\frac{1}{2}}/\eta$ differ by only 12%. We do not understand why the values for H_2 and He differ so badly from the values for the rest of the compounds, but one is inclined to associate the difficulty with the light masses of these two substances. We conclude that our analysis of the gas flow in the mass spectrometer has a rough validity, and in fact it may have some predictive value. Thus we think that as a first approximation the quantity $(MW)^{\frac{1}{2}}/\eta$ should determine the relationship between P_S and P_M for different substances.

The results of the three experiments where the temperature was changed are somewhat disconcerting. For krypton and methane the P_S - P_M relationships were the same at a source temperature of 135°C and room temperature. For H_2 the source pressure at room temperature was about 20% lower than the corresponding value at 135°C. Because viscosity decreases as temperature decreases, the viscous flow will increase with a decrease in temperature. On the other hand, effusive flow decreases with a decrease in temperature, and both of these effects would lead one to expect that the pressure in the ion source would increase as the temperature decreases. This is contrary to the experimental facts, and we have no explanation to offer for the discrepancy. We are inclined not to discount the validity of our analysis of the flow in the mass spectrometer, and whatever may be the truth of this, the fact is that the relative lack of sensitivity of the flow through the instrument is desirable from a practical point of view in that changes in source temperature will not require extensive recalibration procedures.

Acknowledgement

We wish to acknowledge the competent service of Mr. W. C. Gieger in carrying out the experiments. The machine computations were carried out by Dr. Ben T. Rhodes, and we thank him for his service.

THE DETERMINATION OF FLUORINE IN ZrO_2 CORROSION FILMS
BY SPARK SOURCE MASS SPECTROGRAPHY

H. D. Cook
Bettis Atomic Power Laboratory
Pittsburgh, Pennsylvania

ABSTRACT

The residual fluorine, resulting from etching and air drying zirconium and zircaloy surfaces prior to corrosion testing, may result in defective temper films on core components or irradiation test specimens. The defective areas of the temper film undergo accelerated corrosion when in the reactor environment.

Existing methods of analyses for fluorine in corrosion films are based on the determination of an average fluorine concentration for the entire surface of the test sample. Since localized high fluorine content is significant, total surface analyses of some non-defective films may indicate higher fluorine content than some defective films.

A spark source mass spectrograph was used to investigate the variation in fluorine content in both defective and non-defective corrosion films. The fluorine content varied from 6 ppm in as machined materials to 500 ppm in some defective films. To verify the analyses, fluorine films were deposited on the surfaces of untreated material and non-defective corrosion films.

Typical results are presented as well as correlation between F^+ , ZrO^+ , Zr^+ and O^+ spectra observed for bulk material and defective and non-defective corrosion films.

ANALYSIS OF INSULATING POWDERS BY SPARK SOURCE MASS SPECTROMETRY

By

R. Brown and W. A. Wolstenholme
Associated Electrical Industries Limited
Manchester, England.

INTRODUCTION

To make possible the analysis of insulating powders by spark source mass spectrometry, sample electrodes which fulfil the following requirements must be prepared:-

1. The electrodes must be electrically conducting.
2. The physical strength must be sufficient for them to be clamped in the ion source.
3. There must be minimum interference from the mass spectrum of the support material.
4. Any impurities in the support material must be present at low and known concentrations.
5. For quantitative analysis, the contribution of the support material to the spark and, therefore, to the total ion current, should be constant and consistent.

This paper describes a method based on compounding the sample powder with pure graphite. It has been successfully applied to the quantitative analysis of a variety of samples including powdered rocks of geological interest, aluminium oxide, titanium dioxide, thorium dioxide, magnesium oxide, bauxite, sodium azide, cadmium sulphide, and others.

EXPERIMENTAL

The sample powder is mixed with an approximately equal amount of pure graphite powder in an end mill employing a PTFE vial and rod. The homogeneous mixture of the sample and the graphite is then pressed in a die (Fig.1) to form a conducting rod of dimensions 20 mm x 2 mm x 2 mm. The surfaces of the rod are scraped to remove any surface contamination, and then it is broken in the middle to give two electrodes. The electrodes are mounted in the ion source of the instrument with the freshly broken ends forming the spark gap.

The choice of graphite as the support material can be appreciated if one considers it with respect to the five requirements listed above.

First, the compound electrode must be electrically conducting, and this is satisfied.

Second, the physical strength must be sufficient for the electrodes to be clamped in the ion source. This is satisfied if graphite powder of suitable particle size is used and if the concentration is sufficiently great; usually between 2 and 5 parts atomic of graphite to one of sample.

Third, there must be minimum interference from the mass spectrum of the support material. This is well satisfied since:-

- (a) The intense carbon isotopes at masses 12 and 13 have a large percentage mass difference from the nearest neighbours boron at masses 10 and 11, and nitrogen at mass 14.
- (b) The multiply charged carbon lines only interfere with lithium and this can in any case be determined from the isotope at mass 7.
- (c) The molecular ions corresponding to clusters of 2,3,4 or more carbon atoms, have sufficient mass defect to be easily resolved

POWDER MOULDING DIE.

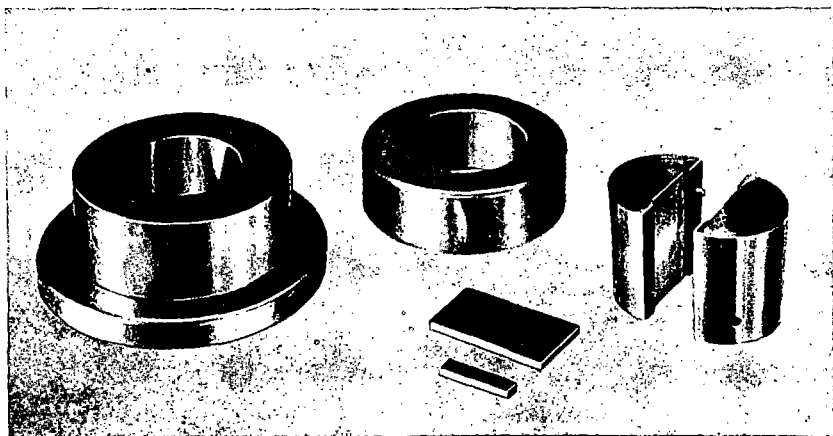


Fig. 1 Electrode forming die (Supplied by Ringsdorffwerke A.G.)

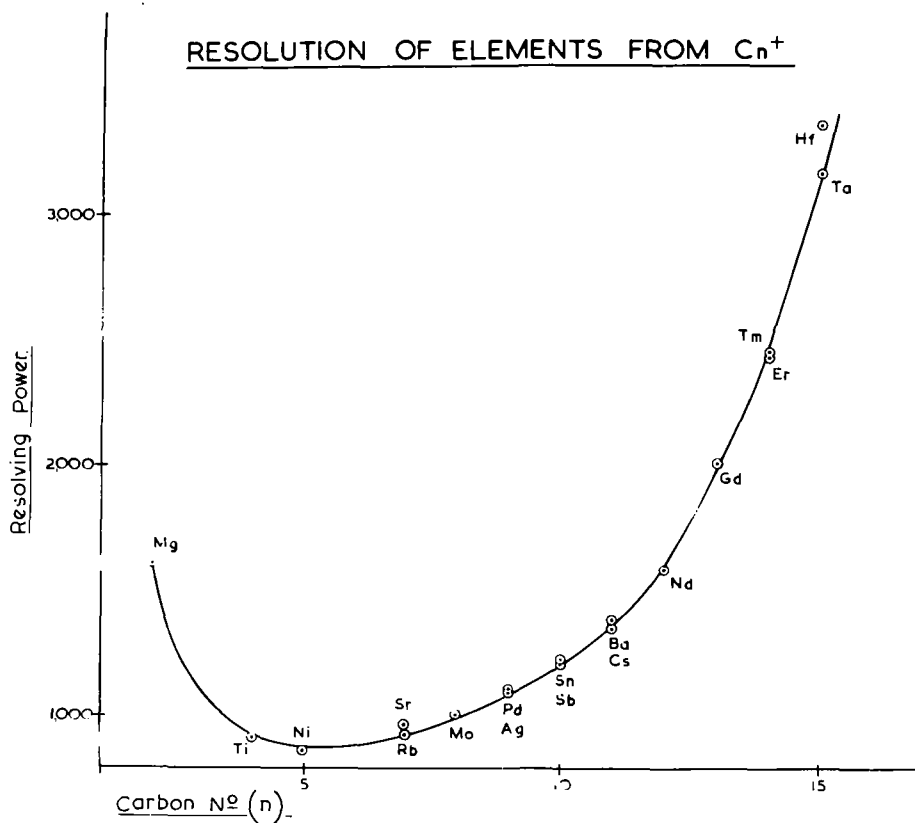


Fig. 2 Resolution required to separate C_n^+ from elements of the same mass number.

from elements at the same mass number. This is illustrated in Fig.2 which shows the resolving powers required to separate the carbon molecular ion C_n^+ from the different elements. Only for the highest carbon numbers is there any problem and for these the intensity of the carbon lines is usually negligible.

Fourth, any impurities in the support material must be present at low and known concentrations. Unfortunately, when the work was started, the purest grades of spectroscopic graphite were only available in solid form and the Ringsdorffwerke RWA grade had therefore to be used. The contribution from the carbon matrix is shown below. However, we understand that the purer Ringsdorffwerke RWS grade is now available as a powder of suitable particle size.

Typical Contribution From Carbon Matrix
(Type RWA Graphite)

Fluorine	} 3 ppm.(atomic)	Aluminium	} 1 ppm.(atomic)
Sodium		Calcium	
Magnesium		Chromium	
Silicon		Iron	
Chlorine			
Potassium			

16 other elements at concentrations between 0.3 and 0.01 ppm.
All other elements below the detection limit.

The fifth requirement was that the contribution of the support material to the spark, and therefore to the total ion current, should be consistent. That this requirement has been met is shown by the reproducibility of repeat analyses which were generally within a 20% standard deviation and compared favourably with the performance obtainable with solid rather than compounded electrodes.

After the electrodes have been pre-sparked for about 10 minutes, analysis is carried out in the usual manner. The voltage required to give an easily maintained spark is about 25 kV, and the speed of analysis is generally comparable to that when conducting samples are being run.

RESULTS

A selection of typical results obtained for powder analysis with the AEI/MS7 is given below.

Rock Samples

Two standard rock samples, granite G1 and diabase W1[‡], have been analysed and parts of the mass spectrum of the granite are shown in Fig.3.

The elements detected in this preliminary work on these rock samples are given in Table I. Silicon was chosen as the internal standard, since it is present in the granite and the diabase at known concentrations, and the densities of lines due to the trace elements were compared with that of the line due to the ^{30}Si isotope.

[‡] Originating from the US Geological Survey, Washington.

PART SPECTRA OF POWDERED GRANITE G1

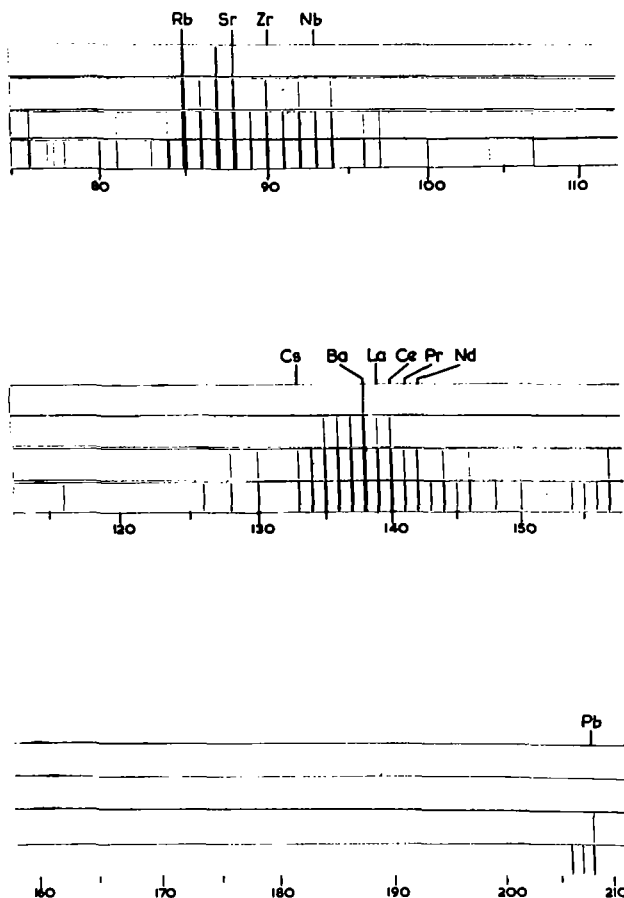
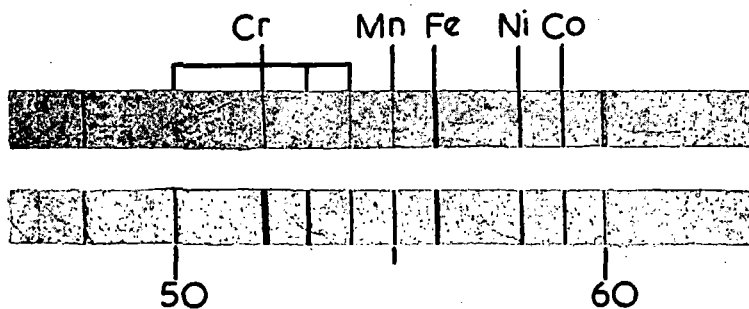


Fig. 3 Part Mass Spectra of Powder Granite G1.

ANALYSIS OF MAGNESIUM OXIDE.



GOOD.

BAD.

Fig. 4 Part Mass Spectra of Magnesium Oxide Samples.

TABLE I
ANALYSIS OF POWDERED ROCKS
Trace Elements Detected (ppm. weight)

<u>Element</u>	<u>Granite</u> <u>G1</u>	<u>Diabase</u> <u>W1</u>	<u>Element</u>	<u>Granite</u> <u>G1</u>	<u>Diabase</u> <u>W1</u>
Uranium	1.3	0.5	Antimony	0.1	0.3
Thorium	6.5	1.3	Tin	5	2
Lead	22	1.9	Niobium	4	4
Thallium	0.4	<0.2	Zirconium	127	104
Tantalum	2	0.5	Yttrium	10	23
Hafnium	5	2	Strontium	382	508
Lutecium	<0.2	0.2	Rubidium	783	83
Ytterbium	0.7	1	Arsenic	3	3
Thulium	0.3	0.3	Gallium	39	39
Erbium	2	4	Zinc	17	72
Holmium	2	1	Copper	9.3	152
Dysprosium	5	5	Nickel	14	78
Terbium	2	1	Manganese	248	1570
Gadolinium	4.6	4.6	Chromium	29	154
Europium	2	2	Vanadium	25	333
Samarium	9.7	5.7	Titanium	1330	8200
Neodymium	48	17	Scandium	11	36
Praseodymium	15	4.5	Chlorine	52	66
Cerium	116	33	Sulphur	3	3
Lanthanum	58	11	Phosphorus	69	495
Barium	1300	257	Sodium	1000	500
Cesium	4.7	2.3	Boron	2.8	18

In Table II some of the mass spectrometric results are compared with those obtained by other analytical techniques⁽¹⁾. Considering that the mass spectrometric results were calculated on the assumption that all elements have equal sensitivity, the agreement between the mass spectrometric and other results is good.

TABLE II
ANALYSIS OF POWDERED ROCKS
Granite G1 - Results in ppm.wt.

<u>Element</u>	<u>Mass Spectrometry</u>	<u>Neutron Activation</u>	<u>Spectrographic</u>	<u>Various</u>
Cr	29	30	18	22
Mn	248	-	250	210
Cu	9.3	16	15	13
Zr	127	-	222	210
La	58	122	124	-
Sm	9.7	11	-	-
Gd	4.6	-	-	-

Alumina

The results for the elements detected in three samples of aluminium oxide are given in Table III. Concentrations were estimated by the visual method on the assumption that all elements have the same sensitivity ⁽²⁾.

TABLE III
ANALYSIS OF THREE ALUMINA POWDERS
Elements Detected (ppm atomic)

<u>Element</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>Element</u>	<u>1</u>	<u>2</u>	<u>3</u>
Uranium	0.08	0.2	<0.02	Rubidium	0.04	<0.02	<0.02
Thorium	<0.02	0.02	<0.02	Bromine	0.4	0.4	<0.04
Bismuth	<0.02	<0.02	0.02	Arsenic	2	0.4	0.1
Lead	<1	0.04	0.1	Gallium	60	150	3
Platinum	<0.06	<0.06	0.4	Zinc	40	4	1
Hafnium	<0.08	0.2	<0.08	Copper	8	3	8
Terbium	<0.02	0.02	<0.02	Nickel	11	8	2
Gadolinium	<0.08	0.2	0.08	Cobalt	0.2	0.6	0.06
Samarium	<0.08	0.08	<0.08	Iron	60	200	20
Neodymium	0.08	2	0.2	Manganese	6	<3	<3
Praseodymium	0.02	0.2	0.06	Chromium	6	2	<1
Cerium	0.2	1	0.6	Vanadium	60	60	20
Lanthanum	0.1	0.8	0.4	Titanium	20	40	6
Barium	0.2	1	0.5	Scandium	<0.2	0.2	0.2
Iodine	0.6	0.6	0.04	Calcium	400	400	10
Tin	0.6	2	<0.2	Potassium	30	30	30
Rhodium	<0.06	<0.06	6	Chlorine	60	60	<6
Molybdenum	0.2	0.8	<0.2	Sulphur	260	80	2
Niobium	<0.06	0.2	<0.06	Phosphorus	15	6	6
Zirconium	0.8	8	0.3	Silicon	80	40	40
Yttrium	0.2	0.5	0.05	Magnesium	6	<3	6
Strontium	2	2	0.6	Sodium	20,000	20,000	400

The concentrations of the elements Fe, Ti, V, Ga and Zn were determined more accurately by scanning their spectra with a microdensitometer, and the results obtained in 3 analyses of the same sample are given in Table IV. Iron was used as the internal standard.

TABLE IV
ANALYSIS OF ALUMINA
Results in ppm.(atomic)

Reproducibility of Analysis using Iron as the Internal Standard

<u>Plate</u>	<u>Ti</u>	<u>Zn</u>	<u>V</u>	<u>Ga</u>
1	36	2.9	57	200
2	45	3.2	53	220
3	30	2.2	57	140

The values indicate that the reproducibility of the method is of the order of 20% which is comparable to that obtained when conducting solids are analysed.

The average mass spectrometric values of four determinations of the concentrations of a number of elements in two alumina samples were converted to the equivalent oxide concentrations, and in Table V the results are compared with the known values obtained by chemical methods. The mass spectrometric results are again calculated on the assumption of equal sensitivity for all elements.

TABLE V
ANALYSIS OF TWO ALUMINA POWDERS
Results in % wt.

	<u>Sample 1</u>		<u>Sample 2</u>	
	<u>MS7</u>	<u>Chemical</u>	<u>MS7</u>	<u>Chemical</u>
SiO ₂	0.020	0.025	0.017	0.021
TiO ₂	0.005	0.006	0.003	0.004
Na ₂ O	1.46	0.73	1.12	0.46
Fe ₂ O ₃	0.036	0.034	0.028	0.043
Ga ₂ O ₃	0.036	0.016	0.021	0.016
ZnO	0.0004	0.001	-	-
V ₂ O ₅	0.010	0.010	0.003	0.005

Work on aluminium oxide included the analysis of a sample of powdered bauxite, and the elements detected are given in Table VI; again, all elements were assumed to have equal sensitivity.

TABLE VI
ANALYSIS OF POWDERED BAUXITE
Elements Detected (ppm atomic)

<u>Element</u>	<u>ppm (atomic)</u>	<u>Element</u>	<u>ppm (atomic)</u>
Uranium	1	Palladium	0.7
Thorium	10	Rhodium	0.1
Bismuth	0.3	Molybdenum	2
Lead	40	Niobium	30
Tungsten	1	Zirconium	300
Tantalum	0.3	Yttrium	150
Hafnium	2	Strontium	100
Lutecium	0.7	Rubidium	1
Ytterbium	2	Arsenic	100
Thulium	0.7	Gallium	60
Erbium	3	Zinc	20
Holmium	0.7	Copper	4
Dysprosium	3	Nickel	80
Terbium	0.8	Cobalt	10
Gadolinium	5	Iron	80,000
Europium	1	Manganese	200
Samarium	8	Chromium	200
Neodymium	40	Vanadium	200
Praseodymium	10	Titanium	7,000
Cerium	150	Scandium	70
Lanthanum	80	Calcium	300
Barium	10	Potassium	300
Cesium	0.1	Sulphur	20
Iodine	0.3	Phosphorus	300
Antimony	2	Silicon	13,000
Tin	8	Magnesium	250
		Boron	90

Thorium Dioxide

Thorium metal, prepared by reduction of the oxide, is added to magnesium alloys to give the desired metallurgical properties for special applications. The selection of the thorium dioxide is normally based on an assay of ThO₂. However, in Table VII, where the results of the analysis of three different grades are given, the wide variation in elemental composition suggests the need for a detailed analysis of this type.

TABLE VII
ANALYSIS OF THREE THORIUM DIOXIDE SAMPLES
Elements Detected (ppm atomic)

<u>Element</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>Element</u>	<u>1</u>	<u>2</u>	<u>3</u>
Bismuth	0.03	1	<0.03	Strontium	2	50	1
Lead	0.6	0.3	6	Zinc	6	20	2
Tantalum	1	0.3	20	Copper	10	30	1
Samarium	30	50	7	Nickel	40	40	4
Neodymium	100	160	16	Cobalt	3	300	3
Praseodymium	50	30	3	Iron	400	400	80
Cerium	1000	300	20	Manganese	3	10	1
Lanthanum	40	20	10	Titanium	40	4000	20
Barium	2	1400	2	Sulphur	500	4000	100
Niobium	1	30	0.1	Phosphorus	100	20	5000
Zirconium	20	200	20	Silicon	1200	20,000	1200

Magnesium Oxide

Fig.4 shows parts of the mass spectra of two samples of magnesium oxide. One of these samples had been in use as an insulator for 2,000 hours before it failed, and the other was the unused material. The analysis was performed to determine whether there had been any contamination of the magnesium oxide by the materials in contact with it. The analytical results for the region of the spectrum shown are given in Table VIII.

TABLE VIII
ANALYSIS OF MAGNESIUM OXIDE
Results in ppm. (atomic)

<u>Element</u>	<u>Sample 1</u> <u>unused</u>	<u>Sample 2</u> <u>used</u>
Ni	50	50
Co	30	30
Fe	100	100
Mn	4	50
Cr	15	1,800
V	1	2

The results indicate that the used magnesium oxide had become contaminated with chromium and manganese. These impurities might well have been responsible for its failure.

Titanium Dioxide

Several samples of titanium dioxide have been analysed (3). This material is used as a pigment, and the presence of certain trace impurities can affect its physical properties. The elements which are responsible for the differences are not completely known and a survey analysis for trace impurities is particularly valuable. Some of the elements detected in an analysis of two different grades of the powder are given in Table IX.

TABLE IX
ANALYSIS OF TWO TITANIUM DIOXIDE SAMPLES
Elements Detected (ppm atomic)

<u>Element</u>	<u>1</u>	<u>2</u>	<u>Element</u>	<u>1</u>	<u>2</u>
Lead	5	5	Copper	1	15
Tungsten	6	3	Cobalt	2	1
Hafnium	8	3	Iron	10	50
Antimony	30	20	Chromium	3	3
Tin	20	10	Calcium	40	200
Molybdenum	2	4	Potassium	30	300
Niobium	300	300	Sulphur	100	3
Zirconium	20	150	Phosphorus	100	1000
Zinc	4	20	Silicon	100	4000
			Aluminium	40	10,000

CONCLUSIONS

Insulating powders can be analysed by spark source mass spectrometry by mixing with pure graphite powder and forming electrodes in a die. Reproducible spectra are obtained and the speed of analysis is comparable to that when conducting solids are analysed.

The method is not, of course, limited to insulating powders, and it opens up a new wide field of application of the spark source mass spectrometer.

ACKNOWLEDGEMENTS

The authors wish to thank the Directors of Associated Electrical Industries Limited, Manchester, for permitting publication of this paper.

REFERENCES

- (1) M. Fleisher and R. E. Stevens, *Geochimica et Cosmochimica Acta*, Vol.26, May 1962, p.525.
- (2) R. D. Craig, G. A. E-rook and J. D. Waldron, "Advances in Mass Spectrometry", Vol.1, Ed. J. D. Waldron, Pergamon, 1959, p.136.
- (3) R. Brown, R. D. Craig and R. M. Elliott, "Advances in Mass Spectrometry", Vol.2, Ed. R. M. Elliott, Pergamon, 1963, p.141.

CONSTRUCTION DETAILS OF AND FIRST RESULTS OBTAINED
WITH A NEW COMMERCIAL MATTAUCH-TYPE MASS SPECTROGRAPH

K. E. Habfast
Atlas MeB- und Analysentechnik GmbH
Bremen, Germany

ABSTRACT

In the new Atlas Mass Spectrograph SM 1 a spherical condenser has been built in with the result of better sensitivity. Four of the most important parameters of geometry are adjustable from outside during operation. This gives a good control of high resolution. An electron bombardment ion source and a spark ion source, on the one hand, and photographic plate and electrical detecting system, on the other hand, are exchangeable. Data on resolution, sensitivity, and accuracy for both ion sources and both detecting systems will be given.

A NEW DOUBLE FOCUSING MASS SPECTROMETER FOR ORGANIC ANALYSIS

By

M. Barber, R. D. Craig, R. M. Elliott and B. N. Green,
Associated Electrical Industries Limited,
Manchester, England.

INTRODUCTION

The object of this paper is to give a brief account of a high resolution mass spectrometer specifically designed for organic work, to illustrate the performance obtainable and to indicate some applications in which it might be employed.

DESCRIPTION OF THE INSTRUMENT

The instrument, the A.E.I. MS9, has been designed to meet the following requirements:

- (1) High resolution and precise mass measurement for identification and structural analysis.
- (2) Rapid selection of optimum resolution, scan time and method of sample introduction.
- (3) Provision for conventional quantitative analysis.

A schematic diagram of the instrument is shown in Fig. 1 and a photograph of the complete unit in Fig. 2.

Principal features are:

Inlet system:	(1) room temperature reservoir (calibration gas) (2) heated reservoir (350°C) (3) direct evaporation
Ion detection:	(1) electron multiplier (high resolving power, fast scanning) (2) monitor collector (total ion current) (3) plate collector (low resolution, quantitative work)
Mass range:	1 - 800 at 8kV; 8 - 6,400 at 1kV
Mass measurement:	by oscilloscope peak matching

PERFORMANCE

1. Resolution

For high resolution work the instrument is usually set for resolution 10,000 on the 10% valley definition. However, any resolving power from 500 up to the maximum can readily be obtained by varying the source and collector slit widths. Selection of the optimum combination of slit width controls for a particular value of resolving power can be made in 10 seconds.

The maximum value of resolving power obtainable is maintained from day-to-day by a simple adjustment process taking only 10 minutes. If this process is not carried out daily, the loss in resolving power over a week would, however, not be more than 5% for an initial value of 10,000.

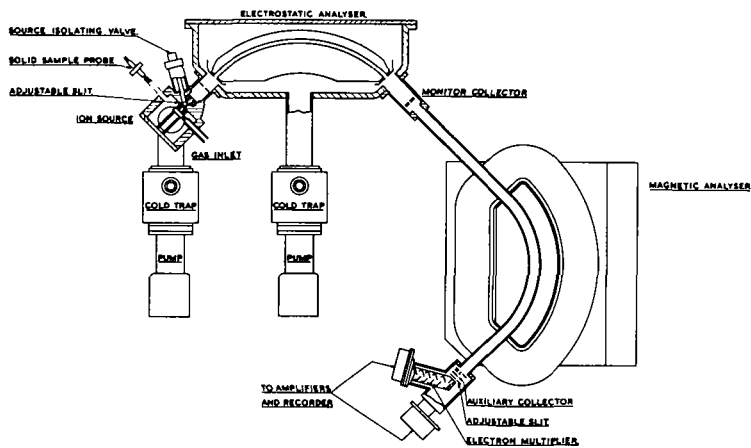


Fig. 1 Schematic diagram of MS9 mass spectrometer, showing Nier-Johnson type analyser system with 15" radius electric analyser and 12" radius magnetic analyser.

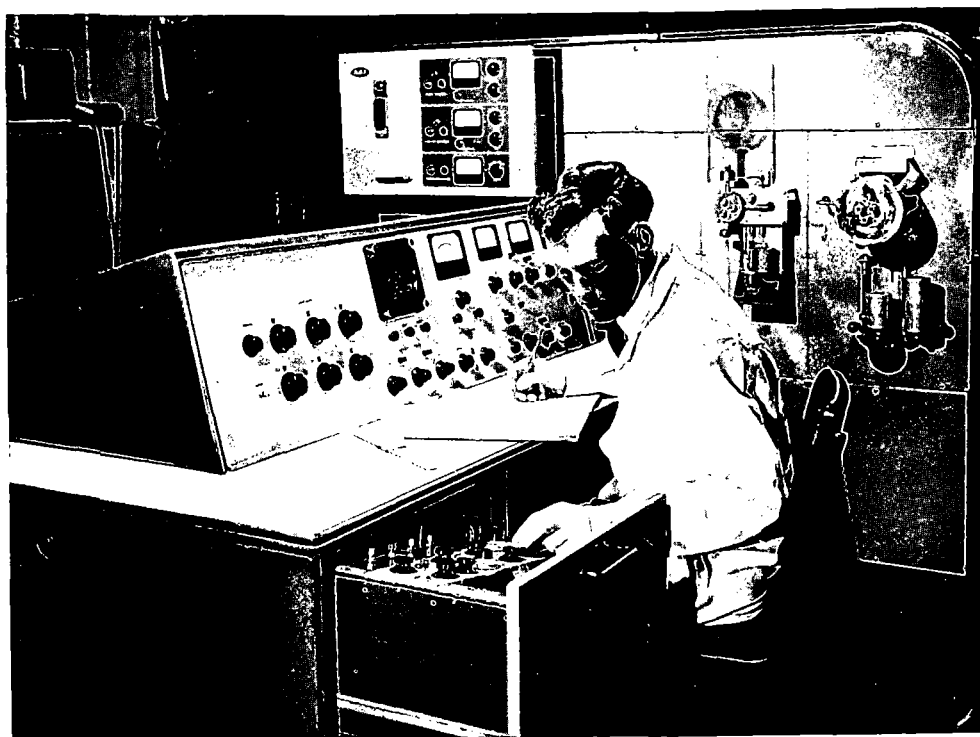


Fig. 2 A.E.I. MS9 mass spectrometer.

Although the "10% valley" definition of resolving power, used above, is appropriate for quantitative work, it is unduly pessimistic for distinguishing doublets. In such work, if the two peaks are separated by their "width at half height" the doublet will generally be distinguishable, provided the intensity ratio is not greater than 10:1. This is illustrated in Fig. 3 where a typical MS9 peak shape has been used to construct synthetic doublets according to the "10% valley" and "width at half height" definitions of resolution for intensity ratios from 1:1 to 100:1. It is to be noted that the resolving power on the "width at half height" definition is almost exactly twice the conventional value.

The point is further illustrated in Fig. 4 which shows an actual recording of a 5-component multiplet at m/e 130 with the instrument set for R.P. 12,000 on the "10% valley" definition; the $^{13}\text{C} - ^{12}\text{C}$ H doublet on the extreme right is clearly distinguishable as a doublet although the separation is only 1 part in 29,000.

Other components in this multiplet are due to doubly charged ions containing oxygen and sulphur and to xenon which was admitted as a reference.

2. Mass Measurement

The system is basically that described by Nier⁽¹⁾ where the two peaks whose masses are to be compared are displayed alternately on an oscilloscope. The measurement consists of adjusting decade controls until the two peaks coincide. The mass ratio is read directly from the decades and the system can be used up to a ratio of two in mass between the unknown and reference peaks. However, it is usually possible to choose a reference mass within 10% of the unknown, with the advantage that errors will be less.

The accuracy of mass measurement is always within 5 p.p.m. of the true value provided the reference mass is within 10% and provided a simple correction is made for one of the known systematic errors. The average time for a mass measurement, including admission of the reference and selection of peaks, is 5 minutes and the correction adds only a further 30 seconds.

Still higher accuracy is obtainable by using peaks with masses within 1%, or better still, the components of a doublet, and by making further corrections for other systematic errors. Thus, in the measurements on chlorine and krypton shown below, using hydrocarbon peaks as reference at mass differences of 0.2% and 0.06% respectively, the discrepancy between the measured values and those in the literature are less than 0.3 p.p.m. and the estimated errors are of the same order.

ACCURACY OF MASS MEASUREMENT

"Unknown" Ion	Reference Ion	Measured Mass of "Unknown"	Literature Values
Cl_2^+	$\text{C}_5\text{H}_{10}^+$	69.959962 ± 21	69.959944 ± 22
$^{84}\text{Kr}^+$	CH_2Cl_2	83.938190 ± 22	83.938178 ± 3

Note: for Cl $\pm 21 = \pm 0.3$ ppm

for Kr $\pm 22 = \pm 0.26$ ppm

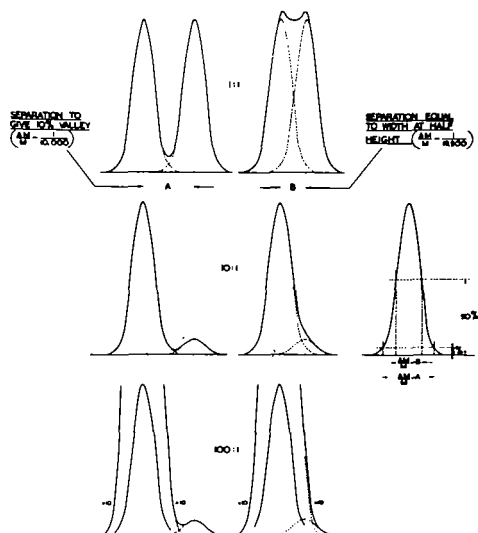


Fig. 3 Synthetic doublets based on the actual MS9 peak shape shown on the right.

On the left: Resolution 10,000 on 10% valley definition, i.e. peaks with separation $\frac{\Delta M}{M} = A$ = peak width at 5% height points.

In centre: Resolution 19,500 on "width at half height" definition, i.e. peaks drawn with separation $\frac{\Delta M}{M} = B$ = peak width at 50% height points.

(Note: The 10% valley definition is used throughout this paper).

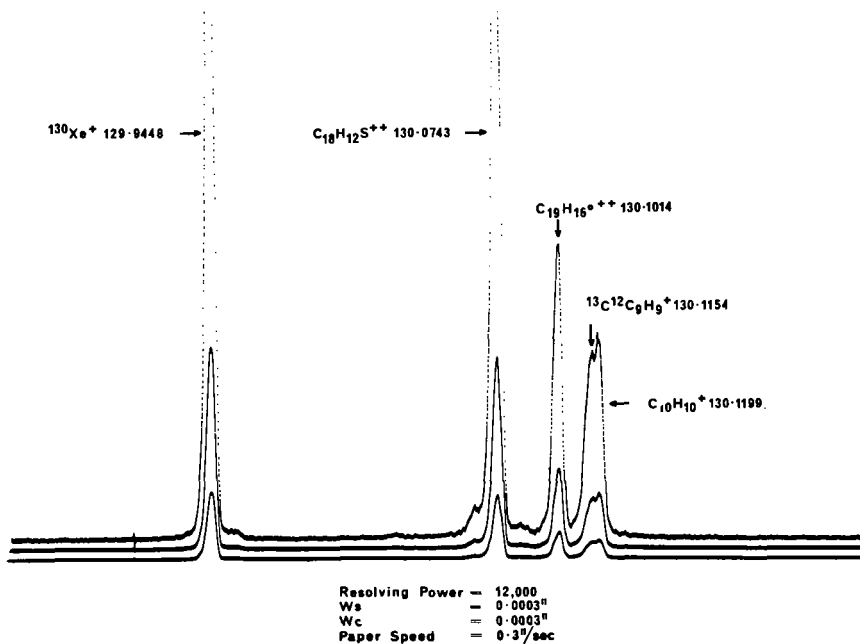


Fig. 4 Mass 130 multiplet from a four component mixture. The $^{130}\text{Xe}^+$ peak is from xenon admitted as a reference for accurate mass measurement.

3. Scanning

The scan speed and amplifier time constant are adjustable to suit the problem.

For low resolution scans up to mass 800, the most commonly used scan speed is 3 minutes for a factor of two in mass; a portion of such a scan is shown in Fig. 5a. In Fig. 5b there is shown a fast scan of the same spectrum taken at the rate of 5 sec. for a factor of two in mass. Compared with the normal scan this has a factor of eight loss in signal-to-noise, a 40% clipping of the peaks and a factor of two loss in effective resolution due to "filling-in" of the valleys, nevertheless, all the principal features of the spectrum are well preserved.

For high resolution work, optimum results are obtained by very slow scanning of selected mass numbers at the rate of $\frac{1}{2}$ minute each. An example is the 238 multiplet shown in Fig. 6, the recording of the peak itself taking 15 sec. in this case. However, in some cases a general survey of a limited mass range will be run to identify the multiplet peaks. With a resolving power of 10,000, such a scan would usually be done at a rate equivalent to 20 minutes for a factor of two in mass (3 minutes for a 10% change in mass).

Typical scanning speeds employed under various conditions are summarised as follows:

LOW RESOLUTION (R.P. 800)

Normal: 3 min. for a factor of two in mass
Fast : 5 sec. " " " " " " "

HIGH RESOLUTION (R.P. 10,000)

Detail: $\frac{1}{2}$ min. per mass number
Survey: 20 min. for a factor of two in mass

4. Sensitivity

For a resolving power of 800, the sensitivity of the MS9 is approximately half that of the equivalent single focusing instrument, the effect of shorter slits and increased path length being compensated by the higher voltage employed.

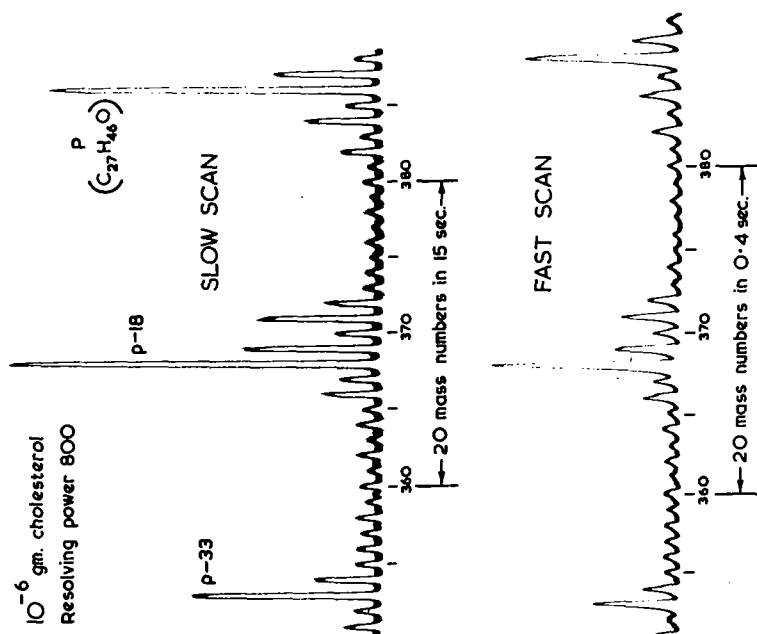
For quantitative or semi-quantitative work it is usual to use about 100 micrograms of sample, which is held in a reservoir and is used up at the rate of 0.3% per minute, but for identification work using direct evaporation techniques, the normal sample size is 1 microgram. The spectrum shown in Fig. 5 at a resolving power of 800 was obtained from 1 microgram of cholesterol and these peak heights were maintained for over an hour.

For a resolving power of 10,000 the sensitivity is reduced by a factor of about twenty but is still generally sufficient for stable spectra to be obtained from a microgram. The parent peak region of the same cholesterol sample is shown in Fig. 7 at a resolving power of 10,000.

APPLICATIONS

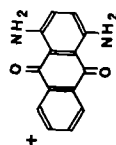
It is not the object of this paper to review in detail all applications of high resolution mass spectrometry, but merely to indicate one or two possibilities.

10⁻⁶ gm. cholesterol
Resolving power 800

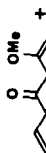


Figs. 5a Portions showing the parent peak region, taken from slow and fast scans of a 10⁻⁶ gm. cholesterol sample.

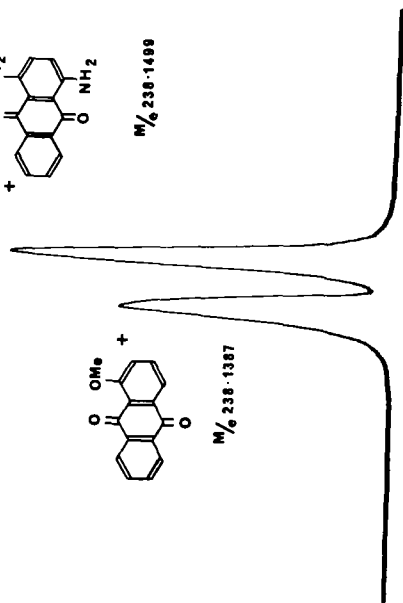
M/e 238



M/e 238-1498



M/e 238-1387



Resolving Power = 21,200
(("5%" peak width definition)
W_{1/2} = 0.0001"
W_c = 0.001"
Paper Speed = 0.1"/sec.

Fig. 6 Mass 238 doublet from the parent peaks of 1-methoxy-antraquinone and 1,4-diamino-antraquinone.

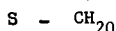
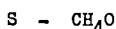
1. Analysis of Oxygenated Compounds in Petroleum

The quantitative determination of oxygenated compounds in mixtures of polynuclear aromatic hydrocarbons, such as petroleum distillates, has proved a laborious process in the past⁽²⁾ and recourse has had to be made to prolonged separations and a variety of spectroscopic techniques.

The potential advantage of high resolution mass spectrometry is demonstrated in Fig. 8, which shows a portion of the mass spectrum of a trinuclear aromatic concentrate from the middle distillate of petroleum. With a resolving power of 10,000 the peak due to the oxygenated compound at mass 208 is clearly separated from the hydrocarbon, permitting not only identification by mass measurement but also direct quantitative determination of the concentration. The low mass component of the doublet was, in fact, identified by precise mass measurement as $C_{15}H_{12}O$.

2. Analysis of Compounds containing Sulphur

An interesting extension of existing quantitative mass spectrometry techniques is the analysis of petroleum products containing sulphur compounds. The possibilities of high resolution in this field are illustrated by the multiplet in Fig. 9 which shows the separation obtainable at mass 260 for the doublets



3. Labelled Compounds

Use of isotopes as a means of labelling specific parts of a molecule, or as a means of following the course of a reaction, are standard techniques in certain branches of chemistry. Of particular interest are carbon-13 and deuterium.

Carbon-13 labelling has been used to obtain information on electron impact phenomenon and fragmentation modes. The special potential advantage of a high resolution instrument lies in its ability to distinguish peaks at the same nominal mass but containing different numbers of carbon-13 atoms. Separation of the $^{13}C - ^{12}CH$ doublet is involved and at mass 100 this requires a resolving power of 22,000.

The multiplet shown in Fig. 10 was plotted with this resolving power and the separation of the doublet on the extreme right indicates that this value of resolving power would be sufficient for measurement of $^{13}C - ^{12}CH$ doublets at mass numbers considerably higher than 118.

Deuterium has been used extensively as a tracer in following catalytic hydrogenation and exchange reactions of the lighter hydrocarbons. While low resolving power spectra can be used for this work, the interpretation may be considerably simplified and extra information obtained from a high resolution spectrum in which the $D - H_2$ doublets are resolved to give separate peaks for different numbers of deuterium atoms in the ion. This is illustrated in Fig. 11 which shows the multiplet at m/e 30 corresponding to ions with 0, 1, 2 and 3 deuterium atoms from a mixture of deuterated ethanes. This particular multiplet revealed a significant amount of undeuterated C_2H_6 in the mixture, although low resolution analysis involving subtraction of the deuterated species from the total peak height had suggested that no C_2H_6 was present.

10^{-6} gms. cholesterol
Resolving power 10,000.

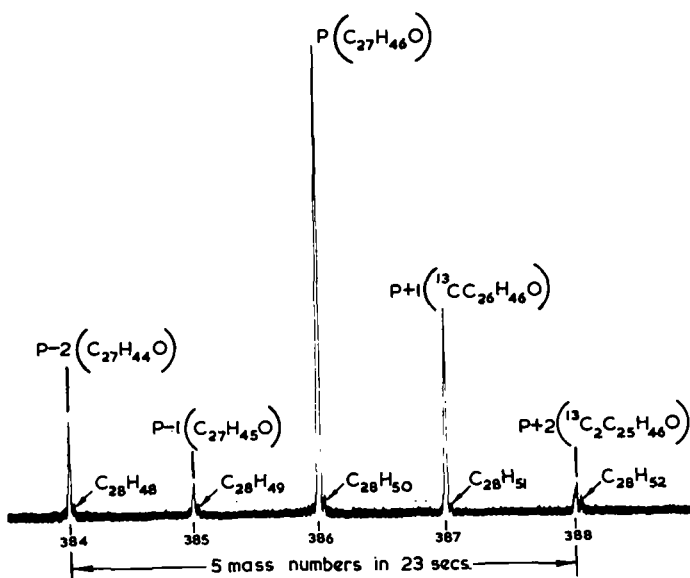


Fig. 7 High resolution scan of the parent peak region for the same 10^{-6} gm. cholesterol sample as in Fig. 5.



Fig. 8 High resolution scan of a trinuclear aromatic concentrate from the middle distillate of petroleum. Range factors are 1, 3, 10 and 30 and thus the oxygenated $C_{15}H_{12}O$ peak is only 0.2% of the $C_{16}H_{14}$ peak.

4. Identification of Unknown Compounds

Perhaps the most useful single piece of information which can be derived from the mass spectrum of a compound is the exact mass of its parent peak; from this the atomic composition can be deduced.

For example, a peptide whose identity was unknown was admitted to the instrument and the parent peak mass measured relative to a reference peak in the spectrum of dibromobenzene. The steps in the deduction of the molecular formula were:

Reference ion	=	$^{13}\text{C}^{12}\text{C H}_4$	$^{79}\text{Br } ^{81}\text{Br}$
∴ reference mass	=	236.9446	
measured ratio	=	$\frac{\text{unknown mass}}{\text{reference mass}}$	= 1.001174 ± 2
∴ measured mass	=	237.2228	± 5
Calculated mass of $\text{C}_{12}\text{H}_{19}\text{N}_3\text{O}$	=	237.2231	

It is interesting to note how certainly this measurement identifies the molecular formula. This is illustrated in Fig. 12, where the masses of all possible⁽³⁾ combinations of C, H, N and O are shown diagrammatically, the eight combinations between 237.210 and 237.240 being plotted individually. It can be seen that the limit of experimental error of ± 2 p.p.m. in the mass ratio measurement is sufficiently small to enable a unique determination of the atomic composition of the peptide to be made.

In a similar way, by making precise mass measurements on the principal fragment peaks, the atomic composition of the fragments can be established.

5. Identification of Impurities

Identification of impurities in a nominally pure substance is illustrated by the case of the 10^{-6} gm. cholesterol sample referred to earlier.

On continuing the scan above the parent region, a group of peaks was found at p+14 as shown in Fig. 13a. No further peaks were to be found at higher mass and an impurity of molecular weight p+14 or p+16 was therefore suspected.

This region of the spectrum was therefore rescanned at high resolution to obtain more information. Surprisingly, the p+14 peak appeared to be a triplet, as shown in Fig. 13b and confirmed in the detail plot shown in Fig. 14.

The identity of the three components A, B and C of the p+14 multiplet was then determined by mass measurement relative to the parent cholesterol peak as follows:

Peak	<u>Measured Mass Ratio</u>	<u>Mass - $\text{C}_{27}\text{H}_{46}\text{O}$</u>	<u>Identification</u>	<u>∴ Molecular Formula</u>
A	1.036180 ± 5	13.9828	$\text{O}-\text{H}_2 = 13.9837$	$\text{C}_{27}\text{H}_{44}\text{O}_2$
B	1.036272 ± 5	14.0183	$\text{CH}_2 = 14.0201$	$\text{C}_{28}\text{H}_{48}\text{O}$
C	1.036360 ± 10	14.0523	$\text{C}_2\text{H}_6 - \text{O} = 14.0566$	$\text{C}_{29}\text{H}_{52}$

thus establishing the presence of two impurities, $\text{C}_{27}\text{H}_{44}\text{O}_2$ and $\text{C}_{28}\text{H}_{48}\text{O}$. The third peak, C, corresponding to $\text{C}_{29}\text{H}_{52}$, is believed to be due to hydrocarbon contamination introduced in the sample handling.

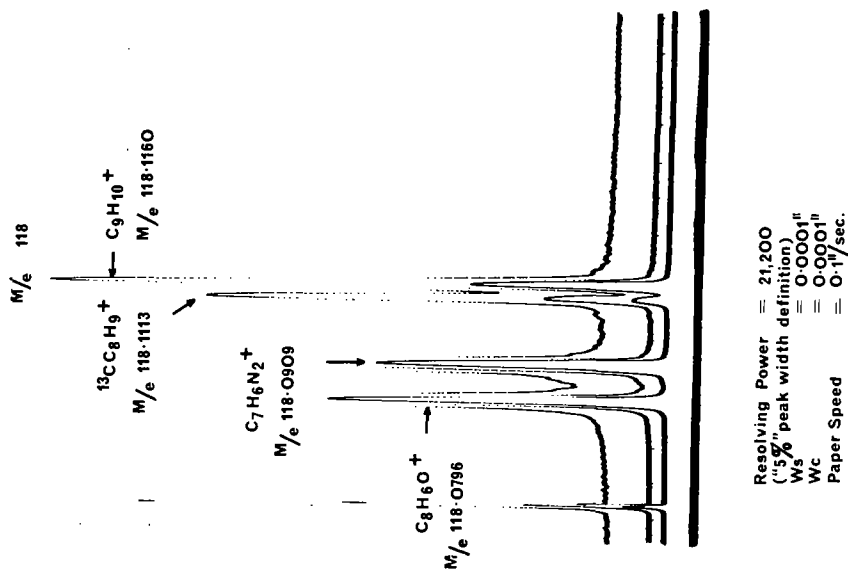


Fig.10

Parent peak spectrum of a mixture of coumarone, indane and 7-azaindole.

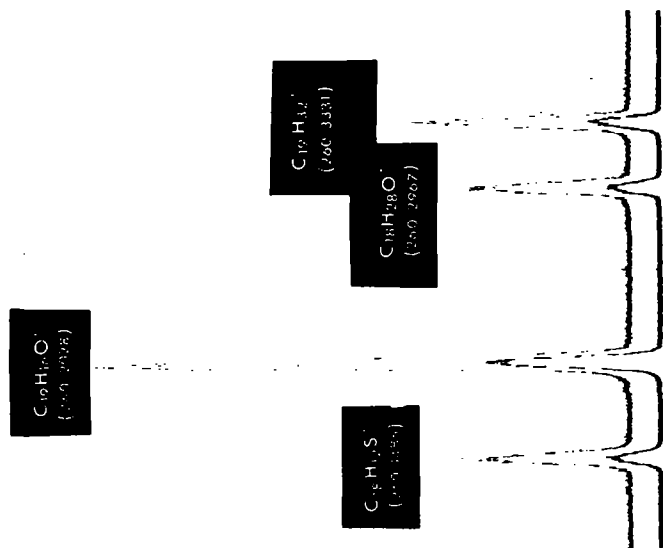


Fig. 9 Parent peak spectrum of tri-decyl benzene, phenyl undecyl ketone, 1,2 dimethyl-4-benzoyl naphthalene, 2,2 naphthyl benzo-thiophene.

In a similar manner, mass measurement of the $p+16$ peak established that this was predominantly due to a third impurity, $C_{27}H_{46}O_2$. The parent ion intensities for the above three impurities were 3, 4 and 2% respectively of the cholesterol parent ion.

ACKNOWLEDGEMENTS

The authors wish to thank the Directors of Associated Electrical Industries Limited, Manchester, for permitting publication of this paper.

REFERENCES

- (1) Nier, A. O., Nuclear Masses and their Determination (Hintenberger, H., ed.), pp.89-102, Pergamon Press, 1959.
- (2) Bartz, K. W., Aczel, T., Lumpkin, H. E., Stehling, F. C., Analytical Chemistry, p.1814, 34, 1962.
- (3) Beynon, J. H., Mass Spectrometry and its Applications to Organic Chemistry, Elsevier, 1960.

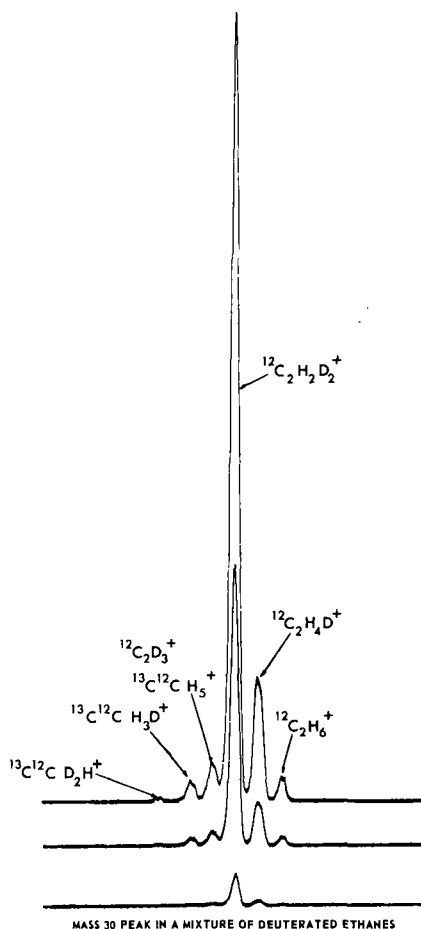


Fig.11 Multiplet at mass 30 from a mixture of deuterated ethanes.

MASS VALUES OF COMPOUNDS HAVING A NOMINAL MASS OF 237

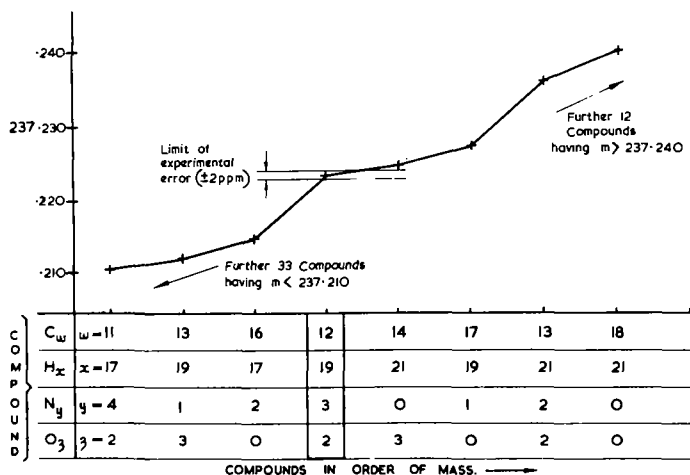


Fig.12 Diagrammatic plot of possible combinations of C, H, N and O(3) giving a mass in the region 237.210 to 237.240. (Measured mass and experimental limit of error is indicated by the two horizontal lines).

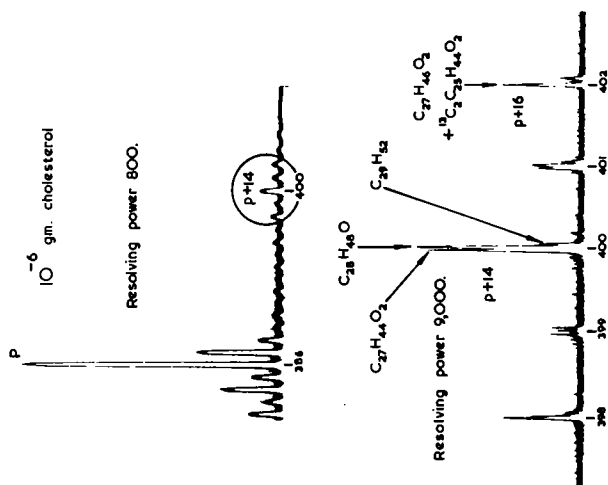


Fig.13 Low and high resolution scans of the $p+14$ region for the cholesterol sample referred to in Figs. 5 and 7.

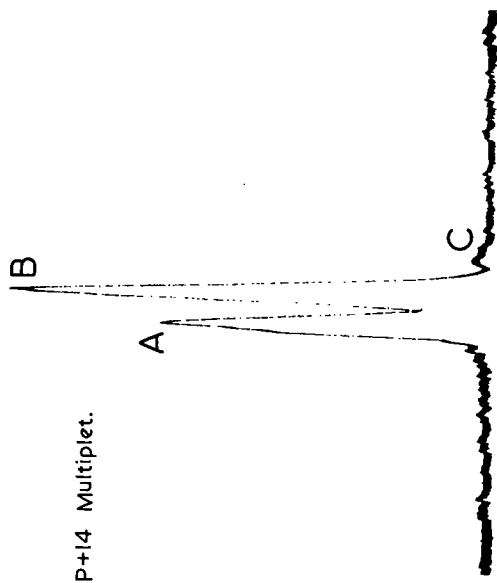


Fig.14 Repeat scan of the $p+14$ multiplet in Fig.13 showing the three peaks A, B and C with improved signal-to-noise

ELEMENTAL ASSOCIATIONS OBSERVED IN THE RADIO-FREQUENCY SPARK SOURCE

F. Neil Hodgson, Monsanto Research Corporation,
Dayton, Ohio
Michel Desjardins, University of Cincinnati
Cincinnati, Ohio
William Baun, Materials Central, Aeronautical Systems
Division, Wright-Patterson Air Force
Base, Ohio

INSTRUMENT

A double focusing mass spectrograph of the Mattauch-Herzog design was used for this work. The instrument, which was built by Bell and Howell Research Center under contract with the United States Air Force, has been described previously. A prototype of Consolidated Electrodynamics Corporation's model 21-110, the instrument utilizes a radio-frequency spark source operated at an instantaneous voltage of 100-150 kv of rf voltage and a photographic recording device, using 2" x 15" photographic plates. Spark repetition rates could be varied from 1 to 10,000 pulses per second and the pulse length from 5 to 50 microseconds.

RESULTS

Graphite, diamond and amorphous carbon Dörnenburg and Hintenberger¹ have shown that ions up to C_{28}^+ and above can be observed in the spark mass spectrum of graphite. The lines due to these associations alternate in intensity with maxima occurring at every fourth carbon atom association for ions above C_{10}^+ . This observed catenation or association pattern has been related to structure and bonding. The phenomena has been observed many times for graphite electrodes used in our laboratory. We have recently studied the behavior of other forms of carbon in the spark source. Figure 1 shows the catenation pattern of graphite, amorphous carbon and diamond. Since amorphous carbon and diamond are non-conductors, the samples were run by packing the materials into hollow electrodes made of high purity aluminum. Sparking conditions did not markedly affect the catenation pattern. Ilford Q2 photographic plates were used to record the mass spectra and the plates were scanned with a microdensitometer. A calibration curve was drawn, using the carbon isotopes in a graded scale of 10 exposures. Both line width and blackening were taken into consideration in preparing the calibration curve.

Amorphous carbon and diamond give many less associated species than graphite, with C_9^+ the upper limit in most spectra. Additionally, amorphous carbon does not show the typical alternation in intensity. Diamond shows an increase at C_5^+ and C_7^+ which is not seen in amorphous carbon. One must be careful in the measurement of C_5^+ in diamond at mass 60, since frequently nickel is used as a catalyst in the production of synthetic diamond as was the case with our diamond sample. Any work of this type must either be done on a very pure sample or an instrument that has a resolution of 1600 or better should be used in order to resolve Mg - C_2 at mass 24, Ti - C_4 at mass 48, Ni - C_5 at mass 60 and other closely spaced doublets. Our instrument is capable of this resolution. Figure 2 shows resolution obtained for the Ti - C_4 doublet at mass 48.

Coronene mass spectrum Graphite may be thought to consist of layers of a practically infinite number of condensed benzene rings with weak van der Waal's binding between layers and can be considered as the limiting case of an infinitely extended polynuclear aromatic hydrocarbon.

¹Von E. Dörnenburg and H. Hintenberger, Z. Naturforsch., 14a, 765 (1959).

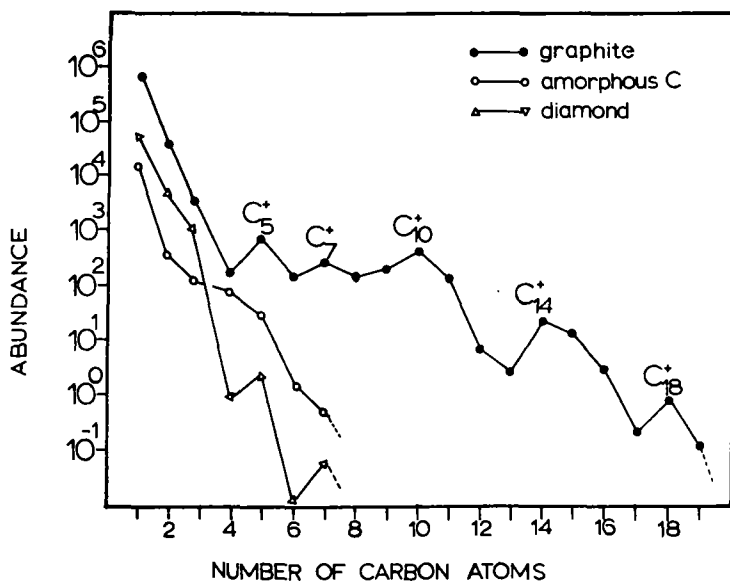


Figure 1. Associations in different forms of carbon.

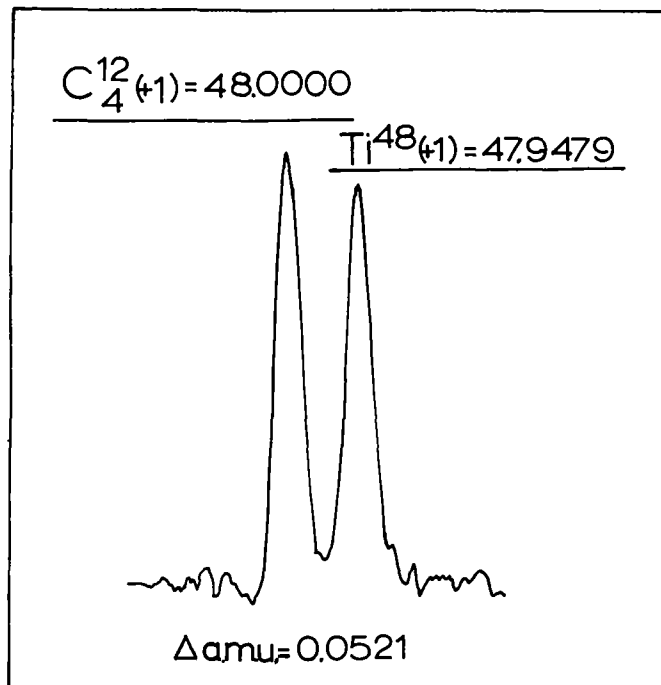


Figure 2. Resolution of carbon and titanium lines.

An aliphatic C - C bond length is 1.54Å, while the olefinic C = C double bond is 1.34Å in length. The hybrid bonds of benzene have the intermediate length of 1.39Å. Generally one would expect that as the number of condensed benzene rings of a compound increases, the average C - C bond length would approach the value for the C - C distance of graphite, 1.42Å. In the light of these observations, it is interesting to examine the spark mass spectrum of a polynuclear hydrocarbon, Coronene, which is extremely stable and inert, is an ideal representative of this type of compound. Figure 3 shows the mass spectrum obtained by sparking coronene in aluminum electrodes. In this mass spectrum, masses of fragment ions up to the molecular weight and above can be observed with the ions being grouped into 24 distinct groups, corresponding to the number of carbon atoms in the molecule. Though not always the strongest line of the group, the first mass of most groups is a multiple of the mass of carbon-12 and it is reasonable to assume that the first lines of the groups are due to ions containing only carbon. Thus groups appear at 12, 24, 36, 48, 60, and so forth, with the other lines of the group resulting from ions with protons associated. The lines in the molecular weight group, in addition to being quite intense, are greatly broadened on the photographic plate, presumably due to a space-charge effect. Since, in this figure, only transmission measurements are plotted, this group of lines is drawn heavier than the others.

Figure 4 shows spark data for a series of fused aromatic hydrocarbons. The data for each are similar to the data of coronene as is illustrated by the column at the right in the figure. In each case, the number of groups of lines equals the number of carbon atoms in the molecule and the intensity of the molecular ion is relatively strong compared to intensities of smaller fragments. One point observed consistently was that the first mass lines of the last several groups are not multiples of the mass of carbon-12. This suggests, as might be expected, that high mass fragments which have no protons attached are unlikely to occur. In Figure 4, the first line of each group is given, with the lines which are not multiples of twelve underlined.

Figure 5 shows the lines of the coronene spark mass spectrum which are due only to carbon, namely the first line of each of the groups. These lines are plotted in the same manner as those of the graphite spectrum. The qualitative similarity of these association curves is obvious and doubtlessly derives from the structural similarity of coronene and graphite.

Elemental associations in the spark have also been observed for carbon in the form of carbides. For example, silicon carbide, to which complete three dimensional covalent bonding imparts giant molecule characteristics, gives a number of associated species. Figure 6 lists these species. In addition to ions containing both silicon and carbon as shown in this figure, species due to the association of carbon atoms only, were observed. In order to plot the abundance of these species, one must be certain that resolution is obtained between certain doublets. These doublets are: $\text{Si}_2^{30}\text{-C}_5^{12}$ at mass 60, $\text{Si}_2^{30}\text{C}^{12}\text{-C}_6^{12}$ at mass 72, $\text{Si}_3^{28}\text{-C}_7^{12}$ at mass 84, and $\text{Si}_3\text{C-C}_8$ at mass 96.

It will be noted that the SiC_4 ion represents the species with the greatest number of carbon atoms combined with a single silicon atom and the Si_4C ion represents the species with the greatest number of silicon atoms associated with a single carbon atom. Figure 7 shows the association pattern of the carbon species observed in SiC mass spectrum. The highest association observed is C_7^+ , which is also more intense than the C_4 , C_5 , or C_6 .

Many of the same species observed in the mass spectrum of silicon carbide can be observed if a mass spectrum is recorded using one electrode of silicon and the other of graphite to produce the spark. The electrode arrangement is shown in Figure 8. When using two electrodes

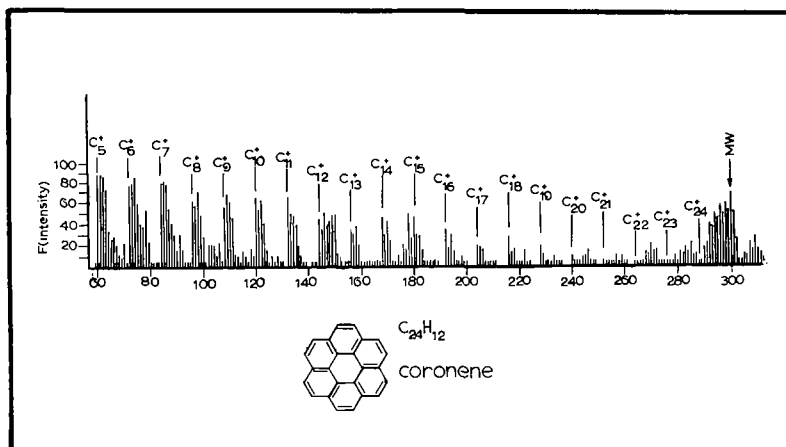


Figure 3. Spark Mass Spectrum of Coronene.

Compound	Structure	Prominent Ions Observed	First Lines of Each Group Mass Numbers
Coronene <chem>C24H12</chem>		Molecular ion, 300 m/e Doubly charged mol. ion group, 146-150 m/e	12, 24, 36, 48, 60, 84, 96, 108, 120, 132, 144, 156, 168, 180, 192, 204, 216, 228, 240, 252, 264, 278, 290
Benzo-perylene <chem>C22H12</chem>		Molecular ion, 278 m/e	12, 24, 36,204, 216, 233, 244, 256, 268
Perylene <chem>C20H10</chem>		Molecular ion, 252 m/e	12, 24, 36,108, 192, 209, 220, 233, 244
Picene <chem>C22H14</chem>		Molecular ion, 278 m/e	12, 24, 36,204, 216, 233, 244, 256, 268
Naphthalene <chem>C18H12</chem>		Molecular ion, 228 m/e	12, 24, 36,144, 156, 172, 185, 197, 209, 223
Chrysene <chem>C18H12</chem>		Molecular ion, 228 m/e Doubly charged mol. ion group, 111.5-114.5 m/e	12, 24, 36,156, 172, 185, 197, 209, 220
Triphenylene <chem>C18H12</chem>		Molecular ion, 228 m/e Doubly charged mol. ion group, 111.5-114.5 m/e	12, 24, 36,156, 172, 185, 197, 209, 220
Pyrene <chem>C16H10</chem>		Molecular ion, 202 m/e	12, 24, 36,144, 156, 173, 185, 197
Anthracene <chem>C14H10</chem>		Molecular ion, 178 m/e Doubly charged mol. ion group, 87.5-90.5 m/e	12, 24, 36,132, 144, 161, 173

Figure 4. Summary lines and line groups due to fragmentation of polynuclear aromatic hydrocarbons in the spark source.

of different materials, it is easily observed that ionization occurs at one electrode in preference to the other. In the prototype instrument used for these studies, one electrode is operated at a peak potential of approximately 100 kv, while the other is operated at a lower potential of approximately 15 kv. It has been commonly observed that the electrode at peak potential is preferentially ionized. When the silicon electrode is the one at higher potential, the species are silicon-rich. When the carbon electrode is at the higher potential, the species are carbon-rich. This effect is shown in Figure 9. Here are shown only species corresponding to the general formulas, Si_xC and SiC_y , although some species of the form Si_xC_y are observed and they also are rich in the preferentially ionized element.

As will be recalled, the highest values of x and y for Si_xC and SiC_y species present in the SiC mass spectrum were x and y equal to 4. As Figure 9 shows, when the carbon electrode is at peak potential, the species SiC_7 is observed.

It is somewhat surprising that sputtering between the electrodes does not completely counteract this effect.

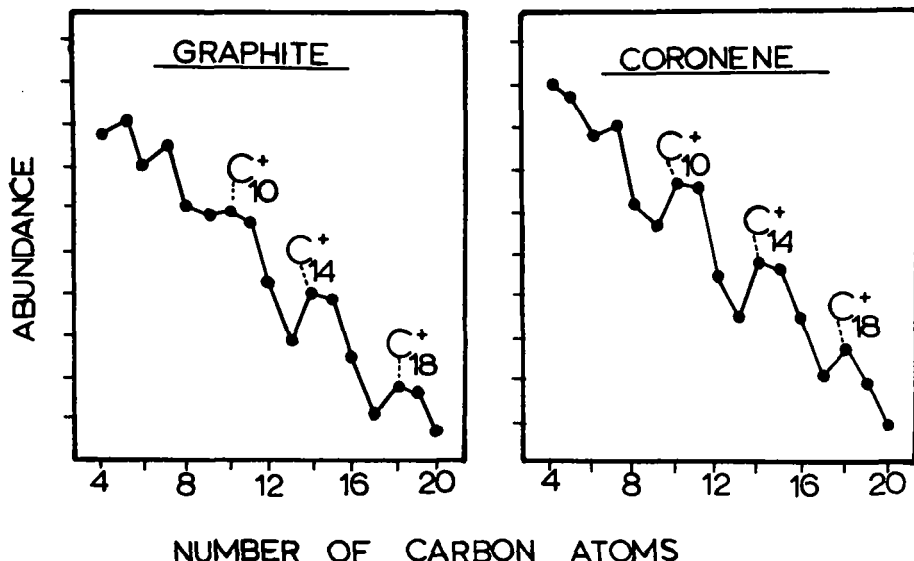


Figure 5. Carbon associations in coronene compared to those in graphite.

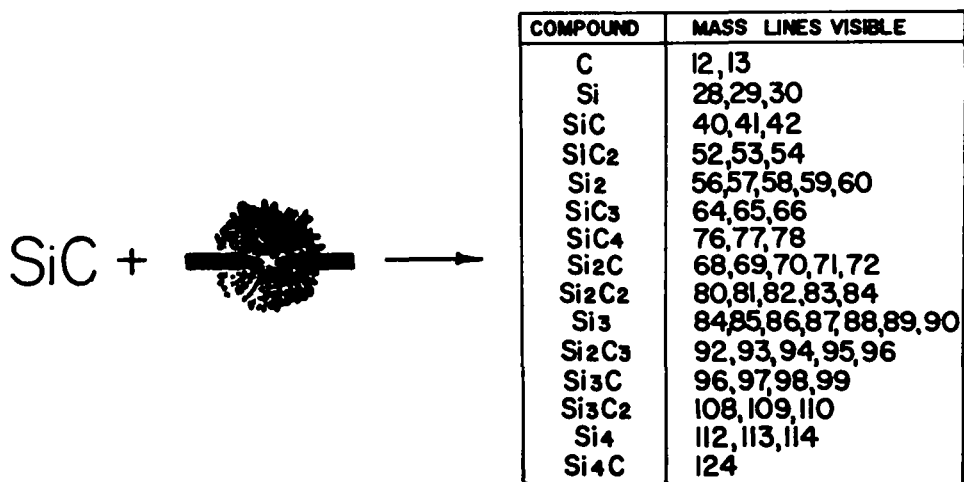


Figure 6. Lines observed for SiC in the spark source.

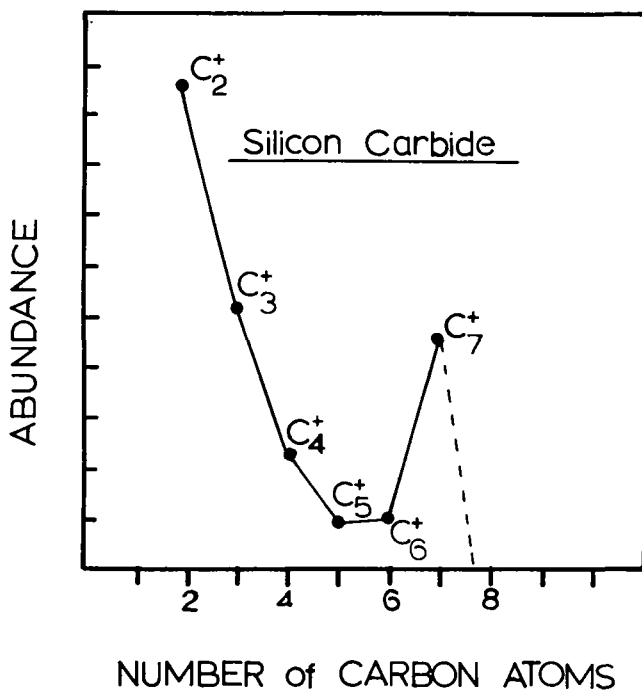


Figure 7. Carbon associations in the SiC mass spectrum.

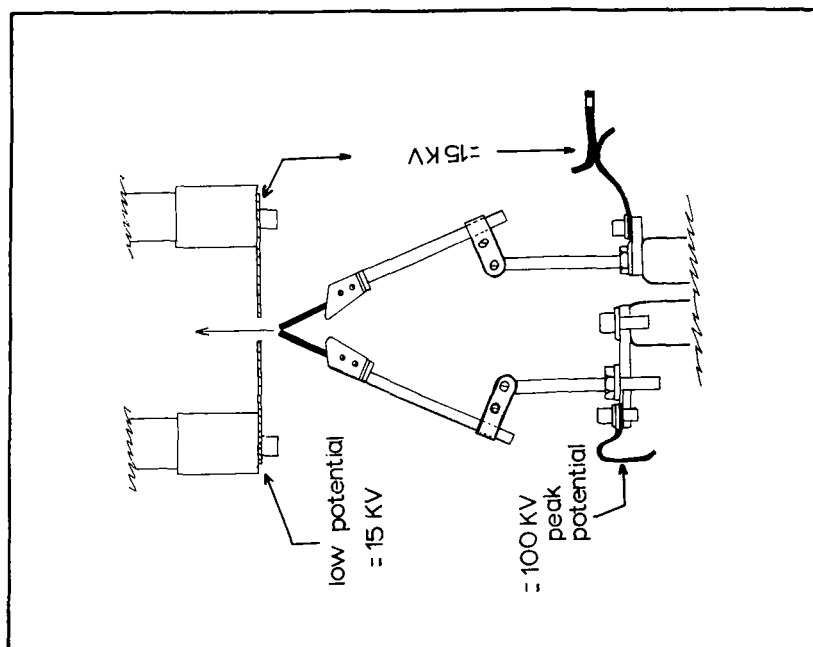


Figure 8. Electrode arrangement in the prototype instrument.

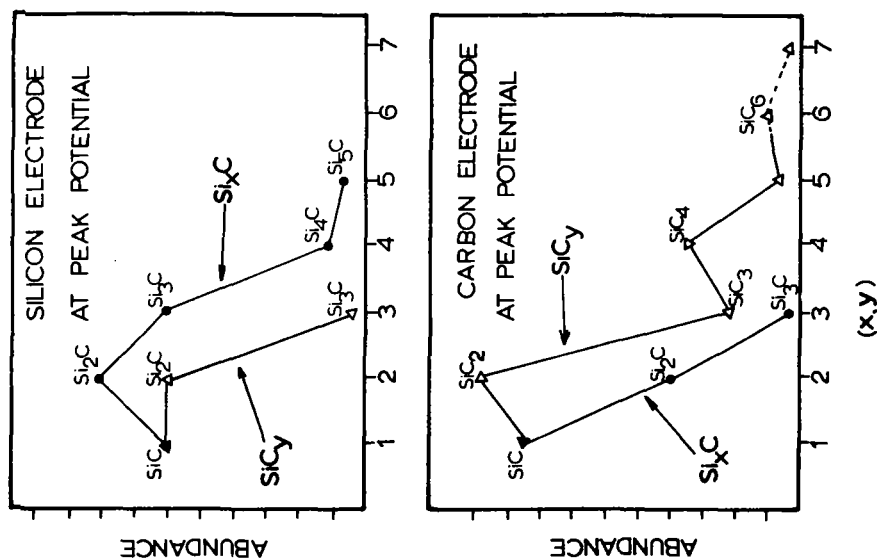


Figure 9. Electrode selectivity with applied potential for two different electrodes; one silicon, the other carbon.

USE OF SPARK SOURCE MASS SPECTROGRAPH AS A MILLIPROBE ANALYZER

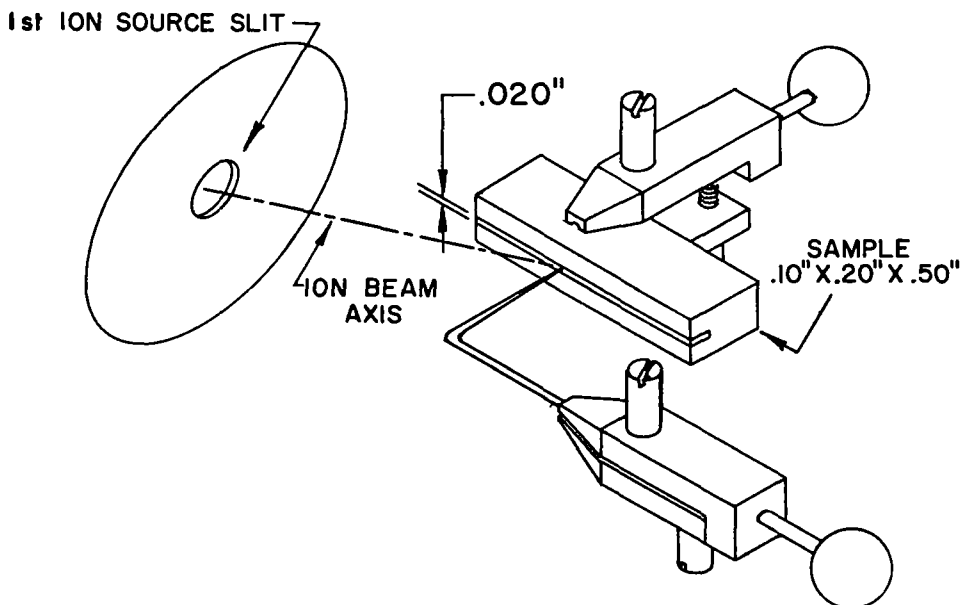
by

Robert A. Wallace and John Roboz
General Telephone & Electronics Laboratories, Inc.
Bayside 60, New York

The objective of this work was to investigate the use of a spark source mass spectrograph as a milliprobe analyzer for the study of striated metallic samples. The zones of interest are usually less than 1 mm wide. The unconfined spark techniques which we apply in order to avoid the use of masks results in sparked areas having a minimum linear dimension of a few tenths of a mm. Therefore, we are using the term milliprobe. In what follows, experimental results will be presented on two types of artificially prepared samples.

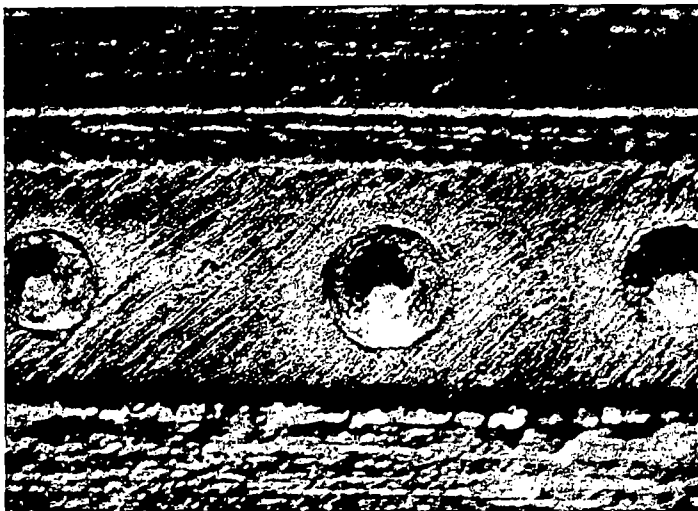
The purpose of the artificial samples was to demonstrate, first, the degree of control on the dimensions of the sparked area as effected by the quality and geometry of the probe electrode and by the manual manipulations of it under a 10-power magnification. Second, the ability to discern small impurity concentration differences in adjacent layers. Both types were prepared by milling a slot 0.02 inch wide into a small section of the base material. Into this slot a previously prepared strip of core material was placed. Intimate contact along the zone boundary was achieved by squeezing this sandwich in a small press. The character of a smooth surface integral sample was then achieved by milling the edge of the sample. This was followed by a cleaning and etching procedure.

Slide (1) shows a dimensioned isometric sketch of the electrodes as they are visible through a binocular microscope. The first artificial sample had a core of ultrapure titanium in a copper base. Our objective was to determine a 10 ppm copper impurity reported in this titanium. The severity of this test should be appreciated since it requires only a few stray sparks to the base material to produce copper line densities equivalent to that expected from the copper impurity in the core material for which an exposure consisting of a few million sparks is required. On the next slide (2) a light micrograph at 60 diameters magnification shows the layer structure and the size of the craters developed to produce the required exposure. It was possible to determine repeatedly the 10 ppm copper impurity in the titanium. The precision of these measurements was essentially the same as that of bulk impurity measurements, that is, within a factor or two. The onset of self-shielding is indicated by the point at which the linearity of a curve relating the total number of pulses and exposure ceases. In general, this does not begin until exposure levels in excess of 10^{-9} coulomb are desired. This implies that attempts to utilize the free spark techniques below 10 ppm may be hampered by electrode interference. In the present case no shielding effect was observed, presumably as a result of a favorable sparking characteristic. An unfavorable case occurred with our second type of artificial sample, where we tested our ability to distinguish between concentration differences of factors two and four. In this sample both the core and base were relatively pure aluminum samples. The iron content of the core was 30 ppm atomic, while that of the base was 60 ppm. In like manner for silicon, these values were 70 and 250 ppm. Experimental results are shown on the next slide (3). The following aspects of these experiments should be considered in evaluating the data. First, because of interferences, only isotopes with low abundances could be used. Second, and more significant, however, was a tendency towards an apparent equalization of concentration which results from the transfer of bulk material to the probe such that, in successive exposures from zone to zone, one finds the material of the previously sparked zone entering the sample in each following exposure. This is an effect of which we were not aware until later on in the work. Its result is always to yield ratios lower than the actual ratios. Third, a strong self-shielding effect caused additional difficulties. The next slide (4) showing a photomicrograph of spark craters in this sample reveals that, in order to obtain the sufficient exposure as required to avoid interferences and to reduce self-shielding, elongation of the normally circular craters was necessary. Nevertheless, the probe control is sufficiently good to allow one to track the zone properly as is clearly evident from the slide.



Slide 1.

ISOMETRIC VIEW of ELECTRODE STRUCTURE for MILLIPROBE ANALYSIS



Slide 2.

The solution to the bulk transfer problem lies in the proper selection of a sparking sequence and requires a separate clean probe for each zone. This sample also contained Mg, Cu, Zn, Pb and Sn as impurities, whose ratios were between 5 and 15. These were clearly observed and could naturally be more readily determined than those selected for our test.

We feel that it is significant that, in all samples we have so far examined, not a single instance of an inverted ratio was encountered, even when no attempt was made to avoid equalization. This, coupled with the fact that in most real analytical cases very little is known about the impurities and their ratios, gives emphasis to the usefulness of the milliprobe method; even if the data for a particular element were only qualitatively signified as being larger or smaller than its neighbor. A particular case of this type which successfully yielded to milliprobe analysis concerned the nitrogen content in a diffusion-strengthened Mo alloy specimen wherein the metallurgical properties of the core were markedly different from those observed in the rest of the sample. This case will be discussed in paper No. 103 on Friday, which discusses gases in metals using the spark source instrument.

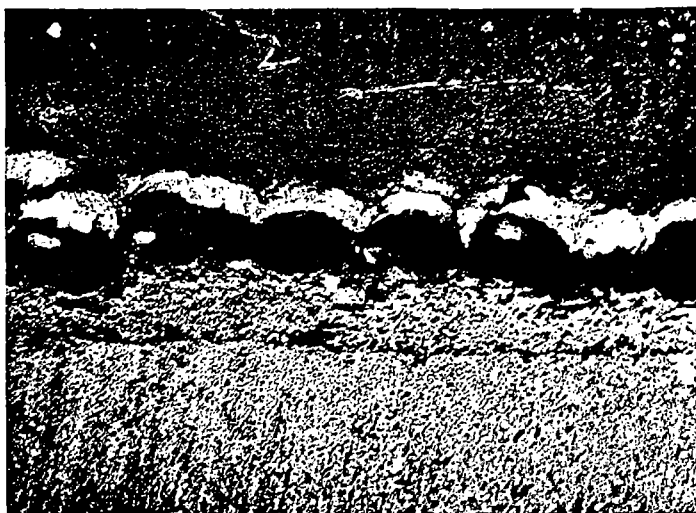
Some thought has also to be given to the selection of the probe material and its geometry. At first it appears sensible to strive for the sharpest possible point and use the same material in the probe as in the sample. However, it must be remembered that good sparking characteristics for the probe are quite important and that usually one does not have very much insight into what is to be expected from the base material. Also, an extremely sharp and hair-like point is subject to vibration and mechanical damage. We have experienced one instance in which a fine point was bent to a hook from contact with the bulk sample, and it became extremely difficult to obtain stable and intense sparking to the smooth sides of the hook. Mechanically breaking off the hook immediately restored the usual good sparking. Our probe electrodes are about 1/2 in. long and 1/2 mm in diameter, and are tapered over 3/4 of their length in a cone whose apex angle is between 3 and 10 degrees, and whose apex diameter is from 1 to 3 mils. Refractory materials of the highest possible purity lend themselves well to this application. An ultrapure Ti and some refined Mo have proved to be most useful in this work. Ta, W, Re, and Nb are other materials which merit investigation for particular cases. Any probe of material different from the sample demands a price in a reduced sensitivity. In addition the analyst must correct for the effect of the probe's contribution to the total charge as indicated on the exposure monitor. The weak exposure required for the matrix calibration curve may require as much as a factor of two corrections when the calculations involve the much longer exposures where the probe is completely coated with zone material. This is an extreme case, and in actual practice the lines due to the probe are always present though sometimes at reduced intensities. Therefore, the effect does not constitute a major error, and an estimate of its magnitude can easily be made. The next slide (5) shows a micrograph of the surface of a 10 mils thick Mo sheet in which several spark craters have been formed as a result of exposures using a zone-refined Mo probe of the type just described. The craters for the weaker exposures are difficult to show because they hardly mark the surface and consist of a scattering of small spark regions confined to an area about one mil in dia. As sparking progresses, however, a distinct crater appears which at first is dish-shaped but then becomes approximately hemispherical. The left side of the next slide (6) shows these crater diameters as a function of their corresponding exposures. It is evident from this curve that our selection of an artificial zone width of 0.5 mm was dictated primarily by the low level of impurities expected in the samples. We have found that, with careful probe control and when material sparking characteristic permits, impurities at the few ppm level can be determined in zones as small as 10 mils. On the right side of this slide another curve relates these same exposures to the volume of material removed from the craters. The volumes were calculated by assuming the craters to be segments of spheres and taking a depth and diameter measurement on each crater. Up to 10^{-8} coulomb, this latter relationship appears to be quite linear. Beyond this point the curve will undoubtedly break and flatten out as self-shielding effects arise, at which time the probe is usually being manipulated to maintain the average beam current such that crater diameter ceases to be a characteristic parameter. Also shown on this curve is the application

RATIO DETERMINATIONS OF Fe and Si IN Al

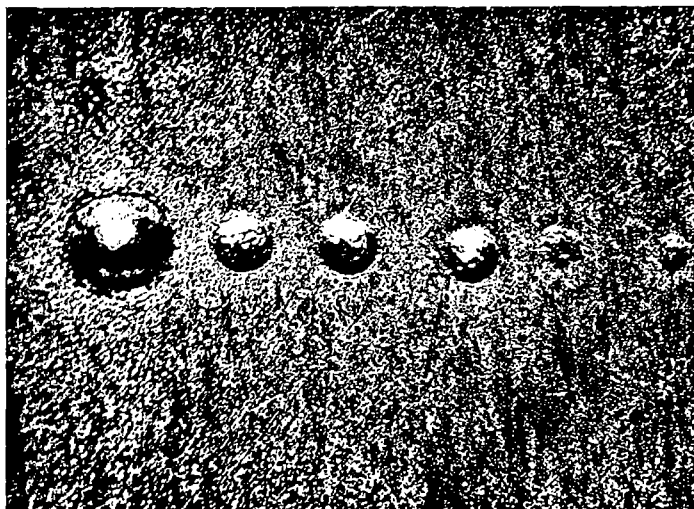
0.020 in. ZONE, Mo PROBE

$\frac{\text{base}}{\text{Ratio, core}}$	Fe	Si
Expected	2	4
Found	1.5 avg. of 2 detns.	2.6 avg. of 4 detns.
Based on	^{57}Fe	^{28}Si
% Isotopic abundance	2.19	4.7

Slide 3.



Slide 4.



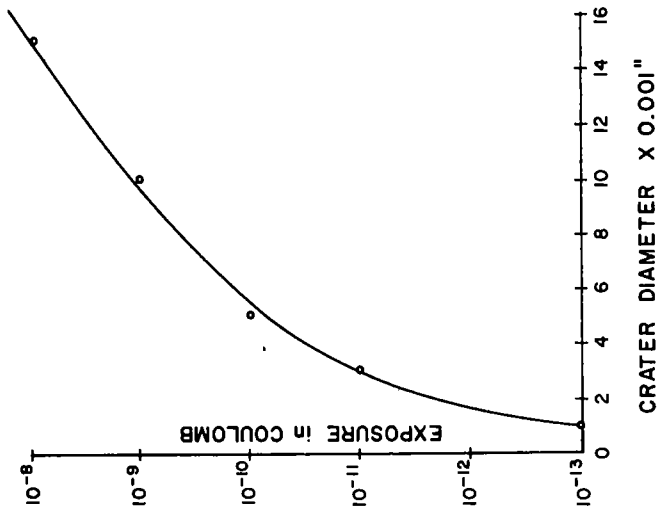
Slide 5.

of the density value for Mo resulting in a new set of abscissa values in micrograms of material removed. The amount of material usually consumed in probe work lies in the range of 1 to 100 μg .

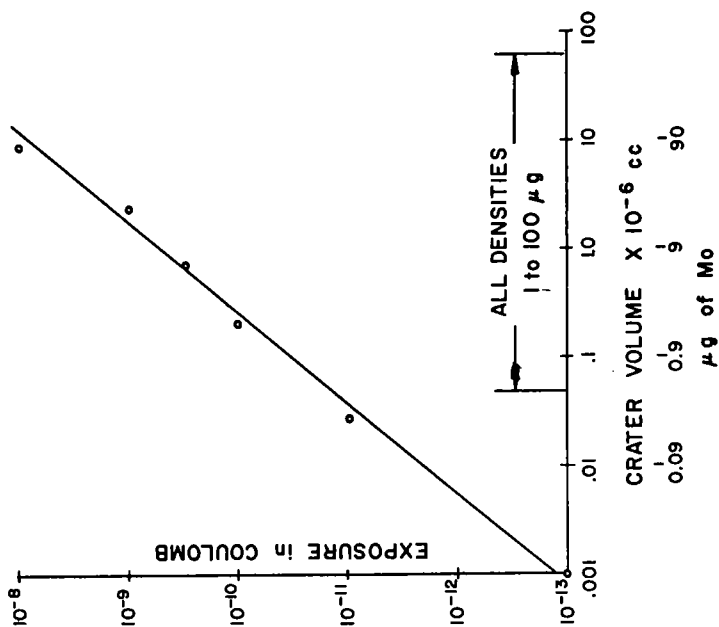
For densities ranging from 2 to 20 g/cc one covers the general range indicated above the abscissa. Of course, for different material systems the curve shown would not apply directly and in a few cases radical departure may occur. Nevertheless, we found these curves to be very useful in obtaining preliminary estimates of our ability to make analyses to required sensitivities. Using probes of refractory metals, the curves can be used with quite some confidence for most samples.

In summarizing, the use of an unconfined spark in milliprobe work appears to be a convenient and useful tool to investigate impurities and differences in impurities in structures having zones or inclusions whose dimensions fall in the range from 0.1 to 0.5 mm. The spark-source mass spectrograph therefore becomes a valuable complement to the electron microprobe, especially when simultaneous analysis of many elements is desired and whenever gases or elements of low atomic number are of interest.

EXPOSURE vs CRATER DIAMETER
for Mo-Mo SYSTEM



EXPOSURE vs VOLUME of MATERIAL
REMOVED, Mo-Mo SYSTEM



Slide 6.

A METHOD FOR STUDYING THE CHEMISORPTION AND EXCHANGE OF GASES ON SURFACES*

Y. L. Sandler and W. M. Hickam
Westinghouse Research Laboratories
Pittsburgh 35, Pennsylvania

Abstract

A mass-spectrometric method is discussed which makes it possible to obtain a detailed picture of chemisorption and exchange processes proceeding when a gas is adsorbed on a surface. Application of the method to the silver-oxygen system is described. O^{16}_2 + neon is preadsorbed on the silver; O^{18}_2 + argon is then allowed to react with the system. The inert gases are used in excess. A complete analysis of the concentration changes in the gas phase and adsorbed phase is made as a function of time without reference to adsorption isotherms. The information obtained on the adsorbed phase and other applications of the method are briefly discussed.

Introduction

Isotopic exchange methods provide a powerful tool in investigations of catalytic surface properties of solids.

In the following an exchange technique involving a preadsorbed gas will be discussed. The method reveals a considerable amount of detail of the adsorption process. The technique used here involves the use of two different inert gases, admixed (in excess) to the isotopic reactive gases. The amounts of the inert gases in the gas phase, which are unchanged by the oxygen adsorption, are determined by expansion into a standard volume. By measuring the changing composition of the gas phase at certain time intervals, the concentration of the active gases in the gas phase and the adsorbed phase can be accurately determined at any time, without reference to independently determined isotherms.

The details of the method and the type of information obtained will be explained by means of an example, viz. adsorption of oxygen on silver.

The Silver-Oxygen System

Silver forms one of the most interesting oxidation catalysts as far as efficiency and selectivity is concerned. Its ability to oxidize ethylene to ethylene oxide¹ and to form organic peroxides² are examples of its specificity. Previous studies of catalytic reactions of this kind and of adsorption^{3,4} and isotopic exchange⁴ phenomena with silver have indicated the existence of two types of oxygen chemisorption on silver, one dissociative, i.e. in form of atoms, and one molecular. The present work was undertaken to confirm tentative conclusions from previous exchange work⁷ and to determine the kinetics of the adsorption and the isotopic exchange as individual processes.

The high solubility of oxygen in silver causes difficulties in a quantitative oxygen exchange study because of diffusion to the surface of oxygen retained by the bulk or, conversely, by loss of adsorbed oxygen to deeper layers. Consequently, to desorb the oxygen, and also to clean the surface, in the present work the silver powder was first subjected to a prolonged heat treatment with hydrogen and oxygen at successively lower pressures, followed by pumping at 500°C. The reaction was studied at 200°C.

Experimental Procedure

Figure 1 shows a schematic diagram of the set-up. The center portion and the numbered valves, V, are standard equipment of a Consolidated Electrodynamics Mass-Spectrometer, model 21-103C. The 3 liter expansion volume and micro-manometer in this part are used for collecting and measuring the gas amounts withdrawn from the reaction vessel during sampling and in the final expansions for determining the total amounts of the inert gases present.

*Work supported by the Advanced Research Projects Agency and sponsored by the U. S. Army Electronics Research and Development Agency.

Table 1
Exchange of Preadsorbed O^{16}_2 + Ne with O^{18}_2 + A on Silver at 200°C

Measurements

Time Min.		Neon	A	MOLE %			Neon	Argon
				O^{16}_2	O^{16}_2	O^{18}_2	O^{16}_2	O^{18}_2
0	Admitted 25 mm O^{16}_2 + Neon	88.24		11.55		.05	7.64	
20	O^{16}_2 + Neon, No. 1	93.78		6.22			15.08	
50	Added O^{18}_2 + A 25 mm		92.11	.06	1.08	6.71		13.73
55	Sample No. 2	42.77	50.47	2.97	.53	3.26	14.40	15.48
65	Sample No. 3	42.90	50.22	3.27	.55	2.76	13.12	18.30
80	Sample No. 4	42.91	50.49	3.64	.68	2.28	11.79	22.14
110	Sample No. 5	42.70	50.71	3.92	1.06	1.60	10.86	31.69
170	Sample No. 6	43.12	50.41	4.07	1.59	.81	10.59	62.23
230	Sample No. 7	42.35	51.10	4.11	1.90	.54	10.30	94.63
290	Sample No. 8	44.18	49.48	4.02	1.97	.35	10.99	141.37

Table 2
Balance Sheet for Oxygens in Entire System

	cc. of Neon	A	O^{16}_2	O^{16}_2	O^{18}_2
O^{16}_2 + Neon added	2.7685		.3623	.0015	
Sample No. 1 withdrawn	.0494		.0032		
Balance:	2.7190		.3590	.0015	
O^{18}_2 + A Added		2.8501	.0018	.0334	.2076
	2.7190	2.8501	.3609	.0349	.2076
Sample No. 2	.0184	.0217	.0012	0.00023	.0014
	2.7005	2.8283	.3596	.0347	.2062
Sample No. 3	.0252	.0297	.0019	.0003	.0016
	2.6753	2.7986	.3577	.0344	.2045
Sample No. 4	.0228	.0268	.0019	.0003	.0012
	2.6524	2.7718	.3558	.0340	.2033
Sample No. 5	.0214	.0254	.0019	.0005	.0008
	2.6310	2.7463	.3538	.0335	.2025
Sample No. 6	.0227	.0266	.0021	.0008	.0004
	2.6082	2.7197	.3516	.0327	.2021
Sample No. 7	.0234	.0283	.0022	.0010	.0003
	2.5848	2.6914	.3494	.0316	.2018
Sample No. 8	.0215	.0241	.0019	.0009	.0002
	2.5632	2.6672	.3474	.0306	.2016
Removed at Room Temp.	2.5632	2.6672	.2244	.1122	.0195
Residuals	0.0	0.0	.1230	-.0816	.1821
Total O_2 added			.3642	.0349	.2076
Total O_2 removed			.2412	.1165	.0255
			.1230	-.0816	.1821

Heavy oxygen of about 92% O^{18} content* was mixed with argon and stored in a vessel, shown at the right end of Fig. 1. An envelope around the vessel for pumped liquid nitrogen makes it possible to recondense the unused portion of the gas mixture into the storage vessel. Oxygen was mixed with neon. 20 gram of silver powder was used in a quartz vessel of about 150 cc volume. The powder consisted of particles of about 10 micron diameter.

Results

To illustrate the principle of the measurements and the kind of result obtained, only one run will be discussed here. Table 1 gives the mass-spectrometric analyses for this run. About 25 mm Hg of the O^{16}_2 + neon mixture were bled into the system at 200°C and allowed to adsorb. The analysis of the admitted gas is shown in the first row of the Table. After 20 minutes the analysis given in the second row shows that about one half of the admitted gas was adsorbed. The analysis of the O^{18}_2 + argon mixture is given in the third row. After 50 minutes a dose of this mixture, about equal to the first dose but containing about one half the oxygen concentration, was admitted. An exchange of the oxygens now took place which can be recognized from the changes in the ratios inert-gas/oxygen given in the subsequent analyses: the ratio neon/ O^{16}_2 decreased (desorption of O^{16}_2) while the ratio argon/ O^{18}_2 increased (adsorption of O^{18}_2).

An analysis of the different oxygens in the gas phase and in the adsorbed phase can now be made. The system is completely determined by the measured ratios and by measurement of the amounts of inert gases withdrawn - in the samples and in the repeated final expansions of the remaining inert gases into the expansion volume.

Table 2 gives the total amounts of the various components in the various stages of the experiment. The changes occurring in the gas phase are represented graphically in Figure 2.

The amounts of the various types of oxygen and their totals are plotted versus time. Of the 0.36 cc of O^{16}_2 admitted, about one half is seen to be adsorbed. After 50 minutes 0.207 cc of O^{18}_2 , plus some $O^{16}O^{18}$ contained in the heavy oxygen, are admitted. It is seen from the curve "Total O_2 " that a further small adsorption takes place. Immediately upon contact of the O^{18}_2 , O^{16} is slowly evolved in molecular form while O^{18} is adsorbed. The initial lag in the evolution of $O^{16}O^{18}$ is in part due to the $O^{16}O^{18}$ content of the adsorbing O^{18}_2 . In the dashed curve "Generated $O^{16}O^{18}$ (Actual)" the portion of $O^{16}O^{18}$ remaining in the gas phase is deducted. For comparison, the other dashed curve "Generated $O^{16}O^{18}$ (Surface Equilibrium)" gives the $O^{16}O^{18}$ generation curve calculated from the actual concentrations of O^{16} and O^{18} on the surface under the assumption that a complete isotopic equilibrium is instantly established on the surface. From the disagreement of the two curves it is seen that adsorption and exchange are two distinct processes which, in the present case, occur at comparable rates.⁵

For the present discussion the important point is that the method is capable of giving a detailed picture of the adsorption process and facilitates a kinetic study of adsorption and exchange processes and individual reactions.

Conclusion

It is obvious that the method can be applied to other pairs of isotopic gases. The method should also more generally be useful for study of catalytic reactions between chemically different gases or in investigations of the mutual displacement of gases from surfaces.

* Procured from the Isotope Dept., Weizmann Institute of Science, Rehovoth, Israel.

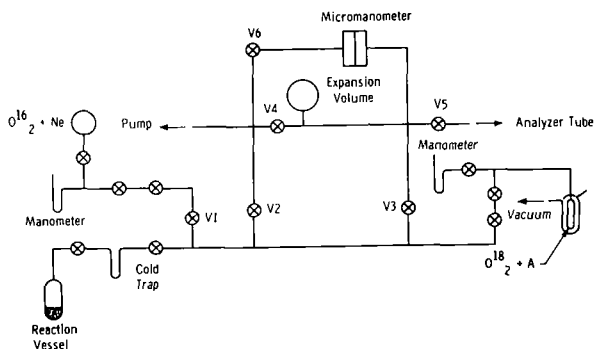


Fig. 1 - Diagram of Set-up on Mass-Spectrometer.

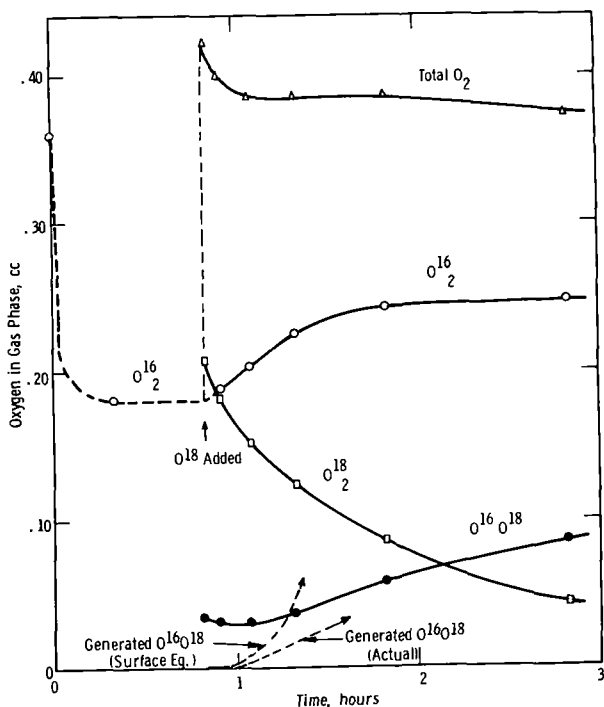


Fig. 2 - Exchange Experiment - Plot of the Amounts of the Various Oxygens in the Gas Phase Versus Time.

References

1. G. H. Twigg, Proc. Roy. Soc. (London) 188A, 92, 105, 123 (1946).
2. J. H. de Boer, "Second International Congress on Surface Activity", Butterworths (1957), Vol. II, p. 337.
3. Smeltzer, Tollefson and Cambron, Can. J. Chem. 34, 1046 (1956).
4. Meisenheimer, Ritchie, Schissler, Stevenson, Voge and Wilson, "Second International Congress on Surface Activity", Butterworths (1957), Vol. II, p. 299.
5. Meisenheimer, Ritchie, Schissler, Stevenson, Voge and Wilson, ref. 4, p. 307.

EVALUATION OF ACCURACY OF SURFACE IONIZATION
MASS SPECTROMETER DATA

H. O. Finley, M. R. Clickner, and E. E. Leuang, Jr.

In previous reports,^{1,2} two measurement methods were compared:

1. The "Four Component" method. This involved the measurement of the four uranium isotopes at the same total ion beam intensity and slit setting. With this technique, the relative ion beam intensities of the isotopes limit the optimum range positions of the vibrating reed electrometer, VRE, so that sufficient deflections for one or more minor peaks cannot be obtained. It was shown that these insufficient voltage deflections contribute a greater error than that shown by the large scale deflections obtained by the second method.

2. The "Direct Measurement" method. In this technique, the relatively larger peak deflections of the major isotopes obtained with a wide resolving slit are first compared. Then the signals of the minor isotopes, measured with a smaller resolving slit and slower amplifier response time, are compared to an ion signal of one of the major isotopes. This method was found to be generally more precise and accurate than the four component method.

In the present report, the direct measurement method is further evaluated for accuracy by analyzing National Bureau of Standards (NBS) certified standards in the 0.5 to 93.3 per cent U^{235} range. Although the differences found between the NBS values and the New Brunswick Laboratory (NBL) results for all four isotopes in most of the standards fell within the expected limits, the slightly larger per cent differences found for U^{235} in the region below 50% U^{235} prompted the preparation and analysis of gravimetrically prepared synthetic "standards" covering this range. The analyses of a uranium material in the normal range, also a one-to-one U^{235} to U^{238} content (50% U^{235} material) available from NBS, were also carried out.

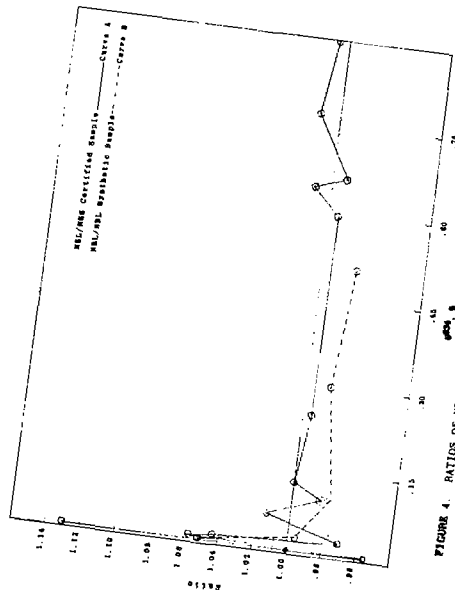
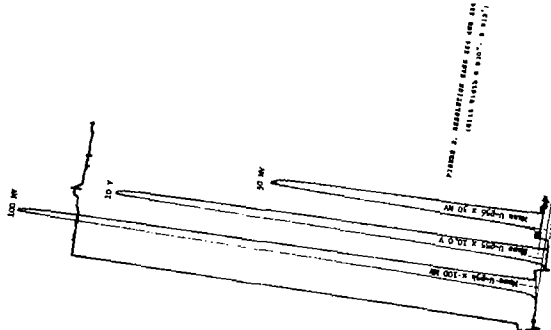
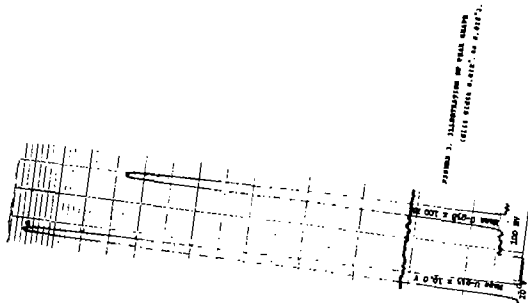
In the standardization of the instrument and procedure used to measure ion currents, certain conclusions were reached and are summarized briefly as follows:

1. The largest single error of measurement was due to the nonlinearity of the measuring recorder or to the vibrating reed electrometer and amplifier system.

2. The time constant for the vibrating reed electrometer with an input resistor of 1×10^{12} ohms contributed little to the inaccuracy if the currents are 10^{-15} ampere or higher. Also, the scan rates and resolution were sufficient to produce flat-top peaks; a 3 second or longer time on each peak assured adequate response as shown in Figures 1 and 2.

3. The many sources of noise from the mass spectrometer shielding, and pulses due to alpha particle activity contributed only a small error to currents above 10^{-16} ampere. Further, the voltage effect for different levels of intensities measured by the 1×10^{11} and 1×10^{12} ohm input resistors did not contribute significantly to the total nonlinearity of the measuring system. This latter conclusion was based on measurements with a constant current supply and the two input resistors which indicated that contributing errors were within the standard deviation of the data obtained with the U^{235} ion beam measurements.

4. The ionization processes were assumed to follow somewhat the processes associated with the Saha-Langmuir theory. It was believed that an equilibrium was reached which at the high ion production rates tended to "swamp out" any other competing mechanism at the temperature used: 2000°C for the center filament, 1300°C to 1800°C for the side filaments. Accordingly, it was believed to be unnecessary to apply a mass correction when measurements were of the U^+ ion. If such a correction were made, a measurement would result which would be completely out of line when compared to those of other instruments.



5. In measuring the small peaks at the 10^{-15} ampere level, impurities from all sources were considered. However, neither the $(K_6^{39})^+$ ion at mass 234 nor the $(K_5^{38}K^{41})^+$ ion at mass 236 were measured, since a resolution of about 1100 was sufficient to resolve them from the uranium peaks. There was no measurable uranium spectrum from the tungsten filament at 2100°C ; the amount present, therefore, did not contribute a measurable error when 10^{-4} to 10^{-5} g. samples were used. Other impurities were adequately reduced by cleaning the filaments in a vacuum system at temperatures above that necessary to vaporize the uranium.

6. With the use of a constant 15,000 volt ion source, no measurable source or voltage discrimination was present or measured, as magnetic scanning was used. Any other effects present were considered to be a part of the total error.

7. No measurable error existed due to the ion beam signal in the ion beam collector. The ion beam collector had a constant electron suppressor voltage supplied by batteries. The suppressors were at 45 volts negative, the defining slit 45 volts positive to ground. Also a U-shaped permanent magnetic field was parallel with the defining slit and the Faraday cage collector.

Experimental

The instrument was adjusted for optimum resolution, ion-source efficiency, transmission, etc. by analyzing NBS uranium standard No. 940. The complete series of NBS uranium isotopic standards from No. U-005 to No. U-940 containing from 0.48 to 93.27 wt. % U^{235} , were then analyzed. The data to be presented in graphical form are the ratios between the results obtained and the NBS nominal certification values. Also presented, is a comparison of the results on normal as well as the one-to-one (U^{235} to U^{238}) material prepared by NBS.

In Figure 3, Curve A, is shown the ratios between the NBL values and the NBS certificate values for the U^{235} . It can be seen that the differences from unity are very small and within the expected limit for the U^{235} isotopic levels above 20%. However, there are large differences for the U^{235} content at levels below 20%.

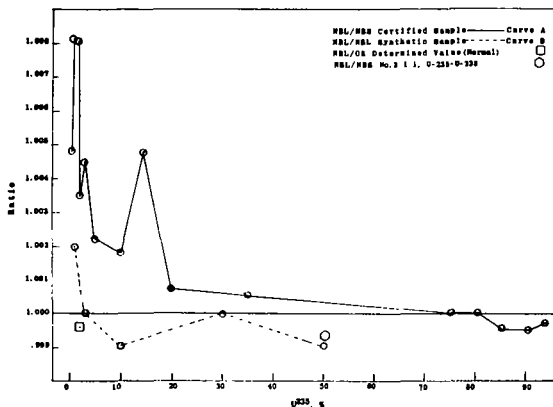


FIGURE 3. RATIOS OF NBS CERTIFIED VALUES AND NBL RESULTS FOR U^{235} .

The cross-over point on the curve is observed to be some point between 35 and 85% U^{235} . The exact point is uncertain because no certified standards are available for points between these two levels.

All points, then, below about 50% show a positive difference. It was for this reason that the study was continued with the preparation and analysis of synthetic "standards" with a U^{235} content of 1 to 50 wt. % (Curve B).

The results obtained with the synthetic gravimetrically prepared "standards" are shown in Figure 3, Curve B. As shown, the differences are not as pronounced for the synthetic standards as those shown for the NBS standards. The 1% level, however, still shows a positive instrumental difference. The differences appear to be negative for the 10% and the 50%, in contrast to those measured for the NBS standards which are always positive below 50%.

TABLE 1

NEW BRUNSWICK LABORATORY MEASURED VALUES OF
NATIONAL BUREAU OF STANDARDS CERTIFIED STANDARDS

<u>NBS No.</u>	<u>Wt. %</u> <u>U-234</u>	<u>S_x</u>	<u>NBS No.</u>	<u>Wt. %</u> <u>U-234</u>	<u>S_x</u>
<u>U-005</u>			<u>U-050</u>		
NBS ($\pm 10\%$)	0.0023		NBS ($\pm 5\%$)	0.0280	
NBL	0.0026	0.0001	NBL	0.0272	0.0001
Difference	0.0003		Difference	- 0.0008	
<u>U-010</u>			<u>U-100</u>		
NBS ($\pm 10\%$)	0.0054		NBS ($\pm 1\%$)	0.0670	
NBL	0.0054	0.0001	NBL	0.0680	0.0010
Difference	0.0000		Difference	0.0010	
<u>U-015</u>			<u>U-150</u>		
NBS ($\pm 10\%$)	0.0090		NBS ($\pm 4\%$)	0.0990	
NBL	0.0086	0.0001	NBL	0.0973	0.0013
Difference	- 0.0004		Difference	- 0.0017	
<u>U-020</u>			<u>U-200</u>		
NBS ($\pm 8\%$)	0.0120		NBS ($\pm 4\%$)	0.1250	
NBL	0.0127	0.0003	NBL	0.1250	0.0020
Difference	0.0007		Difference	0.0000	
<u>U-030</u>			<u>U-350</u>		
NBS ($\pm 5\%$)	0.0180		NBS ($\pm 4\%$)	0.2490	
NBL	0.0188	0.0001	NBL	0.2478	0.0004
Difference	0.0008		Difference	- 0.0012	

Note: Values in parenthesis are relative uncertainties reported on NBS certificates.

TABLE 2

NEW BRUNSWICK LABORATORY MEASURED VALUES OF
SYNTHETIC "STANDARDS"

<u>Standard</u>	<u>U-234</u> <u>95% C. L.</u>	
<u>No. 1</u>		
Calculated Wt. %	0.0097	0.0001
Measured Wt. %	0.0102	0.0003
Difference	0.0005	0.0003
<u>No. 3</u>		
Calculated Wt. %	0.0299	0.0003
Measured Wt. %	0.0296	0.0010
Difference	- 0.0003	0.0010
<u>No. 10</u>		
Calculated Wt. %	0.1017	0.0009
Measured Wt. %	0.0993	0.0017
Difference	- 0.0024	0.0019
<u>No. 30</u>		
Calculated Wt. %	0.303	0.003
Measured Wt. %	0.299	0.002
Difference	- 0.004	0.003
<u>No. 50</u>		
Calculated Wt. %	0.506	0.004
Measured Wt. %	0.495	0.002
Difference	- 0.011	0.005

An NBS prepared 50% material is also shown (NBS No. 3). The sample is composed of equal amounts of U^{235} and U^{238} atoms and the ratio is known to 0.1 of a per cent or 1.000 ± 0.001 . The NBL measured ratio was 1.0006 for four charges of material. This result is in excellent agreement with the known NBS value. It thus also confirms the assay of the NBL synthetic 50% material.

A normal uranium was analyzed and found to contain 0.7104 wt. % U^{235} . The value determined by a gas instrument at Oak Ridge for this material is 0.7107 wt. %. This difference is also shown in Figure 3.

The standard deviations attached to the NBL values are very low and do not completely account for the differences shown.

The results obtained with the NBL gravimetrically prepared "standards" for the 1 to 50% synthetic U^{235} also have very low standard deviations. The 95% C. L. for the difference in the 10 and 50% synthetic do not account for the measured difference, while the confidence limits for the 1, 3, and 30% standards do not indicate a significant difference between the calculated and the measured values.

Before any conclusions can be drawn, it is necessary to evaluate the data or measurements of the small peaks. The 234 comparison is shown in Figure 4.

As shown by Figure 4, Curve A, there is a random distribution of the differences, but these differences are well within the error certified by the NBS.

Figure 4, Curve B, indicates the agreement between the U^{234} (gravimetric value) determined from the primary standard materials selected to blend the synthetic materials, and the NBL measured values. These comparisons are well within the NBS limits for these small values.

Tables 1 and 2 show the differences and confidence limits.

There were several considerations taken in regards to the evaluation of data. It was desirable to report a total error with due regard to accuracy based on the NBS certified values, rather than only internal precision or the average precision based on repetitive analyses. In the process of evaluating the accuracy of the NBL values, the following considerations were felt to be most important:

1. The tendency to correct for bias and report a small error rather than report the bias, which may change from time to time, as a part of the error, was considered not acceptable, if the reported confidence limit is smaller than that of the standards used.
2. Each level of NBS material had to be evaluated. A procedure for the position of the range switches, recorder deflection, pressure, temperature and many other conditions had to be evaluated as to their effect on the mean value. The instrument, therefore, had to be under control at all times.
3. Control charts had to be prepared to determine the average precision acceptable.
4. The internal precision of a measurement had to be evaluated and included in the total error or as a part of the confidence limit reported.

The method used at NBL is considered to be an absolute method in that no corrections are made in the data recorded or the reported value. The reported values have confidence limits which are a function of the accuracy based on the NBS isotopic standard for the equivalent level of U^{235} , plus the precision of the measurement. The internal precision must fall within the control limits or the data is rejected.

An estimate of the total error is determined by the use of the following method: First, the average reproducibility is determined. Figure 5 and 6 show graphically the reproducibility as obtained from a number of independent analyses. The following are included:

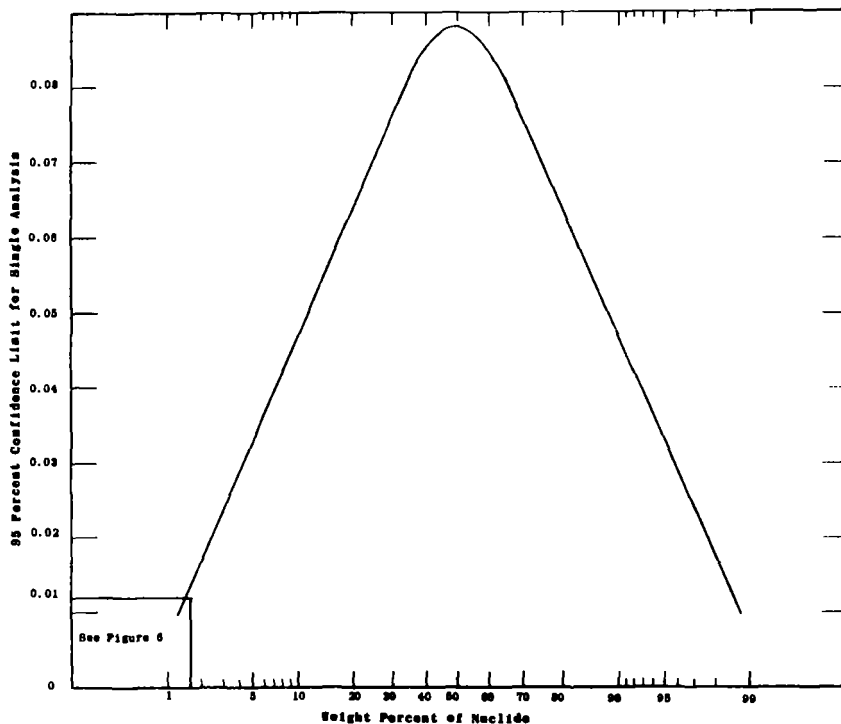


FIGURE 5. UNCERTAINTIES FOR U^{235} AND U^{238} DETERMINATIONS.

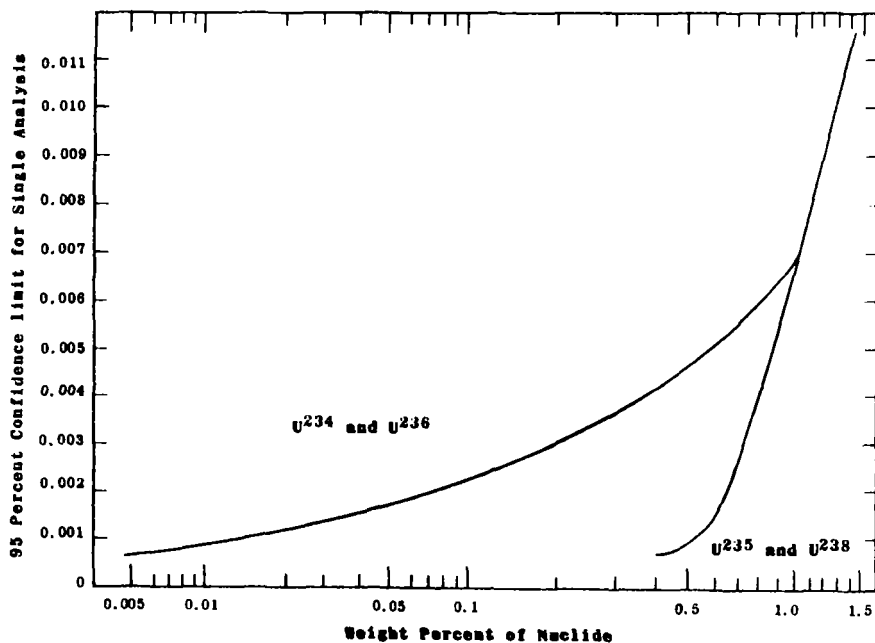


FIGURE 6. UNCERTAINTIES FOR U^{234} , U^{235} , U^{236} , AND U^{238} DETERMINATIONS.

1. One of each of the NBS standard samples, 0.5 to 93 per cent U^{235} .
2. One of each of five NBL synthetic standard samples through the range 1 to 50 per cent U^{235} .
3. A few normal and 1% U^{235} standards and analytical samples.

The method given below then was used to establish the total error for the analysis of unknowns and is illustrated in Tables 3 and 4.

TABLE 3

EVALUATION OF RESULTS OF NBS $U-O_3O$

<u>NBS $U-O_3O$ (3% U^{235})</u>	<u>U^{234}</u>	<u>U^{235}</u>	<u>U^{236}</u>	<u>U^{238}</u>
Certified Value, Wt. %	0.018	3.01	0.020	96.95
NBS Estimated Uncertainty	$\pm 5\%$	$\pm 0.5\%$	$\pm 5\%$	$\pm 0.05\%$
NBL Measured Value, Wt. %	0.0188	3.024	0.0202	96.938
Standard Deviation	0.0001	0.001	0.0002	0.001
Reproducibility (Figure 5)		± 0.025		
Difference between NBL and NBS		0.014		

1. A standard was analyzed. A control chart was used to determine the difference in the value obtained with the control value obtained for that standard to date with the same instrument settings. For this measurement, the two numbers were equal, 3.024; therefore, it was acceptable.

2. The confidence limit for this range was then taken from the reproducibility curve, Figure 5. It was found to be 0.025.

3. The difference was determined between the NBL and NBS value. The value was 0.014.

4. The unknowns were then analyzed. The results for four different aliquots of uranium oxide are shown in Table 4. The reproducibility is shown

TABLE 4

UNKNOWN SAMPLES

<u>Sample No.</u>				
1	0.0189	3.003	0.0190	96.959
2	0.0195	3.004	0.0192	96.957
3	0.0194	3.006	0.0195	96.955
4	0.0194	3.008	0.0191	96.953
Mean	0.0193	3.005	0.0192	96.956
Std. Dev. (Ind. Meas.)	0.0003	0.002	0.0002	0.003

$$\text{Error} = 0.014 \pm \sqrt{0.025^2 + 0.015^2} = 0.014 \pm 0.029$$

but not used in the calculation of the reported error.

5. Each individual measurement or analysis is evaluated by use of control charts and if acceptable, the following error or accuracy is reported for all unknowns in the 3% range:

$$\begin{aligned} \text{The difference } 0.014 \pm \sqrt{(\text{NBL Reproducibility})^2 + (\text{NBS Uncertainty})^2} \\ = 0.014 \pm \sqrt{0.025^2 + 0.015^2} = 0.014 \pm 0.029. \end{aligned}$$

Each sample was assigned this error (± 0.029) until another standard was run or another U^{235} range was to be evaluated.

Conclusions

1. By analyzing a series of NBS uranium isotopic standards, it was found that the direct measurement method and instrumentation were satisfactory for the analysis of all levels of U^{234} , U^{235} , and U^{236} . Most of the measurements agreed with the NBS values within the NBS assigned uncertainties. The values that do not fall within the assigned uncertainty assume a larger error.

2. The values obtained with the NBS standards for U^{235} indicated a positive difference in the 1 to 50% range. The analysis of synthetic, gravimetrically prepared standards in this range also indicated a positive difference at the 1% level. The reason for the different levels at which positive difference occurs cannot be explained at the present time. Further studies must be made to determine the cause of the positive difference below 50% U^{235} and the apparent negative difference above 50% U^{235} .

3. A systematic procedure is presented to permit the reporting of an isotopic measurement with an error which includes accuracy based on NBS standards for each level of U^{235} from 0.5 to 93% U^{235} . This systematic procedure is especially useful when evaluating differences between methods, instruments, or laboratories. Also, it has been shown that gravimetrically prepared materials may be useful in determining the accuracy of instruments or methods when determining small concentrations of U^{234} and U^{236} rather than procedures using a spiking method.

REFERENCES

1. Finley, H. O. and Leuang, E. E., Jr., NBL-159 (May 1960), p. 108.
2. Finley, H. O. and Leuang, E. E., Jr., NBL-170 (August 1961), p. 74.
3. Finley, H. O. and Leuang, E. E., Jr., "Ibid.", p. 67.
4. Payne, E. C., NBL-153 (June 1959), p. 48.
5. Finley, H. O., Clickner, M. R., and Leuang, E. E., Jr., NBL-188, (December 1962), p. 73.

MASS SPECTROMETRIC STUDY OF SODIUM AND RUBIDIUM DIFFUSION IN TUNGSTEN

H. M. Love and J. J. White*
Department of Physics
Queen's University
Kingston, Ontario, Canada

ABSTRACT

The method described by Love and McCracken (1) to measure the diffusion of alkali metals in tungsten has been extended.

Sodium atoms were allowed to diffuse through a tungsten ribbon in the form of a single crystal. The ribbon constituted the surface ionization source for a mass spectrometer in which the ions emerging from the ribbon were analyzed. The use of an electron multiplier detector made possible the detection and measurement of the small ion currents necessary for significant measurements of diffusion coefficients for sodium.

Results will be presented for the diffusion coefficients of sodium and rubidium in tungsten.

* Present address: University of British Columbia.

1 Love and McCracken, Canadian Journal of Physics, 41, 83 (1963).

PRECISION, ACCURACY, AND SENSITIVITY IN SPARK MASS SPECTROMETRY

By: C. M. Judson and C. W. Hull

Consolidated Electrodynamics Corporation
Pasadena, California

The study of accuracy in spark mass spectrometry reported at this meeting last year by C. W. Hull¹ has been extended with emphasis on empirical approaches to calibration and to corrections in analysis. We have tested the accuracy of analyses based on sensitivity coefficients referred to standards of known concentrations by analysing two different Bureau of Standards iron samples. The measured sensitivity coefficients J_x are shown in Table I, each value being an average of several measurements, usually two different isotopes at two different exposure levels. The precision, measured as average deviation between measurements at different exposure levels, is not as good as in some of our previous work. However it is good enough to permit some significant observations about differences in sensitivity between samples and between elements.

Table I
Sensitivity Coefficients

at. wt.	element	sample S-466		sample S-463	
		J_x	av. dev.	J_x	av. dev.
11	B	----	---	0.15	15%
48	Ti	3.4	15%	6.1	10%
51	V	1.7	5%	2.7	18%
52	Cr	1.4	5%	2.5	5%
55	Mn	2.1	5%	1.3	5%
59	Ni	1.3	10%	0.5	15%
59	Co	0.9	5%	1.2	5%
64	Cu	2.2	50%	0.7	5%
73	Ge	6.1	5%	2.6	10%
75	As	7.0	5%	1.3	45%
91	Zr	0.39	5%	1.3	5%
93	Nb	1.0	15%	1.0	20%
96	Mo	0.7	15%	0.5	5%
108	Ag	18.0	5%	1.7	10%
119	Sn	4.8	15%	1.6	50%
181	Ta	0.45	---	0.37	5%
184	W	0.31	---	0.20	10%
207	Pb	9.3	5%	2.0	33%

The significant conclusions which we have drawn are:

1. There are significant variations in sensitivity between elements. In spite of differences between samples, accuracy of analysis will be better if sensitivity coefficients are used than if they are ignored.
2. Any consistent variation in plate sensitivity with mass is disguised by larger specific element effects.
3. A few elements which show particularly high sensitivity coefficients in one sample also show poor agreement between samples and between measurements.

The probable cause of high and non-reproducible sensitivity appears to be either overheating of the sample or lack of control of accelerating voltage. We plan to carry out experiments to determine whether either or both of these effects are actually causing significant errors. While use of a low voltage vibrator spark, as suggested by Hintenberger², offers one possible method of minimizing errors from these sources, it is not clear that this is the only way, or even the best way, to solve this problem.

The method of analysis used in obtaining these data requires first a calibration curve relating exposure in coulombs to optical transmittance of the plate. Typical calibration curves are shown in Fig. 1. The experimental points generally fit the curve within 25%. We have previously given an equation for the calibration curve for Ilford Q2 plates in the form:

$$\frac{T - T_{\infty}}{1 - T_{\infty}} = \frac{1}{1 + (KE)^R} \quad (1)$$

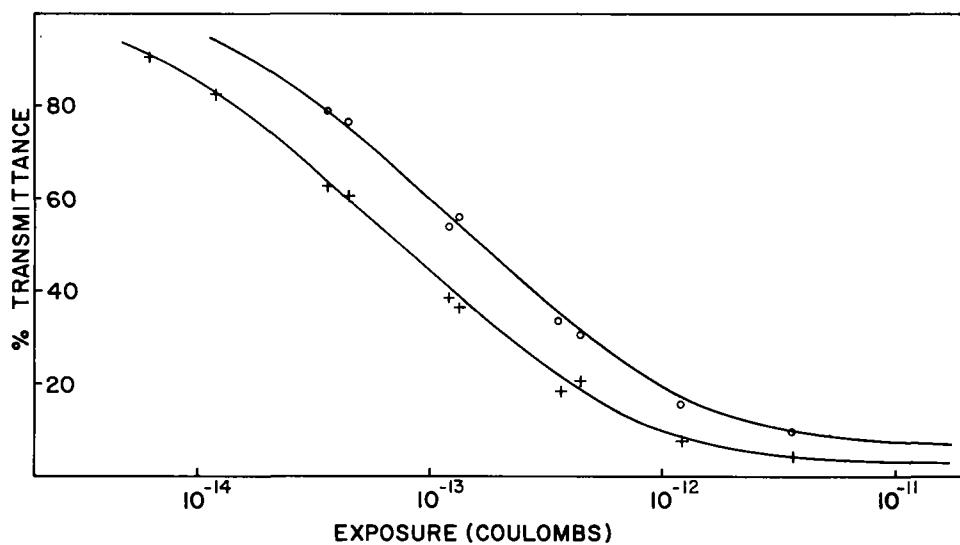


FIG. 1

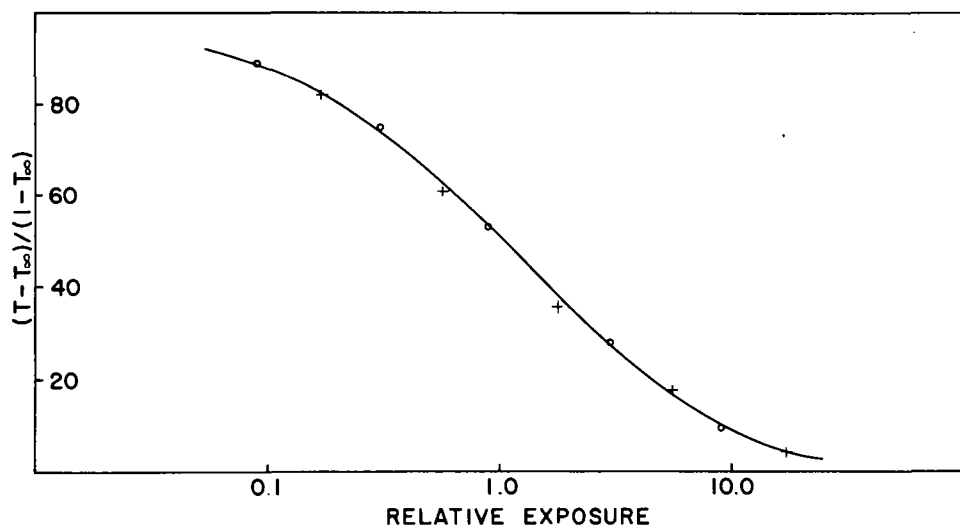


FIG. 2

where T is the minimum transmittance of a line due to an exposure E , T_{∞} is the transmittance at very large E , and K and R are constants. This equation can be written in a simpler form defining the left hand side of equation (1) as normalized transmittance T' and defining KE as normalized exposure E' so that the constants K and T_{∞} are eliminated:

$$T' = \frac{1}{1 + (E')R} \quad (2)$$

The two curves in Fig. 1 represent plates from two different batches with significantly different values for K and for T_{∞} . Expressed in normalized form T' vs E' , however, they both fit the same curve as shown in Fig. 2. The constant R is the same for these two plates, is nearly constant for all Q2 plates, and is near to unity. T_{∞} is a constant for a particular batch of plates which may change slowly with age. The sensitivity coefficient K is apparently variable between individual plates.

Equation (1) can be written in a rearranged form

$$(KE)^R = \frac{1 - T_{\infty}}{T - T_{\infty}} \quad (3)$$

The coefficient R can be determined by writing equation (3) for two different values of E and dividing and the coefficient K can then be determined. The calibration curve can be obtained most objectively by such a calculation of values for R and K but in most cases a satisfactory calibration can be obtained by simply drawing a curve through the experimental points.

If one wishes to fit the data to a curve without making any assumptions about the form of the curve, the isotope ratio method of Owen³ can be used. We find that the isotope ratio method requires more measurements to get the same precision than calibration using equation (1) and do not generally use this method.

Calibration curves can also be made by plotting $\log T$ against E or against $\log E$. Straight lines can be obtained in these curves over a limited range. Care must be exercised not to extrapolate these straight lines beyond the region of application. The straight line in the $\log T$ vs $\log E$ plot fails at transmittances above 50%. The straight line in the $\log T$ vs E plot fails at transmittances below 70%. Since one commonly works in the region of 50% transmittance, the linear regions of these curves are of limited use. One can obtain a reasonably good linear plot over a wide region based on equation (3) by plotting E^R or approximately by plotting E against $(1 - T_{\infty}) / (T - T_{\infty})$. However, it is not clear that a plot in this form is as useful as a simple calculation from the equation.

Correction for unexposed plate transmittance should be made both in calibration and in analysis by dividing all observed transmittances by a transmittance representing a nearby unexposed region of the plate. Where there is a background contribution from nearby lines, one must also make a correction for background exposure, the observed exposure being the sum of the exposure in the line and the background exposure. This is best seen by writing the complete equation for the exposure:

$$E_x = Q_T A_x C_x \left(\frac{W_o}{W_x} \right) J_x + E_B \quad (4)$$

where E_x is the exposure observed in a line due to a particular isotope of a particular element, Q_T is the total charge on the beam monitor, A_x is the abundance of the isotope, C_x is the concentration of the element in the sample, (W_o/W_x) is the ratio of the widths of the standard and unknown lines, J_x is the overall sensitivity for a particular element in a particular matrix, and E_B is the background exposure. The background exposure is calculated from the background transmittance immediately adjacent to the line, corrected for plate transmittance as are all transmittances.

The width correction term arises from the fact that plate darkening is determined not by total number of ions but by number of ions per unit of line width. The line width is obtained by determining E_x and E_B from the line and background transmittances using the calibration curve and calculating $E_{1/2}$ by the equation:

$$E_{1/2} = \frac{E_x - E_B}{2} + E_B = \frac{E_x + E_B}{2} \quad (5)$$

The calibration curve is then used to calculate $T_{1/2}$ corresponding to $E_{1/2}$ and the width on the densitometer chart is measured at $T_{1/2}$.

In calibration the terms C_x and J_x are generally unity by definition and the background and width corrections can generally be neglected so that E_x becomes simply Q_{TA_x} . If background or width corrections are required in calibration, they must be made by approximation methods.

For analysis one uses the complete equation (4) rearranging to solve for C_x . Where J_x is not known it may have to be assumed to be unity even though this may not be a very good assumption.

The overall sensitivity coefficient J_x for impurity x in matrix m referred to calibration with element s can be considered to be made up of four terms:

$$J_x = \frac{I_x K_x}{I_m K_s} \quad (6)$$

where K is the pure element sensitivity coefficient as defined by equation (1) and I is a relative ionization efficiency coefficient referred to the yield of ions at the beam monitor.

Acknowledgement:

The experimental data reported were obtained by R. F. Howard.

References:

1. C. W. Hull, Photographic quantitative analysis with a solids spark mass spectrograph, ASTM Mass Spectrometry Conference, 1962.
2. H. Hintenberger, Instrumentation and techniques of high resolution mass spectrometry, ASTM Mass Spectrometry Conference, 1963.
3. Edward B. Owens, Ion charge distribution in an RF spark ion source and its effect on quantitative analysis, ASTM Mass Spectrometry Conference, 1962.

ANALYTICAL TECHNIQUES*

by

Arthur J. Socha and Robert K. Willardson
Bell & Howell Research Center
Pasadena, California

ABSTRACT

Substantial progress on the problem of rapid, accurate mass spectrographic analyses has been made. For spark source analyses, a dual sample holder is utilized to facilitate comparative results. Samples and sample holders are cleaned in situ by a glow discharge prior to sparking. Cryopumping is used to minimize water and hydrocarbon backgrounds. The line densities recorded on photographic plates are converted into parts per million of impurity concentration using a computer. The programming of the computer involves corrections for background, plate sensitivity, ion mass, isotopic abundance, and multiple ionization. Methods have also been developed to permit accurate concentration determinations from doubly charged ions.

* * * * *

INTRODUCTION

The analysis of semiconductor materials by mass spectrographic methods was first demonstrated in 1954 by Hannay⁽¹⁾ and Ahearn.⁽²⁾ Since that time improved instruments based on their version of a double focusing spark source mass spectrometer have been developed^(3,4) and have been used for the analysis of semiconductors and other solids.

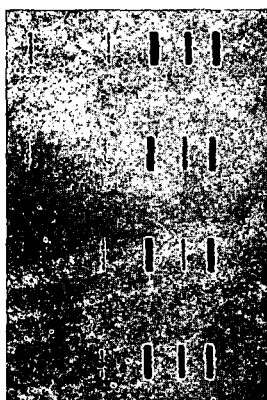
Photographic plates are often used as the ion collector because of their ability to integrate ion exposures over long periods of time. Ions strike the plate and produce a permanent record of both the sample impurities and their concentrations. The analytical techniques described here are those which were developed for the analysis of solid samples using a spark source mass spectrometer and include the procedures developed for the determination of impurity concentrations of materials from a photographic collector.

Sample Handling and Sparking Techniques

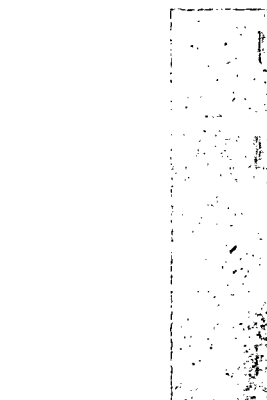
Dual Sample Holders. Comparative analytical results between samples are often as informative as the actual impurity concentrations of each sample. In order to provide a better comparison between one sample and another on the same photographic plate, a set of dual sample holders were constructed with which two pairs of samples could be mounted. The sample holders were constructed of tantalum⁽⁴⁾ and not only improve the accuracy of comparative results, but also permit two samples to be analyzed with the same pumpdown of the mass spectrometer. Comparative results are especially useful in the study of the properties of semiconductors and the distribution of impurities in zone refined materials.

Sample Preparation. Samples are cut into bars approximately 2 x 2 x 10 mm and then chemically etched to remove gross surface contaminants which may have been introduced during cutting and handling. Samples which are either of small size, fragile structure, or have low electrical conductivity are potted in indium prior to placing them in the sample holders. This technique insures good electrical contact between the sample and the holder, besides alleviating any mechanical stress placed on fragile crystals and platelets.

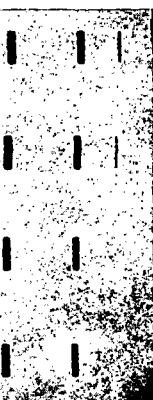
* Supported in part by Aeronautical Research Laboratories, Office of Aerospace Research, U. S. Air Force.



13



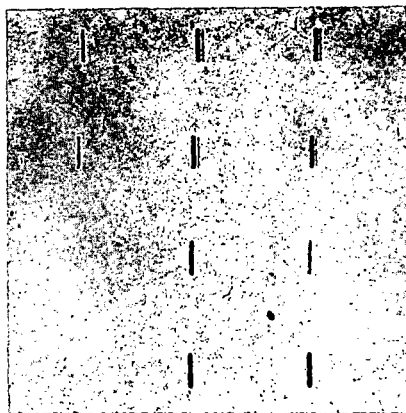
14



17

18

Figure 1. Section of photographic plate showing effects of N_2 flushing, cryogenic pumping, and cathodic etch.



26

27

28

Figure 2. Section of photographic plate showing effects of N_2 flushing, cryogenic pumping, and cathodic etch.

Indium was selected as potting material because its low melting point reduces the possibility of diffusion of material into the sample. Furthermore, its two isotopes generally do not interfere with normal analysis (in the case of a stray spark).

Reduction of Contaminants. The reduction of contaminants in the ion beam is an important factor in accurate mass spectrographic analyses. Residual gases in the source are ionized and are difficult to distinguish from similar ions arising from impurities in the sample. The photographic plate also experiences heavier backgrounds from ions which are scattered by excessive residual gases in the instrument.

The following procedures were developed for minimizing residual gases in the source and collector sections of the instrument and for the removal of surface impurities from the sample just prior to sparking.

Upon placing the samples in the instrument the source sector is pumped out and then flushed with dry nitrogen. Following the dry nitrogen flush a cathodic etch is used to remove surface impurities from the sample. This is accomplished by initiating a glow discharge with 5000 volts in a nitrogen atmosphere of about 25 microns.

High vacuum is obtained in the instrument utilizing three diffusion pumps which are cold trapped with liquid nitrogen. When ultimate pressures are reached using these conventional diffusion pumps, cryogenic pumping is used in the source and collector sections of the instrument. This is accomplished by filling with liquid nitrogen, dewars located in the source and collector sections. These dewars are filled following the cathodic etch and the additional pumping usually reduces pressures by a factor of 2 or 3.

Figures 1, 2, and 3 are segments of the same photographic plate each showing the effects of the nitrogen flush, cathodic etch, and cryogenic pumping. The exposures shown in these figures are 3×10^{-8} coulomb exposures and were made in the following manner: The top exposure was made after the samples were chemically etched; the second exposure following the dry nitrogen flush; and the third after cryogenically pumping source and collector sections of the instrument. Exposure 4 was made following the cathodic etching of the sample and the cryogenic pumping of the instrument. In Figure 3, the fifth exposure was made without the cryogenic pumping of the collector sector only.

In Figure 1, the reduction of CH at mass 13, the reduction of OH and NH₃ at mass 17, and H₂O at mass 18 are readily apparent following cryogenic pumping. The slight increase in NH₃ after the cathodic etch on the fourth exposure indicates the addition of this compound by the nitrogen ion bombardment of the cathodic etch. In Figure 2, the reduction of hydrocarbons at masses 26, 27, and 28 is apparent following the N₂ flushing. The complete absence of these lines occurs after the cryogenic pumping in the third exposure. At mass 28 there is also a reduction of CO after the cryogenic pumping. The increase of N₂ at mass 28 on the last exposure is from the cathodic etch. In Figure 3, covering masses 40 to 44, note the reduction of hydrocarbons after each procedure and the reduction of CO₂ at mass 44. The decrease of calcium is readily apparent at mass 40 after the cathodic etch, indicating that the calcium in the first three exposures is a surface impurity on the sample.

Table I shows the partial pressures at 10^{-9} Torr which were obtained prior to the sparking of the sample shown in Figures 1, 2, and 3. These partial pressures were obtained from a residual gas analyzer which is located in the source sector of the instrument.

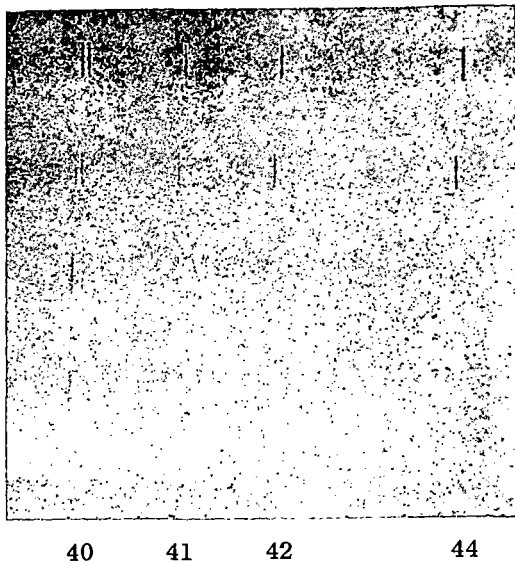


Figure 3. Section of photographic plate showing effects of N_2 flushing, cryogenic pumping, and cathodic etch.

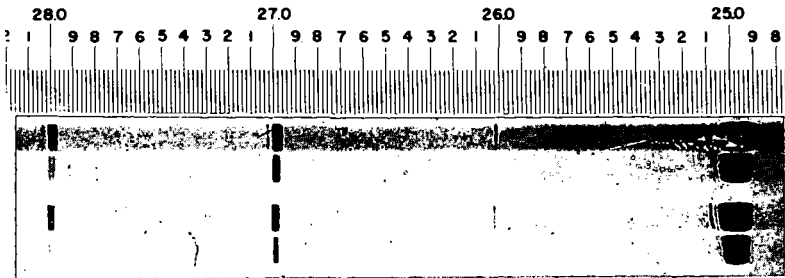


Figure 4. Enlargement of a mass scale with a portion of a photographic plate.

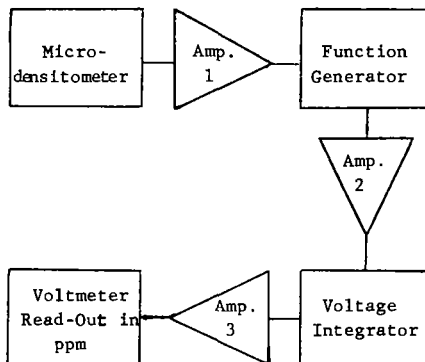


Figure 5. Block Diagram of a Computer Arrangement for the Integration of Mass Lines

TABLE I. PARTIAL PRESSURES OF RESIDUAL GASES
($\times 10^{-9}$ TORR)

Mass	Chemical Etch	After N ₂ Flushing	After Cryopumping	After Cathodic Etch and Cryopumping
14	8	4	3	3
15	8	2	2	2
16	35	15	6	5
17	110	70	20	20
18	300	200	48	40
28	110	60	45	50
30	13	4	3	2
44	53	25	13	12

In reference to Table I, the partial pressures after the N₂ flush indicate that a general reduction in the overall pressure of the source was obtained. The largest reductions, however, were in the hydrocarbons at masses 14, 15, and 16. Substantial reductions in partial pressures are noted following the cryopumping of the source and collector sections. This is especially true of H₂O and HO. The variations in partial pressures following the cathodic etch are slight. The cleaning action of the cathodic etch, however, was indicated by the reduction of calcium at mass 40 in Figure 3.

The systematic reduction of contaminants in the instrument permitted an increase in sensitivity of the analyses because of the general reduction of pressures in both the collector and source sections of the instrument. This allowed heavier exposures to be made without an increase in background from ions scattered by residual gases in the collector section. Referring again to Figure 3, the first, second, and fifth exposures were performed without cryogenic pumping. The darker backgrounds indicate the importance of low gas pressures in the instrument.

QUALITATIVE ANALYSIS

Mass Scale. Data is obtained from the mass spectrometer by the interpretation of the lines which appear on the photographic plate. To facilitate the identification of these lines, a mass scale was developed which is dimensionally proportional to the square root of the mass of the ions. This scale permits the rapid identification of mass lines to the fraction of a mass number as shown in Figure 4. This figure is an enlargement of a portion of the mass scale which is 15 inches long and covers masses 1 to 40. A portion of a photographic plate is located beneath the scale. At mass 25 one of the matrix components is identified at $^{75}\text{As}^+$. At mass 26, C₂H₂ is easily identified occurring at mass 26.015. The lines at mass 27 are aluminum and C₂H₃ and at mass 28 are, from right to left, silicon, CO₂, N₂, and C₂H₄, all of which are easily identified. A number of these mass scales were developed, each one covering a given group of mass numbers which correspond with different magnetic field strengths of the mass spectrometer.

QUANTITATIVE ANALYSIS

General Procedure. After completing the identification of the lines on the photographic plate, the following techniques were developed for the conversion of the line densities into impurity concentrations. A microdensitometer is used to scan the line to be analyzed. The density of the line is dependent on the numbers of ions which have struck the photographic plate at that particular mass number. The density and width of a line, however, are not uniform and allowances for these factors must be made. These variables are best evaluated by performing a numerical integration of the line by converting the density of each small unit area of the line into a number of ions, and then summing the number of ions of all of the areas. A density to number of ions curve is

developed for the particular type of photographic plate which is being used. Corrections for the background on which the lines appear are necessary because part of the line's density is due to background. (Variations in the background density are generally due to the scattering of ions by residual gases in the instrument.) The background corrections are made by subtracting the background density from that of the line density.

Initially, the microdensitometer output was plotted by an X-Y recorder as the microdensitometer scanned the line to be analyzed. Corrections for line width and background were made from the plotted curves. In order to perform the numerical integration rapidly, a computer system was developed which would perform the integration and apply any required corrections simultaneously.

The Computer. Figure 5 is a block diagram of the computer arrangement used for the integration of mass lines. The output of the microdensitometer is fed into Amplifier 1 which converts the microdensitometer voltage into a voltage range suitable for the function generator. (All amplifiers are high gain linear amplifiers.) The function generator provides the conversion of density into a number of ions (H & D curve) as determined by the density-ion curve which is programed into the function generator. The output of the function generator is fed into Amplifier 2.

Amplifier 2 is used to calibrate the computer for each type of plate and emulsion, and its gain is adjusted to compensate for their variations in sensitivity. The output of Amplifier 2 is summed over a number of short, equally spaced intervals by the voltage integrator. This sum is then multiplied by another factor at Amplifier 3. The gain of Amplifier 3 is adjusted for the appropriate abundance of each isotope that is scanned, and also can be used to apply the inverse square root mass correction.⁽⁵⁾ The output of Amplifier 3 is then read on a voltmeter which is calibrated to read in ppm for a given exposure level.

In designing the computer, a zero center meter was selected for setting the background correction. In scanning the area near the line which is to be integrated, the output from the microdensitometer is set such that the meter indicates within the vicinity of the meter's zero. Ten-turn potentiometers are used to set the gains of Amplifier 2, correcting for plate sensitivity, and Amplifier 3, for the mass and isotopic abundance corrections. Other features incorporated in the design are immediate reset of the integrator section and an additional multiplier section for simple multiplications when needed. Also, the output of each amplifier section, the power supply, and input voltages can be checked separately to insure that the computer is functioning correctly.

Methods for applying the background corrections have been discussed.^(6,7) For accuracy in the work which has been completed, lines which have adjacent background transmissions of less than 50% were not used. Likewise, lines which have a transmission of less than 5% were not used because of the inaccuracies of the slope of the H & D curve in that region.

The principle advantages of the computer are the rapid and accurate conversion of line densities into impurity concentrations. Factors such as variations in the H & D curve, corrections for background density, plate sensitivity, isotopic abundance, and the variation in line density with mass are quickly and conveniently adapted to the program of the computer. Other advantages of the computer are: rapid determination of abundances of several isotopes of the same impurity which offers a cross-check of the H & D curve of each plate; repeated scanning of a line in several regions and averaging them to reduce local variations in the emulsion; impurity concentrations of previously run plates can be readily rechecked by resetting the computer for that particular plate sensitivity and cross-checking any lines which had been previously analyzed.

PLATE AND EMULSION SENSITIVITIES

Variations in plate and emulsion sensitivities have been well established.^(8,9) Table II shows maximum density, average background, and relative sensitivities of various Ilford QII emulsions. The relative sensitivities are indicated by the multiplier settings which were used for Amplifier 2 of the computer. The multiplier settings were obtained by taking an isotope such as $^{33}\text{S}^+$ which is of known abundance in CdS and calibrating the computer output to read that concentration.

TABLE II. MAXIMUM DENSITY, AVERAGE BACKGROUND, AND RELATIVE SENSITIVITIES OF VARIOUS ILFORD QII EMULSIONS

	Plate No.	Multiplier Settings		Maximum Density	Background in %
		Sample "A"	Sample "B"		
Emulsion #4158	255	2.3	---	2.00	78
	258	2.0	2.2	1.90	81
	259	2.5	2.5	1.95	80
	260	2.0	2.0	1.90	81
	Average	2.2		1.95	80
Emulsion #4003	211	4.1	---	1.55	72
	220	4.2	5.1	1.50	70
	224	4.6	5.2	1.47	68
	Average	4.6		1.50	70
Emulsion #4052	212	1.5	---	2.20	62
	213	1.8	---	2.20	58
	Average	1.65		2.20	60

Emulsion No. 4052 was most sensitive with an average computer setting of 1.65. This is also implied by its maximum density of 2.20. The background, however, was unsatisfactory with an average background transmission of 60%. (Backgrounds were determined from unexposed areas of the plate.) Emulsion No. 4003 was the least sensitive with an average of 4.6 with a low maximum density of 1.50 and a background of 70%. Emulsion No. 4158 was satisfactory with an average multiplier setting of 2.2, a maximum density of almost 2.0, and a background transmission of 80%. It should be noted that within any one type of emulsion, the settings are relatively close to each other. Likewise, densities and backgrounds are also similar. Small variations in the multiplier settings are required because of plate-to-plate variations in the emulsion.

Similar variations in the multiplier settings are made necessary by changes in the number of multiply charged species. Sample-to-sample variations in such physical properties as electrical resistivity cause large changes in the number of multiply charged ions produced. Such variations are illustrated in Table II, where for each plate, settings were determined for two different samples.

Variations in the H & D curve also occur.⁽¹⁰⁾ In the analysis of many matrices, however, it is possible to monitor variations in the H & D curve from one emulsion to another by utilizing the range in abundances of the various isotopes of one of the matrix elements.

The shape of the H & D curves for the three emulsions listed in Table II have been examined using the isotopes of cadmium. In Table III the natural abundance of cadmium isotopes 108, 106, 113, and 114 are given. The values obtained using the computer are normalized to cadmium 116 and are listed for two plates for each of the three emulsions. In this experiment it was necessary to

use the same exposure for all the determinations. It was not possible to obtain quantitative values of mass 108 for Emulsions 4052 and 4003 because of the exposure level. With the particular H & D curve which was programed into the function generator, the maximum deviation was $\pm 12\%$. Thus no significant difference was observed in the shape of the H & D curve for these three radically different emulsions.

TABLE III. ABUNDANCE OF CADMIUM AS DETERMINED
FROM VARIOUS ISOTOPES AND ILFORD QII EMULSIONS
(Normalized to ^{116}Cd)

Cd Isotope and % Abundance	108 (0.88)	106 (1.2)	116 (7.6)	113 (12.3)	114 (29)
<u>Plate No. - Emulsion #4158</u>					
258	108	102	100	104	92
259	96	98	100	104	94
<u>Plate No. - Emulsion #4052</u>					
212	---	104	100	112	110
213	---	100	100	96	108
<u>Plate No. - Emulsion #4003</u>					
211	---	100	100	104	92
220	---	90	100	88	88

CONCENTRATIONS DETERMINED FROM MULTIPLY CHARGED IONS

In the analysis, lines due to the sample matrix occasionally interfere with the analysis of some impurities. However, lines due to multiply charged ions can be used for the determination of impurity concentrations. For some isotopes of high abundance, they even offer better sensitivity than can be obtained using singly charged low abundance isotopes. To use this method the computer sensitivity is set such that the voltmeter will indicate the known abundance of a calibration isotope, by scanning the line formed by its doubly charged ions. Then lines created by other doubly charged ions with similar ratios between the first and second ionization potential can be scanned and their concentration determined.

In CdS, silicon can be determined by subtraction from the combination of $^{112}\text{Cd}^{+4}$ and $^{28}\text{Si}^{+}$; however, it is preferable to use $^{30}\text{Si}^{+}$ or $^{28}\text{Si}^{+2}$. Doubly charged ions have been used where the density of the line for $^{30}\text{Si}^{+}$ is less than that of $^{28}\text{Si}^{+2}$. Experiments were conducted where both $^{28}\text{Si}^{+2}$ and $^{30}\text{Si}^{+}$ were of an appropriate density. Also, $^{40}\text{Ca}^{+2}$ and $^{40}\text{Ca}^{+}$ were used as an added check of the validity of the use of doubly charged ions. Concentrations based on these isotopes are shown in Table IV. The results indicate comparative determinations can be obtained, thereby permitting the use of the doubly charged ion method for other samples. Note that in the case of silicon a singly charged, low abundance isotope was compared with the doubly charged, large abundance isotope. For calcium the same isotope was used, but different exposures were required to achieve nearly equal line densities.

TABLE IV. CONCENTRATIONS OF SILICON AND CALCIUM IN CdS
DETERMINED FROM SINGLY AND DOUBLY CHARGED IONS
SAMPLE "A"

Exposure in Coulombs	Isotope	Isotopic PPM	Total PPM
10 ⁻⁸	30Si ⁺	3.13	101
10 ⁻⁸	28Si ⁺²	92.7	100
10 ⁻⁹	40Ca ⁺	23.3	24
2x10 ⁻⁸	40Ca ⁺²	26.1	27
SAMPLE "B"			
3x10 ⁻⁹	30Si ⁺	6.0	195
3x10 ⁻⁹	28Si ⁺²	194	210

DISCUSSION

The method used for the conversion of line densities to number of ions is easily adaptable to computer programs. In actual practice the conversion of line densities into ppm is a continuous integration limited only by the micro-densitometer slit which scans the line. Improved analyses have been obtained by the use of approximate solutions to the problem of line width and variations in line density. One of the better methods utilizes the half-width approximation;⁽¹¹⁾ however, numerical integration not only gives greater accuracy, but is readily adapted to computer programming.

The criterion for the metal used for sample holders, first aperture, and other items located near the spark are that they be machineable or readily plated on other metals and have only one major isotope. To minimize interference from multiply charged ions, an isotope of odd mass number and relatively high mass is desirable. Tantalum is an obvious choice. In the event that an analysis for tantalum is desired, the sample holders may be plated with rhodium.

The substitution of argon or helium in the cathodic etch may be made when an accurate analysis for nitrogen is necessary.

Cryogenic pumping with liquid nitrogen has been shown to be effective in reducing hydrocarbons and water vapor. The CO background can be reduced by using liquid helium.

REFERENCES

- (1) N. B. Hannay, Rev. Sci. Instrument 25, 644 (1954).
- (2) N. B. Hannay and A. J. Ahearn, Anal. Chem. 26, 1056 (1954).
- (3) R. D. Craig, G. A. Errock, and J. D. Waldron, "Advances in Mass Spectrometry," (Pergamon Press, London, 1959), p. 136.
- (4) C. F. Robinson, G. D. Perkins, and N. W. Bell, "Instruments and Measurements," (Academic Press, London, 1961), Volume 1, p. 260.
- (5) W. Rudloff, Z. Naturforsch. 17a, 414 (1962).
- (6) D. A. Resnik and R. K. Willardson, "Impurities in Semiconductors," Metalurgy of Semiconductor Materials, edited by J. B. Schroeder, (Interscience Publishers, New York, 1962), p. 209.
- (7) E. B. Owens, Proceedings of Mass Spectrometry Conference of ASTM, New Orleans, Louisiana, June 1962, p. 403.
- (8) E. B. Owens, Applied Spectroscopy 16, 148 (1962).
- (9) W. Rudloff, Z. Naturforsch. 17a, 417 (1962).
- (10) W. Rudloff, Z. Naturforsch. 17a 418 (1962).
- (11) C. W. Hull, Proceedings of Mass Spectrometry Conference of ASTM, New Orleans, Louisiana, June 1962, p. 404.

MINIATURIZED BENDIX TIME-OF-FLIGHT MASS SPECTROMETERS

J.F. Betts and G.J. O'Halloran

The Bendix Corporation
Research Laboratories Division

Recent work in mass spectrometry at The Bendix Research Laboratories Division has stressed application of the Time-of-Flight Mass Spectrometer as an absolute partial pressure sensor for multicomponent gas samples. The Time-of-Flight Spectrometer equipped with a gated electron multiplier is uniquely suited to this application because of its ability to provide continuous, simultaneous readout of selected components of the gas sample.

A gas partial pressure sensor is an important tool for research in generation and control of closed-cycle life-supporting atmospheres. In a fully developed system for manned space probes, the partial pressure sensor would detect any deviations from the model atmosphere. This information would be fed into a computer which would actuate appropriate controls to correct the abnormality. The degree of correction would be determined by the partial pressure sensor, thus completing the feedback loop.

The primary requisite of a gas partial pressure sensor is maintenance of a stable, linear transfer function between inlet partial pressures of gas sample components and voltage outputs to recording or telemetry equipment. Adaption of a mass spectrometer to the peculiar requirements of a partial pressure sensor is relatively straightforward as partial pressure sensors is a corollary program* to develop miniaturized equipment to perform a similar function. The ultimate need for such equipment is evident, since it is obviously impractical to fly a typical laboratory-type mass spectrometer in a space probe.

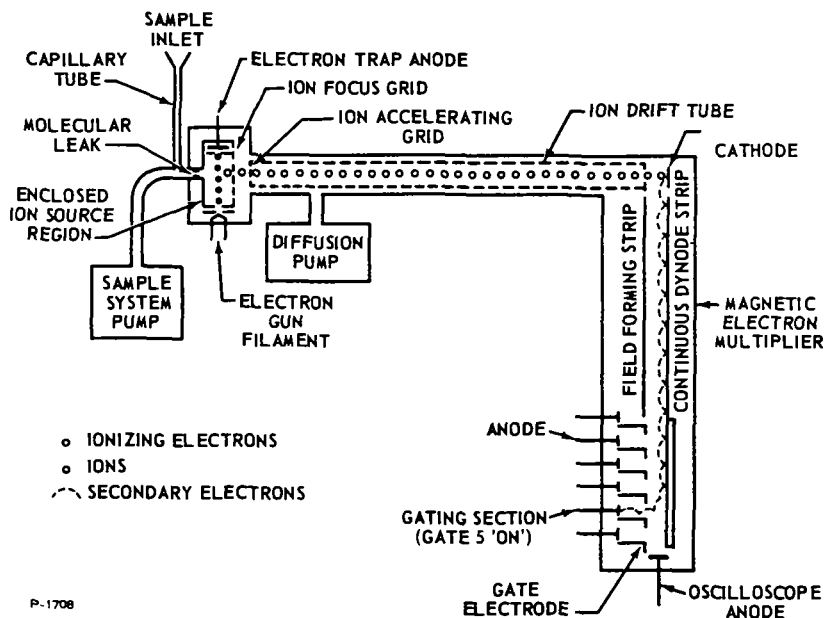
Several laboratory-type Bendix Time-of-Flight Mass Spectrometers are currently being used as gas partial pressure sensors in space simulator systems. Applications range from medical research on human subjects to evaluation of space suits. A logical outgrowth of the successful development of laboratory-type time-of-flight instruments as partial pressure sensors is a corollary program* to develop miniaturized equipment to perform a similar function. The ultimate need for such equipment is evident, since it is obviously impractical to fly a typical laboratory-type mass spectrometer in a space probe.

For many of the Time-of-Flight Mass Spectrometer components, there is no direct relation between size and stability; miniature versions can be designed without sacrificing stability. Unfortunately, this does not apply in all areas. It particularly does not apply to the sample pumping system, where stability of transfer function is almost directly related to pump size.

When this problem is considered from the over-all system point of view, however, it becomes evident that other trade-offs exist which can effectively improve performance of a miniature partial pressure sensor. One alternative is to design the instrument to perform a fairly specific function, thus limiting the conditions under which it must meet specified performance figures. In effect, versatility is traded for improved performance in a specific application. Actually, this is not a serious limitation, because in manned space flight, the gas partial pressure sensor would normally be required to function unattended.

The miniature instrument which is the subject of this paper has been designed to a size, weight, and power consumption suitable for installation in a space vehicle, while retaining much of the performance characteristics of the larger laboratory instruments.

*Part of the effort involved in conducting this program was supported by the Air Research and Development Command, United States Air Force Edwards Air Force Base, California, under Contract AF 04(611)-8171.



P-1708

Figure 1 - Time-of-Flight Mass Spectrometer--Schematic Diagram

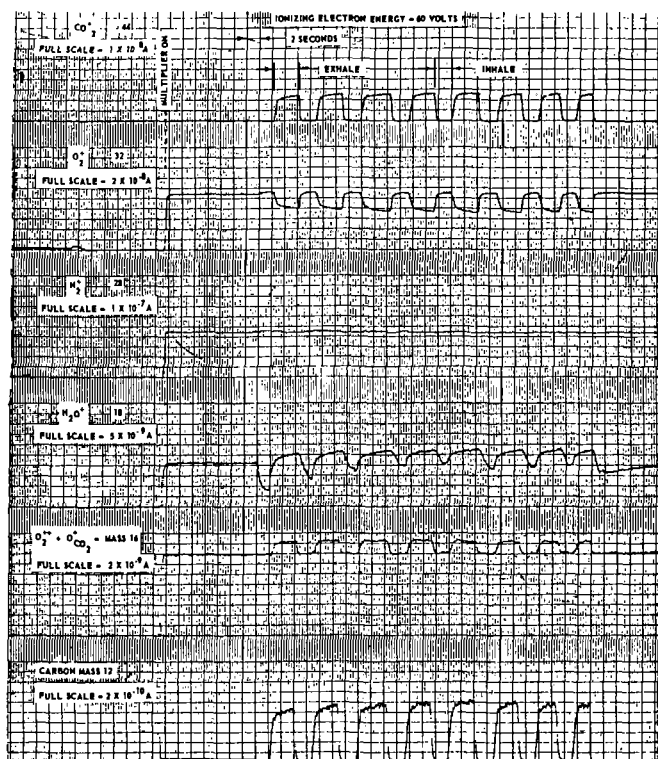


Figure 2 - Breath-by-Breath Analysis of Respiratory Gases Using Multi-Channel Time-of-Flight Mass Spectrometer

This instrument has been developed for the specific application of monitoring the breathable atmosphere in a space helmet or in the "shirt sleeve" environment of a space vehicle cabin.

The operation of the complete instrument will first be described briefly, followed by a more detailed discussion of areas of special interest. In describing the various design features, it is convenient to categorize the instrument into three principal areas. These are (1) the gas sample handling system, (2) the mass analyzer, and (3) the output system.

Figure 1 is a schematic diagram of the instrument. The dynamic pressure range at the gas sample inlet is from 1 atmosphere to 1/4 atmosphere. Sample gas from space helmet or cabin is pumped through a stainless steel capillary tube which is heated to achieve dimensional stability. The conductance of the sample pump tube is adjusted to produce a pressure of 1 Torr in the sample chamber when the sample inlet pressure is 1 atmosphere. Viscous flow prevails throughout the region from sample inlet to sample pump. Sample gas flows into the mass analyzer ion source via a molecular flow leak from the sample chamber. The conductance out of the ion source is restricted to a value well below the pumping speed of the diffusion pump so that ion source pressure is essentially determined by the exit conductance, and not by the pump characteristics.

Sample gas molecules in the ion source are ionized by a pulsed electron beam, and subsequently accelerated into the drift tube at a uniform energy level. As the ions travel through the drift region they become time focussed as a function of mass for singly charged ions. Time focussed ion bunches are detected and amplified by a magnetic electron multiplier. At the outboard end of the multiplier is an eight channel gating system which employs accurately timed pulses to deflect selected electron bunches, corresponding to the desired mass peaks, onto discrete anodes. The average current flowing to each anode is then measured with an electrometer. Mass spectra are initiated at 50 microsecond intervals, so that relative to the rate of change of gas composition normally encountered in gas dynamics at atmospheric pressure, response of the mass analyzer is instantaneous for all sample gas components.

The mass analyzer is mounted on a test stand which provides facilities for initial pumpdown and calibration of the instrument. A single magnet produces the B-field for both pump and multiplier. Inclusion of the getter pump elements in the multiplier housing increases pumping speed by nearly an order of magnitude over the pumping speed which would be obtained with a commercially available pump of comparable volume. In addition, there is a substantial weight reduction in eliminating the pump magnet.

The magnetic circuit is designed so that the multiplier, which requires a 240 gauss field, operates in the fringe field region of the magnet. The getter pump is located directly between the magnet poles, in a 1000 gauss field region. Soft iron shunts are trimmed to produce a uniform multiplier field over the entire multiplier region at the 240 gauss level. The upper shunt has been removed to show details of the rectangular multiplier header.

Vacuum seal is maintained by an aluminum gasket and a single knife-edge on the multiplier housing. The recesses around the feedthru-blocks permit use of a thin section lightweight multiplier header by eliminating the possibility of cracked feedthrus due to deforming of the header as it is pulled down against the knife-edge.

The tube protruding from the ion drift region provides the connection to initial pump-down facilities in the test and calibration stand. When the system has been pumped down to background level, and the internal getter pump is operating, the pump-down tube connection is pinched off with a special tool which produces a tight seal. Use of the pinch-off tube eliminates a bulky gate valve which would otherwise be required.

The complete electronics system consists of seven circuit boards stacked to form a module which fits within the rectangle defined by projection of the mass analyzer outline dimensions. The complete system, excluding the sample pump, measures 8.5" x 15" x 2.75", weighs 19.75 pounds, and requires 30 watts of power. The system is designed to operate from a nominal 28 volt d-c power source.

Since the instrument will be operated unattended for long periods of time, exceptional stability has been incorporated into the electronic circuitry, which is completely transistorized with the exception of electrometer tubes. All critical power supplies and potentials are chopper stabilized to achieve drift figures of less than 10 parts per million per degree centigrade. The ion source electron beam is stabilized by a feedback-type trap current regulator controlling filament emission.

The output system employs six linear electrometers with their associated pulse delay circuits to continuously monitor six mass peaks selected from the spectrum. A seventh channel repetitively scans the spectrum to detect mass peaks not assigned to one of the six fixed channels. The scanning channel is equipped with a logarithmic electrometer which provides a five decade dynamic range.

The scanning circuit is connected to the first multiplier output channel, which takes precedence over all other channels in collecting the multiplier output pulses. Thus a complete spectrum is seen at the scanning channel output. In addition, as the scanner sweeps over the mass peaks assigned to the fixed channels, their outputs momentarily drop to zero, which serves as an automatic zero check on these channels.

Figure 2 is a typical readout from a multichannel Time-of-Flight Mass Spectrometer, showing the human respiratory cycle.

The ability of a mass spectrometer to read out absolute partial pressures is critically dependent on the sample system design. In a miniature system, this problem is compounded by the necessity of using relatively small pumps. The final design of the sample system for the partial pressure sensor necessarily represents a number of compromises on conflicting performance requirements.

The basic philosophy of the sample system design is that if the same gas flow mechanism pertains for flow into and out of a given region of the sample system, then true gas composition will be preserved in that region. Since the pressure at the gas sample inlet is of the order of one atmosphere, it is evident that a transition from viscous to molecular flow must take place somewhere in the system. Therefore the sample system must provide for the transition from viscous to molecular flow without affecting sample composition, and at the same time, it must satisfy a number of other conditions. Since the instrument is designed to monitor a life support environment, response time must be fast. A response time of 1 second from gas inlet at atmospheric pressure to analyzer output is desired. Fast sample system response is easily attained at high sample gas flow rate. However, it is desirable that the sample gas requirement be as small as possible to reduce the load on the sample pump, or to prevent excessive loss when pumping overboard, using outer space as an infinite pump.

The high degree of stability necessary in an absolute pressure sensor requires that gas flow orifices used in the sample system be dimensionally stable and relatively free from the possibility of clogging. It is equally important that the effects of variations in pumping speed of the getter pump and of the sample system pump be minimized.

Instabilities due to variations in pumping rates are minimized by conductance limiting of the sample gas flow in critical regions. Thus, the gas flow is established by passive elements of the system, and instabilities in the active elements have little effect on over-all system stability.

Consider first the viscous flow region of the sample system from sample inlet to sample pump. In a viscous flow system, gas flow through a conductance is proportional to the difference of the squares of the absolute pressures at either end of the conductance. Therefore if the pressure drop across a conductance is at least 10:1, the error in neglecting the pressure at the low end is 1 percent or less. With a sample inlet pressure of 1/4 atmosphere or more, and a sample chamber pressure of the order of 1 Torr, the condition is easily met, and sample gas flow through the capillary can be considered a function of inlet pressure only.

If variations in sample pump speed are to produce no more than 1 percent output error, the pressure drop across the pumping line constriction must always be at least 10:1. When this condition pertains, sample chamber pressure will follow sample inlet pressure with an error of 1 percent or less. If a 1 Torr sample chamber pressure

corresponds to a 1 atmosphere sample inlet pressure, then the sample chamber pressure will be 0.25 Torr at 1/4 atmosphere, and the sample pump ultimate pressure must be at least a factor of 10 lower, or less than 25 microns.

Referring to Figure 3, we find that the sample flow rate necessary for a 1 second response time through a 3 foot capillary at 0.25 atmosphere is about 2 ml./min. Constant mass flow then requires a 15 liter pump at 25 microns. Commercially available pumps with this capacity and ultimate pressure are hardly companion pieces for a low power miniature mass spectrometer.

It is evident that both pump ultimate pressure and pumping speed requirement can be eased by raising the sample chamber pressure. However, this necessitates reducing the size of the molecular flow leak into the ion source. At 1 Torr, the mean free path for air is 50 microns. Ideally, the molecular leak dimensions would be a fraction of a mean free path. Thus, the sample chamber pressure cannot be raised appreciably without requiring a leak diameter in the micron region, with attendant problems in dimensional stability and possible clogging.

This problem has been resolved by modifying a commercially available 18 liter pump to adapt it for space vehicle installation.

A similar problem exists in the molecular flow region. Gas flow through the molecular leak into the ion source is essentially dependent on the sample chamber pressure, since the pressure in the ion source is negligible relative to the 1 Torr pressure level in the sample chamber. Gas flow out of the ion source is limited by the conductance of the ion exit orifice. It should be noted that the size of this orifice does not determine resolution of the Time-of-Flight Mass analyzer. The orifice size is adjusted only to regulate gas flow.

In a molecular flow region, volume flow through an orifice is the same in either direction regardless of pressure differential. Thus, errors due to back streaming of particles into the ion source can be minimized by raising the ion source pressure well above the pressure level in the remainder of the vacuum housing. If the pressure differential is 100:1, for example, then a 100 percent change in diffusion pumping rate would be reflected as a 1 percent error in ion source pressure. In the viscous flow regions, the same immunity from pump speed variations was achieved with a 10:1 pressure differential, due to the p^2 factor in the viscous flow mechanism.

In large laboratory-type systems, a 100:1 pressure differential across the ion exit orifice is relatively easy to achieve using an exit conductance of the order of 1 liter/second, and a 100-150 liter/second diffusion pump.

A 100 liter diffusion pump is not practical in a compact system, however. Location of the titanium getter diffusion pump in the multiplier housing has resulted in greatly increased pumping speed over that attainable with a separate pump, partly because the conductance into the pump is at a maximum, and also because the pump housing is the optimum configuration for our system, permitting inclusion of more pumping elements. A large diameter drift tube housing increases the conductance between pump and ion source to take full advantage of the increased pumping speed. The system used provides a pumping speed of about 8 liters/second. A 100:1 pressure differential would require an 80 milliliter/second ion exit conductance. A conductance this small would result in a serious reduction in sensitivity by reducing the effective ionizing area. It would also slow response of the system to changes in gas composition, since the source volume would be pumped through the 80 milliliter conductance.

In resolving this problem, we have taken advantage of the fact that the miniature gas partial pressure sensor is intended for a specific application. Under normal circumstances, the sample gas composition will be essentially invariant, and the dynamic sample pressure range is only 4:1. In the event that unusual variations in gas composition occur, reduced accuracy can be tolerated until conditions return to normal. On this basis, the ion source exit conductance has been increased to 0.8 liter/second which provides a 10:1 pressure differential between source and vacuum housing. Thus, a 100 percent change in pumping speed for a given sample gas constituent would result

in approximately a 10 percent readout error. The constancy of the normal gas sample makes the probability of large pump speed variations extremely remote, however. Occasional recalibration is sufficient to maintain partial pressure readout accuracy of the order of 1 percent.

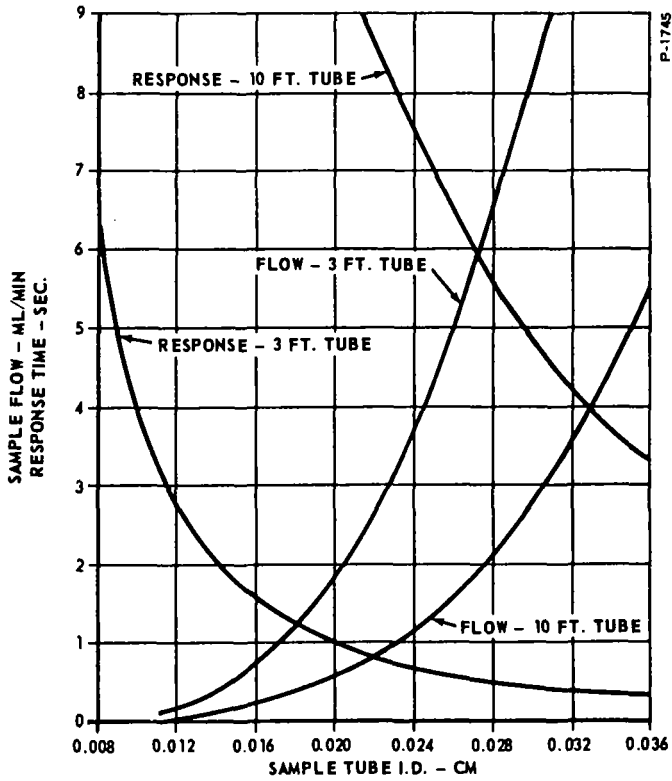


Figure 3 - Sample Flow vs. Response Time for Capillary Tube at 190MM Hg Sample Gas Pressure

AN IMPROVED OSCILLOGRAPHIC CAMERA TECHNIQUE FOR TIME-RESOLVED MASS SPECTROMETER DATA RECORDING*

Richard T. Meyer
Sandia Corporation
Albuquerque, New Mexico

INTRODUCTION

The application of mass spectrometers to time-resolved studies of chemical and physical processes occurring on the time scale of milliseconds and microseconds has received wide attention in recent years. In part, this is the result of the development of rapid scanning time-of-flight mass spectrometers. Simultaneously, various techniques have been advanced for the extraction, recording, and processing of the rapidly changing mass spectral data.

Figure 1 is a schematic summary of several of these data recording techniques. Shown in the upper left is the typical amplitude vs mass display observed with an oscilloscope output for a Bendix Time-of-Flight Mass Spectrometer. The methods of Damoth¹ and Kendall² for recording amplitude vs time both utilize electron beam intensification and Polaroid film recording.

The revolving drum camera technique consists of the high speed movement of a strip of film vertically past the standard oscilloscope display in order to time-resolve and permanently record successive scope traces of amplitude vs mass. Kistiakowsky and Kydd³ employed this data recording method for the study of gas phase chemical reactions induced by flash photolysis and shock wave. However, low overall photographic sensitivity and time-consuming data reduction have been limiting features. This paper describes several improvements which have been made which now render the drum camera method a means for legible data recording and efficient data reduction.

Desirable features of this oscillographic camera technique for time-resolved mass spectrometer data recording are as follows. First, any and all mass spectral signals occurring within the mass range being displayed by the oscilloscope will be simultaneously recorded on the film strip. This is particularly important for those systems producing intermediate species such as atoms, free radicals, or other molecular fragments, which may be completely absent at both the beginning and end of a transient experiment and which may be unknown to exist prior to the experiment. Second, each trace of the film record carries a baseline for zero amplitude reference which is common to all the masses under observation. Third, absolute mass identification is provided by interpolation between known masses. Fourth, essentially independent coordinate axes are utilized to display amplitude, mass, and time. This minimizes problems of signal overlapping and mass and time resolution.

PHOTOGRAPHIC SENSITIVITY

Factors controlling the effective photographic sensitivity are listed in Table I, along with a numerical estimate of the sensitivity obtained in this work relative to that utilized by Kistiakowsky and Kydd.³ The first two factors, the CRT phosphor and the film emulsion, are conveniently considered together. The combination of a P16 phosphor with Agfa Isopan Record film yields a net loss in sensitivity of approximately a factor of one half in comparison to the combination of a P11 phosphor with Kodak Linagraph Pan film. The shorter persistence, 0.1 μ sec, of the P16 phosphor is required with the overall increased sensitivity provided by the other factors. The vertical motion of the film strip causes image streaking with

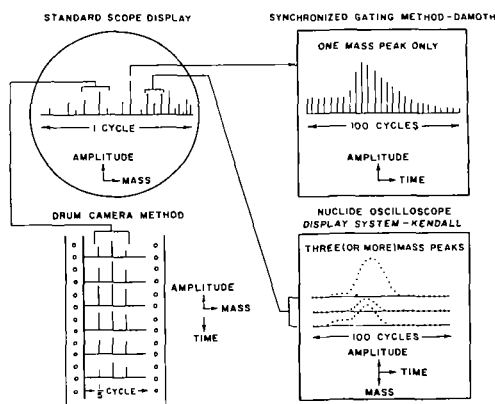


Fig. 1 Schematic summary of three data recording techniques for time-resolved mass spectrometry.

TABLE I. FACTORS CONTROLLING EFFECTIVE PHOTOGRAPHIC SENSITIVITY

ITEM	KISTIAKOWSKY AND KYDD ³	THIS WORK	RELATIVE SENSITIVITY
CRT PHOSPHOR	P11 (30 μ sec, 4550A)	P16 (0.1 μ sec, 3850A)	1/2
FILM	LINAGRAPH PAN (2600) ^a ROYAL-X PAN (6300) AGFA ISOPAN RECORD	AGFA ISOPAN RECORD ROYAL-X PAN (600) AGFA ISOPAN RECORD	1/10 ^b 1/5 ^c
ACCELERATING POTENTIAL	10 kv	28.5 kv 12 vs 24 kv 12 vs 28.5 kv	10 6 8
SWEEP RATE	1 μ sec/cm	1 μ sec/cm 1.0 / 0.1 μ sec/cm	1 3/4
LENS APERTURE	f 3.5	f 2.3	9/4
FILM PROCESSING	—	20 min in Rodinal at 68°F or Sensitized	—

a. Relative CRT - Film Speed, ref. 4.

b. Data on Royal-X Pan film taken from ref. 4.

c. Data on Agfa Isopan Record film obtained in this work.

the longer persistence phosphors. The effect of the increased emulsion speed of the Agfa Isopan Record is appreciated by noting that the relative sensitivity would be one-thirteenth if the Kodak Linagraph Pan were used with the P16 phosphor.⁴ Indirect experiments indicate that Agfa Isopan Record may be faster than Kodak Royal-X Pan at 3850A for this type of data recording by a factor of two; at least, clearer, less noisy negatives are obtained from the Agfa film.

The loss in sensitivity with this phosphor-film combination is regained with a larger effective lens aperture. A Beckman and Whitley Model 364-2 Oscillographic Camera, equipped with a Wollensak f 1.9 Oscillo-Raptar lens, is used. In actual application, the lens system has an effective aperture of f 2.3.

The most significant single factor contributing to the increased trace recording capability is the 28.5 kv accelerating potential on the electron beam of a modified Tektronix Type 517A oscilloscope. Actual experiments have shown, with the P16 phosphor, that by stepping up the potential from 12 kv to 24 kv a gain of a factor of six in sensitivity is achieved; boosting the potential to 28.5 kv raises this to a factor of eight. It is estimated, therefore, that the sensitivity ratio for 28.5 kv vs 10 kv is approximately ten. Variation in the horizontal sweep rate has only a minor effect on the sensitivity over the range of 1.0 to 0.1 $\mu\text{sec/cm}$.

The effect of the mode of film processing is significant. Extended development can increase the film speed by a factor of two to ten, depending upon the particular emulsion. Kodak data⁴ indicate that, for Royal-X Pan film exposed to a P16 phosphor, increasing the development time in Kodak D-19 from 4 to 15 minutes increases the film speed by a factor of twenty. In our work, a 20 minute development time was used for both Royal-X Pan in Kodak D-19 and Agfa Isopan Record in Rodinal. We have also tried chemically sensitizing our exposed films prior to development. For the recording of mass spectral signals, we have found no significant net increase in sensitivity. However, the development time could be halved to obtain the same image density.

Overall, it is estimated that a factor of ten increase in photographic sensitivity has been achieved for time-resolved mass spectrometer data recording with a revolving drum oscillographic camera. Reproductions of actual film records which have been obtained with 20 kc pulsed operation of a Bendix TOF Mass Spectrometer are shown in Figs. 2 and 3. Figure 2b demonstrates the recording of mass signals due to only a very few ions per cycle on the average; note that the mass 14, 16, and 18 peaks do not appear in every trace. Figure 3 illustrates film recordings of higher mass species at faster sweep rates, the faster sweeps being used to achieve increased mass separation in the oscilloscope display.

SYNCHRONIZING CIRCUITS

This data recording system has been assembled for the purpose of performing time-resolved chemical kinetics studies of gas phase reactions excited by flash photolysis. Figure 4 illustrates the auxiliary electronic components which have been instrumented to synchronize the flash lamp with the 20 kc pulsed operation of the spectrometer and to provide effective shuttering action for the oscillographic camera. The principle component of the synchronizing circuit, which is a modification of a scheme developed by Schellenbaum,⁵ is a 5696 tetrode thyatron. The shield grid is biased negatively in the stand-by position, which prevents indiscriminate triggering of the thyatron by 20 kc pulses from

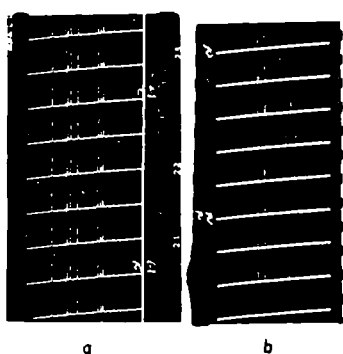


Fig. 2 (a) Mass spectrum of H_2O_2 and CO_2 mixture; masses 44, 34, 32, 28, 18, 17, 16, 14, 12, left to right; (b) Mass spectrum of residual air; masses 32, 28, 18, 16, 14, left to right; masses 14-18 appear randomly; 1.0 $\mu\text{sec}/\text{cm}$ sweep.

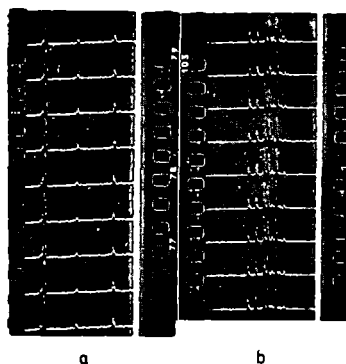


Fig. 3 (a) Mass spectrum of SF_6 ; masses 127, 108, 89, left to right; 0.5 $\mu\text{sec}/\text{cm}$ sweep; (b) Mass spectrum of Xe isotopes; masses 136, 134, 132, 131, 130, 129, 128, 126, left to right; 0.2 $\mu\text{sec}/\text{cm}$ sweep.

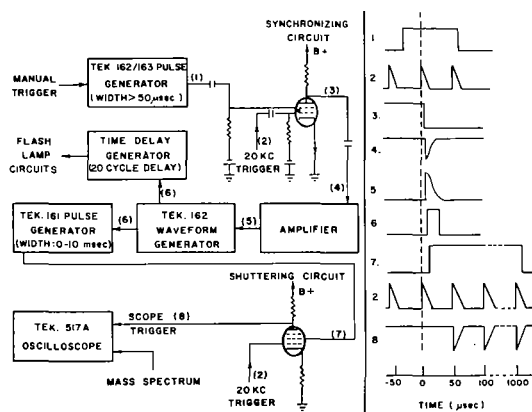


Fig. 4 Electronic components and associated waveforms for synchronization of flash photolysis - time-of-flight mass spectrometer apparatus with shuttering action of the data recording oscillographic camera.

the mass spectrometer appearing continuously on the control grid. When the desired drum speed of the oscillographic camera is attained, a Tektronix Type 163 pulse generator is triggered. This produces a positive pulse of duration greater than the 50 μ sec interval between spectrometer pulses and of amplitude sufficient to offset the negative bias on the control grid of the thyatron. The thyatron fires on the next 20 kc trigger pulse, and subsequent stages in the circuit become synchronized to the mass spectrometer. The thyatron remains conducting, serving as a lockout against multiple triggering. The output signal is differentiated, amplified, inverted and applied to a waveform generator, which simultaneously triggers a time delay generator and a variable width pulse generator.

The camera shuttering circuit utilizes a 6AK5 pentode. It conducts the 20 kc spectrometer pulses applied to the control grid only for the duration of the screen grid gating pulse, which is derived from the variable width pulse generator. The width of the gating pulse is adjusted to be equal to or less than one revolution of the camera drum. Thus, the shuttering action is achieved by triggering the horizontal sweep generator of the oscilloscope a selected number of times rather than by a mechanical shutter. The additive finite risetimes associated with the circuits between the thyatron and the pentode cause the first scope trigger pulse (Fig. 4, waveform 8) to be one pulse later in time than the 20 kc pulse which fires the thyatron. Compensation for this 50 μ sec lag may be achieved with the time delay generator.

The principle function of the time delay generator is to delay the firing of the flash lamp for 20 cycles or so, in order to record on film the mass spectral signals prior to the initiation of the reaction. A short duration electromagnetic pickup from the discharge of the flash lamp distorts the output of the mass spectrometer. This interference is illustrated in the fourth and fifth horizontal sweep traces of Fig. 5a. The principal portion of this interference persists for less than 50 μ sec. Therefore, fine adjustments of the time delay generator may be made to position the discharge in a region of the spectrum which does not contain useful information.

FLASH HEATING EXPERIMENT

Data obtained in experiments in which gaseous nitrogen dioxide was flash heated is recorded in Figs. 5 and 6, as an example of the application of the oscillographic camera technique and the associated electronic circuitry to time-resolved mass spectrometer studies. The nitrogen dioxide was subjected to flash heating rather than flash photolysis for these particular experiments, as a result of both the radiation emitted by the flash lamp and the absorption by the gas favoring wavelengths above the decomposition wavelength. The effect of the flash heating was to increase the gas density in the reaction chamber. This is clearly demonstrated, in the film record of Fig. 5, by the increase in the amplitude of the NO^+ (the major ionization fragment of NO_2) signal subsequent to the flash. Figure 6 is composed of data transferred from three films to graphical representation by our data reduction procedures. The lamp was flashed at time zero, after the spectrum of the nitrogen dioxide had been recorded for one millisecond. The time lag between the lamp flash and maxima in the NO_2^+ and NO^+ amplitudes is a result of non-uniform heating of the gas sample followed by gas flow to the sampling orifice of the ionization chamber. The NO^+ to NO_2^+ ratio remains constant, which is what one expects in the absence of any photochemical decomposition.

In as much as quantitative data reduction can be a very time-consuming process, a brief description follows of methods and facilities used to render data reduction from the film records

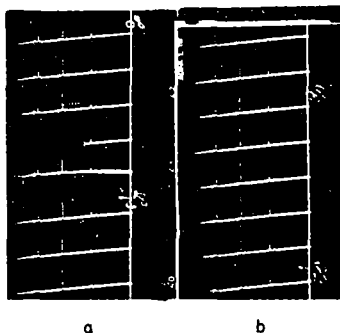


Fig. 5 Flash heating of NO_2 ; masses 46, 32, 30 (NO-major peak), 28, 16, 14, left to right; top of (b) follows bottom of (a) in time; lamp flashed during fourth trace of (a) causing signal interference; 50 μsec between traces; 1.0 $\mu\text{sec/cm}$ sweep.

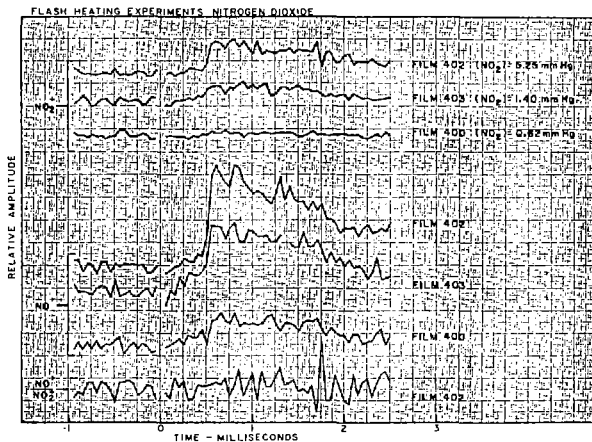


Fig. 6 Time-resolved flash heating of nitrogen dioxide at various gas pressures; NO and NO_2 ion signals recorded before and after lamp flash (time zero).

more efficient and accurate. A semi-automatic film reader is employed to read and record on punched cards the mass position and peak amplitude of each mass spectral signal in the time-resolved mass spectrum. The punched cards are sorted automatically according to mass and supplied to a x,y-coordinate plotter which provides amplitude vs time data plots similar to those shown in Fig. 6. The data cards are also available as an information source for numerical computer programs. For example, in chemical kinetics experiments, it may be necessary to reference numerically each measured amplitude to an internal, inert standard substance in order to account for systematic error; or concentration ratios of reactant to product and intermediate to parent may be required to interpret the detailed chemical processes. A specific example of the latter is the NO^+ to NO_2^+ ratio plot of Fig. 6, for which the interpretation has already been cited.

SUMMARY

A revolving drum camera - oscilloscope data display and recording system has been assembled. It provides an effective photographic sensitivity an order of magnitude greater than that previously reported for utilization in time-resolved mass spectrometer analyses of rapidly occurring physical and chemical processes. A gas phase flash heating phenomenon, recorded with a Bendix TOF Mass Spectrometer operating at 20 kc, is cited as an application of the improved data recording system and as an example of time-saving data reduction procedures.

REFERENCES

1. D. C. Damoth, paper presented at the Eighth Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Atlantic City, New Jersey (1960).
2. B. R. F. Kendall, Proceedings of Tenth Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, 1962, p. 306.
3. G. B. Kistiakowsky and P. H. Kydd, J. Amer. Chem. Soc. 79, 4825 (1957).
4. Kodak Films for Cathode-Ray Tube Recording, Kodak Publication No. P-37 (Eastman Kodak Company, Rochester, 1962).
5. R. L. Schellenbaum, Rev. Sci. Instr. 33, 1112 (1962).

*This work performed under the auspices of the U. S. Atomic Energy Commission.

PLASMA ANALYSIS WITH THE BENDIX
TIME-OF-FLIGHT MASS SPECTROMETER*

G. J. O'Halloran and R. A. Fluegge⁽¹⁾

The Bendix Corporation
Research Laboratories Division
Southfield, Michigan

ABSTRACT

The results of a recent experimental program⁽²⁾ which saw the demonstration of the feasibility of using a Bendix Time-of-Flight Mass Spectrometer for the direct sampling of a high energy density plasma are discussed. Data which confirms the capability of this instrumentation to provide qualitative information about the plasma phenomenology is presented. Plans for experimentally evaluating the quantitative capabilities of the equipment are summarized.

The mass spectra obtained using an argon plasma operating at temperatures greater than 5000 °K, in a room-air atmosphere, showed the presence of

^{40}Ar , $^{28}\text{N}_2$, $^{32}\text{O}_2$, and $^{18}\text{H}_2\text{O}$; and $^{40}\text{Ar}^+$, $^{28}\text{N}_2^+$, $^{18}\text{H}_2\text{O}^+$, $^{16}\text{O}^+$, $^{14}\text{N}^+$,

$^{44}\text{CO}_2^+$, $^{63}\text{Cu}^+$, $^{65}\text{Cu}^+$, $^{32}\text{O}_2^+$, and $^{17}\text{OH}^+$

for the respective neutral and ionized species of the plasma. The mass spectra indicate that the relative ion concentration is about 2.5×10^{-6} and that the ion density is about 5.2×10^{12} ions cm^{-3} . The variation of

$^{40}\text{Ar}^+$, $^{28}\text{N}_2^+$, and $^{32}\text{O}_2^+$

ions as a function of longitudinal position in the plasma stream is presented and the variation of $^{40}\text{Ar}^+$ and $^{28}\text{N}_2^+$ ions with respect to plasma generator power is shown.

INTRODUCTION

This paper summarizes work which was accomplished at the Bendix Research Laboratories Division in developing a specialized inlet system and the Time-of-Flight Mass Spectrometer with which it was used in order to allow direct sampling from a high energy density, 760 mm Hg plasma. Mass spectra for both the neutral and ion species for such a plasma were obtained and a cross section of the experimental results is included.

The plasma which was used in our experiments was generated by a Gianninni Model M-4 Arc Plasma Generator operating at indicated power levels through the range of 8 to 35 kilowatts. The inlet system was designed using the philosophy that the shockwave or severe discontinuity occurring as the result of the rapid expansion of the sampled plasma can be best coped with by using a supersonic nozzle design which permits the attachment of the shockwave or discontinuity to the nose of the nozzle. A Model 12 Bendix Time-of-Flight Mass Spectrometer was used and a small amount of additional circuitry was provided for use with the instrument in order to facilitate the experiments. The mass spectra were recorded by using Polaroid photographs of the spectra displayed on a Tektronics Type 545 oscilloscope. A comprehensive discussion of our investigation is being prepared (Reference 1) and is expected to be available in the near future.

The Time-of-Flight Mass Spectrometer accomplishes its analysis by pulsing the sample ions to a common kinetic energy. Consequently, the mass-to-charge ratio and velocity of the ions are related. The velocities of the ions are measured by determining the flight time required for the ions to travel a fixed distance.

(1) Present address: Cornell Aeronautical Laboratory, Inc., of Cornell University, P.O. Box 235, Buffalo 21, New York.

(2) Part of the effort involved in conducting this program was supported by the Aeronautical Systems Division, Air Force Systems Command, United States Air Force, under Contract AF 33(616)-8374.

Table 1 - Comparison of Measured Ion and Neutral Plasma Species

PLASMA IONS				PLASMA NEUTRALS				
M/e	READING	$\sqrt{M}$ CORRECTION	CORRECTED RATIO	CORRECTED RATIO	IONIZATION EFFICIENCY	$\sqrt{M}$ CORRECTION	READING	M/e
14	0.003	1.69	0.005	0.025	--	1.69	0.015	14
16	0.003	1.58	0.005	0.032	--	1.58	0.02	16
17	0.0005	1.53	0.0008	0.0031	--	1.53	0.002	17
18	0.005	1.49	0.0075	0.0045	--	1.49	0.003	18
20	--	--	--	0.0013	--	1.42	0.0009	20
28	0.3	1.18	0.353	1.85	2.28	1.18	0.69	28
30	0.014	1.16	0.016	0.017	1.5	1.16	0.01	30
32	0.06	1.12	0.067	0.377	2.1	1.12	0.16	32
40	1.0	1.0	1.0	1.0	1.0	1.0	1.0	40
44	0.02	0.95	0.019	--	--	--	--	44
--	--	--	--	--	--	--	--	--

P-1709

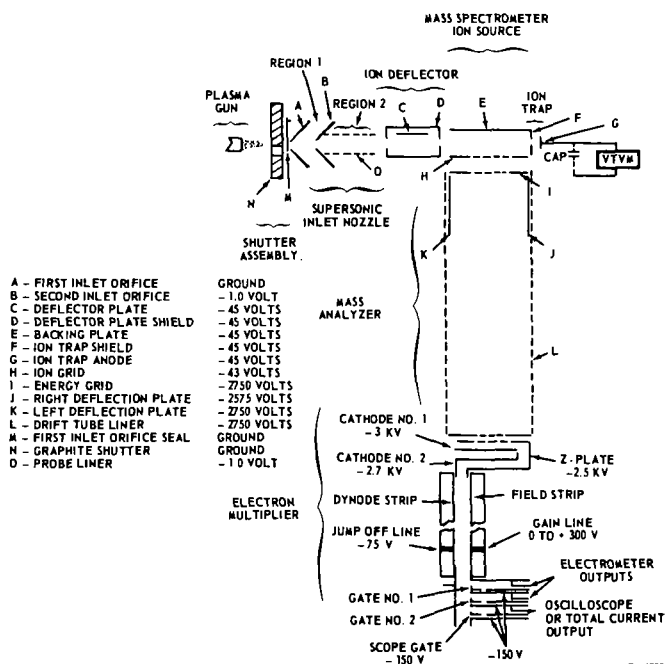


Figure 1 - Overall Schematic of Plasma Inlet-Mass Spectrometer

The success of the Bendix Time-of-Flight Mass Spectrometer results directly from the application of two important inventions made at the Bendix Research Laboratories Division. One of these was the development of the double grid source (Reference 2) which focuses all mass peaks with the same set of instrument operating parameters. The other (Reference 3) was the development of a unique ion detector of simple and rugged construction which has an unusually high gain and extremely wide bandpass characteristics.

The focusing action of the source is such that the time interval during which a particular mass peak is detected is much shorter than the time interval during which the original ionization took place. This makes possible a very substantial increase in the signal-to-noise ratio over that which can be obtained using instruments which utilize continuous ionization and detection, and substantially greater resolving power than has heretofore been available in time-of-flight instruments.

The ion detector is a magnetic electron multiplier which employs crossed magnetic and electric fields to control the electron trajectories. The numerous dynodes of the more conventional multipliers have been replaced with a continuous dynode and a field forming strip each consisting of a high resistance coating which has been fired onto an insulating support. This eliminates the need for special cathode and dynode contours and provides for a straightforward mechanical design of a gating section which can be mounted at the output end of the multiplier. The use of an appropriately designed gating section allows complete versatility in the design of output systems for use with the Time-of-Flight Mass Spectrometer (Reference 4). Some of the experiments which are considered in this paper were performed by using an oscilloscope spectrum display; however, a great deal of the data has been taken while using an Analog Scanner (Reference 5). This type of output system is expected to see frequent use in our future work.

A complete mass spectrum is completed in the period of a few microseconds so that the mass analyses can be repeated at a very high repetition rate. Though Time-of-Flight Mass Spectrometers have been produced with repetition rates as high as 100 kilocycles and as low as 2 kilocycles per second, the more routine applications usually use repetition rates between 10 and 50 kilocycles per second. Our plasma experiments were accomplished using a 10 kilocycle per second repetition rate.

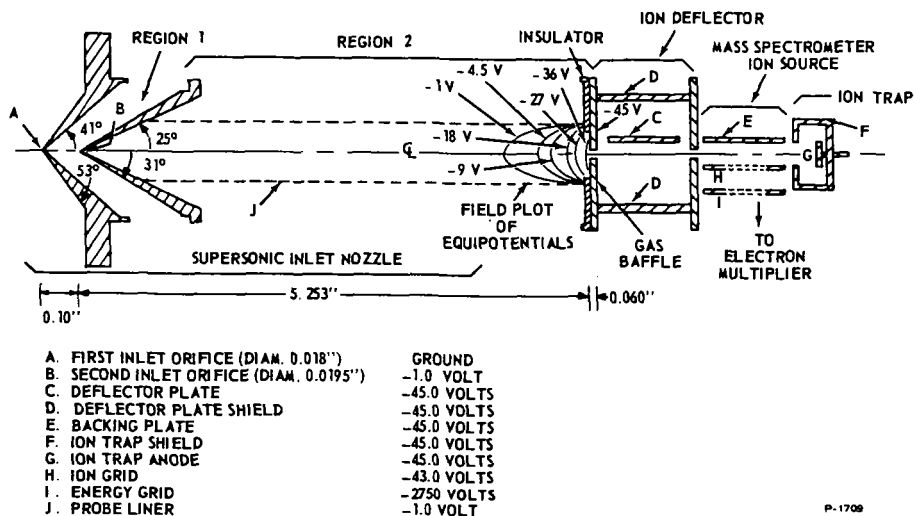
The Bendix Model 12 Time-of-Flight Mass Spectrometer has a resolution in excess of 225 AMU and its speed of response remains several orders of magnitude greater than the requirements of our experiments.

The important details of the inlet and mass spectrometer are shown in Figure 1.

In the more routine uses of the time-of-flight instrument, it is operated in such a way that the ions take a virtually line-of-sight path from the ion source to ion detector. The instrument can readily cope with samples which have a velocity component along the analyzer axis or with a velocity component or a velocity spread along either of the two transverse axes. However, samples which have a velocity spread in the direction of the analyzer axis will rapidly reduce the resolution achievable with the instrument (References 6 and 7).

The inlet system used in the plasma experiments was designed and installed in such a way that the plasma species entered the spectrometer source with an appreciable velocity in a direction transverse to the analyzer axis. The inlet provided optically aligned collimating slits so that the velocity spread of the sample species in the direction parallel to the line-of-sight of the axis was held to a value corresponding to less than 0.05 electron volt. In this way, the basic resolution of the spectrometer was not degraded.

The effects of large sample velocities perpendicular to the analyzer axis can be readily overcome by the use of the deflection plates (J and K) that are similar in operation and function to those which are used in a cathode ray tube. A consideration of the potentials applied to the deflection plates and the geometry of the system provides a straightforward method of computing the magnitude of the transverse velocity.



P-1709

Figure 2 - Principal Components of the Supersonic Probe

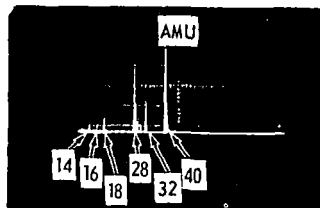
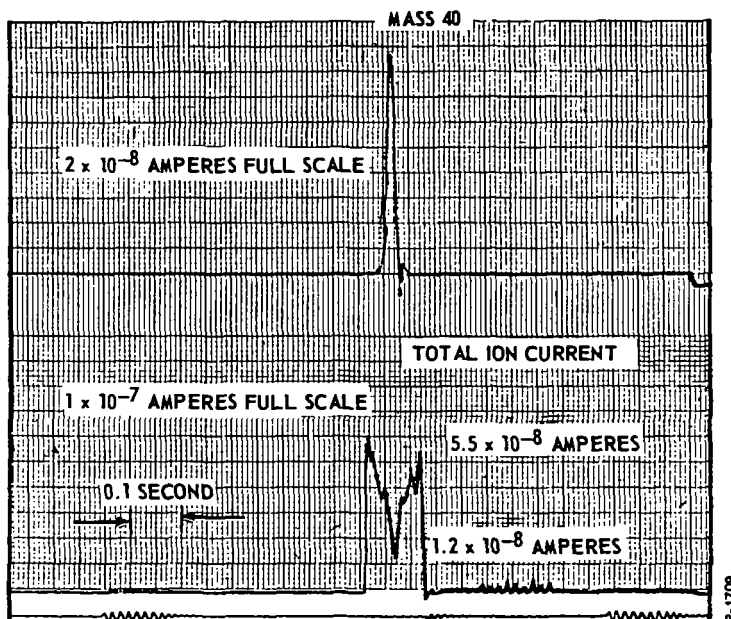


Figure 3 - Plasma Ion Spectrum at 24.6 KW Power



P-1709

Figure 4 - System Performance Verification Using Argon Ions

INLET PROBE

The principal components of the supersonic inlet probe are shown in Figure 2. The design of the supersonic nozzle (A) of the probe was based upon the work of Kantrowitz and Grey (Reference 8), Owen and Thornhill (Reference 9), Skinner (Reference 10), and Deckers and Fenn (Reference 11).

Prior to an analysis, the first inlet orifice (A) is sealed by a silastic RTV Number 731 seal in contact with the probe tip. This seal is controlled by a rotating graphite shutter that prevents the plasma jet from streaming on the probe tip except during an approximately 0.12 second "open" time in which the sample runs are made. The open time of the shutter was necessarily limited to short periods to prevent the thermal evaporation of the first orifice nozzle. The inlet seal is removed just prior to the time that the plasma contacts the probe tip and it is subsequently repositioned to reseal the probe in preparation for the next sample run.

Before a sample run is made, the pressure in region 1 is about 6×10^{-3} mm Hg, in region 2 and in the mass spectrometer proper is about 1×10^{-7} mm Hg. The influx of plasma species after removal of the silastic seal causes these respective pressures to become 3.8×10^{-2} mm Hg, about 10^{-4} mm Hg, and 5×10^{-5} mm Hg.

As the plasma species enter the inlet probe, an expansion takes place which produces a Mach 7 stream at the second inlet cone (B). This cone is designed so that the shock-wave or discontinuity which occurs at its orifice becomes attached to its leading edge. The sample species which pass through the orifice proceed toward the mass spectrometer ion source. The neutral species drift and upon entering the spectrometer source are ionized by a pulsed electron beam and analyzed by the mass spectrometer. The ion species are accelerated by an electric field due to the potential difference between the probe liner (J) and the gas baffle (D) so that they enter the mass spectrometer ion source with a transverse velocity corresponding to approximately 45 electron volts. Of course, the spectrometer electron beam is turned off during ion analyses, and ions which are not pulsed from the source and analyzed are collected by the ion trap anode (G). The deflector plate (C) is included so that the ions can be rejected when neutral analyses are being made.

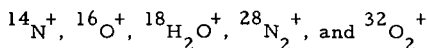
Each of the major elements of the inlet probe is constructed so that electric potentials can be applied to them. This permits the establishment of an assortment of electric fields within the individual regions of the probe. Consequently, the characteristics of the motion of ingested ion species under several conditions of operation can be readily investigated. Nominal operating potentials for each of the probe elements are shown in Figure 2. (All potentials in Figure 2 are referenced to the stainless steel probe-mass spectrometer vacuum housing.)

It is believed that the design of the inlet cones and their orifices is one of the major keys to the success of the plasma probe.

EXPERIMENTAL RESULTS

A Polaroid photograph of a typical oscilloscope spectrum is reproduced in Figure 3. This spectrum was obtained with the instrument sampling plasma ion species with a one inch separation between the plasmatron head and the first inlet orifice.

All of the experimental results presented in this paper were obtained by using argon in the plasma jet exhausting directly into the room air. The largest ion species sampled is $^{40}\text{Ar}^+$ due to the plasmatron operating gas. This figure also shows the



ion species due to the participation of the entrained air in the plasma processes.

Several experiments were performed to assure proper sequencing of the shutter, inlet seal, and instrumentation. A typical data recording for such a test is reproduced in Figure 4. The bottom trace records the sum of the amplitudes of all of the mass peaks in the ion spectra which are not specifically gated into another channel. The top trace records the output of one gated channel as it scans over the $^{40}\text{Ar}^+$ peak. A 0.1 second time interval is identified on the data record with time increasing to the

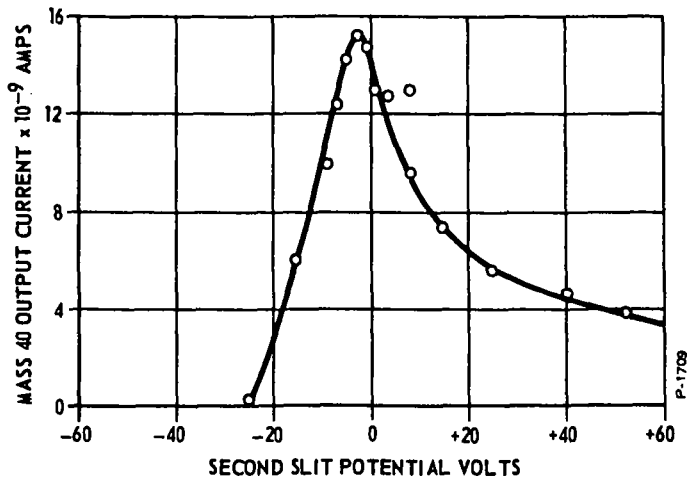


Figure 5 - Effects of Second Inlet Orifice Potential on $^{40}\text{A}^+$ Output

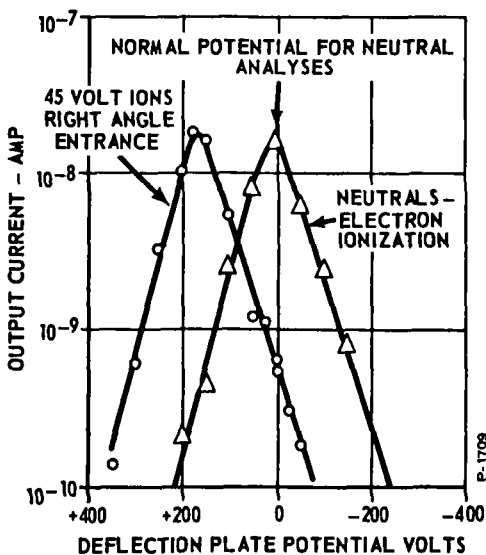


Figure 6 - Comparison of Deflection Plate Potential for Neutral and Ion Species

observer's right. The bottom record shows that ions are sampled for about 0.1 second, and that the output due to the $^{40}\text{A}^+$ peak is removed proportionately as this peak is scanned.

Comparison of this trace with others (not shown) shows that the total shutter "on" time (0.12 second) is much less than the time (0.25 second) required for the total spectrometer pressure to exceed the maximum permissible operating value (above which the equipment is automatically disabled). Since the total current exists for the shorter period of time, the entry of the plasma species into the remainder of the instrumentation is controlled by the shutter.

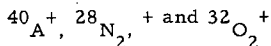
The effects on the $^{40}\text{A}^+$ output of the potential applied to the second inlet cone are shown in Figure 5. As is shown in the figure, the number of ions entering the orifice of the second inlet cone is a maximum at close to zero potential difference between the cones. This implies that the greatest number of ions traverse the space between the cones when their velocity is nearly the same as that of the neutral species.

The (positive) current flowing to the second inlet cone when it was operated with a negative bias and the ion and gas computed velocities were used to estimate the ion density in the plasma. Number densities of about 10^{13} ions/cm³ are estimated by this procedure.

Investigation of the effects of varying the potential difference of these deflection plates was carried out. The results are summarized in Figure 6. Data for both ions entering with velocities corresponding to 45 electron volts energy and (for comparison) ions formed with almost zero velocity are shown. The latter were obtained by operating the spectrometer in the conventional manner and ionizing the neutral species with an electron beam.

The data shows that the "temperature" of the ions is about the same for each run and that the velocity due to the 45 volt bias used in the inlet is compensated by about 175 volts applied to the deflection plate J in Figure 1. Several attempts to relate the 45 volt entrance energy, the 175 volt deflection plate potential, and the spectrometer geometry failed to produce a reasonable explanation for the trajectories of the ions in the system. Future experiments are planned to study this.

Figure 7 shows a plot of the amplitudes of the



ion peaks as a function of the separation between the inlet and the plasmatron head. This separation is felt to be related to, but not precisely the same as, the longitudinal position in the plasma, since the presence of the "cold" inlet in the plasma likely causes some modification of the plasma.

The figure indicates that the density of each of the species falls off exponentially. This suggests that the diffusion dominantly governs ion transport at the high plasma densities.

The variation of the intensity of the $^{40}\text{A}^+$ and $^{28}\text{N}_2^+$ ion peaks as a function of plasma generator power level is shown in Figure 8. The linearity of these plots suggest a proportional loss of power from the plasma system for increasing input powers. A temperature of 3000°K or 4000°K was obtained for plasma generator powers near 10 KW. Much higher temperatures are expected to exist at the higher generator power inputs.

Considerable evaluation of the data so far obtained is planned. Our efforts will be directed toward a better understanding of the operation of the probe and a better knowledge of the processes which obtain in the plasma system.

For comparison, the results of several experiments are brought into juxtaposition in Table 1. The corrected ratios of each of the species concentration to the Argon concentration for the neutral and the ion plasma species are compared. All of the entries are normalized to argon. The $\sqrt{M}$ correction is applied since "molecular flow" from near the second inlet to the spectrometer source is believed to occur (for both ion and neutral species).

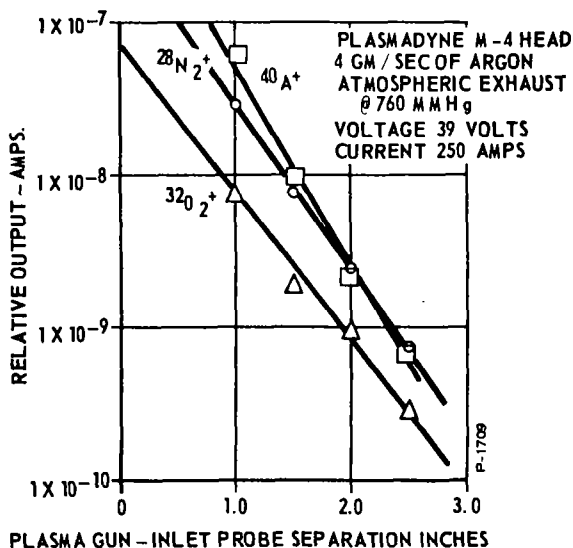


Figure 7 - Intensity of 40Ar^+ , 28N_2^+ , and 32O_2^+ versus Inlet-Plasma Gun Separation

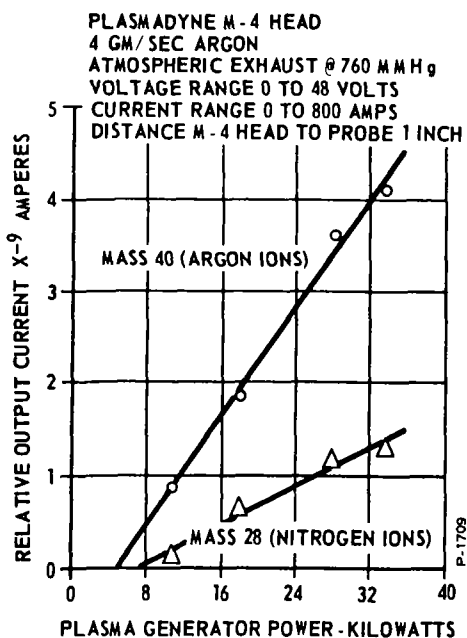


Figure 8 - Intensity of 40Ar^+ and 28N_2^+ versus Plasma Gun Power Level

The table shows entries for several mass-to-charge ratios. The identity of the species responsible for these entries is discussed below.

Entires for M/e , 14 and 16, occur under both ion and neutral headings. Each entry is due to N and O respectively but for quite different reasons. The $^{14}\text{N}^+$ and $^{16}\text{O}^+$ ions are sampled from the plasma, while the ^{14}N and ^{16}O neutrals are not. The latter two dominantly result from the dissociative ionization of the $^{28}\text{N}_2$ and $^{32}\text{O}_2$ in the mass spectrometer source.

Results obtained so far show a dynamic range for either ion specie or neutral specie analysis of at least one thousand. Computations based on the intensities of the peaks in the output mass spectra indicate the ion density in the plasma is about 5×10^{12} ions cm^{-3} and that the relative ion concentration is about 2.5×10^{-6} .

The 5×10^{12} ions cm^{-3} obtained in this way compares favorably with the 1×10^{13} ions cm^{-3} inferred from the second inlet cone current measurements (discussed above).

It is interesting to note that the instrumentation and experimental results described above were obtained in a one-year program. Each sample run is followed by a period of at least twenty minutes during which the spectrometer and inlet vacuum systems are pumped back down to starting pressures.

We plan a considerable amount of additional effort in both the development of refined experimental technique and in the better understanding of the plasma mechanism.

REFERENCES

1. O'Halloran, G. J.; Fluegge, R. A.; Betts, J. F.; Everett, W. L., "Summary Technical Report, Bendix Time-of-Flight Mass Spectrometer Plasma Jet Analyses Program," Report No. 2102, Aeronautical Systems Division Contract AF 33(616)-8374, Wright-Patterson Air Force Base, Ohio.
2. Wiley, W. C. and McLaren, I. H., "Time-of-Flight Mass Spectrometer with Improved Resolution," The Review of Scientific Instruments, Vol. 26, No. 12, pp. 1150-1157, December 1955, and U.S. Patent Number 2,685,035.
3. Wiley, W. C. and Goodrich, G. W., "Resistance Strip Magnetic Electron Multiplier," The Review of Scientific Instruments, Vol. 32, No. 7, pp. 846-849, July 1961.
4. Betts, J. F.; Pauve, E. H.; and Wiley, W. C., "Output Systems for Time-of-Flight Mass Spectrometers," Applied Spectroscopy, Vol. 14, No. 5, pp. 119-123, 1960.
5. Instruction Manual, Analog Output System Electronic Chassis, The Bendix Corporation, Research Laboratories Division.
6. O'Halloran, G. J., "Development of a Miniaturized Bendix Time-of-Flight Mass Spectrometer," Presented at the Eighth Annual Meeting of the ASTM Committee E-14 on Mass Spectrometry, Atlantic City, New Jersey, 26 June through 1 July 1960.
7. Fluegge, R. A., "The Use of the Spark Source Time-of-Flight Mass Spectrometer," Presented at the Ninth Annual Meeting of ASTM Committee E-14, Chicago, Illinois, 8 June 1961.
8. Kantrowitz, A. and Grey, J., "A High Intensity Source for the Molecular Beam," The Review of Scientific Instruments, Vol. 22, No. 5, p. 328, 1951.
9. Owen, P. L. and Thornhill, C. K., "Reports and Memoranda," Report No. 2616, September 1948.
10. Skinner, G., The Physics of Fluids, Vol. 4, No. 9, pp. 1172, 1961.
11. Deckers, J. and Fenn, J., Review of Scientific Instruments, Vol. 34, No. 1, p. 96, 1963.

CONVERSION AND EVALUATION OF DIFFUSION TO IONIC PUMPING
IN ISOTOPE RATIO MASS SPECTROMETER

W. S. Updegrove
Sinclair Research
Tulsa, Oklahoma

Manuscript Withdrawn

A DIRECT DETERMINATION OF THE ${}^3\text{H}$ - ${}^3\text{He}$ MASS DIFFERENCE†

P. E. Moreland, Jr.* and K. T. Bainbridge

Harvard University, Cambridge, Massachusetts

ABSTRACT

The ${}^3\text{H}$ - ${}^3\text{He}$ mass difference has been measured directly utilizing the high resolving power obtainable with the Harvard 50-inch, double-focusing mass spectrometer. A value of $19.83 \pm 18 \mu\text{u}$ (${}^{12}\text{C} = 12$) is found for the mass differences of this doublet. A brief description of the mass spectrometer and measurement techniques used is given. Results obtained for the doublets HD - ${}^3\text{H}$, HD - ${}^3\text{He}$, and H_2 - D are also presented.

INTRODUCTION

The initial mass measurements with the large double focusing mass spectrometer at Harvard have been made on the lightest nuclides. Among these the doublet T - ${}^3\text{He}$ was chosen for study. This mass difference, between two nuclei linked by a beta decay, has received a fair amount of investigation over a period of years, but has had a history of rather large discrepancies in the measured values. No prior direct measurement of T - ${}^3\text{He}$ has been reported but there has been one indirect mass-spectrometer measurement in which T and ${}^3\text{He}$ appeared in the doublets D_2 - HT , HT - ${}^4\text{He}$, and HD - ${}^3\text{He}$. There have been a number of measurements of the tritium beta-ray spectrum. The extrapolated beta-ray energy end points of these spectra should theoretically be equal to the T - ${}^3\text{He}$ mass difference.¹ In addition to providing another independent datum for this reaction Q , this measurement also was a convenient test of the resolution capability of the instrument. Other doublets measured are HD - T , HD - ${}^3\text{He}$ as a check on the T - ${}^3\text{He}$ measurement, and H_2 - D .

TECHNIQUE

The Harvard instrument has been described previously at several phases of its construction and initial operation.^{2,3} However, a number of additions and modifications for improved performance had been made by the time of these measurements in 1962. It was found that the battery supplies used for the magnet and electrostatic analyzer have sufficient stability without regulation for use with a "peak-matching"⁴ measurement technique. Figure 1 gives the basic plan view of the instrument along with a simplified schematic of the electronic instrumentation employed with the peak matching scheme in use during these measurements. With this scheme, the ion beam is modulated at the image slit in a sinusoidal manner with an AC modulation field provided by a coil in the gap of the magnet. The modulation frequency can be varied, but is normally derived from the 60 cps AC line. At the end of each modulation cycle, the acceleration and electrostatic analyzer voltages are switched by an amount sufficient to cause members of the doublet to follow identical trajectories and be focused at the image slit with precisely the same value of magnetic field on alternate cycles. This coincidence is accurately determined by observing the mass peaks in the ion detector output on an oscilloscope whose time base is proportional to the modulation current. The high speed switching is accomplished with mercury contact relays driven with a Strobotron light link.

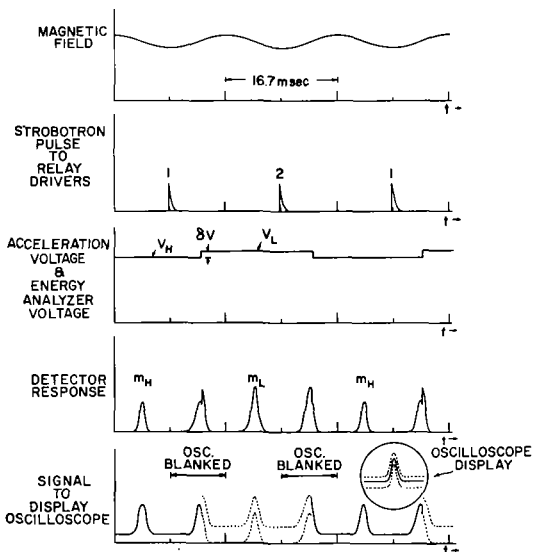
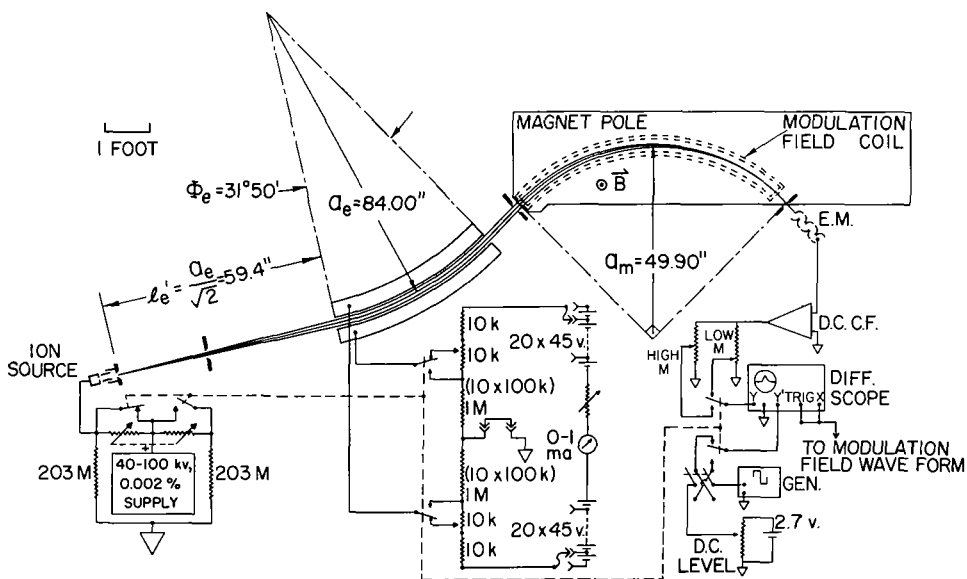
The peak display circuit** includes provision for matching the amplitude of the doublet peaks and for separating the peaks vertically. In addition, one peak can be superposed on a high frequency square wave, appearing as two traces symmetrically displaced from the other peak on the display. In order to avoid the display of the return trace and any switching transients present, the oscilloscope is blanked during half (or more) of each cycle. The phase relation of the various waveforms is illustrated in Fig. 2. Figure 3 shows the appearance of a single mass peak during a resolving power measurement, exhibiting a resolving power of 300,000 (full width at half height).

† This work supported by the Office of Naval Research

* Present address, Argonne National Laboratory, Argonne, Illinois

** We are indebted to Dr. J. W. Dewdney for the design and fabrication of this circuit.

FIG. 1 THE HARVARD DOUBLE FOCUSING MASS SPECTROMETER



Phase Relationships in Peak Matching Circuits. Field and Voltage Variations Shown Exaggerated. "+Slope" Convention Shown for Magnetic Modulation Field.

Fig. 2

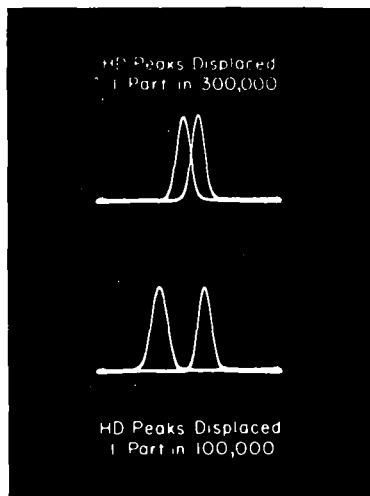


Fig. 3

The measurement of the fractional mass difference $\Delta M/M_L^*$ consists of measuring the fractional change in potential required to produce a peak match. This comes about from the requirement that $\Delta M/M_L = -\Delta V/V_H$, imposed by the fact that the ions must have the same momentum at peak match. By virtue of the energy focusing property of the instrument, the acceleration voltage change need not be highly precise. The accuracy of the mass measurement thus depends on the precision with which the fractional potential change at the energy analyzer is known. This potential is derived from a calibrated precision voltage divider, as shown in Fig. 1. For wide doublets the dispersion must be calibrated by the use of hydrocarbons and the ^{12}C standard.

MEASUREMENTS

Over one hundred peak matchings were made of each of the four doublets over a period of days. Figure 4 shows the general appearance of the display at peak match. The atomic ion beams produced by our electron bombardment source were rather weak, resulting in poor signal to noise ratio for these doublets. Using a resolving power of 300,000 to 330,000, the T- ^3He doublet, with a separation of about 1 part in 150,000, is just resolved, as shown in Fig. 4.

A relativistic correction factor $[1 + 2T/M_0c^2]$, where T is the kinetic energy of the ions, was applied to the average of the calibrated voltage divider readings to obtain final values of $\Delta M/M_L$. At an acceleration potential of about 80 kV, this correction is nearly equal to the quoted errors for these doublets. The mass differences for the four doublets are shown in Table I. The errors were obtained by applying a consistency factor^{5,6} to the standard error of the readings and adding an estimated limit of error for the voltage divider calibration. Since consistency factors ranged from 3 to 11, there are errors much larger than the standard error of the readings would indicate. However, after consistency factor adjustment under the assumption that these errors are random, the final reading error is still of the same magnitude as the calibration error. While these doublet values may still be affected by one or more systematic errors, more recent calibration of the instrument against ^{12}C and ^1H shows that a measured systematic error in $\Delta M/M_L$ is small compared to the errors quoted in Table I.

TABLE I. Doublet Mass Differences in μ
 $^{12}\text{C} = 12$

Doublet	BNL	Minn.	Harvard
T - ^3He	$20.03 \pm .21^a$	—	$19.83 \pm .18$
HD - T	—	—	$5\ 877.22 \pm .72$
HD - ^3He	$5\ 898.03 \pm .07^a$	—	$5\ 896.84 \pm .42$
H_2 - D	$1\ 548.78 \pm .18^a$ $1\ 548.08 \pm .10^b$	$1\ 547.2 \pm 4^c$	$1\ 547.77 \pm .28$
(HD- ^3He)-(HD-T)	—	—	$19.62 \pm .84$

^aFriedman and Smith, Phys. Rev. 109, 2214 (1958)

^bL. G. Smith, Phys. Rev. 111, 1606 (1958)

^cQuisenberry, Scolman, and Nier, Phys. Rev. 102, 1071 (1956)

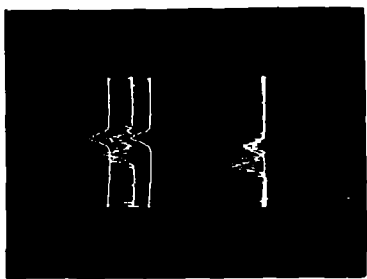
Previous mass spectrometer measurements of these doublets from the Brookhaven National Laboratory and the University of Minnesota are shown in Table I. The agreement is seen to be good in most instances, although the mass spectrometer results of Smith are slightly larger in every case than the conventional mass spectrometer values.

The mass excesses for D, T, and ^3He were obtained by combining the doublet data of Table with the ^1H mass value obtained by Konig, et al. These values are shown in Table II.

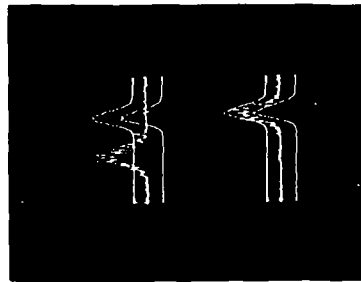
* Subscripts, L and H refer to the low and high mass members of the doublets, respectively.



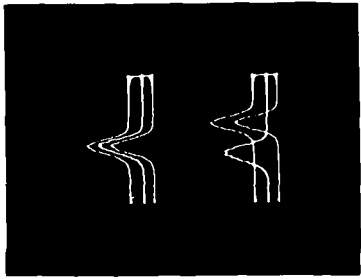
TOP: He^3 , H^3 PEAKS
RESOLVED. BOTTOM: PEAK
MATCH OF $\text{H}^3 - \text{He}^3$.



TOP: PEAK MATCH
OF $\text{HD}-\text{H}^3$, HD PEAK SPLIT.
BOTTOM: PEAK MATCH OF
 $\text{HD}-\text{H}^3$, PEAK SPLITTING NOT
USED.

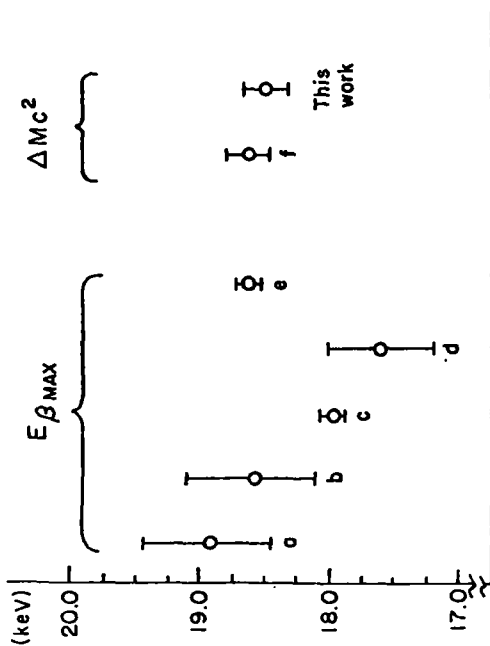


TOP: H_2-D PEAKS
DISPLACED 1 PART IN 10^5 .
BOTTOM: PEAK MATCH OF
 H_2-D , H_2 PEAK SPLIT.



TOP: PEAK MATCH
OF D_2-He^3 , D_2 PEAK SPLIT.
BOTTOM: He^3 PEAK DISPLA-
CED 1 PART IN 10^5 FROM
 D_2 PEAKS.

Fig. 4



- G. L. Hanna and B. Pontecorvo, PR 75, 983 (1949).
- S. C. Curran, et al., PR 76, 835 (1949).
- L. M. Langer and R. D. Moffat, PR 88, 689 (1952).
- D. R. Hamilton, et al., PR 92, 1521 (1953).
- F. T. Porter, PR 115, 450 (1959)
- L. Friedman and L. G. Smith, PR 109, 2214 L (1958)

FIG. 5 $3\text{T} - {}^3\text{He}$ MEASUREMENTS

TABLE II. Mass Excess in μu
 $^{12}\text{C} = 12$

Isotope	BNL	Minn.	Harvard
H - 1	$7\,825.00 \pm .10^a$	$7\,824.7 \pm .2^c$	$7\,825.22 \pm .08^e$
D - 2	$14\,101.90 \pm .10^a$	$14\,102.2 \pm .5^c$	$14\,102.67 \pm .38$
T - 3	$16\,048.19 \pm .38^b$	—	$16\,050.74 \pm .81$
^3He - 3	$16\,028.15 \pm .22^b$	—	$16\,030.98 \pm .60$

^aL. G. Smith, Phys. Rev. 111, 1606 (1958)

^bL. Friedman and L. G. Smith, Phys. Rev. 109, 2214 (1958)

^cQuisenberry, Giese, and Benson, Phys. Rev. 107, 1664 (1957)

^dGiese and Benson, Phys. Rev. 110, 712 (1958)

^eKönig, Mattauch, and Wapstra, Nuc. Phys. 31, 18 (1962)

The previous measurements of the tritium decay energy along with the value obtained here are presented in Fig. 5. Good agreement is found between the two mass spectroscopic measurements of Friedman and Smith and ourselves, and also with the work of Porter using an iron free beta ray spectrometer and the earlier value of Curran using a gas proportional counter. The weighted average of these four measurements is $18.57 \pm .08$ kV.

REFERENCES

- ¹J. J. Sakurai, Phys. Rev. Letters 1, 40 (1958).
- ²T. L. Collins and K. T. Bainbridge in Nuclear Masses and Their Determination, H. Hintenberger, ed., Pergamon Press, London, 1957, p. 213.
- ³K. T. Bainbridge and P. E. Moreland Jr., in Proceedings of the International Conference on Nuclidic Masses, H. E. Duckworth, ed., University of Toronto Press, 1960, p. 460.
- ⁴L. G. Smith and C. C. Damm, Rev. Sci. Instr. 27, 638 (1956).
- ⁵J. H. E. Mattauch in Proceedings of the International Conference on Nuclidic Masses, H. E. Duckworth, ed., University of Toronto Press, 1960, p. 14.
- ⁶R. T. Birge, Phys. Rev. 40, 207 (1932).

The determination of the absolute value of the Deuterium
content of hydrogen and water by Mass Spectrometry

R. Botter
Centre D'Etudes Nucleaires De Saclay, France

Abstract -

In a former publication we have described a method for the determination of the absolute deuterium content of water.

The absolute value of the isotopic composition of hydrogen gas has been made by total combustion of hydrogen gases, and comparison of the water obtained with standard waters whose absolute content has been determined by the preceding method.

Having the possibility of obtaining highly depleted hydrogen by gas chromatography or thermal diffusion we will be able to check the absolute value determined by the preceding method.

During this last few years the use of isotopic analysis of hydrogen by mass spectrometry has widened its scope of applications, specially in glaciological and meteorological application.

The accuracy of the analysis becoming higher it has been shown that there were notable differences between the values determined by various laboratories for the same sample of water. If absolute values can be assigned to the deuterium content of hydrogen samples. This makes it difficult to link the values obtained for different samples from different laboratories. For instance the values published by the National Bureau of Standards (1) for the water standard NBS I range from 149 ppm D_2 to 154 ppm D_2 .

The availability of zero content deuterium hydrogen gas (i.e. containing theoretically less than 0.1 ppm D_2) obtained by thermal diffusion and gas chromatography makes it possible to check those values of hydrogen gas.

In this paper we describe a method used to make those absolute determinations for hydrogen gas by comparison with absolute values previously assigned to standard water samples.

The check performed on the hydrogen gas phase will therefore serve as an independant confirmation of the accuracy of values assigned to the water samples.

I) Mass Spectrometer :

The mass spectrometer used have been described in a preceding paper (2).

These spectrometers are specially designed for isotopic analysis of hydrogen at low deuterium content (less than 1 % D)

* ppm = parts per million in atom.

TABLE I

Reproducibility of the reduction method

<u>NUMBER</u>	<u>MASS SPECTROMETER VALUES</u>	
	<u>Sample I</u>	<u>Sample II</u>
1	151,5	116,4
2	152,6	115,8
3	152,2	116,4
4	152,5	115,7
5	152,5	116,2
6	152,5	116,3
7		116,4

TABLE II

Reproducibility of the oxydation method

<u>NUMBER</u>	<u>MASS SPECTROMETER VALUES</u>	
	<u>Sample I</u>	<u>Sample II</u>
1	28,1	123,0
2	28,0	122,8
3	28,0	122,9
4	28,1	123,0
5	28,0	122,9

TABLE III

Comparison of water after passing through
the combustion apparatus with the initial hydrogen

<u>Initial value</u>	<u>Final value</u>
123,2	123,2
123,2	123,3
123,2	123,2

The sensitivity is 0.1 ppm in deuterium and the precision 0.1 per cent above 100 ppm D.

One of the apparatus is equipped with a classical gas line, and is destined for analysis of hydrogen gas.

The second apparatus has a special reduction line for the analysis of water. The water sample is introduced with a micro-syringe and vaporised into a 250 ml flash. Then it flows through a uranium furnace, located in the low pressure part of the mass spectrometer, where it is reduced to hydrogen.

The amount of water necessary for an analysis is about 0,5 mg.

2) Determination of the absolute deuterium content of water by the equilibration method :

The absolute value of the isotopic composition of water was determined by an indirect method (2). This method was the following.

Standard waters were prepared by mixing weighted amounts of water of low deuterium content and heavy water. This provides a serie of standards differing by known amounts in D content though their absolute content in D cannot be assigned. This difference is known with a prevision better than 0,1 ppm (2).

Hydrogen sulphide is equilibrated with these standard waters and both H_2S and H_2O were analysed on the mass spectrometer with the reduction line.

The values for the waters and the H_2S are plotted on the same graph on the abscissa scale and on the ordinate the differences in absolute value of the standard waters with an arbitrary origin. Two straight lines are obtained, one for H_2O and one for H_2S , and their intersection correspond to the concentration zero of D (the origin of the absolute values) as H_2O and H_2S cannot have the same isotope content except at zero deuterium concentration.

The values thus obtained for NBSI is $154 \pm 0,4$ ppm.

3) Absolute content in deuterium of the hydrogen gas by comparison with the water standards.

This comparison cannot be made directly on a mass spectrometer equipped with the reduction line. In this case the inlet leak is a capillary, of 10 cm lenght and 0,2 mm in diameter. The hydrogen flow in this capillary, at the correct working pressure is a KNUDSEN flow. But water vapor is introduced at a different point of the apparatus as it has to be reduced over uranium, and the flow in the earlier part of the line is not a molecular flow. Therefore the values of the readings taken on the mass spectrometers may not be the same for hydrogen and water of the same deuterium content. In either case independant calibration of the instrument is required.

The comparison of deuterium content of water and hydrogen can be made in one of two ways :

a) Reduction of water to hydrogen outside of the mass spectrometer, and comparison of the gases.

b) Combustion of hydrogen and comparison of the water obtained with reference water.

TABLE IV

COMPARISON OF HYDROGEN AFTER AN CYCLE
COMBUSTION-REDUCTION WITH THE INITIAL HYDROGEN

<u>Number</u>	<u>Initial value</u>	<u>Difference after oxydation and reduction</u>	<u>Mean Value</u>
1	122,9	+ 1,0	123,0
2	122,9	- 0,1	
3	122,9	- 0,9	
4	122,9	+ 1,1	
5	122,9	- 0,2	
6	122,9	- 0,5	
7	122,9	+ 0,6	

TABLE V

ABSOLUTE VALUES FOR THE REFERENCE GASES

<u>Référence</u>	<u>Absolute value</u>
E I	134,1
E II	28,0
R I	122,9
R II	33,5

E I and E II : standard waters

R I and R II : reference gases

TABLE VI

VALUE OF DEPLETED HYDROGEN

<u>Reference</u>	<u>Value</u>
R II	122,9
R I	33,5
D ₀	2,9
G ₀	2,4

D₀ = depleted hydrogen by thermal diffusion

G₀ = depleted hydrogen by gas chromatography

- a) Reduction of water. About 40 mg water were reduced in a uranium furnace, containing about 100 g uranium turnings, at 600 °C.

The hydrogen thus obtained was used for the calibration of the hydrogen mass spectrometer and for the determination of the absolute content of reference gases.

This method was rejected because the reproducibility of hydrogen thus obtained by reduction of water outside the mass spectrometer line is only about $\pm 0,5$ ppm for water of 120 ppm D content (Table N°I).

- b) Combustion of hydrogen. Total oxydation of hydrogen is carried out on platinum filaments.

The apparatus is shown schematically on figure I.

After carefull degassing under vacuum the apparatus is filled with a dried mixture of O_2 and A ($O_2/A = 1/2$)

The argon is dried in a cold trap filled with molecular sieve at dry-ice temperature. Oxygen is first passed over a platinum catalyst in order to convert the residual hydrogen to water and then water is trapped in cold trap.

The mixture of A and O_2 is circulated with the glass circulation pump. The platinum wires are heated to about 400°C. Then 1 liter of hydrogen gas is introduced in small fractions (200 cc) with the toepler pump. Sufficient time is allowed for the total combustion of one hydrogen fraction between successive introduction. The water formed is trapped in a dry ice-acetone mixture.

The completion of the oxydation is verified by mass spectrometric analysis of the residual hydrogen in the A - O_2 mixture. Collected water is then analysed on the mass spectrometer equipped with the reduction line. The reproducibility of the analysis for a serie of combustions is that of the mass spectrometer (0,1 ppm) (see table N°II

We have cheked the apparatus for systematic errors.

- First we have introduced into the apparatus containing the oxygen-argon mixture, water instead of hydrogen and verified that the D content of this water does not change after passing in the apparatus (table N°III).

- Second we have reduced water obtained from a combustion of a hydrogen sample and this hydrogen was compared with the original hydrogen. (The mean value is the same) (table N°IV)

RESULTS.-

1) The results obtained for two reference gases are given in table V.

The absolute value for R I and R II are obtained by comparison with water standards E I and E II, known by the equilibration method.

The difference between R I and R II is known with a precision of 0,2 ppm due to the error of the analysis on both samples.

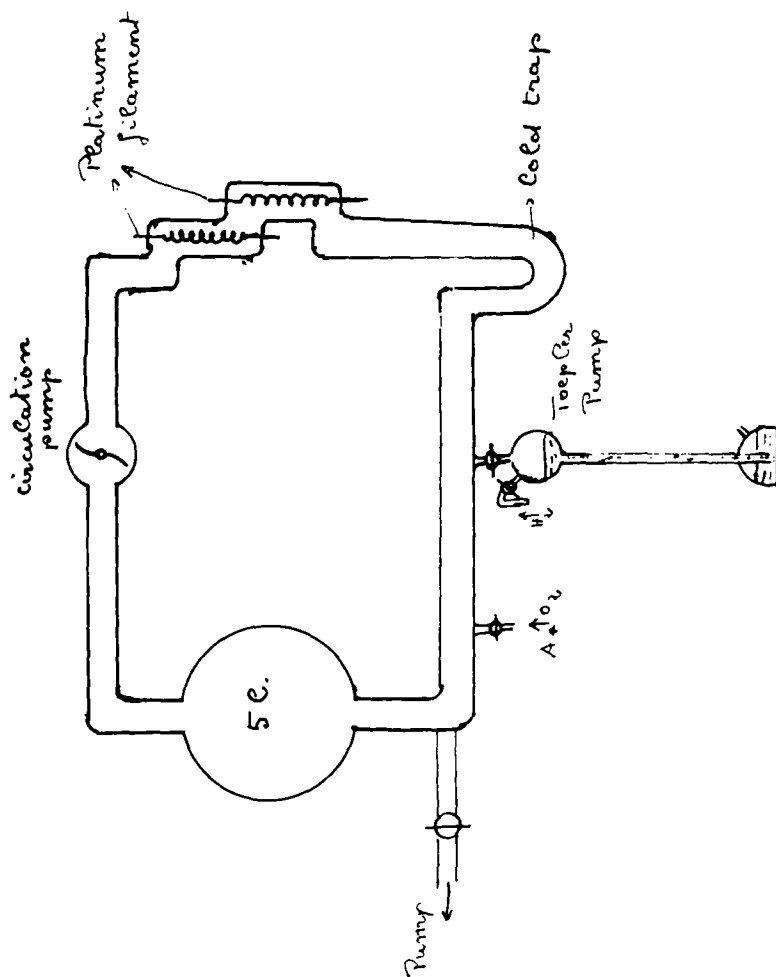
2) Preparation of hydrogen at low deuterium content :

a) Thermal diffusion -

The thermal diffusion unit has an available length for enrichment of 550 cm.

The column was filled with hydrogen of about 30 ppm in D; the known enrichment factor of the column lead us to a value for the

Diagram of the
Combustion apparatus



depleted hydrogen lower than 3.10^{-2} ppm.

b) Gas chromatography -

A frontal gas chromatographic separation was made on a molecular sieve 13 X.

The column has a length of 3 m

The initial hydrogen has a deuterium content of about 30 ppm

Only the head fractions are collected in several parts. An exact estimation of the D content of this gas was not made up to now.

The results for both gases D_0 (diffusion sample) and G_0 (gas chromatography sample) are given in table VI.

The value for D_0 is higher by about 0,5 ppm than the value for G_0 .

So D_0 must have been contaminated, and we will repeat these experiments to estimate the D content of the depleted hydrogen obtained by gas chromatography in order to obtain an other determination of the absolute D content of hydrogen and water.

ACKNOWLEDGMENTS -

We are indebted to MM. LERAT and MOLINARI for the preparation of depleted hydrogen by thermal diffusion, and to Mrs. F. BOTTER and Mr. S. TISTCHENKO for the preparation of depleted hydrogen by gas chromatography.

Résumé

Dans une publication antérieure nous avons décrit une méthode de détermination en valeur absolue de la composition isotopique de l'hydrogène de l'eau.

Pour déterminer la valeur absolue de la composition isotopique de gaz hydrogène nous avons effectué une combustion totale de gaz hydrogène et comparé l'eau ainsi obtenue à des eaux standards dont le titre a été déterminé par la méthode précédente.

Ayant la possibilité d'obtenir par diffusion thermique ou par chromatographie en phase gazeuse de l'hydrogène très appauvri en deutérium, nous pouvons vérifier les valeurs absolues déterminées par la méthode précédente.

R E F E R E N C E

- 1) NATIONAL BUREAU OF STANDARDS
Technical Note 51
Isotopic abundance ratios reported for reference
samples stocked by the National Bureau of Standards.
- 2) R. BOTTER - G. NIEF
Analysis of simple hydrogen compounds
Advances in Mass Spectrometry - Pergamon Press (1959)

THE PRODUCTS OF FLASH PYROLYSIS OF PHENOL-FORMALDEHYDE
BY TIME-OF-FLIGHT MASS SPECTROSCOPY

Henry L. Friedman

General Electric Company, Space Sciences Laboratory, King-of-Prussia, Pa.

ABSTRACT

A sample of phenol-formaldehyde was flash pyrolyzed eleven times in the reaction chamber of a time-of-flight mass spectrometer. Quantitative analyses were determined for pyrolysis products which were present within ten seconds after each flash. A high degree of consistency between compositions of products from consecutive flashes resulted. A discussion of the results is presented.

INTRODUCTION

As plastics undergo ablation, pyrolysis products are injected into the boundary layer between the plastic and the environment. Material and energy transfer during ablation depends, in part, on the energy that is associated with the decomposition process, and the enthalpy of the decomposition gases. Many studies have been carried out wherein the decomposition products were analyzed by techniques which were suitable only for handling stable products. Under some conditions, it is quite probable that a considerable quantity of free radicals, atoms, or unstable complex molecules are evolved. Such species may have a marked influence on material and energy transfer.

Kistiakowsky and co-workers have used a time-of-flight mass spectrometer to study the intermediates of several reactions. Kistiakowsky and Kydd¹ flash photolyzed ketene and nitrogen dioxide in the reaction chamber of the mass spectrometer. Bradley and Kistiakowsky studied the thermal decomposition of nitrous oxide² and the polymerization and oxidation of acetylene³ by shock waves, where the mass spectrometer leak was at the end of the driven section of the shock tube. Nelson and co-workers⁴⁻⁶ have demonstrated that plastics may be heated to very high temperatures by radiation from xenon filled discharge tubes. Therefore, it seemed appropriate to attempt to study the products of flash pyrolysis of plastics in the reaction chamber of a time-of-flight mass spectrometer in order to observe compositions which might simulate those that are present during ablation. While techniques for studying transitory products are still being developed, it has been possible to determine quantitative analyses for the more stable products which are present about ten seconds after the flash. This paper describes only the work which has been performed for the more stable products.

EXPERIMENTAL

The standard Model 14-100 Bendix Time-of-Flight Mass Spectrometer with several additions and modifications were used for these studies. The mass spectrometer is equipped with a Model 112 Bendix Two Channel Analog Output System. The Model 321 Scanner Channel was used as is, while the Model 311 Controller Channel was converted to a second scanner channel. The Model E-104 Bendix Trap Current Regulator was used to maintain a constant ionizing current. The high voltage supply to the multiplier field and dynode strips was regulated by the circuit that is shown in Figure 1*. The multiplier noise was reduced by placing a 0.1 microfarad capacitor between the multiplier scope anode and ground**. The D. C. voltages throughout the instrument were kept constant by use of a Model CUL Sola Constant Voltage Transformer. A Model 450 Hewlett-Packard Amplifier was used to amplify the signal which was generated by the multiplier.

The flash lamp and sample geometry that was used for these experiments is described elsewhere⁷. A schematic diagram of the flash lamp and sample, as mounted in the reaction chamber of the mass spectrometer, are shown in Figure 2. In operation, the assembly is placed in the reaction chamber of the mass spectrometer with a solid sample in place. The glass lead from the hollow electrode is fastened to the external vacuum system, and the lamp is evacuated at 10^{-6} mm Hg for several hours. Meanwhile, the reaction chamber is evacuated through the mass spectrometer leak and through the reaction chamber pumping port by the external vacuum system. The lamp is then filled to about 40 mm Hg with xenon. A 220 microfarad capacitor bank at 5000 V is discharged through the lamp in order to produce the flash.

* This modification was recommended by Mr. Edward Younginger of the Bendix Corporation.

** This modification was recommended by Prof. Stig Claesson, Head of the Institute of Physical Chemistry, Uppsala, Sweden.

DEGRADATION PRODUCTS FROM FLASH PYROLYSIS OF PURE PHENOL-FORMALDEHYDE SAMPLE
AS DETERMINED BY THE BENDIX TIME-OF-FLIGHT MASS SPECTROMETER

TABLE 1 (ABSOLUTE YIELD)

Yield in Arbitrary Units, Proportional to Moles (Flash Number →)											
Component	1	2	3	4	5	6	7	8	9	10	11
H ₂	149.7	250.0	291.9	309.5	283.1	261.1	221.3	190.3	172.7	170.3	181.9
CH ₄	33.8	52.4	61.3	73.6	61.7	50.9	40.9	34.8	33.7	32.6	32.5
H ₂ O	176.9	131.3	82.7	86.5	67.5	54.2	33.9	33.3	29.5	23.8	32.3
CO	94.2	153.0	152.6	175.3	138.8	124.8	100.0	67.8	55.4	54.6	61.0
C ₂ H ₂	22.9	15.1	13.1	10.9	9.0	10.1	10.1	6.7	4.6	5.4	3.3
C ₂ H ₄	21.9	11.1	13.7	12.7	11.6	6.3	6.6	12.2	7.3	9.4	6.8
C ₂ H ₆	11.8	7.8	8.6	8.7	7.9	9.0	8.0	7.0	6.2	6.4	4.9
C ₃ H ₄	4.2	1.5	2.5	2.8	2.1	2.9	2.5	2.2	1.7	1.7	1.3
C ₃ H ₆	9.7	5.8	4.2	4.5	6.0	5.4	6.4	5.5	3.9	4.7	2.9
C ₃ H ₈	9.9	5.4	4.8	4.8	4.4	4.1	3.9	2.8	1.8	2.1	1.9
CO ₂	23.6	16.2	11.3	10.3	8.0	7.1	5.9	4.7	3.9	4.3	5.1
C ₄ H ₂	0.4	0.9	1.2	1.2	1.0	1.0	0.8	0.7	0.4	0.4	0.5
C ₄ H ₄	0.3	1.4	1.2	1.5	0.9	0.9	1.0	0.3	0.4	0.6	0.5
C ₄ H ₆	0.6	1.1	0.8	1.6	1.0	1.4	0.8	0.6	0.6	0.5	0.6
C ₄ H ₈	1.8	1.8	0.7	1.6	1.3	2.0	2.5	1.8	1.4	1.6	1.2
C ₅ H ₆	0.3	2.2	3.1	3.0	2.7	2.2	2.0	1.6	1.3	1.1	1.4
C ₅ H ₈	0.9	1.7	1.8	2.1	1.9	0.9	1.2	0.8	1.0	0.8	1.3
C ₆ H ₆	1.2	2.5	3.6	4.0	3.2	2.6	1.9	1.6	1.2	1.1	1.3
C ₇ H ₈	0.6	1.0	1.2	1.3	1.0	0.8	0.6	0.6	0.4	0.4	0.4
C ₈ H ₈	0.6	0.8	1.0	1.0	0.8	0.6	0.5	0.4	0.3	0.3	0.2
C ₉ H ₁₂	-	-	trace	trace	trace	trace	trace	-	-	-	-

TABLE 2 (RELATIVE YIELD)

Mole Percent (Flash Number →)											
Component	1	2	3	4	5	6	7	8	9	10	11
H ₂	26.5	37.7	44.1	43.2	46.1	47.6	49.2	50.7	52.7	52.9	53.3
CH ₄	6.0	7.9	9.3	10.3	10.1	9.3	9.1	9.3	10.3	10.1	9.5
H ₂ O	31.3	19.8	12.5	12.1	11.0	9.9	7.4	8.8	9.0	7.4	9.5
CO	16.7	23.1	23.1	24.4	22.6	22.8	22.2	18.1	16.9	17.0	17.9
C ₂ H ₂	4.0	2.3	2.0	1.5	1.5	1.8	2.2	1.8	1.4	1.7	1.0
C ₂ H ₄	3.9	1.7	2.1	1.8	1.9	1.1	1.5	3.1	2.2	2.9	2.0
C ₂ H ₆	2.1	1.2	1.3	1.2	1.3	1.6	1.8	1.9	1.9	2.0	1.4
C ₃ H ₄	0.7	0.2	0.4	0.4	0.3	0.5	0.5	0.6	0.5	0.5	0.4
C ₃ H ₆	1.7	0.9	0.6	0.6	1.0	1.0	1.4	1.5	1.2	1.5	0.8
C ₃ H ₈	1.7	0.8	0.7	0.7	0.7	0.8	0.9	0.8	0.6	0.7	0.5
CO ₂	4.2	2.4	1.7	1.4	1.3	1.3	1.3	1.2	1.2	1.3	1.5
C ₄ H ₂	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1
C ₄ H ₄	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.1
C ₄ H ₆	0.1	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
C ₄ H ₈	0.3	0.3	0.1	0.2	0.2	0.4	0.6	0.5	0.4	0.5	0.3
C ₅ H ₆	0.1	0.3	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
C ₅ H ₈	0.1	0.3	0.3	0.3	0.3	0.2	0.3	0.2	0.3	0.2	0.4
C ₆ H ₆	0.2	0.4	0.5	0.6	0.5	0.5	0.4	0.4	0.4	0.4	0.4
C ₇ H ₈	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
C ₈ H ₈	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C ₉ H ₁₂	-	-	trace	trace	trace	trace	trace	-	-	-	-

Average pressure in reaction chamber during duration of analog sweep in mm Hg
relative to room temperature

3.54	4.15	4.14	4.48	3.84	3.43	2.81	2.35	2.05	2.01	2.14
------	------	------	------	------	------	------	------	------	------	------

A single two mil diameter gold foil leak was used for these experiments. The decomposition products were ionized with 70 Volt electrons. All spectra were recorded with the ion lens of the mass spectrometer in operation. The liquid nitrogen trap of the mass spectrometer was filled as the lamp electrodes were being charged. The lamp was discharged two minutes after the trap was completely filled, in each case. The analog spectra were recorded by the following method.

In normal operation, the multiplier receives a new mass spectrum every 100 microseconds (10 KC). The analog gate is activated only for a fraction of a microsecond during each mass spectrum, and sweeps to either higher or lower mass numbers slowly from cycle to cycle. Thus, one may integrate a large number of events with the analog. The starting mass may be selected manually by choice of an initial voltage. The mass range is swept by continually increasing or decreasing this voltage. The entire process is controlled by the 10 KC master pulse of mass spectrometer. During flash pyrolysis experiments, it was necessary to start analog scan at the same time with respect to the flash for each flash experiment in order to obtain data that could be compared with a minimum of errors. The following procedure was found to give reproducible timing. The flash strikes a phototube, which generates a pulse. The pulse triggers the Tektronix Model 543 Oscilloscope after a pre-set time delay (three seconds for these experiments). A rising voltage which is generated by the oscilloscope, at a predetermined rate, replaces a similar voltage source in the analog and drives the gate towards an increasing mass range. A photograph of the mass spectrum is obtained by opening the camera shutter with the oscilloscope set for single sweep before striking the flash, and closing the shutter after the desired mass range has been swept. It was desirable to use the second channel to study a greater mass range in shorter periods of time and to provide a wider range of sensitivity. Since the gate of the first channel is at the correct time relationship with respect to the master pulse, the gate signal of the first channel was used as a pulse to trigger the gate of the second channel. The starting mass of the second channel was set manually at the desired value. The gates of the two channels then began to sweep at the same predetermined time delay with respect to the flash and covered their respective mass ranges during the same interval of time. Calibration spectra were photographed in the same manner so that they could be compared with the unknowns more accurately. Analog channel 2, which covered the higher mass range, was set to a higher sensitivity than channel 1. Channel 1 covered m/e 1 to 100, while channel 2 covered m/e 12 to 130. Analog sweep was completed in seven seconds. Reference samples of n-butane were run periodically to standardize the instrument.

A sample of pure phenol-formaldehyde was flash pyrolyzed eleven times in the reaction chamber of the mass spectrometer. Each flash was applied only after the products of the previous flash were pumped away, a process which took about $\frac{1}{2}$ hour. The mass spectroscopy data were analyzed by the following method.

Calibration samples of pure Hydrogen, Methane, Carbon Monoxide, Ethane, Ethylene, Acetylene, Water, and Carbon Dioxide were run in order to obtain their mass spectra. Comparison of these spectra with the Mass Spectral Tables of the American Petroleum Institute showed that they were quite similar to spectra which were obtained at the National Bureau of Standards. Therefore, N.B.S. spectra were used for compounds which were not tested directly. Where N.B.S. spectra were not available, those spectra which were found to be most like N.B.S. spectra, for other compounds, were used. Note that the A.P.I. Mass Spectral Tables were used only for minor components, so that small discrepancies in the pattern and sensitivity would not be too important. Direct calibration spectra were obtained by a technique which simulated part of the flash pyrolysis experiment. Samples of known pressure were introduced to the reaction chamber from the three liter reservoir. At the appropriate moment, the valve which separates the reaction chamber from the reservoir was closed. The analog system was triggered manually at that instant, and the oscilloscope was triggered after a time delay of three seconds.

The first few analyses of data were performed by starting at the high mass end and assigning peaks to the compounds from which they probably originated. The lower mass fragment contributions which could be attributed to these compounds were then subtracted from the remaining mass spectrum in order to see if the choices were reasonable. Changes were made when necessary. When a consistent set of compounds was obtained for several flash experiments, a matrix was derived for application to the other flash experiments. The matrix method was much faster than the earlier systematic elimination procedure.

RESULTS AND DISCUSSION

The results of these experiments are shown in different forms in Tables 1 and 2. Table 2 shows that a high degree of consistency is associated with the analysis. Absolute yields of the various products are plotted as a function of flash number in

TABLE 3

FLOW OF PURE GASES FROM THE REACTION CHAMBER INTO THE MASS SPECTROMETER

(Initial Pressure - 67 microns)

Gas	m/e	$\frac{M}{M_0}$
H ₂	2	$-(1.13 \pm 0.02) \times 10^{-2}$
CH ₄	16	$-(4.25 \pm 0.12) \times 10^{-3}$
n-C ₄ H ₁₀	58	$-(2.33 \pm 0.05) \times 10^{-3}$

Gases compared	Theory	Experiment
H ₂ /CH ₄	2.828	2.7 ± 0.1
H ₂ /C ₄ H ₁₀	5.385	4.9 ± 0.2
CH ₄ /C ₄ H ₁₀	1.904	1.8 ± 0.1

TABLE 4

COMPARISON OF ARC-IMAGE AND FLASH PYROLYSIS DATA

Component	Arc Image Furnace	Relative Yield, moles/mole H ₂ (Flash Number →)										
		1	2	3	4	5	6	7	8	9	10	11
H ₂	1	1	1	1	1	1	1	1	1	1	1	1
CO	.377	.629	.612	.523	.566	.490	.478	.451	.356	.321	.320	.336
CH ₄	.244	.266	.210	.210	.238	.218	.195	.185	.183	.195	.191	.179
fraction 2*	.198	.714	.272	.212	.196	.188	.192	.219	.234	.186	.217	.158

Relative Yield, grams/mole H₂

fraction 3**	38.6	23.3	11.9	7.9	7.9	6.9	5.9	4.9	5.1	4.9	4.1	5.1
--------------	------	------	------	-----	-----	-----	-----	-----	-----	-----	-----	-----

* Fraction 2 in arc image furnace experiment consists of components which are not volatile at liquid nitrogen temperatures and distill from a CO₂ ice cooled trap. For the flash pyrolysis experiments, this fraction is assumed to contain all C₂, C₃, and C₄ hydrocarbons and CO₂.

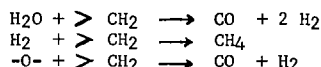
** Fraction 3 in arc image furnace experiment consists of components which are not volatile at CO₂ ice temperatures and distill from a trap at room temperature. For flash pyrolysis experiments, this fraction is assumed to contain all C₅ and heavier hydrocarbons and H₂O.

TABLE 5

SURFACE TEMPERATURE CALCULATED FROM WATER GAS EQUILIBRIUM

Flash Number	Temperature, °K
1	2025
2	2090
3	1790
4	2030
5	1880
6	1755
7	1495
8	1480
9	1450
10	1305
11	1385

Figures 3 to 5. Examination of the individual yields shows several trends. H_2 , CO, CH_4 , C_4H_2 , C_5H_6 , C_6H_6 , C_7H_8 , and C_8H_8 show a maximum yield at about the fourth flash with comparatively smooth increases in the earlier flashes and decreases in the later experiments. C_4H_4 , C_4H_6 , and C_5H_8 showed the same general behavior as the above, with several small variations. H_2O , CO_2 , C_2H_2 , and C_3H_8 showed a more or less continual decrease in yield. C_2H_4 , C_2H_6 , C_3H_4 , and C_3H_6 showed an early decrease in yield, followed by a leveling off and then a comparatively gradual decrease. C_4H_8 showed a rather different trend. The yield of C_4H_8 was very irregular with the maximum yield at the seventh flash. In general, however, H_2 , CO, CH_4 , and C_4 and heavier hydrocarbons showed one type of behavior, while H_2O , CO_2 , C_2 , and C_3 hydrocarbons showed a different type. This information could conceivably lead to understanding of the mechanism of high temperature degradation of phenol-formaldehyde and other complex plastics. For example, Ouchi and Honda⁸ observed that H_2O was an early decomposition product of phenol-formaldehyde and suggested that it was probably produced by condensation of a pair of hydroxy groups to form an ether linkage and by reaction of a hydroxy group with a hydrogen of a bridge CH_2 group. CO_2 was also observed to be an early product. H_2 , CO, and CH_4 formed later, but at about the same time. The following reactions were thought to be responsible for their formation.



$>CH_2$ and $-O-$ represent bridge methylene and ether groups, respectively. The observations of the current experiment do not disagree with these findings of Ouchi and Honda.

Although the analytical data show great consistency, there are several possible sources of error. One type of error is normal instrumental error. Another source of error may be chemical reactions which occur among the products during the time of analog scan. A further source of error may be caused by continued generation of gases from the hot surface long after the flash is extinguished. Another type of error is due to the fact that the lighter gases will be pumped out of the 100 cc reaction chamber through the two mil diameter leak more rapidly than the heavier gases. This error is not very large and is rendered less serious than otherwise because the lighter masses are scanned earliest. In fact, it is possible to correct for this error to some extent, and some experiments have been carried out to that end. Samples of hydrogen, methane, and n-butane were admitted into the mass spectrometer at initial pressure of 67 microns. In each case, the gate of one analog channel was focussed at the parent peak. At the appropriate time, the stopcock, which isolates the reaction chamber from the reservoir, was closed and ion current was monitored as a function of time. Figure 6 shows plots of the logarithm of ion current as a function of time. Kinetic theory shows that for effusive flow

$$\ln I = \ln I_0 + \sqrt{\frac{M}{M_2/M_1}} t$$

where I = ion current
 I_0 = initial ion current
 $\sqrt{\frac{M}{M_2/M_1}}$ = a constant
 M = molecular weight
 t = time

so it is reasonable that the plots are linear. The interrelationships between the slopes are shown in Table 3. Note that the experimental and theoretical $\sqrt{M_2/M_1}$'s are quite close to each other, but the experimental values are somewhat lower. This could mean that the pressure is slightly too high for effusive flow through a two mil hole in some cases. A study with n-butane at a variety of higher pressures showed that the slope increased (smaller negative number) with increasing pressure which also indicated that flow was not effusive, at least at the higher pressures. Reference to Table 2 shows that the pressures were too high for this type of correction to be applied. Future experiments will be carried out with smaller samples.

A sample of phenol-formaldehyde was pyrolyzed in the Space Sciences Laboratory Arc-Image Furnace Facility according to the procedures which are described in References 9 and 10. A partial qualitative analysis disclosed the presence of H_2 , CO, CH_4 , N_2 (traces), CO_2 , C_2H_2 , C_2H_4 , C_2H_6 , H_2O , benzene, styrene, toluene, and xylene. Quantitative comparisons of some of the products with those of the flash pyrolysis experiments are listed in Table 4. The agreement of results is very good, considering the differences in the experiments. Because of the pumping error associated with the analog readings, the relative yields of the flash experiments are probably too low.

Examinations of plastic samples after flash pyrolysis have disclosed that the finish of the surface influences the absorption of energy. In some cases, the surface

appears to be blackened rather uniformly, while in others, some parts are hardly blackened. Machining notches, which are readily discerned by the eye, appear to be readily blackened. It would certainly be helpful to have a technique to produce a standard and uniform surface finish on samples if one desires to compare different samples of the same material. In addition, the energy flux is not uniform over the surface of the sample. Still, it would be helpful to know an average energy input and/or surface temperature. Knowledge of the pressure in the reaction chamber would also be helpful. It is planned that such measurements will be carried out in the future.

Since H_2 , H_2O , CO , and CO_2 were major decomposition products for the eleven flash experiments, temperatures were calculated based on the possibility that the water gas equilibrium was important. The water gas equilibrium temperature would be valid if these four products came to equilibrium on the surface and then were cooled rapidly upon leaving the surface. Equilibrium constants were calculated from Table 1 and temperatures were determined from Reference 11. They are listed in Table 5. The temperatures and trend are thought to be quite reasonable. One might expect that, during earlier flashes, the sample would start to blacken and might become a better receptor of radiant energy. However, with each flash, solids which are driven off from the plastic surface could coat the lamp and may thus reduce its energy output. A portion of the decomposition gases could come from the lamp surface and other surfaces of the reaction chamber.

ACKNOWLEDGMENTS

The author particularly wishes to express his indebtedness to George A. Griffith for carrying out most of this work, for helping to write parts of this report, and for the many ideas that he contributed to the program. He is also grateful to Jesse E. Brown, Richard L. Everett, James D. Graham, Jr. and George Parks for their help. He also wishes to thank the Bendix Corporation, Dr. Eugene Levy of the Atlantic Petroleum Refining Co., Prof. Stig Claesson, Dr. H. E. Hall, and David A. Rogers for their help and advice in mass spectroscopy and instrumentation. His discussions with Joseph A. Golden, Dr. Milton J. Linevsky, Dr. Walter E. Kaskan, and others were very valuable.

This work was carried out under the auspices of U. S. Air Force Ballistic Systems Division Contract AF 04(647)-617 and U. S. Air Force Aeronautical Systems Division Contract AF 33(616)-6841.

REFERENCES

1. G. B. Kistiakowsky and P. H. Kydd, J. Am. Chem. Soc. **79**, 4825 (1957).
2. J. N. Bradley and G. B. Kistiakowsky, J. Chem. Phys. **35**, 256 (1961).
3. J. N. Bradley and G. B. Kistiakowsky, J. Chem. Phys. **35**, 264 (1961).
4. J. L. Lundberg and L. S. Nelson, Nature **179**, 367 (1957).
5. J. L. Lundberg, L. S. Nelson, and M. Y. Hellman, Proc. 3rd Conf. on Carbon, Buffalo, N. Y., 1957.
6. L. S. Nelson and N. A. Kuebler, Physical Chemistry in Aerodynamics and Space Flight, A. L. Myerson and A. C. Harrison, eds., Pergamon Press, Oxford, England, 1961, pp. 61-67.
7. J. A. Golden and H. L. Friedman, G. E. TIS R62SD67, July 1962.
8. K. Ouchi and H. Honda, Fuel **38**, 429 (1959).
9. H. L. Friedman, Ballistic Missile and Space Technology. IV. Re-Entry and Vehicle Design, D. P. LeGalley, ed., Academic Press, N. Y., 1960, pp. 3-29. Also G. E. TIS R60SD380, May 1960.
10. H. L. Friedman, G. E. TIS R62SD57, May 1962.
11. JANAF Interim Thermochemical Tables, December 31, 1960.

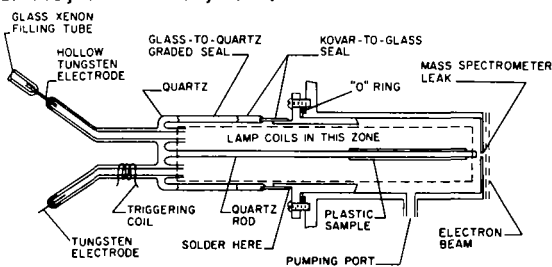
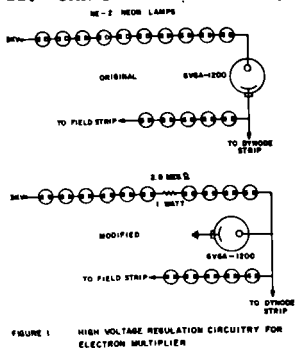


FIGURE 2 Flash Lamp and Plastic Sample as Mounted in the Reaction Chamber of the Mass Spectrometer

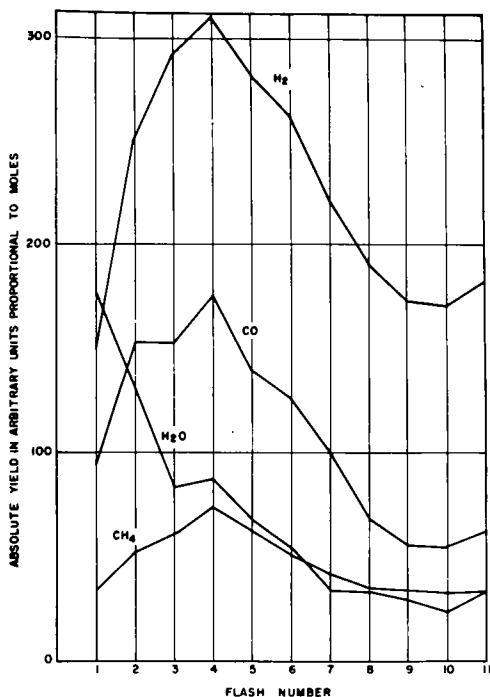


FIGURE 3 PRODUCT YIELDS FROM FLASH PYROLYSIS OF PHENOL-FORMALDEHYDE (H_2 , H_2O , CO , CH_4)

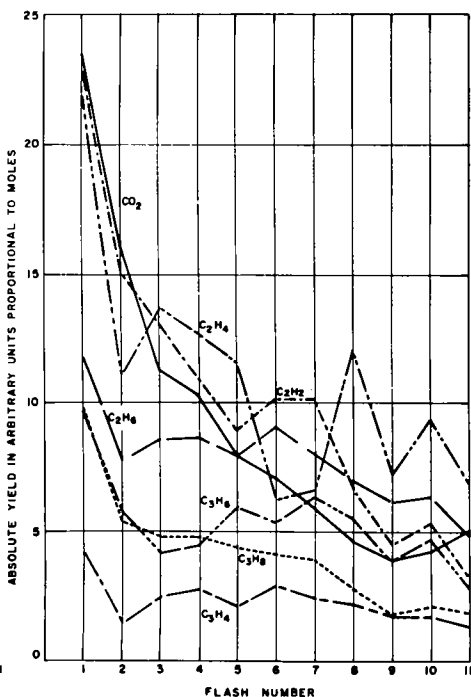


FIGURE 4 PRODUCT YIELDS FROM FLASH PYROLYSIS OF PHENOL-FORMALDEHYDE (CO_2 , C_2 & C_3 HYDROCARBONS)

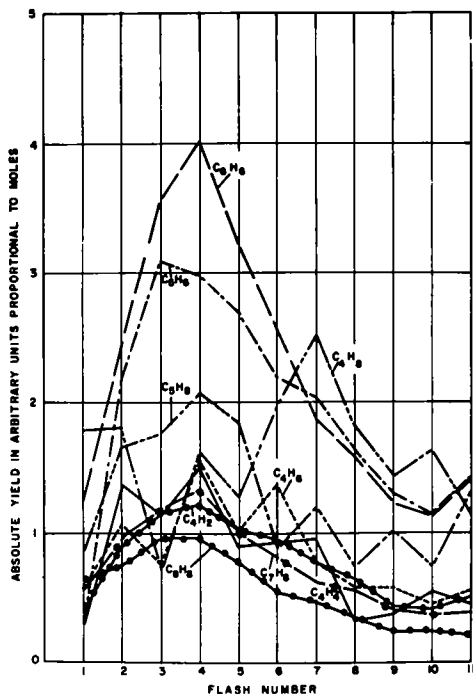


FIGURE 5 PRODUCT YIELDS FROM FLASH PYROLYSIS OF PHENOL-FORMALDEHYDE (C_4 TO C_9 HYDROCARBONS)

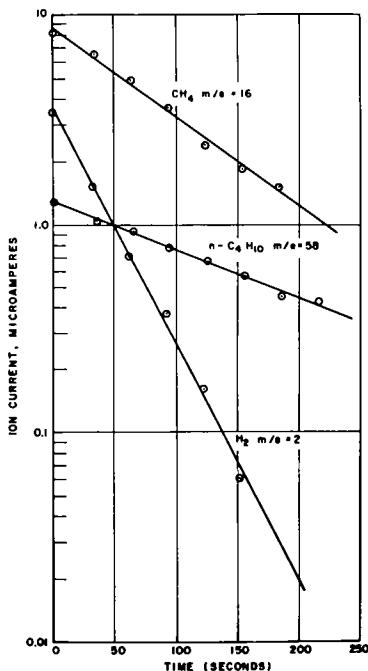


FIGURE 6 FLOW OF PURE GASES FROM FLASH PYROLYSIS REACTION CHAMBER INTO THE MASS SPECTROMETER

IDENTIFICATION OF DECOMPOSITION PRODUCTS OF POLYTETRAFLUOROETHYLENE
("TEFLON"-1 AND "TEFLON"-6) AND POLYFLUOROETHYLENEPROPYLENE ("TEFLON"-100)*

Richard E. Kupel, Melvin Nolan, Robert G. Keenan,
Mark Hite, Sc.D.⁺ and Lester D. Scheel, Ph.D.

Two types of polytetrafluoroethylene, 1 and 6, and polyfluoroethylenepropylene 100 were studied in this investigation. Each type was placed in a furnace operating at temperatures of 350°, 490°, 565°, 670°, 760° and 875°C and the decomposition products formed were analyzed with a time-of-flight mass spectrometer. The atmospheres used in this study included air, oxygen and nitrogen. The effect of varied amounts of moisture in air on the nature of the decomposition products was also investigated.

The decomposition products formed at each temperature with the specific atmospheres and humidities were identified.

Introduction

Considerable experimental work (1,2) has been reported in the literature on the nature of the decomposition products of polytetrafluoroethylene (PTFE) and polyfluoroethylenepropylene (PFEP) in vacuo. However, to date no systematically developed data have been reported where PTFE was admitted to a closed experimental system containing air or oxygen and the decomposition products studied subsequently under reproducibly controllable conditions. We have designed and used the equipment required to overcome these objections. In addition, our instrumentation has permitted the immediate introduction of the sample into the furnace pre-set at the desired operating temperature. This approach was made to avoid the possibility of forming decomposition products at a temperature lower than the desired experimental temperature. Thus, a difference in products at different experimental temperatures should not be missed with this technique. In this paper, we shall present a report of the experimentation which we have conducted with this specially designed system whereby the effects of oxygen, air, and nitrogen atmospheres, of varied operating temperatures from 350 to 875°C, and of varied humidities were studied. The decomposition products formed with these parameters were analyzed using a time-of-flight mass spectrometer.

Experimental System

The decomposition chamber consisted of a 1-inch O.D., 3/4-inch I.D., Monel 400 tube, 18 inches long. This chamber was installed in a tube furnace with a maximum range of 875°C. The temperature of the furnace was controlled by a powerstat and read on a thermocouple, self-balancing indicator, accurate to within $\pm 5^\circ\text{C}$. A stainless steel cap, provided with two holes and a welded entry port for the introduction of the experimental atmosphere, was sealed on one end of the decomposition chamber. The thermocouple sheathing tube was sealed into one of the holes in the cap with the bimetallic junction positioned in the hottest portion of the decomposition chamber. A 1/4-inch stainless steel tube, for the introduction of the sample, was sealed into the second hole of the cap. This sample tube also extended into the hottest portion of the chamber. A plunger, mounted within the sample tube, enabled us to push the sample through this tube and into the decomposition chamber when the desired experimental conditions were established. At the other end of the chamber there was a micro-meter valve connected to the tubing leading to the mass spectrometer. This valving allowed a portion of the chamber atmosphere to be sampled and analyzed continuously. A series of low-flow flowmeters permitted us to select the flow rate necessary for the separate experiments. In those experiments where increased humidity was desired, a bubbler was installed in the atmospheric introductory system at the front end of the decomposition chamber.

* Teflon is the registered trademark of the Du Pont Company for its TFE and FEP fluorocarbon resins. The use of trade names in this paper does not indicate the endorsement of these materials by the Public Health Service.

U. S. Department of Health, Education & Welfare
Public Health Service
Division of Occupational Health
Cincinnati 2, Ohio

⁺ Present Address:
Industrial Health and Medical Department
Dow Chemical Company
Freeport, Texas

TABLE I. MASS SPECTROMETER OPERATING CONDITIONS

Electrometer	1 nanoampere
Scale Range	2
Scan Rate	5
Time Constant	0.05 seconds
Gate Width	6 units
Electron Energy	65 electron volts
Filament Current	2.6 - 3.0 amperes
Control Grid Bias	0.25 microamperes
Trap Current Level	0.135 microamperes
Operating Pressure in Drift Tube	1×10^{-5} Torr

TABLE II. PTFE NO. 1 IN AIR
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	2	6	20	5	22
F	19	0	1	2	1	<1	2
CF	31	0	3	13	24	3	20
CO ₂	44	0	4	38	53+	53+	53+
OCF	47	0	28	40	3	<1	<1
CF ₂	50	0	1	6	9	1	11
OCF ₂	66	0	12	19	<1	0	0
CF ₃	69	0	5	38	53+	8	53+
C ₂ F ₃	81	0	0	1	2	0	<1
OCF ₃	85	0	<1	3	7	3	0
C ₃ F ₃	91	0	0	1	6	<1	3
C ₂ F ₄	100	0	<1	4	8	1	1
C ₂ F ₅	119	0	<1	3	12	2	21
C ₃ F ₅	131	0	<1	3	9	2	1
OC ₂ F ₅	135	0	<1	1	0	0	0

TABLE III. PTFE NO. 6 IN AIR
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	3	4	5	21	26
F	19	0	<1	<1	<1	<1	3
CF	31	0	1	15	6	6	32
CO ₂	44	0	35	37	53+	53+	53+
OCF	47	0	10	4	<1	<1	<1
CF ₂	50	0	1	5	2	5	24
OCF ₂	66	0	4	1	0	<1	0
CF ₃	69	0	4	34	22	40	53+
C ₂ F ₃	81	0	0	1	<1	0	<1
OCF ₃	85	0	4	<1	<1	8	0
C ₃ F ₃	91	0	0	2	<1	0	3
C ₂ F ₄	100	0	<1	10	2	0	1
C ₂ F ₅	119	0	<1	4	3	10	30
C ₃ F ₅	131	0	0	10	2	0	1
OC ₂ F ₅	135	0	0	<1	0	0	0

TABLE IV. PFEP NO. 100 IN AIR
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	4	4	4	19	35
F	19	0	<1	<1	<1	<1	3
CF	31	0	4	15	10	12	36
CO ₂	44	0	39	43	53+	53+	53+
OCF	47	0	9	4	2	<1	<1
CF ₂	50	0	3	5	3	5	20
OCF ₂	66	0	3	<1	<1	<1	<1
CF ₃	69	0	21	34	27	40	53+
C ₂ F ₃	81	0	0	1	<1	<1	<1
OCF ₃	85	0	3	1	<1	5	0
C ₃ F ₃	91	0	<1	3	2	2	3
C ₂ F ₄	100	0	1	13	3	2	1
C ₂ F ₅	119	0	2	4	2	7	14
C ₃ F ₅	131	0	1	11	4	2	1
OC ₂ F ₅	135	0	<1	<1	0	0	0

Experimental Procedures

A 0.2 gram sample was weighed out to the nearest milligram for each experiment, after cleaning a portion of PTFE with alcohol and drying. The chamber was raised to the desired temperature and allowed to equilibrate while the experimental atmosphere was introduced at a flow rate of 20 ml per minute. The sample was then placed in the cool region of its introductory tube. After equilibrium had been established, the micro-meter valve was opened and the pressure in the mass spectrometer increased to a predetermined level. A background scan was made to establish the base spectrogram of each run. The sample was then pushed out of the introductory tube into the hot zone of the decomposition chamber and allowed to decompose. After a predetermined time (zero seconds at 875°C but extending to 10 minutes at 490°C), the recorder was started and the spectrograms of the decomposition products were reproduced on the light sensitive paper of the recorder. During each run the oscilloscope was monitored continuously. These spectrograms were prepared periodically during each run to make sure that all of the decomposition products were being produced continuously. This repeated scanning pointed out the necessity of zero pre-recording time at 875°C and varied incremental periods at the lower operating temperatures. The mass spectra were scanned from masses 12 to 250 and all peaks above the base spectrogram were tabulated.

The experimental procedure was applied to PTFE Types 1 and 6 and to PFEP 100. Each type was studied in atmospheres of air, of oxygen, and of dry nitrogen obtained from cylinders. The experiments were conducted at the following temperatures: 350°, 490°, 565°, 670°, 760°, and 875°C. These temperatures were selected on the basis of the nature and the extent of the decomposition products obtained during preliminary experimentation. Studies of the effects of varied relative humidities in air were limited to experiments with PTFE 1. The operating parameters of the mass spectrometer were held constant throughout the entire experimentation and these are shown in Table I.

Results

The mass spectrometric data obtained from the decomposition of PTFE 1 in air at the indicated temperatures are presented in Table II. These data show that the temperature at which the carbonoxyfluoride compounds form without further decomposition into CO_2 , CF_4 and other high mass fractions is approximately 490°C. Masses 66 and 47 represent a portion of the cracking pattern of COF_2 (carbonyl fluoride), this substance being of greatest interest to our toxicologists at the present time. Mass 66, assigned to COF_2 , is the parent peak for this substance while Mass 47, assigned to COF , is the major peak. Mass 44, which is due to CO_2 , has not reached its maximum at 490°C, showing that a greater degree of decomposition occurs at the higher temperatures. It is noteworthy, for those who are interested in generating COF_2 for experimental purposes, that the concentration of this substance can be built up in the decomposition chamber by holding the temperature at 490°C and feeding PTFE into the chamber continuously. In Table II, and in all of the other tables presented in this report, the results are expressed in terms of recorder chart units, with 53 units representing a full scale peak corresponding to 2 nanoamperes.

Tables III and IV present the mass spectrometric data obtained when PTFE 6 and PFEP 100 were decomposed in dry air. Inspection of these tables shows that the decomposition temperature favoring the production of COF_2 would appear to be lower for the PTFE 6 and PFEP 100 than for PTFE 1. This finding is supported by evidence developed in an oxygen atmosphere to be mentioned later.

Tables V, VI, and VII present the data on the cracking patterns observed when the three types of plastics were broken down in pure oxygen. As shown for the 490°C cracking pattern the COF_2 peak is triple that observed in an atmosphere of air. It is also significant that the CF_3 peak, which is an important decomposition product formed in inert atmospheres, and at higher temperatures in oxygen-containing atmospheres, is beginning to increase at 490°C in the pure oxygen system. Other investigators have reported that the production of a prominent CF_3 peak at temperatures exceeding 600°C indicates the formation of CF_4 in the chamber (4). Note also that with the increase in temperature CF_3 builds up as COF_2 is diminishing.

In view of our previous observation that PTFE 6 and PFEP 100 may decompose preferentially to carbonoxyfluorides at temperatures below 490°C, additional experimentation in oxygen atmospheres was performed to determine the optimal decomposition temperatures for each of these plastics. These were established as 425°C for PFEP 100 and 480°C for PTFE 6. These observations were reproduced repeatedly demonstrating that these decomposition temperatures are rather sharply defined. As the decomposition temperature of PTFE 6 did not drop significantly when the atmosphere of oxygen was substituted for

TABLE V. PTFE NO. 1 IN OXYGEN
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	11	5	9	11	28
F	19	0	4	2	2	3	3
CF	31	0	10	19	45	11	14
CO ₂	44	0	53+	53+	53+	52	53+
OCF	47	0	53+	53+	22	27	0
CF ₂	50	0	4	16	11	8	10
OCF ₂	66	0	42	53+	5	9	0
CF ₃	69	0	16	53+	53+	53+	53+
C ₂ F ₃	81	0	0	<1	4	0	<1
OCF ₃	85	0	17	15	4	1	0
C ₃ F ₃	91	0	<1	2	5	<1	2
C ₂ F ₄	100	0	1	12	12	<1	<1
C ₂ F ₅	119	0	2	15	3	4	18
C ₃ F ₅	131	0	1	8	12	<1	1
OC ₂ F ₅	135	0	1	5	0	0	0

TABLE VI. PTFE NO. 6 IN OXYGEN
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	17	2	7	0	22
F	19	0	6	1	1	<1	2
CF	31	0	17	10	53+	45	12
CO ₂	44	0	53+	53+	53+	53+	53+
OCF	47	0	53+	53+	11	<1	0
CF ₂	50	0	6	10	21	15	9
OCF ₂	66	0	53+	49	3	<1	0
CF ₃	69	0	19	53+	53+	53+	53+
C ₂ F ₃	81	0	0	<1	7	4	0
OCF ₃	85	0	14	14	<1	0	0
C ₃ F ₃	91	0	<1	2	12	11	1
C ₂ F ₄	100	0	1	10	24	14	<1
C ₂ F ₅	119	0	2	12	20	24	16
C ₃ F ₅	131	0	1	8	31	19	<1
OC ₂ F ₅	135	0	1	5	0	0	0

TABLE VII. PFEP NO. 100 IN OXYGEN
Results Expressed As Chart Units With 53+ Off-Scale

Ion +	Mass	350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	9	18	0	1	19
F	19	0	1	2	0	1	2
CF	31	0	3	14	39	53+	10
CO ₂	44	0	53+	53+	53+	53+	53+
OCF	47	0	22	41	16	1	0
CF ₂	50	0	2	7	22	14	8
OCF ₂	66	0	9	14	4	1	0
CF ₃	69	0	14	53+	53+	53+	53+
C ₂ F ₃	81	0	0	<1	10	8	<1
OCF ₃	85	0	18	15	2	0	<1
C ₃ F ₃	91	0	<1	<1	17	15	0
C ₂ F ₄	100	0	<1	5	35	20	<1
C ₂ F ₅	119	0	1	7	16	13	12
C ₃ F ₅	131	0	<1	3	50	33	<1
OC ₂ F ₅	135	0	<1	2	0	0	0

air, we conclude that PTFE 1 and PTFE 6 decompose to carbonoxyfluorides at essentially the same temperature.

Table VIII, IX, and X present the mass spectrometric data on the cracking patterns observed when the three types of plastics were heated in pure, dry nitrogen. Inspection of these data shows at most only a trace of Mass 66, COF_2 , and Mass 47, COF, in these nitrogen runs. However, there is a strong peak for carbon dioxide which, at the moment, cannot be explained as the nitrogen was free of a detectable amount of oxygen and the Mass 44 peak does not appear in blank runs where the plastic was omitted.

Table XI provides data showing the effect of increased relative humidity in an atmosphere of air at 490°C on the plastic decomposition products as shown by the cracking patterns. At a relative humidity of 3.8 percent, the patterns are similar to those produced in atmospheres of dry air. However, at higher humidities, the production of carbonoxyfluorides drops off greatly reaching zero at 25 percent humidity. It is noteworthy that HF was formed in the chamber maintained at the 3.8 percent humidity; this is the only experiment where we detected HF repeatedly.

It is interesting to point out that, at temperatures exceeding 490°C , the cleavage of the polymer resulted in the formation of the monomer, C_2F_4 , Mass 100. A small amount of heptafluoropentane and cyclofluorobutane were identified at these higher temperatures. A small peak was recorded at Mass 200 which may be due to perfluoroisobutylene.

Summary

The carbonoxyfluoride compound, COF_2 , which is of great interest to the toxicologists was not detectable when the PTFE and PFEP plastics were decomposed in nitrogen at any of the six operating temperatures extending from 350° to 875°C . However, this compound does form both in atmospheres of air and oxygen at 490° and 565°C . As the temperature is increased above 600°C production of this compound ceases when the materials are decomposed in air.

No decomposition products were formed at 350°C even though the materials were held at that temperature for 4 hour periods.

HF was detected in only one experiment in the entire study, that conducted with an atmosphere of air maintained at 3.8 percent relative humidity.

At temperatures in excess of 490°C , the cleavage of the PTFE polymers formed the monomer, C_2F_4 with a Mass of 100 and higher mass fragments. The PFEP 100 polymer also formed these compounds but in larger quantities.

The establishment of the experimental conditions for the decomposition of these plastics into compounds of primary interest to the toxicologists now permit us to design the experimental animal exposure system required for the study of the toxicity of these substances and their decomposition products.

References

1. Treon, Joseph F.; Stemmer, Klaus L.; Larson, Edwin and Cappel, John. (1954). The Toxicity of the Products Formed by the Continuous Thermal Decomposition of Teflon. (Supplement to the Report of April 26, 1954.)
2. Treon, Joseph F.; Cleveland, Frank P.; Larson, Edwin; Cappel, John; Shaffer, Fred; Stemmer, Klaus; Denham, Ralph. (1954). The Immediate Toxicity of the Thermal Decomposition Products of Teflon and Kel-F.
3. Sites, John R. and Baldock, Russell. (1952). Mass Spectrometer Studies of High Vacuum Materials. ORNL-1405.
4. Simons, J. H., Editor. (1950). Vol. 1, P. 423. Fluorine Chemistry. Brice, T.J.: Thermal Stability of Fluorocarbons.
5. Lewis, E.E. and Naylor, M.A.; J. Am. Chem. Soc., 69, 1968, (1947).
6. Florin, R.E.; Wall, L.A.; Brown, D.W.; Hyme, L.A.; and Michaelsen, J.D., J. Res. Nat. Bur. Stds., 53, No. 2, Aug., 1954. Research Paper 2524, P. 121.
7. Madorsky, S.L.; Hart, V.E.; Straus, S.; and Sedlak, V.A., J. Res. Nat. Bur. of Stds., 51, No. 6, Dec. 1953. Res. Paper 2461, P. 327.

TABLE VIII. PTFE NO. 1 IN NITROGEN

Ion +	Results Mass	Expressed As Chart Units With 53+ Off-Scale					
		350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	4	4	12	10	6
F	19	0	0	1	1	1	2
CF	31	0	21	41	18	42	16
CO ₂	44	0	50	20	53+	53+	53+
OCF	47	0	0	<1	0	0	0
CF ₂	50	0	8	10	3	6	10
OCF ₂	66	0	0	0	0	<1	0
CF ₃	69	0	53+	20	25	53+	53+
C ₂ F ₃	81	0	4	11	2	3	<1
OCF ₃	85	0	3	1	3	2	3
C ₃ F ₃	91	0	2	3	3	7	<1
C ₂ F ₄	100	0	11	22	5	8	<1
C ₂ F ₅	119	0	10	2	2	3	10
C ₃ F ₅	131	0	10	19	9	14	<1
OC ₂ F ₅	135	0	0	0	0	0	0

TABLE IX. PTFE NO. 6 IN NITROGEN

Ion +	Results Mass	Expressed As Chart Units With 53+ Off-Scale					
		350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	4	4	4	5	<1
F	19	0	<1	<1	2	2	2
CF	31	0	13	50	53+	53+	17
CO ₂	44	0	53+	24	28	37	53+
OCF	47	0	0	<1	<1	2	0
CF ₂	50	0	4	13	15	11	10
OCF ₂	66	0	0	<1	<1	<1	<1
CF ₃	69	0	27	31	53+	53+	53+
C ₂ F ₃	81	0	2	12	9	4	<1
OCF ₃	85	0	5	<1	2	2	0
C ₃ F ₃	91	0	1	5	10	14	<1
C ₂ F ₄	100	0	4	35	22	9	<1
C ₂ F ₅	119	0	5	2	3	9	11
C ₃ F ₅	131	0	5	28	27	14	<1
OC ₂ F ₅	135	0	0	0	0	0	0

TABLE X. PFEP NO. 100 IN NITROGEN

Ion +	Results Mass	Expressed As Chart Units With 53+ Off-Scale					
		350°C	490°C	565°C	670°C	760°C	875°C
C	12	0	6	3	4	5	33
F	19	0	<1	1	2	2	1
CF	31	0	32	53+	53+	53+	31
CO ₂	44	0	53+	46	21	35	53+
OCF	47	0	0	2	<1	<1	0
CF ₂	50	0	8	17	10	9	21
OCF ₂	66	0	0	<1	<1	0	0
CF ₃	69	0	53+	53+	53+	53+	53+
C ₂ F ₃	81	0	6	11	6	4	<1
OCF ₃	85	0	4	1	<1	2	0
C ₃ F ₃	91	0	4	12	9	12	3
C ₂ F ₄	100	0	14	50	14	8	2
C ₂ F ₅	119	0	8	18	3	5	20
C ₃ F ₅	131	0	17	51	20	13	2
OC ₂ F ₅	135	0	0	0	0	0	0

TABLE XI. PTFE NO. 1 IN AIR AT 490°C. AND AT VARIOUS HUMIDITIES

Ion +	Results Mass	Expressed As Chart Units With 53+ Off-Scale			
		Relative Humidity at 23°C			
		50%	25%	12.5%	3.8%
C	12	4	3.5	3.5	4
F	19	0	0	0	1
HF	20	0	0	0	3
CF	31	0	<1	<1	2.5
CO ₂	44	53+	53+	46	33
OCF	47	0	0	5	25
CF ₂	50	<1	<1	<1	1
OCF ₂	66	0	0	2	11
CF ₃	69	2	1.5	2	3
C ₂ F ₃	81	0	0	1.5	0
OCF ₃	85	0	1	0	2
C ₃ F ₃	91	0	0	0	0
C ₂ F ₄	100	0	0	0	0

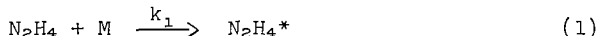
MASS SPECTRAL STUDIES OF KINETICS BEHIND SHOCK WAVES
THE THERMAL DECOMPOSITION OF HYDRAZINE*

R. W. Diesen
The Dow Chemical Company
Midland, Michigan

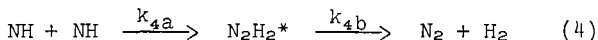
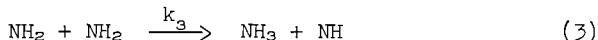
SUMMARY

The decomposition of hydrazine, diluted in argon, has been studied over the temperature range 1200° to 2500°K. and pressure range 0.06 to 0.25 atmospheres using a shock tube coupled to a time-of-flight mass spectrometer. The time resolved mass spectra (25 microseconds) enable the simultaneous identification and determination of N_2H_4 , NH_3 , N_2 , H_2 and the NH_2 radical, the five major species observed. The material balance is within the experimental error (10%) during reaction up to complete decomposition.

The primary process in the dissociation of hydrazine is shown to be the rupture of the N-N bond to give NH_2 radicals. The observed rate constants for the disappearance of hydrazine are those expected of a unimolecular reaction:



at or near the second order region where collisional activation (1) is rate controlling. At the higher temperatures, the results are consistent (within experimental error) with the very simple reaction scheme of reaction (1) and (2) followed by:



At the lowest temperatures the reaction:



appears to become important.

From the experimental concentrations a value of

$$k_3 = 2.5 \times 10^{13} \text{ cc./mole-sec. (2000°K.)}$$

is obtained. An order of magnitude estimate gives

$$k_4 \sim 10^{14} \text{ cc./mole-sec. (2000°K.)}$$

*This work was sponsored by the Office of Naval Research under Contract Nr. Nonr-3814(00).

DETERMINATION OF HYDROCARBON TYPES IN KEROSENE RANGE DISTILLATES
BY MASS SPECTROMETRY

L. R. Snyder, H. E. Howard and W. C. Ferguson
Union Oil Company of California
Brea, California

ABSTRACT

A method has been developed which determines eight hydrocarbon compound types and one sulfur type in any petroleum stream boiling between 350°F and 550°F. These compound types include alkanes, non-condensed naphthenes, condensed naphthenes, alkylbenzenes, indanes-tetralins, naphthalenes, biphenyls, fluorenes and benzothiophenes. In addition, the carbon number distribution of C₁₀ through C₁₅ naphthalenes is obtained. When olefin and sulfur types other than benzothiophene are present, their concentrations are determined by some supplementary means, then integrated into the final results.

ANALYSIS OF PARAFFIN WAX IN THE C₁₆-C₃₆ RANGE BY MASS SPECTROMETRY

F. J. Galbraith, V. A. Cirillo

A more reliable method of analysis of paraffin wax has been the subject of interest for the past several years. Lack of pure compounds, particularly the non-normal type has hampered the development of a routine method. Recent advances in physical separation techniques have made available fractions of wax rich in non-normal content for evaluation.

This paper illustrates a technique for the calculation of paraffin wax in the C₁₆-C₃₆ range by mass spectrometry.

The calculation provides for the determination of compound types present by molecular weight distribution.

The spectrometer used in obtaining spectral data reported is a modified Consolidated 21-103A instrument. The sample is introduced through a heated sintered disc sealed with indium. Care is exercised in heating the sample in order to eliminate the possibility of thermal decomposition. Samples and calibrations are run at relatively constant pressures. The operating conditions are shown below:

Box temperature	575°F
Sintered disc temp.	~ 710°F
Isatron temp.	500°F (varies)
Magnet current	1.30 amp
Ionizing current	75 μ a
Scan time	IAV 3000 $\rightarrow$ end 19'

Compound	Peaks m/e	Pattern Ratio Fragment/Parent
nC ₁₆	127 226	1.45 $\pm$.02
nC ₃₀	197 422	4.50 $\pm$.25

Past experience in this laboratory has emphasized the importance of maintaining stable fragmentation patterns. n-Hexadecane and n-triacontane have been selected as standard calibration compounds. In practice, the ion source temperature is varied in order to maintain the n-hexadecane 127/226 peak ratio at 1.45 ± 2 . The temperature is adjusted at the beginning of each day and is held constant for that day's operation. The disc temperature is raised to 700°F for the n-triacontane compound. The peak ratio 197/422 is 4.50 ± 25 .

Earlier work in this laboratory (2) has shown that the hydrocarbons present in wax are fairly simple in structure; i.e., n-paraffins, mono methyl branched paraffins, 1 cyclopentyl and 1 cyclohexylparaffins with minor concentrations of more complex structures. Mono aromatic type compounds are also present in low concentration.

The n-paraffin fragmentation results from cleavage of successive carbon-carbon bonds. The relative intensity of the parent ions as well as the fact that they are little affected by other types present permits their use in a parent peak method of calculation. The sensitivity decreases with molecular weight but parent ions have been detected to nC₄₂. Predominant fragment peaks at m/e 71, 85 have been selected for use in the type analysis.

The iso-paraffin fragmentation results from cleavage of the long chain adjacent to the substituted carbon atoms. The low intensity of parent ions along with the fact that the parent ions are the same m/e as the n-paraffin precludes their use. In practice use is made of the predominant fragment peaks in the parent region. The peaks used are based on the predicted fragmentation of the iso-paraffin isomers.

The 2 methyl compounds fragment to give a peak at parent -15 and parent -43, the 3 methyl compounds a peak at parent -29, the 4 methyl a peak at parent -43 and the 5 methyl a peak at parent -57. The m/e 71, 85 are used in the type analysis.

Both the cyclopentyl and cyclohexyl compounds fragment alpha to the ring. The parent ions are intense enough to use in the parent peak method. The major fragments at 67, 68, 69, 81, 82, 83, 96 and 97 are used in the type analysis.

FIGURE 1

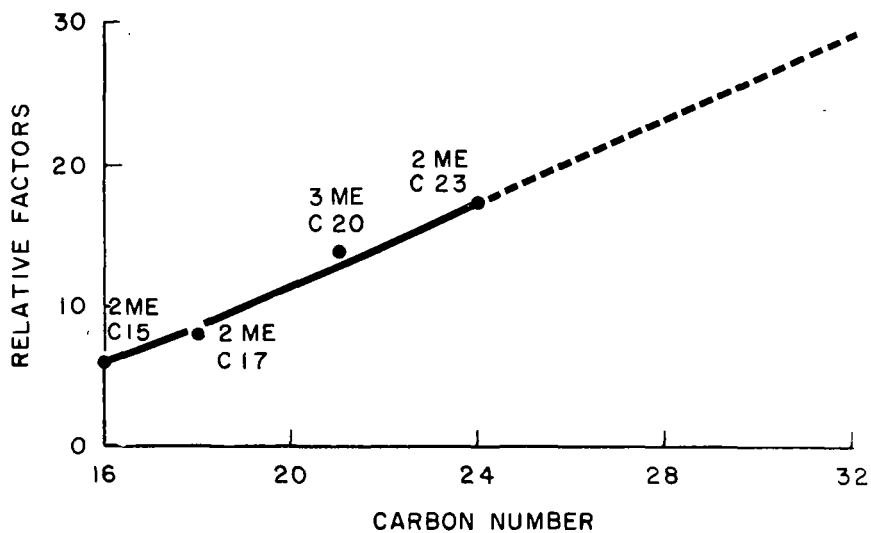
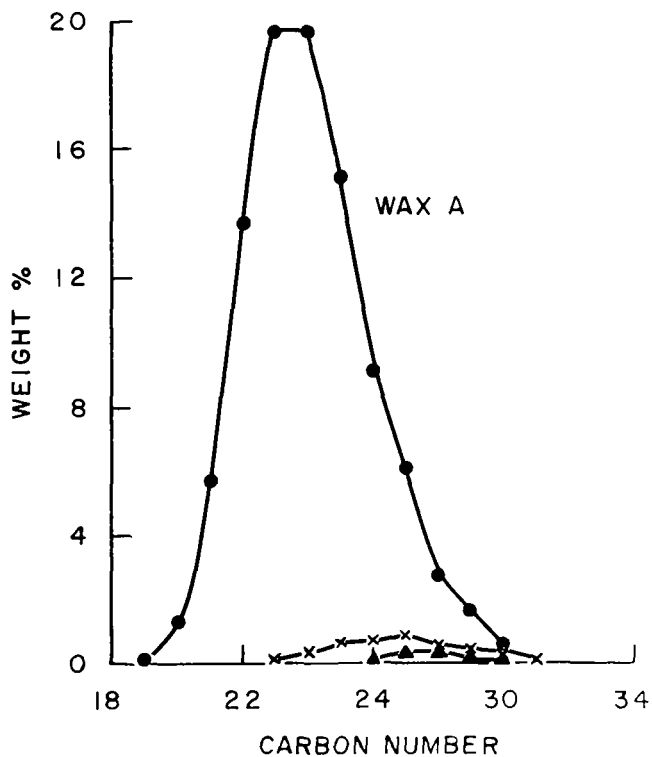


FIGURE 2



The aromatic hydrocarbons have the most intense parent ions due to the greater stability of the aromatic nucleus. The fragmentation results from cleavage beta to the ring. There is no contribution from other types present. The 91, 92, 105, 106, to 175, 176 peaks are used in the type analysis.

The major components of paraffin wax are, by far, the normal paraffins. Pure compounds prepared by API Project 42, and others isolated from various petroleum fractions, have been most helpful in determining the fragmentation patterns of the straight chain paraffins. However, relatively little information is available on the cracking characteristics of the non-normal compounds present in wax. Although these compounds make up the lesser concentration, their importance in interpretation of the total wax should not be minimized. Relative sensitivities are most critical.

Calculation

To illustrate the application of this method to a wax sample the following tables show a portion of the calibration data and steps used in the calculation. The full mass range is scanned under the same conditions in order to eliminate any effect on patterns and sensitivities due to change in magnet current and electron current. For this reason the $\Sigma 71$, $\Sigma 67$ rather than $\Sigma 43$, $\Sigma 41$ are used in the type analysis for the calculation of paraffin, cycloparaffin content.

The record is read for $\Sigma 71$, $\Sigma 67$ and $\Sigma 91$ as well as for the peaks in the C_{14} - C_{36} parent peak region. The peaks are corrected to a monoisotopic basis using factors from Esso tables⁽³⁾. Table I shows values used over the range.

Table I

C#	m/e	(-)	(+)	C#	m/e	(-)	(+)
C ₁₆	224	.1778	.0167	C ₂₉	406	.3222	.0536
	225	.1778			407	.3222	
C ₂₀	280	.2222	.0258	C ₃₃	462	.3667	.0691
	281	.2222			463	.3667	
C ₂₅	350	.2778	.0400	C ₃₅	490	.3889	.0776
	351	.2778			491	.3889	

Table II shows the calculated patterns of n-paraffin contributions to the C_nH_{2n+1} peaks used in the determination of iso-paraffin content of a wax.

Table II
n-Paraffin Contributions to C_nH_{2n+1} Peaks

m/e	C ₁₆	C ₁₈	C ₂₀	C ₂₂	C ₂₅	C ₂₇	C ₂₉	C ₃₀	C ₃₃	C ₃₅	C ₃₆
197	26	66	115	167	258	356	425	472	770	1015	1136
225	1	26	81	113	187	243	327	373	547	770	890
253		1	30	73	140	197	262	300	445	570	660
281			1	32	114	161	217	239	349	449	515
309				2	65	120	165	195	280	346	400
351					2	38	110	149	236	287	312
379						3	51	83	207	267	287
407							3	5	137	197	230
421								4	99	170	201
463									5	68	108
491										5	3
505											6

C_nH_{2n+1} + 2 peaks 100%

Table III shows the calculated patterns of n-paraffin contribution to the C_nH_{2n} peaks used to determine cycloparaffin content of a wax. Additional correction made to these peaks for effect of iso-paraffins. Both Tables II and III show the regularity of the n-paraffin fragmentation patterns.

Table IV shows factors used for calculating weight fractions of n-paraffins, cycloparaffins and alkylbenzenes. Weight sensitivity coefficients for the n-paraffins are based on data obtained from pure compounds. In this range over 50% of the n-paraffin compounds are available from API Project 42⁽¹⁾. The compounds are nC₁₆, nC₁₇, nC₁₈, nC₁₉, nC₂₀, nC₂₃, nC₂₄, nC₂₆, nC₂₈, nC₃₂, nC₃₅, and nC₃₆. A number of others were isolated by physical separation techniques in this laboratory.

The cycloparaffin sensitivities were calculated on the available pure

FIGURE 3

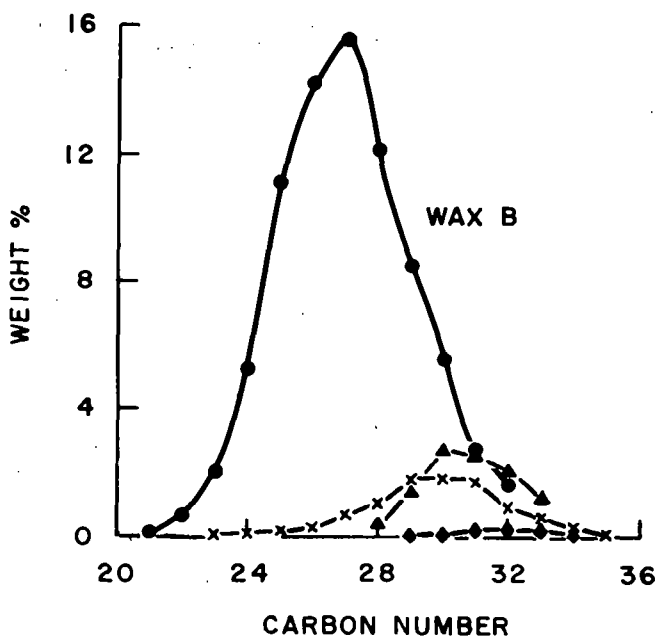


FIGURE 4

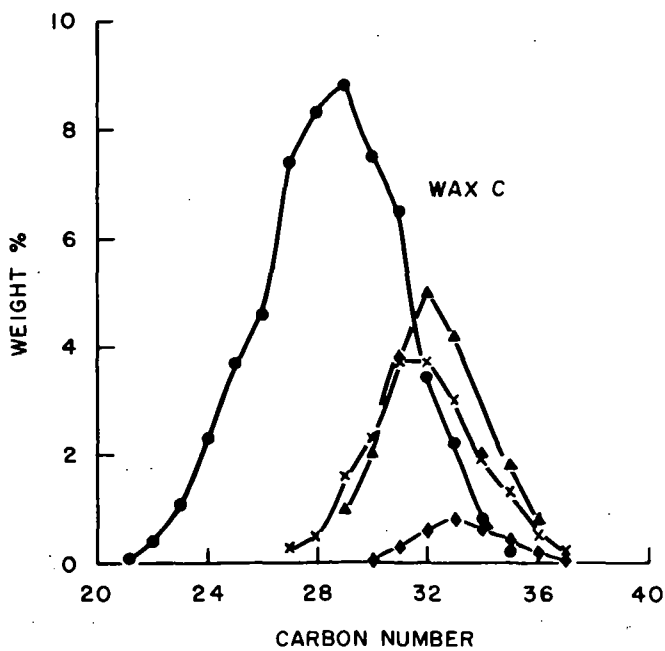


Table III
n-Paraffin Contributions to C_nH_{2n} Peaks

m/e	C ₁₆	C ₁₈	C ₂₀	C ₂₂	C ₂₅	C ₂₇	C ₂₉	C ₃₀	C ₃₃	C ₃₅	C ₃₆
196	3	24	44	60	103	145	197	225	379	502	580
224	2	10	26	44	82	106	145	170	280	380	439
252		2	9	24	51	86	117	137	203	280	353
280			4	13	35	54	91	106	162	216	243
308				4	20	39	65	80	132	175	199
350					5	14	30	45	83	114	134
378						8	15	22	53	83	97
406							8	1	42	60	70
420								11	33	54	60
462									12	24	37
490										12	26
504											14

$C_nH_{2n} + 2$ peaks 100%

Table IV
Factors for Calculating Weight Fractions of
n, cyclo and alkylbenzenes

C#	K ₁	K ₂	K ₃
16	.347	.069	.039
18	.461	.092	.039
20	.606	.121	.039
22	.847	.175	.045
25	1.515	.303	.051
27	2.083	.417	.054
29	2.857	.571	.057
30	3.333	.667	.059
33	4.348	.870	.065
35	4.762	.952	.069
36	5.000	1.000	.072

$$K = \frac{1}{\text{Wt. Sens.}}$$

compound data and extrapolated to cover the range of interest. Compounds available from API Project 42 were:

	MW	C#
1 Cyclohexyloctane	196	14
1 Cyclopentyldecane	210	15
1 Cyclohexyldecane	224	16
1 Cyclopentylheneicosane	364	26
1 Cyclohexyleicosane	364	26

The selection of these compounds is based on identification of cycloparaffin types present in narrow fractions from crystallization and gas chromatography. Alkylbenzene sensitivities are based on pure compound data for the most part. Figure 1 shows a plot of relative sensitivity factor values for the 2 and 3 mono methyl branched paraffins. The compounds available from API Project 42 were:

	MW	C#
2 Methylpentadecane	226	16
2 Methylheptadecane	254	18
3 Methylleicosane	296	21
2 Methyltricosane	338	24

The data was extrapolated to cover the wax range. Work with fractions from gas chromatographic runs substantiated the data. The 2 and 3 methyl types comprise to date better than 70% of the branched paraffins present. Little change in relative sensitivities was noted for the 4, 5, and 6 isomers. In calculation the average carbon number of the normals is determined and the relative sensitivities of the isoparaffins selected from the curve.

Table V shows a portion of a wax spectrum in the C₂₇-C₃₁ range. Starting on the left the first column shows m/e read from spectrum. Peak height values shown in column #2. Column #3 shows monoisotopic peak values.

Column #4 shows the $C_nH_{2n} + 1$ and C_nH_{2n} -residual peak height values after correction for n-paraffin pattern contributions and in the case of C_nH_{2n} peaks the additional correction for effect of isoparaffins. The residual peaks are a measure of the isoparaffinic and cycloparaffinic content of the sample. Deltas are checked at the $C_nH_{2n} + 1$ and C_nH_{2n} peaks. The m/e 197 is used to check the overall calculation of the sample. After removing the effects of n-paraffin contributions the peak is further corrected for the effect of isoparaffins. A study of the data available indicated the average pattern is ~14%. The aromatic content is calculated directly from parent peaks. The values on the right under weight fractions indicate the relative concentrations of compound types present in this portion of the wax.

Table V
Portion Wax Spectrum

<u>m/e</u>	<u>Heights</u>	<u>Peaks</u>		<u>n</u>	<u>Weight Fractions</u>		
		<u>Mono</u>	<u>Residual</u>		<u>iso</u>	<u>CP</u>	<u>AB</u>
378	7.2		-.35				
379	18.0	15.34	12.89		.40		
380	9.5	4.43		9.23			
392	6.4		0.43			.21	
393	14.1	12.11	10.71		.61		
394	7.0	2.93		7.15			
400	0.5						
406	6.0		1.42			.31	
407	11.1	9.17	8.59		1.08		
408	5.0	1.75		5.00			.03
414	1.1						
420	4.7		2.45			1.63	
421	6.0	4.43	4.23		1.05		
422	2.7	0.97		3.23			.06
428	1.9						
434	3.3		1.98			1.47	
435	3.7	2.56	2.54		.98		
436	1.5	0.43		1.59			.11
			Wt. %	75.6	11.9	11.9	0.6

As an internal check samples are calculated by the type analysis method as well. Table VI shows the pattern and sensitivity data used.

Table VI
Type Analysis

<u>CA</u>	<u>Type Analysis</u>			<u>Weight Sensitivities</u>	
	<u>Σ 71/Σ 67</u>	<u>Σ 67/Σ 71</u>	<u>Σ 71</u>	<u>Σ 67</u>	<u>Σ 91</u>
20	36	4	110	240	328
21	38	4	107	235	306
22	40	4	104	231	284
23	43	5	101	226	266
24	45	5	99	220	248
25	47	5	97	214	232
26	49	6	94	210	218
27	51	6	92	204	210
28	53	6	90	199	202
29	55	7	89	195	194
30	57	7	87	190	188

Σ 71 = 71, 85

Σ 67 = 67, 68, 69, 81, 82, 83, 96, 97

Σ 91 = 91, 92, 105, 106, 119, 120 etc. ---- 175, 176

The following three figures show results obtained on three waxes. These waxes were selected in order to illustrate the application of the method over a range of average carbon number as well as concentration level of n-paraffins.

Figure 2

Wax A

	<u>Wt. %</u>	<u>Average C#</u>
n-Paraffins	95.3	24.0
iso-Paraffins	3.7	26.3
cyclo-Paraffins	1.0	27.9
Type Analysis	Total Paraffins 98	
	Cycloparaffins 2	

Figure 3

Wax B

	<u>Wt. %</u>	<u>Average C#</u>
n-Paraffins	79.3	27.0
iso-Paraffins	9.6	29.3
cyclo-Paraffins	10.2	30.3
Alkylbenzenes	0.9	31.7
Type Analysis	Total Paraffins 87	
	Cycloparaffins 12	
	Alkylbenzenes 1	

Figure 4

Wax C

	<u>Wt. %</u>	<u>Average C#</u>
n-Paraffins	57.3	28.5
iso-Paraffins	19.0	31.8
cyclo-Paraffins	20.6	32.3
Alkylbenzenes	3.1	33.3
Type Analysis	Total Paraffins 74	
	Cycloparaffins 23	
	Alkylbenzenes 3	

Conclusion

The parent peak method of analysis has been applied to a large number of waxes, both plant and laboratory in origin, and the data has been related to physical properties of the waxes. A precise knowledge of the hydrocarbon types-present as well as the molecular weight distribution by this technique have been most helpful in the evaluation of paraffin wax physical characteristics.

The further advantages of the method are:

1. A definite reduction in instrument calibration time. Once calibrated, the relative patterns and sensitivities can be checked by running several pure compounds.
2. Shorter calculation time per sample is required. The method can be computerized to further reduce sample handling time.
3. This method reports a more reliable distribution of compound types present. Although the absolute accuracy of the iso-cyclo split cannot be checked, the n-paraffin concentration has been confirmed by other analytical techniques.

Acknowledgment

The authors gratefully acknowledge the advice given by F.W. Melpolder, the work done by J. A. Kieras in obtaining fractions by crystallization, members of the Analytical group for spectra used and B. M. Hollis for assistance in the calculations.

References

- (1) The American Petroleum Institute Research Project 42. Pennsylvania State University, University Park, Pennsylvania.
- (2) Levy, E. J., Galbraith, F. J., and Melpolder, F. W., Advances in Mass Spectrometry, Oxford, England, Vol. 2.
- (3) McAdams, D. R., Isotope Correction Factors for Mass Spectra of Petroleum Fractions. Esso Research Laboratories, Baton Rouge, La., October 1957.

ISOTOPIC MASS SPECTROMETRY OF THE ELEMENTS

E. J. Spitzer
J. R. Sites
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Many mass spectrometry laboratories are now determining relative isotopic abundances from solid samples, and others are becoming interested. For many years the Analytical Mass Spectrometry Section of the Oak Ridge National Laboratory has been analyzing isotopes for the Stable Isotopes Separations group. All 55 of the polyisotopic elements have been separated. The resulting enriched isotopes have been analyzed and made available for loan or sale. Isotopic changes in the products of irradiation, as well as in fission products, are also determined. Thus, successful analytical mass spectrometric experience with every pertinent element has been obtained. It is the purpose of this report to indicate the equipment, to outline the general methods used, and to list the variations in technique obtained for each element.

All data reported herein were obtained by means of 60° deflection, sector-type, non-commercial, metal mass spectrometers. Conventional ion-focusing and accelerating slit systems were used, the ionization chambers being so constructed as to accept expendable bases of the sample-supporting filaments. The filaments are resistance heated using current regulated power supplies. The magnet current control permits one to repetitively scan up and down at various rates over a mass range continuously adjustable from a fraction of a mass unit to the full mass range. The magnetically analyzed ion currents, collected on a vane behind an adjustable slit, go through the 10^{10} ohm input resistor of a vibrating reed electrometer. The mass spectra are displayed on a strip-chart recorder.

The base used to support the sample filament has a standard octal configuration, with two opposite pins eliminated. The 0.060 inch diameter pins can carry heavy currents. Usually, a single filament is spot-welded across the center pins. The four side pins can be used either for alignment with the sides of the ionization chamber or to support a second filament. These bases cost less than 50 cents each. A long dimple is formed in most of the filaments, greatly aiding in the retention of the sample material in the central portion. Simple hand-drawn pipets used for samples in solution are discarded after use. A micromanipulator is not needed in any of these loading techniques.

Apparatus

A stereomicroscope is essential. The filament base is supported on a small bell jar flange under the microscope. Thus, a filament can be baked under vacuum to eliminate surface contamination, to fuse a sample, or to reduce an oxide. Accessories are pipets, hemostats, small spatula, and tweezers. Triply distilled water from a polyethylene bottle gives no extra background ions.

Compounds

For the separated stable isotopes, it was hoped that the preferred inventory compound of the element could also be used for the mass analysis. For most elements this is true; however, for some, specially prepared compounds are much better. In a few cases, any simple compound of the element can be used.

A suitable compound should be chemically stable at room temperature. Also, it is desirable for it to be soluble in water or dilute acid. Sometimes the evaporated coating pops off the filament as a result of loss of water of hydration. In order to get stable vaporization, unusual compounds that give thermal decomposition products of high vapor pressure are necessary; for example, BaSiF_6 for silicon and Ag_6TeO_6 for tellurium. Treating CaO and CaCO_3 with HI gives much more steady ion beams of Ca ions than without. Initial heating of a tantalum filament in air to give a faint blue oxide layer makes the cesium ion beam much more stable.

Loading

Most compounds load very easily on the filament when deposited from a dilute solution of their nitrates, for example, uranium. A few finely divided powders will slurry with a droplet of water or dilute nitric acid, as the rare-earth oxides. Some fuse on, as does NaCl. Silicon dioxide is very hard and bounces off at the slightest vibration. Fluffy, and hard materials are crimped into a folded canoe-type filament. The usual procedure for loading a platinum group metal is to fuse it to the proper filament material at a high temperature under vacuum. Boron compounds are added to fused sodium hydroxide on the filament, and further heating forms sodium tetraborate. Watching the many loading procedures through the microscope enables one to see phase changes, completion of reactions, or as is sometimes the case, only crust from an impure sample.

Filaments

The most commonly used filament is a 0.001 by 0.030 by 0.500 inch dimpled tantalum ribbon. Filaments of tungsten, iridium, rhenium, and platinum are also used. A double filament is used for lithium halides which are vaporized from a ribbon filament and ionized on a hot tungsten wire helix. Prebaking the filaments is necessary for the analysis of potassium, calcium, strontium, and barium. This can be done in the mass spectrometer to determine the amount of background ion intensity at operating temperatures, or in an auxiliary vacuum chamber using a heating cycle that has been proven to be satisfactory.

Heat-up

A bit of experience and finesse is needed in the sequence of raising the filament temperature for some compounds, or the sample may be lost. Also, a few analyses are made at a temperature near the melting point of the filament material; for example, some of the platinum-group elements. In many cases, a few sets of data are taken at each increase in ion intensity, in case the ion beam deteriorates after the next temperature increase. Frequently, a sub beam-taking temperature is maintained for a phase change, for background reduction, or for smoother vaporization conditions. A small amount of rubidium in a strontium sample will bake out at a lower temperature than that at which the strontium data are taken. On the other hand, stable ion intensities for some elements such as the rare-earth elements, can be had by setting the filament supply to the proper current.

Data

The magnet scanning speeds and the electrometer scales are selected manually while data is taken. Enough sets of ion peaks are obtained to get 10 sets of measurements. The peaks on the strip-chart are measured with drafting scales, estimating to the nearest tenth of a millimeter. After several years of checking, we have determined that in most cases the "range" method of finding the relative standard error for the 95% confidence interval is applicable. We do not use more modern data-handling equipment than a desk calculator.

Interferences

Circumstances continually arise that keep mass spectrometry from becoming too routine. Interferences are often present. For electron bombardment ion beams, the hydrocarbon background from pump oil or fingers may be very persistent. Water in the sample or a small air leak may hinder. All filament materials give sodium, potassium, rubidium, strontium, cesium, and barium ions. Rhenium contains molybdenum, and iridium contains rhodium.

The submitted sample may be "clean" to the chemist or the optical spectroscopist and still give bothersome ions of the sodium, potassium, etc. In cleaning a uranium solution by extraction, salting with $(\text{NH}_4)_2\text{CO}_3$ instead of CaCO_3

permits steady uranium ion beams of high intensity. Residues of resins and other organics can prevent smooth vaporization and ionization.

Isobars can cause false peak heights, as among rare-earth elements, and for rubidium and strontium. But vapor pressures differ enough so that isobar interference appears in the form of an ion beam of changing intensity with respect to interference-free ions.

Memory from one run to the next can often be controlled without cleaning the source parts between each run by using removable shields, or by analyzing several samples of nearly the same isotopic enrichment. Sometimes, analyzing a "high temperature" sample or two before changing to a different isotope of a "low temperature" set of samples is sufficient.

Corrections

Corrections for hydrocarbon background can be made by subtracting a typical background pattern for the mass region, using a non-isobaric background peak as a base. Corrections for oxygen isotopes are made when necessary, as in analysis of rare-earth oxide ions.

Radioactivity

For the more radioactive and toxic samples, such as fission-product Cs^{137} and Sr^{90} , a removable ionization chamber liner is used. The used filament bases are wrapped and buried, and the contaminated source parts are carefully cleaned and kept isolated from other "cold" parts. Plutonium is not analyzed because this laboratory is not equipped with double-containment facilities.

Gases

Several elements are analyzed as gaseous samples; sulfur and carbon isotopic abundances are determined using SO_2 and CO_2 . Isotopically modified rare gases are also analyzed on a gas mass spectrometer. He^4 containing He^3 , Ne, Ar, Kr, and Xe from thermal diffusion experiments; argon from KCl irradiation; and fission product Kr and Xe are analyzed, but no hydrogen isotopes are analyzed.

Biological

Although not included in the manual, several isotopic studies have been made on biological materials. Biologists often work with very complicated molecules, but they are usually successful in being able to submit isotopically modified CO_2 , or N_2 . Since organic acids give negative ions of the parent molecules, the C^{13} content of tagged methyl malonic and succinic acids has been successfully measured. Also, the negative ion spectra of a deuterated succinic acid sample has been recorded. These were run using an "internal-external" charge bottle. A small glass retort with a long neck with a heater looped around the bulb was fitted to the back of a filament base so that the sample was not warmed directly by the ionizing electron filament.

Standards

Gravimetrically compounded mixtures of nearly isotopically pure separated stable isotopes have been used as standards to check the accuracy of the mass spectrometers for uranium and boron. In all cases, the data substantiate the accuracy and limits of error as are usually reported. For other elements defined laboratory standards are used.

Manual

Each element of interest has a page in the form shown in Table I.

TABLE I
TELLURIUM (Te_{52})

<u>Preferred Conditions:</u>		Relative Abundance of Isotopes	
Compound	Ag_6TeO_6	<u>Isotope</u>	<u>Atom %</u>
Sample Filament	Tantalum	120	0.089
Filament Size	2 x 60 mils	122	2.46
Ionization	Electron Bombardment	123	0.87
Temperature Range	<200° C	124	4.61
Ion Measured	TeO_2^+	125	6.99
		126	18.71
		128	31.79
		130	34.48

Sample Loading:

Comments:

The preferred conditions, the relative isotopic abundances of the normal element, sample loading techniques, and comments relative to any special operating characteristics are listed. In practice, we refer to the temperature in terms of filament current rather than the actual temperature. The sample size varies from a few nanograms to a few milligrams, depending on availability, radioactivity, and volatility.

This "cookbook" is being issued as an Oak Ridge National Laboratory topical report. It is used daily in the mass spectrometry laboratory, and is the result of the experience and personal notebooks of several people.

Summary

An analytical laboratory has an open door and should be able to try something on any sample that is submitted. We will try a sample once, and if unsuccessful in getting useful information, it is returned to the originator for modification. There is no substitute for a clean sample.

Sometimes several samples, each of a different element, must be analyzed on a given mass spectrometer in a day and it is inefficient not to have a quick-recall aid, such as this manual. It certainly does not contain the ultimate nor exhaustive listing of methods, but these work and we use them.

ISOTOPIC ANALYSES WITH A SPARK SOURCE MASS SPECTROGRAPH

F. D. Leipziger
SPERRY RAND RESEARCH CENTER
Sudbury, Massachusetts

I. Introduction

The increasing number of spark source mass spectrographs has led to advances in low level impurity analysis. However, the technic of these analyses has closely paralleled emission spectrographic technics. The application of these instruments to isotopic analyses should not be overlooked. A mass spectrometer with the power to ionize all the elements of the periodic table is in many ways a great improvement over conventional instruments.

The major problem involved in isotopic measurements with a spark source instrument is the photographic detector. The integrating properties of the plate are a major advantage in some cases, but in general this detector ranks well below the electron multiplier or vibrating reed for precise isotope ratio measurements. Thus, for many elements there is no doubt that electron impact or thermal ionization sources are superior. But in cases where the element of interest cannot conveniently be mass analyzed by either of these machines the spark source instrument will be of great value.

The spectrograph used in these studies was the Metropolitan Vickers MS 7.

II. Plate Calibration

The first step necessary for any isotope ratio measurement with photoplate detection is calibration of the emulsion. The method we are using was developed by Mattauch and Ewald (1). This involves sparking a polyisotopic element such as tin and constructing a curve relating darkening of the plate to the known isotopic abundances of the standard. Then the ratio of the isotopes in question may be determined by measuring their optical transmission on the plate and finding relative abundances from the calibration curve.

A series of problems rises from the use of the spark source and the photographic plate. These include problems generated by the nature of the spark and the geometry of the instrument, and also from the photoplate itself. Some of these are listed in the next slide.

1. Variations in line width
2. Differing ion path lengths
3. Variations in the ratio M^+/M^{++}
4. Variation in ionization
5. Non-linear darkening of the emulsion
6. Photoplate emulsion exhibits ion-mass and ion-energy dependence

In general, we may avoid the consequences of some of these problems merely because we are measuring isotope ratios. Thus, if we are able to adjust the ratio so it is close to 1 as in isotope dilution work we avoid problems due to differing line widths, and similarly measurements on adjacent masses will minimize the effects of different path lengths.

Typical of the accuracy attainable when these conditions are met is the isotopic distribution of antimony shown in the next slide.

	White and Cameron	This Work
Sb 121	57.6 a/o	57.3
123	42.4	42.7

$$R = 1.36$$

III. Isotope Dilution

One of the most accurate and sensitive analyses that can be done on a mass spectrometer is the isotope dilution analysis. In theory the method may be applied to any element that is poly-isotopic or has a long lived radioisotope. In practice, however, some elements cannot be handled with conventional instruments. For example, platinum, copper, titanium, and cadmium are just a few of the elements which will not ionize by normal surface ionization or electron impact techniques.

Briefly, the isotope dilution method involves the addition of a known amount of spike, which has an isotopic composition different from the natural element, to a weighed sample. The change produced in the isotopic composition of the spike by the element in the sample is then directly related to the concentration of the element in question.

One of the major advantages of the method is that once the spike and sample have exchanged there is no need for quantitative recoveries or separations.

Our first choice for a test of the method was copper. This element is not normally mass analyzed nor is it one commonly associated with stable isotope dilution. Also, the electrolysis technic affords an accurate check of the method even at low levels. The material chosen for analysis was a nickel oxide powder, NBS #673. The NBS copper value, which is the average of the work of eleven laboratories, is 20 PPM, with values ranging from 12 to 24 PPM. Our procedure for analysis involved weighing a one gram sample, micropipetting a known amount of Cu^{65} spike, and dissolving the sample. Next the copper was concentrated by electrolysis and re-dissolved, and then coated on pure aluminum electrodes which were placed in the instrument and sparked in the normal manner. Several tin exposures were also made on the same plate for a calibration of the emulsion. After the $\text{Cu}^{65}/^{63}$ ratio had been obtained with the aid of a densitometer, the copper content was calculated using the formula shown in the next slide.

$$R_m = \frac{\text{Cu}^{65} \text{ added} + \text{Cu}^{65} \text{ originally present}}{\text{Cu}^{63} \text{ added} + \text{Cu}^{63} \text{ originally present}}$$

$$\text{wt. of Cu} = \frac{\text{Cu}^{65} - K_i(R_m) \text{ Cu}^{63}}{R_s K_i(R_m - 1)} (1 + R_s)$$

where Cu^{65} = wt. of Cu^{65} added
 Cu^{63} = wt. of Cu^{63} added
 K_i = atom-to-weight conversion factor
 R_s = $\text{Cu}^{63}/^{65}$ in the original sample
 R_m = measured ratio of spike plus sample

The results of six analyses of NBS 673 are shown in the following slide.

Copper Content of NBS 673

Run	PPM Cu
1	21.0
2	21.8
3	22.9
4	21.0
5	20.2
6	19.0

Av'g 21.0 ± 1.3 PPM
 NBS value 20 PPM

These results show a standard deviation of 5%, which is actually a little disappointing for this type of analysis. This figure contains errors in weighing, micropipetting, standardization of the spike, and densitometry. In most of these analyses the ratio $\text{Cu}^{63}/^{65}$ was adjusted to be close to one.

We feel that for cases where the effort is worthwhile there is now no bar to isotope dilution analyses for any element which has stable enriched isotopes or long lived radioisotopes.

IV. Upper Limits of Isotopic Abundance

Another use of the photographic detector is in a search for new isotopes or the establishment of upper limits of isotopic abundance. In the course of a series of impurity analyses on ultra pure metals we noted the ease with which the rarer isotopes may be seen. Pt^{190} , U^{234} , and Ta^{180} for example are detectable on good plates at least a factor of 10^4 above maximum sensitivity. Thus we feel that isotopes abundant to one part in 10^8 would be detectable.

With this in mind we were able to run a series of elements and look for undiscovered isotopes and set new abundance limits. Many of these elements have not been examined in this context for years. Elements not susceptible to mass analysis by thermal or electron impact technics comprised the bulk of this work. A total of twenty-one elements were examined, and in many cases the limiting factor was chemical purity rather than plate sensitivity. For example, a thallium impurity in the lead sample reduced sensitivity at mass positions 203 and 205. On occasion similar difficulties arose from compound ion formation. A peak at mass 76 in the arsenic spectrum is attributed to AsH^+ and reduced sensitivity at that position. Typical results for gold are shown on the next slide.

Upper Limits of Isotopic Abundance for Gold

Mass	This Work	Previous Work
194	<0.000001 a/o	----
195	<0.000001	----
196	<0.000005	----
198	<0.000005	$<.02$
199	<0.000005	$<.02$
200	<0.000005	$<.02$

V. $Pb^{206}/^{207}$ Dating

The dating of uranium bearing minerals by measurement of the radiogenic lead content and composition is typical of many isotopic analyses that are possible with a spark source instrument. The facts that no chemical separations are necessary and that the isotopes of interest are examined in situ are the greatest advantages of this technic. The difficulty encountered in the ratio measurement as opposed to the ease of making precise electrical measurements is a distinct disadvantage.

Dating by $Pb^{206}/^{207}$ ratios depends on the disintegration of U^{235} and U^{238} into Pb^{207} and Pb^{206} respectively. The amount of each end product is then proportional to the half life of the precursor and the age of the mineral may be calculated. The assumptions made are that there has been no alteration of the mineral and that none of the daughters have been lost. The presence of radiogenic Pb^{208} in these minerals is the result of the decay of Th^{232} .

The presence of Pb^{204} is indicative of contamination with ordinary lead since Pb^{204} is not known to be a member of any radioactive decay series. When Pb^{204} is detected in these minerals the associated amounts of Pb^{206} and Pb^{207} must be subtracted from the radiogenic material before the age is determined.

The procedure for the pitchblende and uraninite specimens analyzed by us was quite simple. Samples of the appropriate size were cut from the massive specimens and treated to remove any impurities introduced in the cutting operation. These pieces were placed directly in the instrument, and a series of exposures were made. Again several tin exposures were made on the same plates for calibration purposes. Then, after the ratios were measured and corrected for the presence of normal lead if necessary, the ages were determined with the aid of tables by Stieff et. al. (2)

The last slide shows a comparison of ages by this method and the classical method involving a chemical separation.

Comparison of Uranium Mineral Ages

	Classical	This Work
Pitchblende (Katanga)	650×10^6	630×10^6
Pitchblende (Great Bear Lake)	1.5×10^9	1.7×10^9
Uraninite (Wilberforce)	1.05×10^9	$.96 \times 10^9$

References

1. Mattauch and Ewald, Natur. 31, 487 (1943).
2. Stieff, L. R., Stern, T. W., Oshiro, S., and Senftle, F. E., Geol. Surv. Prof. Paper 334-A (1959).

ANALYTICAL STUDIES WITH SPARK SOURCE MASS SPECTROGRAPH

John Roboz
General Telephone & Electronics Laboratories, Inc.
Bayside 60, New York

Manuscript Withdrawn

MASS SPECTROMETRIC ANALYSES OF B^{10} IN BORON MINERALS

H. O. Finley, A. R. Eberle, and C. J. Rodden

In previous studies reported^{1,2} from the New Brunswick Laboratory (NBL) on the B^{11}/B^{10} ratio of commercially prepared boron materials, significant differences were found in the isotopic ratio obtained with boron metal and boric oxide prepared from minerals from the same geological origin. Differences were also found among other samples of unknown origin. The results are shown in Table 1.

TABLE 1

 B^{11}/B^{10} RATIOS OBTAINED WITH FINAL PROCEDURE

Material	Source	B^{11}/B^{10} Ratio	Standard Deviation of Single Measurement	B^{10} Atom %
Boron Metal from Oxide	American Potash and Chemical Corporation (Searles Lake)	4.019	0.006	19.924 ± 0.002 S. D.
Boric Oxide	American Potash and Chemical Corporation (Searles Lake)	4.070	0.004	19.724 ± 0.002 S. D.
Boron Carbide	Norton Company	4.030	0.008	19.881 ± 0.001 S. D.
Boric Acid	Norton Company	4.039	0.002	19.845 ± 0.001 S. D.
Borax	Searles Lake	4.069	0.003	

Note: Value obtained by (KAPL) is 4.07

The possibility of fractionation during laboratory conversion of the samples to the sodium tetraborate charge material existed because the methyl ester and the direct fusion conversion techniques used have uncertain yields.³ Thus, the isotopic ratio differences found could be due to chemical treatment in the commercial processing, to laboratory conversion or to geological origin.

In the present work, possible variations in the natural isotopic abundance as reported by McMullen et al.⁴ were investigated by analyzing boron minerals from various parts of the world. The samples were kindly supplied by the Smithsonian Institution.

Experimental

The boron was isolated from the minerals by a pyrohydrolysis procedure⁵ identical with that described by Williams et al.⁶ except that a platinum boat and a Burrell high-temperature furnace was used. At a temperature of 1300 to 1350°C, all of the boron is found in the distillate after one hour. Recovery tests carried out on borax, borosilicate glass sand NBS No. 93 and synthetic calcium and beryllium borate mixtures, approximating the composition of the minerals to be analyzed, indicated the boron yield to be essentially 100%. The presence of strontium and rubidium in the product, however, was a potential interference in the mass spectrometric analysis. Accordingly, the distillate was passed through a column of cation-exchange resin in the hydrogen form. No loss of boron was found to occur on the column. The effluent was adjusted to pH 9.3 to 9.4 with dilute sodium hydroxide solution and evaporated to dryness. The residue was taken up in 1 or 2 ml of water for the analysis. No losses of boron occur in the evaporation step; losses occur if the pH is adjusted to below 9.3. The tetraborate was analyzed with a first order, directional focusing mass spectrometer with a homogeneous magnetic field of 60° sector shape and a radius of magnetic deflection of 12 inches. The

surface ionization source employs a single filament arrangement with triple filament geometry. Isotopic ratios were determined by measuring the peaks with a calibrated vibrating reed electrometer. This solid source technique has been shown to be more satisfactory than those involving volatile materials in a "gas" instrument.^{1,7,8}

In order to obtain an estimate of accuracy of the B^{11}/B^{10} abundances, a synthetic sample containing a calculated B^{11}/B^{10} ratio of 3.661 ± 0.007 (standard error) was analyzed. The sample was obtained from the Knolls Atomic Power Laboratory (KAPL). The results are shown in Table 2 and Table 3.

Table 2 shows an estimate of accuracy and Table 3 shows a comparison of the NBL instrument to those used in other laboratories.

TABLE 2

B^{11}/B^{10} RATIO OBTAINED WITH SYNTHETIC STANDARD TETRABORATE

	<u>B^{11}/B^{10} Ratio</u>	<u>Standard Deviation</u>
KAPL Calculated	3.661	0.007
KAPL Measured	3.657	---
NBL Measured	3.665	0.011
NBL Measured/KAPL Calculated	1.0011	
Bias of NBL Measured to KAPL Calculated	0.11%	
Bias of NBL Measured	0.004	
Total Standard Deviation for NBL Value	0.013	

TABLE 3

MASS SPECTROMETRIC ANALYSES OF SYNTHETIC BORON STANDARD

<u>Determination by</u>	<u>Calculated</u>	<u>Observed</u>	<u>95% C. L.</u>
Present Authors	3.661 ± 0.007 (standard error)	3.665	± 0.0074
Knolls Atomic Power Laboratory		3.657	± 0.008
Phillips Petroleum Company		3.666	± 0.05
Oak Ridge National Laboratory		3.668	± 0.025
Average		3.664	

Two aliquots from each of two separate chemical separations of each mineral were analyzed using two different ion sources. The synthetic KAPL material was analyzed at various points between samples of the minerals to evaluate any instrumental changes.

The results are shown in Table 4.

TABLE 4
ISOTOPIC BORON COMPARISONS OF CERTAIN BORON MINERALS

Aliquot	Mineral	Country	Ion Source "A" Ratio B^{11}/B^{10}	Std. Dev. on Mean	N	Ion Source "B" Ratio B^{11}/B^{10}	Std. Dev. on Mean	N
1	Standard	KAPL	3.665	0.008	4	3.664	0.004	5
1	Colemanite	U. S. (Death Valley)	4.002	0.007	2	4.000	0.004	4
2	Colemanite	U. S. (Death Valley)	3.997	0.005	5	3.981	0.004	4
1	Colemanite	Turkey	3.994	0.003	3	3.988	0.003	4
2	Colemanite	Turkey	3.999	0.005	3	3.999	0.010	4
1	Ulexite	Argentina	3.930	0.002	7	3.924	0.003	3
2	Ulexite	Argentina	3.915	0.009	4	(3.918 3.925)	(0.005 0.009)	(3) 3)
1	Howlite	U. S. (California)	3.977	0.002	3	3.963	0.005	3
2	Howlite	U. S. (California)	3.950	0.004	3	3.958	0.007	3
1	Inyoite	U. S. S. R.	4.152	0.003	3	4.136	0.002	4
2	Inyoite	U. S. S. R.	4.139	0.005	2	4.138	0.004	3
1	Szaibelyite	Canada	4.053	0.006	3	4.069	0.004	4
2	Szaibelyite	Canada	4.066	0.007	3	4.066	0.005	3
1	Hambergite	Madagascar	4.030	0.001	2	4.028	0.002	4
2	Hambergite	Madagascar	4.024	0.004	3	4.023	0.002	4
2	Standard	KAPL	3.667	0.005				

The statistical evaluation of the above data indicates significant differences were observed between all minerals analyzed with the exception of Colemanite from U. S. and Turkey.

No differences were observed between the two ion sources used in the analytical work performed. Among the duplicate samples analyzed for each of the minerals, differences were observed between the samples on the Colemanite (U.S.) analyzed on ion source "B" and on the Howlite (U.S.) analyzed on ion source "A".

The standard deviation of a single determination was 0.0076. The standard deviation of an average of four determinations is then 0.0038, giving a figure of 0.008 for the 95% confidence limit. This confidence limit could be applied to each of the average values for the various minerals.

The above agreement with the calculated value for the KAPL standard indicates that the results reported on the minerals are accurate within the error previously shown.

The average B^{11}/B^{10} abundance values obtained with the various minerals examined are shown in Table 5.

TABLE 5
AVERAGE RESULTS FOR THE BORON MINERALS

<u>Mineral</u>	<u>Country</u>	<u>B^{11}/B^{10} Ratio</u>	<u>95% C. L.</u>
Colemanite $Ca_2B_6O_{11} \cdot 5H_2O$	Death Valley California, U. S. A.	3.995	± 0.008
Colemanite $Ca_2B_6O_{11} \cdot 5H_2O$	Turkey	3.995	± 0.008
Ulexite $NaCaB_5O_9 \cdot 8H_2O$	Salar de Cauchari Los Andes, Argentina	3.922	± 0.008
Howlite $Ca_2SiB_5O_8(OH)_5$	San Bernardino Co. California, U. S. A.	3.962	± 0.008
Inyoite $Ca_2B_6O_{11} \cdot 13H_2O$	Lake Inder Kazakhstan, U. S. S. R.	4.141	± 0.008
Szaibelyite $(Mn, Mg)(BO_2)(OH)$	Douglas Lake British Columbia, Canada	4.064	± 0.008
Hamborgite $Be_2(OH)(BO_3)$	Imalo Madagascar	4.026	± 0.008

Discussion

Previous investigations by McMullen et al.⁴ using a surface ionization source for the mass spectrometric determination of boron isotopic ratio composition in minerals gave 4.040 for the B^{11}/B^{10} ratio in borax and 4.068 for the ratio in Tincal. The B^{11}/B^{10} ratio for boric oxide has been reported as 4.18 by Semenov and Zonov⁹, 4.00 by Goris et al.⁷, and 4.071 by Finley and Leuang². The chemical history of some of these chemical products is not known and possible isotopic fractionation of the boron in the chemical treatment cannot be excluded.

From the results given in Table 5 it would appear that from the present work there are significant variations in the B^{11}/B^{10} abundance ratio with all the minerals examined except the Colemanite from the United States and Turkey. The value from the U.S.S.R. is appreciably different from the other minerals. It is interesting to note that Semenov and Zonov⁹ reported a value for the B^{11}/B^{10} abundance ratio of 4.16 on boric oxide. This is in close agreement with the value of 4.14 obtained in the present investigation with Inyoite from the U.S.S.R.

The necessity of selecting samples on the basis of location within a deposit as well as the location of the deposit, as shown by McMullen et al.⁴, was not investigated. The primary interest in this evaluation was to determine a normal isotopic value for untreated boron materials rather than rely upon the commercially prepared boron compounds.

The evaluation of the mass spectrometric measurements and the evaluation of the errors follows essentially that recommended by Cameron¹⁰. The masses used are the EKM¹¹ mass and are recommended for use in determining atomic weights by Cameron and Wichers.¹²

The individual atomic weights and the average atomic weights are shown in Table 6.

TABLE 6
AVERAGE ATOMIC WEIGHT FOR BORON MINERALS

<u>Mineral</u>	<u>B¹¹/B¹⁰ Ratio</u>	<u>95% C. L.</u>	<u>Calculated Atomic Wt.</u>	<u>95%¹³ C. L.</u>
Colemanite	3.995	± 0.008	10.80983	± 0.00039
Colemanite	3.995	± 0.008	10.80983	± 0.00039
Ulexite	3.922	± 0.008	10.80687	± 0.00039
Howlite	3.962	± 0.008	10.80851	± 0.00039
Inyoite	4.141	± 0.008	10.81550	± 0.00039
Szabelyite	4.064	± 0.008	10.81255	± 0.00039
Hambergite	4.026	± 0.008	10.81106	± 0.00039
Average Atomic Weight			10.8106	± 0.0026

The errors for the individual weights were determined as recommended by Ewald and Hintenberger.¹³

The average atomic weight for the above minerals is 10.8106 ± 0.0026, 95% C. L. The error contains the instrumental uncertainties and the natural variations among the seven minerals.

REFERENCES

1. Finley, H. O. and Leuang, E. E., Jr, NBL-170 (August 1961), p. 49.
2. Finley, H. O. and Leuang, E. E., Jr., (June 1961), Ninth Annual Meeting ASTM Committee E-14 on Mass Spectrometry.
3. Russell, H., NBL-170 (August 1961), p. 87.
4. McMullen, C. C., Cragg, C. B., and Thode, H. G., Geochim. et Cosmochim. Acta, **23**, 147 (1961).
5. Eberle, A. R., NBL-177 (March 1962), p. 9.
6. Williams, J. P., Campbell, E. E., and Magliocca, T. S., Anal. Chem., **31**, 1560, (1959).
7. Goris, P., Morgan, T. D., and Nielson, R. A., IDO-14549 (1961).
8. Haas, W. O., Jr., Rourke, E. M., Mewherter, J. L., and McDonald, P. H., KAPL-2062 (October 1959).
9. Semenov, G. A. and Zonov, Yu A., Zhur. Anal. Khim., **14**, 137 (1959).
10. Cameron, A. E., Anal. Chem., **35**, (No. 2), 23A (1963).
11. Everling, F., Konig, L. A., Mattauach, J. H. E., and Wapstra, A. H. Nuclear Chipsico, **18**, 529 (1960).
12. Cameron, A. E. and Wichers, Edward J. Am. Chem. Soc., **84**, 4175 (1962).
13. Ewald, H. and Hintenberger, H., AEC-Tr-5080, (1953).

SOLID COMBUSTION PRODUCTS ANALYSIS BY SPARK SOURCE MASS SPECTROGRAPH

by

A. V. Jensen, B. B. Goshgarian, N. E. Dane

6593 Test Group (Development), Chemical and Materials Branch

Edwards AFB, California

ABSTRACT

This paper presents a spark source mass spectrographic technique for the analysis of solids formed in some rocket propellant combustion processes. Identification and quantitative methods for mass fragment determination are shown and discussed, together with observed sample spectra. Methods for calibrating photographic plates used as detectors are given. Results obtained with boron nitride-containing residues indicate that rocket propellant combustion products in the form of solids can be analyzed by spark source mass spectrography with reasonable accuracy.

INTRODUCTION

Use of radio-frequency spark ion source mass spectrography for the analysis of solids is becoming more prominent. Good results can be obtained for trace contaminants analysis of metals and insulating materials (1,2,3,4). Gorman, Jones and Hipple (5) have shown the suitability of spark ionization source mass spectrography for quantitative analysis of stainless steels for concentration of metals above one percent. Desjardins, Hodgson and Baun (6) have applied the spark ion source for the structural identification of solid organic compounds.

The quantitative identification of ion masses by the use of photographic plates has shown that variations exist between plates. Owens (7) studied the effect of ion mass and ion energy on the sensitivity of Ilford Q-2 plates used as ion detectors in spark ion mass spectrography. He found that the plates must be calibrated individually whenever accurate comparisons between exposures on different plates are desired. Hull (8) presents a method for calibrating photographic plates which provides a good analytical correlation between plates.

Very little work has been reported on spark ion source mass spectrographic analysis of non-homogeneous samples. One paper describes the analysis of powders by using packed metal tubes as sample holder and electrode (2). Another paper describes the techniques of adhering powder samples on carbon electrode surfaces (9). Waldron (10) applies RF spark ion mass spectrography for the analysis of insulating and refractory powder samples. His technique involves the molding of a mixture of the sample with a suitable conducting support material in a Seidel press. The resulting table is broken in two and the clean ends used to form the electrode gap.

The analysis by wet chemical techniques (11) of boron compounds formed in rocket engine chambers during combustion has at times proven inadequate. The bonding of hydrogen to boron nitride polymers, which decreases engine combustion efficiency, cannot be readily determined. This paper presents a method for analyzing engine residues qualitatively and quantitatively for boron, nitrogen, oxygen, and (BNH)_x constituents. Applicability of this method for the analysis of residues containing aluminum and other light metals is presently being investigated.

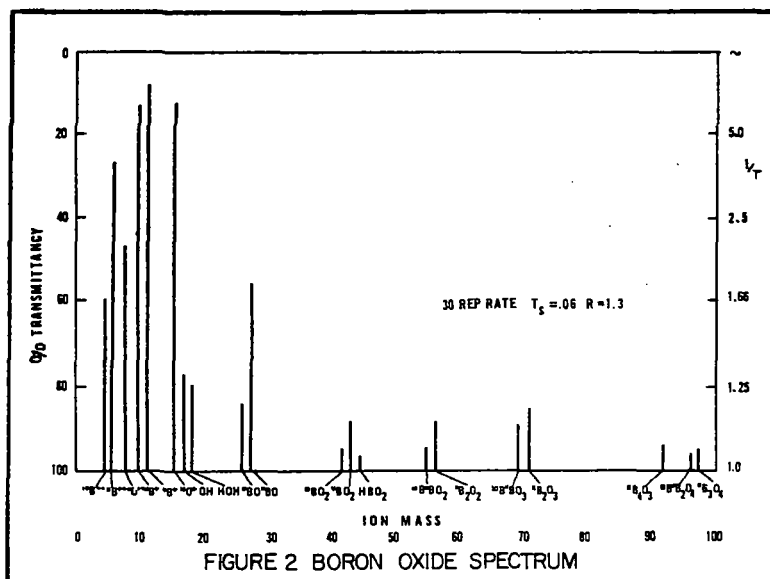
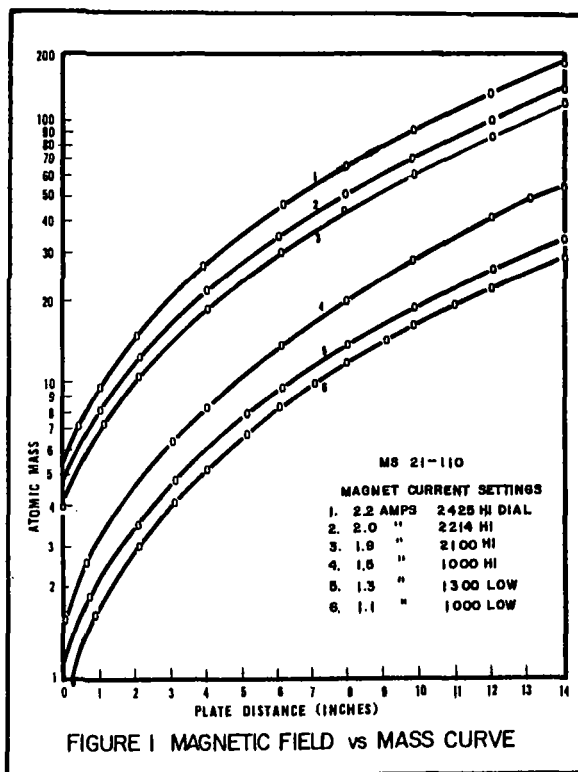
A discussion of instrumental techniques and conditions, together with methods for obtaining plate calibration data are presented. Calculation methods for qualitative and quantitative analysis of elements and fragments in a compound as major constituents, and data obtained from boron, boron nitride, boron oxide, sodium borohydride, and engine residues are given.

EXPERIMENTAL

Instrumental. A Consolidated Electrodynamics Corporation Model 21-110 double-focusing mass spectrograph equipped with a radio-frequency spark source was used in this study. The samples were ionized by an 80 KV radio-frequency spark pulsed at a rate of 30 pulses per second, at 5 microseconds pulse width. Although variable, these parameters were kept constant for all the samples and standards studied. Sparking was continued uniformly for exposure times of 2 to 300 seconds to obtain 2×10^{-11} to 1×10^{-9} coulombs of ion current at the beam monitor.

The magnetic current can be varied as shown in Figure 1, but was kept constant at 2.0 amps, allowing the ions in the mass range of 5-200 to strike an Ilford Q-2 photographic plate.

All samples were sparked with a vacuum of 10^{-6} - 10^{-7} torr in the electrostatic and magnetic sectors. The spark analyzer sector vacuum was initially 10^{-6} - 10^{-7}



torr; however, during firing, the pressure increased to 10^{-5} torr, depending on the sample used.

Electrodes. All electrodes used were of spectrographic assayed purity, and were machined to $3/4$ " lengths by $1/8$ " diameters from spectro grade bar stock. A $1/16$ " x $1/16$ " cup was drilled on the ends of the sample holder electrodes, and points were filed on the ends of the probe electrodes. Electrode material which would not interfere with the sample lines on the photographic plate was chosen. Titanium electrodes were used for plate calibration purposes since the parent isotope lines on the plate were in the mass region of samples to be analyzed. An order of magnitude between Ti^{46} and Ti^{48} abundancies allows one to obtain plate line density saturation while obtaining a plate calibration curve.

Samples. The powder samples fired all contained boron. The standard samples selected were: Boron, 325 mesh crystalline black powder of 99.9+% purity (U.S. Borax and Chemical Corporation); boron nitride, 325 mesh white powder of 99.5% purity (Carborundum Company); boron oxide, white crystalline powder of 95% purity (Fischer Scientific); and sodium borohydride, white anhydrous powder of 100% purity (Callery Chemical Company).

The engine propellant combustion residues analyzed were finely divided, fluffy light-grey-brown powders. Absorbed hydrogen, nitrogen, ammonia, and oxygen were removed from the residue by heating for 18 hours at 80°C at a pressure of 0.1 torr prior to electrode packing and firing.

Maximum ion yield for all the samples was obtained if the spark was maintained at a position somewhat off-center of the slit. The glow which formed around the spark was the reference point used to focus on the slit, not the optical center of the spark gap.

Plate Conditions. The plate, after exposure, was developed in Kodak D-19 developer with continuous agitation for seven minutes, fixed, washed and dried in the usual photographic technique. The developing solutions were kept at 20°C . To insure constant activity of developing solutions, one-half of the solutions were discarded and fresh solution added to the remainder periodically.

The above procedure gives maximum clarity and contrast. Other investigators (12,13) have indicated that shorter development times lead to reversal of some intense lines.

The Ilford Q-2 photographic plates and the development technique gave good results for quantitative and qualitative determinations. Scratches and other marks which were apparently inflicted during packing and/or removal from the black wrapping paper were observed on plates. Although emulsion imperfections occasionally affected the quantitative determination, the mass fragment determinations were not affected.

Densitometry. The transmittancy values obtained for some mass lines varied considerably from the average. These were due in part to the scratches, holes, and spots occurring in the emulsion. The transmittancies of the mass lines on the plate were obtained on a Jarrell-Ash Densitometer. A 2 mm x 5μ slit setting gave maximum line area and averages the emulsion grain variation over the entire line. Shorter slit height settings could not be used because the baseline (100%T) was much too erratic.

RESULTS

Standard Samples. Copper was chosen for the supporting electrode metal since lines due to singly and multiply ionized copper isotopes did not interfere with the sample line determinations. The copper ion intensities obtained do not have any reproducible relationship to the sample ion intensities. This can be expected in such a heterogeneous electrode system.

The parent double- and triply-charged boron isotope fragments were clearly visible on all quantitative plate spectra. No attempt was made to determine the ion intensities of the multiply-charged isotopes with respect to the parent. Diatomic boron was detected in a single instance; a high-yield exposure of elemental boron gave a very faint $^{11}\text{B}_2^+$ line.

The BN^+ fragment was absent in spectra which were useful for densitometric quantitative measurements. A very faint (10^{-14} coulombs) BN^+ line was found in

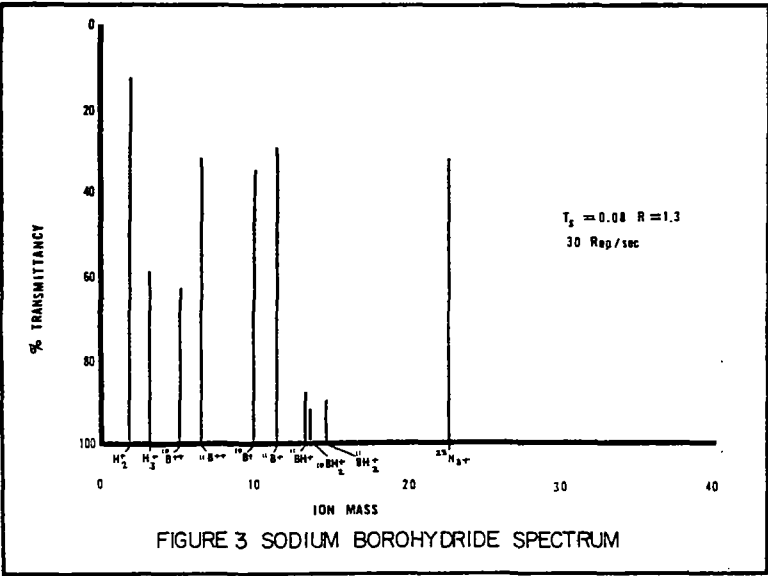


FIGURE 3 SODIUM BOROHYDRIDE SPECTRUM

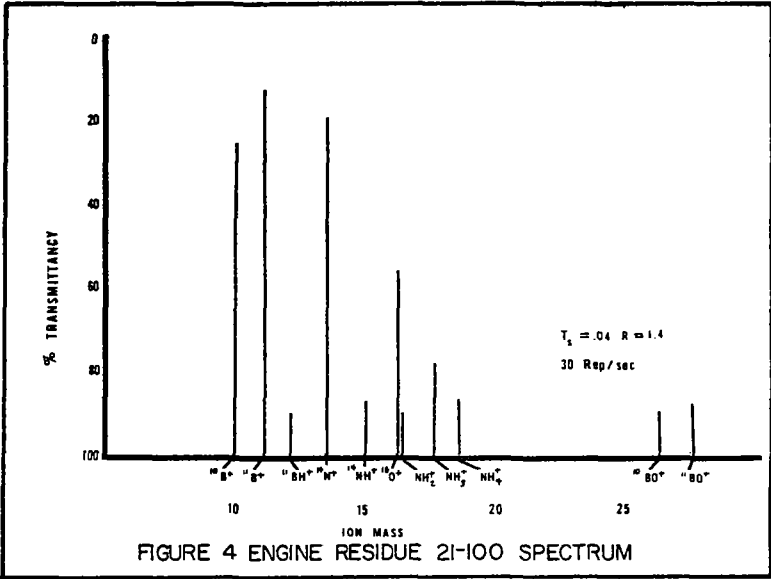


FIGURE 4 ENGINE RESIDUE 21-100 SPECTRUM

extremely high ion yield exposures (1000 times normal).

The boron oxide spectra shown in Figure 2 gave distinct $^{10}\text{BO}^+$ and $^{11}\text{BO}^+$ fragments on the quantitative exposures. Lines corresponding to $^{11}\text{BH}^+$, OH^+ , and OH_2^+ were also detected, apparently from the H_3BO_3 impurity in the B_2O_3 sample. High ion yield exposures showed lines identified as $^{10}\text{BO}_2^+$, $^{11}\text{BO}_2^+$, $\text{H}^{11}\text{BO}_2^+$, $^{10}\text{B}^{11}\text{BO}_2^+$, $^{11}\text{B}^{11}\text{BO}_2^+$, $^{10}\text{B}^{11}\text{BO}_3^+$, $^{11}\text{B}_2\text{O}_3^+$. Additional lines possibly corresponding to $^{11}\text{B}_3\text{O}_4^+$, $^{10}\text{B}^{11}\text{B}_3\text{O}_4^+$, $^{11}\text{B}_4\text{O}_4^+$ were found, but the exact masses were not calculated. Variations in the $^{16}\text{O}^+$ to $^{11}\text{B}^+$ ion intensity found at higher exposures may be due to oxides of copper, as well as background, contributing to the total ion intensity for oxygen.

The spectra obtained from NaBH_4 sample firings contained very distinct fragment lines corresponding to H_2^+ , H_3^+ , $^{11}\text{BH}^+$, $^{11}\text{BH}_2^+$ on high ion yield exposures as shown in Figure 3. The $^{23}\text{Na}^+$ line was by far the most intense and was the broadest line noted. The almost complete absence of copper electrode lines on these plates is explained on the basis that the alkali metal compounds all exhibit a high degree of sensitivity in the spark and thus contribute practically all the total ions striking the plate.

Engine Residue Samples. The first engine residue analysis showed the fragments identified as NH^+ , NH_2^+ , NH_3^+ , NH_4^+ , BH^+ , BN^+ , $^{10}\text{B}^{11}\text{BN}^+$, $^{11}\text{B}^{11}\text{BN}^+$, $^{10}\text{BO}^+$, as well as lines found in pure BN , as shown in Figure 4. The sample therefore contained boron nitride, boron oxide, and $-\text{BNH}-$ constituents. Subsequent samples of engine residue, obtained from modified engine or injector configurations did not exhibit many of the aforementioned fragments.

Some difficulty was encountered during packing of the electrode cup. If the particle size was large, parts of the sample were ejected from the cup during sparking. This was partially overcome by the addition of aluminum powder to a boron sample, effecting a physical bond between particles. This method was discarded because the Al powder adhered to all surfaces which came in contact with the mixture and resulted in a change in sample composition. A Seidel Press and vacuum heating technique appears to have great potential as a means for preparing uniform and compact heterogeneous sample electrodes.

Background. Background lines which were not due to electrode or sample were occasionally noted on plates. Sodium, chlorine, oxygen, and carbon were observed on many plates. Boron, copper, and titanium were observed on a few plates. These background lines were very light (greater than 90% T for quantitative measurements) and, as a rule, did not interfere in mass fragment determinations. In fact, the ^{23}Na , ^{35}Cl , ^{16}O , and ^{12}C were quite often used as mass reference lines. Knowing that these ions do exist, one can subtract them from the sample firing. The amount of sodium background, for example, is increased by burning material like NaBH_4 in the spark followed by a high-yield spark of copper or titanium. Background nitrogen was not observed on spectra of copper electrodes. Oxygen, on the other hand, was almost always observed. This oxygen may have been due to oxides present on the electrode surfaces or in the electrode matrix.

CALCULATIONS

Mass Fragment Identification. The determination of mass fragments, evinced by lines on the photographic plate after development, is accomplished by line distance measurements to within ± 0.0002 inches, using a vernier attachment on a Jarrell-Ash Densitometer and equation (1)(14), programmed into a Burroughs E101 Computer.

$$\sqrt{M} = \sqrt{K} (X_M + A) \quad (1)$$

Where

$$\sqrt{K} = \frac{\sqrt{M_b} - \sqrt{M_a}}{X_b - X_a} \quad A = \frac{X_b \sqrt{M_a} - X_a \sqrt{M_b}}{\sqrt{M_b} - \sqrt{M_a}}$$

$\sqrt{K}$ = constant, dependent on magnetic field and voltage.	X_0 = reference "0" line.
A = constant, independent of magnetic field.	X_M^0 = line distance of sample mass "M" from X_0 .
M_a = atomic weight of standard mass line (a) at a distance X_a from X_0 .	M = computed atomic weight of mass M at distance X_M from X_0 .
M_b = atomic weight of standard mass line (b) at a distance X_b from X_0 .	

The line distances are measured from an arbitrary plate "0" reference line to the center of each line of interest on the plate. Known mass lines are used as standard and are chosen no more than three inches apart. The mass fragments are determined to within ± 0.003 mass units of the true values, the limit of error by the use of the above method.

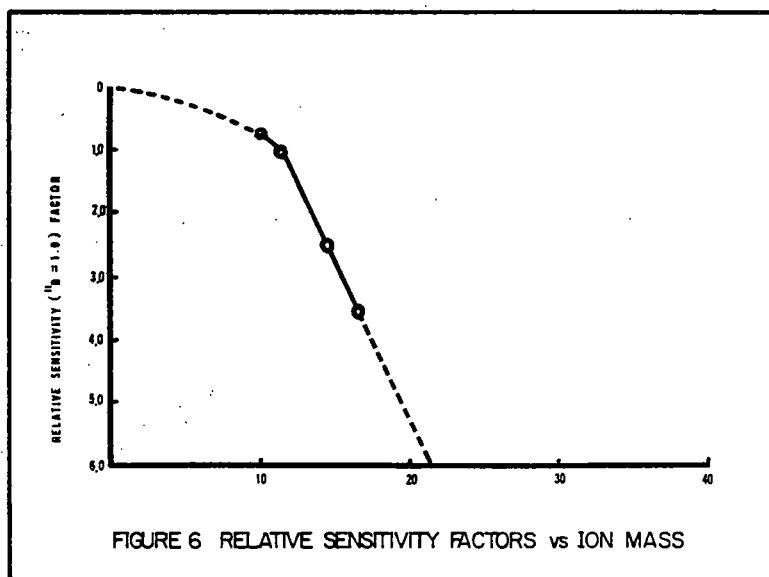
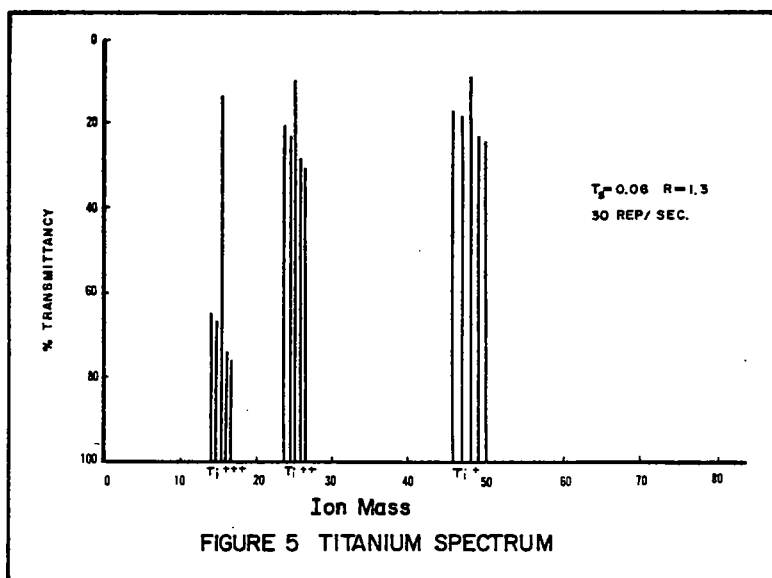


Plate Emulsion Calibration. The Ilford Q-2 photographic plates used as the mass fragment collector are known to have an emulsion of variable sensitivity. Such a variation may cause the quantitative mass determination, based on line density, to vary considerably. Therefore, each plate used for quantitative determination must be calibrated by the use of some standard element. Spectro-grade titanium (Figure 5) was chosen for the standard element, with exposures of from 1×10^{-12} to 1×10^{-9} coulombs. The data obtained from the titanium line transmittancies on the plate are plotted on semi-log paper as percent T (Linear ordinate) vs. E (log abscissa), where E is in absolute values of ion intensity obtained from the beam monitor as exposure in coulombs. The individual titanium isotope curves are then normalized to unity using equation (2) and E as relative exposure (10^{-10} coulombs = 1.00 units). The normalized curve is matched with a calibration curve having the same T_s .

$$T_{(E=1)} = \frac{1 + T_s}{2} \quad (2)$$

The calibration curves are obtained using equation (3)(8) for values of R from 1.0 to 1.6 and T_s of 0.00 to 0.08.

$$\text{Log } E_T = \frac{\log \frac{1 - T_m}{T_m - T_s}}{R} \quad (3)$$

Where

E_T = relative ion intensity at % T_m .	T_s = minimum plate mass line transmittancy.
T_M = transmittancy of line mass "m."	R = plate emulsion calibration constant.

The calibration curve data as obtained from a computer program has been reported earlier (15). The R value for the matched calibration curve of the titanium standard for a particular plate with a given T_s is then used as the plate calibration constant to obtain E values of any line transmittancy occurring on the plate.

The constant R in the equation relating E and T for a plate which does not have standard titanium spectra can be determined by an alternate method of using internal standard mass lines such as ^{10}B and ^{11}B . A percent T for ^{11}B and ^{10}B from one spectrum on the plate, and the transmittancy of the darkest line on the plate (T_s) are read. An E for the percent $T_{11\text{B}}$ is obtained from an R curve of E vs T, where T_s is equal to the one for the plate in question. This E value is multiplied by .32 (average value of $E^{10\text{B}}/E^{11\text{B}}$ from standard spectra). If the value obtained yields a percent T the same as the percent $T_{10\text{B}}$ read from the plate, the plate calibration curve corresponds to the one with that R. If not, the procedure is repeated with a different trial R curve until the E vs. T values obtained match the plate in question.

Atomic Percent Calculations. The relative ion intensity (E) of any line on a plate can be determined by measuring the transmittancy of that particular line and the use of known plate R and T_s .

The relative ion intensity (E) is obtained from the percent T vs E curve of known R and T_s for that plate. The obtained ion intensities (E) of the mass lines on a particular spectrum are then related to the standard mass in the sample, i.e., an internal standard. However, all masses do not darken the plate equally. Therefore, known standards have to be sparked to obtain plate sensitivity constants for the specific masses of interest. The percent transmittancies of the mass lines when converted to ion intensities are then related to an internal standard mass line on the same spectrum. It was decided to study boron-containing compounds; hence ^{11}B was used as the internal standard. The relative sensitivities of the masses are calculated using equation (4).

$$S_m = \frac{E_{11\text{B}}}{E_m} \times \frac{I_m}{I_{11\text{B}}} \quad (4)$$

Where

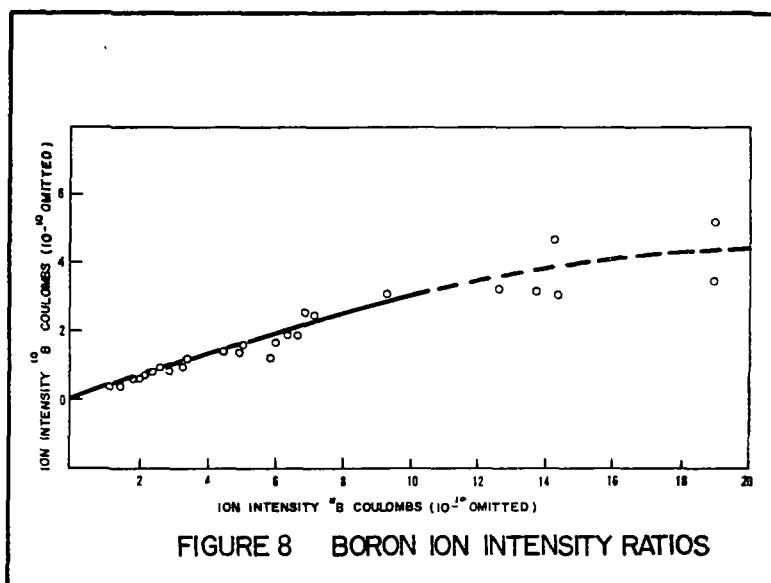
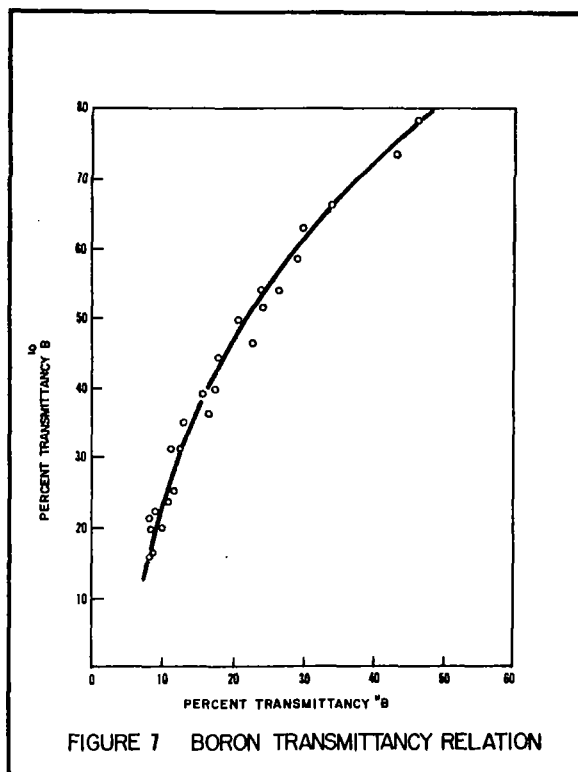
E = ion intensity of ^{11}B line from same spectrum as E_s .
E_m = ion intensity of mass line m on standard sample spectrum.
I_m = isotopic abundance of mass line m.
$I_{11\text{B}}$ = isotopic abundance of ^{11}B .

If the number of atoms of B does not equal the number of atoms M in the standard, then

$$S_m = \frac{E_{11\text{B}}}{(N_B/N_m) E_m} \times \frac{I_m}{I_{11\text{B}}}$$

Where

N_B = number of atoms Boron.	N_m = number of atoms M.
--------------------------------	----------------------------



The ion intensity of a mass line in the sample is then corrected for its sensitivity relative to $S_{11B} = 1.0$ in the same spectrum using equation (5).

$$E_{m_c} = E_m \times S_m \quad (5)$$

Where

- E_m = ion intensity of mass line m from one specific spectrum.
 S_m = sensitivity correction factor for mass line m, obtained from a standard spectrum related to ^{11}B .
 E_{m_c} = ion intensity value for mass line m, corrected for plate position, emulsion variation, and line broadening.

The ion intensities for all masses of interest in a sample spectrum are corrected using equation (5) and summed. Thus, the relative atomic percent of each mass in the sample spectrum can be determined by equation (6).

$$E_{m_c}/E_c \times 100 = \% m \text{ atomic.} \quad (6)$$

Relative Sensitivity Factors. The average sensitivity factors for ^{10}B , ^{14}N , ^{16}O , and ^{23}Na relative to $^{11}B = 1.0$ were obtained by summing all sensitivities for a mass which did not vary more than $\pm 10\%$ from the observed mean value. Values greater than $\pm 10\%$ of the observed mean were disregarded since emulsion variations contributed to line transmittancy errors as described previously. The average relative sensitivities for the masses obtained from at least 8 standard sample spectra of B, BN, B_2O_3 , and $NaBH_4$ are presented in Table I.

TABLE I
Relative Sensitivity Factors

$^{10}B = 0.74$	
$^{14}N = 2.50$	$^{11}B = 1.00$
$^{23}Na = 0.69$	$^{16}O = 3.50 \text{ (based on } B_2O_3)$

These values were used in equation (5) as S_m . Since the instrument conditions were the same for all the studies made in this report, the above sensitivities are valid and applicable for the calculation of percentage concentrations of masses in a sample containing them, and eliminate area and plate distance corrections. The concentration of ^{10}B , ^{11}B , ^{14}N , ^{16}O , and ^{23}Na in a sample can be calculated using equations 5 and 6. The corrected ion intensities for the masses are summed and the individual mass concentrations determined. A curve of relative sensitivity factors vs ion mass is shown in Figure 6. Owens (7) has shown a similar curve for mass 12 to 200 using platinum as the standard mass.

Sample Atomic Percent

Example A

A sample of BN was fired and the following E values obtained from a spectrum:

$E_{10B} = (.93)(.74) = 0.69$	$E_{11B} = 3.03$	$E_{14N} = 1.39$
$E_{c10B} = (0.93)(.74) = 0.69$	$^{10}B = 9.5\%$	$^{10B}^{14N} = 18.4\%$
$E_{c11B} = (3.03)(1.0) = 3.03$	$^{11}B = 42.1\%$	$^{11B} = 81.6\%$
$E_{cN} = (1.39)(2.5) = 3.48$	$N = 48.4\%$	$\% BN = \% B + \% N$
$\Sigma E_c = 7.20$		

Example B

A sample of B_2O_3 was fired and the following E values obtained from a spectrum:

$E_{10B} = 3.03$	$E_{11B} = 9.43$	$E_{16O} = 5.21$
$E_{c10B} = (3.03)(.74) = 2.26$	$^{10}B = 7.55\%$	$^{10B} = 19.2\%$
$E_{c11B} = (9.43)(1.0) = 9.43$	$^{11B} = 31.5\%$	$^{11B} = 80.8\%$
$E_{c16O} = (5.21)(3.5) = 18.25$	$^{16}O = 61.0\%$	$\% B_2O_3 = 5/3 (\%^{16}O)$
$\Sigma E_c = 29.94$		

Quantitative mass calculations for engine residue samples were performed by the preceding method. Mass relative sensitivities were obtained from the relative sensitivity vs ion mass curve (Figure 6).

Sample 21-100	E_m	S_m	E_c	$\% \text{ atomic}$
^{10}B	2.39	0.74	1.77	6.7
^{11}B	9.00	1.0	9.00	33.9
^{11}BH	0.16	1.5	0.24	0.9
^{14}N	3.38	2.5	8.45	31.8
^{14}NH	0.23	3.0	0.69	2.6
$^{14}NH_2$	0.19	3.5	0.67	2.5
$^{14}NH_3$	0.39	4.0	1.56	5.9

Sample 21-100 _B (Cont'd)				
$\frac{m}{m}$	$\frac{m}{m}$	$\frac{S}{m}$	$\frac{E}{c}$	$\frac{\% \text{ atomic}}{p}$
¹⁴ NH ₄	0.24	4.5	1.08	4.1
¹⁶ O	0.88	3.5	3.08	11.6
$\Sigma E_c =$			26.54	

Therefore

BN = 63.6%
B₂O₃ = 19.3%

BH = 0.9%
NH = 15.1%

B = 1.1%

Weight percent values for boron, nitrogen, and oxygen by wet chemical analysis (16) and the converted atomic percent values obtained by this method are shown in Table 2.

The wet chemical method does not show NH and BH found in residues as -BNH- compounds, as shown by the mass spectrographic analysis. Two other engine residue samples analyzed did not contain BH and NH fragments on quantitative spectra. However, these were observed on high ion yield exposures. A mixture containing BN and 7% hydrogen was sparked in an attempt to determine percent recombination to form BH and NH fragments. Results indicate that BH formation was more likely than NH formation. However, the NH formation was a factor of 3 less than found in the engine residue.

TABLE 2
BN Engine Residue Analysis Data

Sample	%B	%B	%N	%N	%O	%O
	MS	WC	MS	WC	MS	WC
21-100 ¹	55.6	56.9	33.5	31.9	10.9	11.2
21-125 ²	48.1	44.5	26.9	36.0	25.0	19.5
21-126 ³	50.3	51.2	29.1	32.9	20.6	15.9

¹Based on 6 analyses. NH and BH fragments found on quantitative exposure.

²Based on 4 analyses. No NH and BH fragments found on quantitative exposure.

³Based on 6 analyses. No NH and BH fragments found on quantitative exposure.

Ion Intensity Limits. As shown in Figures 7 and 8 of percent T_{10B} vs T_{11B} and E_{10B} vs E_{11B}, the transmittancy ratios of the two boron isotopes show little scatter from the fitted curve. However, the E value curve does show a large scatter above an ion intensity value for ¹¹B = 10.0. This generally corresponded to a T of less than 10 percent. The error for obtaining E value from percent T, where T is less than 10 percent, becomes great for a very small percent T variation. While percent T ratios did not vary widely, the E ratios varied considerably. This leads to the conclusion that non-homogeneous samples should be sparked to yield percent T values between 80%-10%, and preferably 80%-20% for best results.

CONCLUSION

Radio-frequency spark source mass spectrography is a very useful analytical technique for the analysis of solids. The elements or fragments present in a compound can readily be resolved and identified to within ± 0.003 mass units of the true values. A wide mass range of 40/1 (lithium to uranium) can be studied on one plate exposure spectrum.

The two methods for obtaining plate calibration constants have proven adequate for the studies presented. Use of the plate calibration curves to obtain ion intensity values from percent transmittancy of a mass line has been applied successfully. Variations in ion intensity values for different plates and plate calibration curves are kept at a minimum providing the values fall between 0.2 and 10.0 relative ion intensity units. This range corresponds to line transmittancies falling between 86% - 12%. Values beyond these limits decrease the accuracy of the presented method.

Sensitivity factors for elements and fragments relative to a sensitivity factor for ¹¹B = 1.00, where the elements and fragments are bonded to boron, can be obtained. The use of these sensitivity factors for quantitative mass fragment determination is satisfactory, providing the instrument settings, e.g., pulse repetition rate, pulse width, plate mass position, are kept constant. When any of the above are varied, the sensitivity factors decrease in accuracy, and calculations based upon them are no longer accurate to $\pm 5\%$ of the ion intensity value (E).

BIBLIOGRAPHY

1. Craig, R. D., Errock, G. A., and Waldron, J. D., Determination of Impurities in Solids by Spark Source Mass Spectrometry, Advances in Mass Spectrometry, Pergamon Press, 1959, pp. 136-155.
2. Hannay, N. B. and Ahearn, A. J., Mass Spectrographic Analysis of Solids, Anal. Chem. 26, 1056 (1954).
3. Hannay, N. B., Mass Spectrographic Analysis of Solids, Science 134, 1220 (1961).
4. Ahearn, A. J., Vacuum Spark Mass Spectrographic Analysis of Solids and Liquids, International Conference on Spectroscopy, 1962.
5. Gorman, J. R., Jones, E. J., and Hipple, J. A., Analysis of Solids with the Mass Spectrometer, Anal. Chem. 23, 438 (1951).
6. Desjardins, M., Hodgson, F. H., and Baun, W., Mass Spectra of Organic Compounds Obtained Using a Radio Frequency Spark Source, Tenth Annual ASTM-E-14 Conference on Mass Spectrometry, June 1962.
7. Owens, E. G., The Effect of Ion Mass and Ion Energy on the Sensitivity of Ilford Q-2 Plates as Ion Detectors in Mass Spectrography, Applied Spectroscopy, Vol. 16, No. 5, P. 148 (1962).
8. Hull, C. W., Photographic Quantitative Analysis with a Solids Spark Mass Spectrograph, Tenth Annual ASTM-E-14 Conference on Mass Spectrometry, June 1962.
9. James, J. A. and Williams, J. L., The Analysis of Non-Conducting Solids by the Mass Spectrometer, Advances in Mass Spectrometry, Pergamon Press, 1959, pp. 157-161.
10. Waldron, J. D., Analysis of Powders by Spark Source Mass Spectrometry, Unpublished Report, May 1962.
11. Research and Development on Analytical Techniques and Equipment in the Chemical, Physical, and Metallurgical Sciences (U); Rocketdyne, Division of North American Aviation, Inc., Canoga Park, California; Contract AF 04 (611)-5963, 31 July 1961, pp. 67-77 (C).
12. Owens, E. G., Ion Charge Distribution in a RF Spark Ion Source and Its Effect on Quantitative Analysis, Tenth Annual ASTM-E-14 Conference on Mass Spectrometry, June 1962.
13. Guthrie, J. W., Sandia Corporation, Private Communication.
14. Consolidated Electrodynamics Corporation Mass Spectrometer, 21-110 Manual, 1961.
15. Jensen, A. V., Goshgarian, B. B., Dane, N. E., Spark Source Mass Spectrometric Analysis of Non-Homogeneous Samples, RTD-TDR-63-1, January 1963, Armed Services Technical Information Agency Document.
16. Research Department, Rocketdyne Division of North American Aviation, Inc.

NEW STUDIES ON THE DIFFUSION OF HYDROGEN THROUGH HOT PALLADIUM

T. W. Martin and R. E. Rummel
Department of Chemistry
Vanderbilt University
Nashville 5, Tennessee

ABSTRACT

The Vanderbilt higher-pressure mass spectrometer has been adapted recently for the study of the rate and probable mechanism of the diffusion of hydrogen gas through hot palladium metal in the temperature range of 150-600°C. The flow rate F (CC STP/min) as a function of pressure differential P (mm) and absolute temperature T is found to fit the general empirical equation

$$\log F = a + b \log P - c/T$$

using a thin palladium tube of 0.003" wall thickness and constant area. The special diffusion cell designed for this study makes it possible to investigate chemical species desorbed from the catalyst within about 1 μ sec. of their formation. Data on the relative rates of desorption of the H^+ and H_2^+ species from the palladium surface and their possible significance on the hydrogen transport mechanism will be discussed.

THE DIFFUSION OF HYDROGEN IN NATURAL AND SYNTHETIC FUSED QUARTZ

R. W. Lee
Research Laboratories, General Motors Corporation
Warren, Michigan

In 1960 I reported to this Committee on the preliminary results of our hydrogen diffusion experiments in fused quartz. Then, as in the more recent studies, the experimental technique involves mass spectrometer detection of the permeation of hydrogen and deuterium through thin walled test tube shaped specimens. Figure 1 is a schematic of the flow-through system with the specimen and its outer coaxial chamber; the gas inlet on the right and the direct connection to the mass spectrometer ion source on the left; together with the oven and thermocouple for temperature control.

Figure 2 shows the type of strip chart data which is generated on a peak height versus time plot. At time zero some pressure of hydrogen (usually one atmosphere) is exposed to the input side of the specimen. This results in a characteristic time lag followed by a rise in the H_2 peak until steady-state permeation is reached. Evacuation of the input gas then results in another time lag followed by a decay of the H_2 peak shown as the evolution curve at the right.

For a strictly diffusion controlled gas transport, the three principal parameters are related as follows:

$$\text{Permeability} = \text{Diffusivity} \times \text{Solubility}.$$

It turns out that permeability, which is calculated directly from the steady-state permeation, is a completely well behaved and predictable parameter in the hydrogen-fused quartz system. It is independent of the type of fused quartz and exhibits a clear first-power pressure dependence characteristic of molecular diffusion. This condition would be highly unlikely without a well behaved molecular hydrogen solubility. Therefore, two of the three parameters seem to obey simple diffusion laws. However, in order for diffusivity to likewise conform, the evolution curves would have to be pure exponentials. Log plots of h versus time should therefore produce straight lines. Except at low temperatures this does not occur as illustrated in Fig. 3. The dashed lines represent the expected results on the basis of simple diffusion theory, whereas the solid lines represent the actual evolution. Since diffusion coefficients are calculated from the slopes of the dashed lines, accurate calculations become increasingly difficult with increasing temperature. However, in addition to this superficial difficulty, the real problem is to account for the high temperature release of up to ten times the normal solubility of hydrogen at rates characteristic of unusually low diffusivities. This phenomenon is what I will call the diffusion anomaly.

Thus far I have given what is essentially a statement of the problem, the consequence of which is a real or apparent concentration dependent diffusivity. In either case a chemical reaction between the diffusing molecular hydrogen and the fused quartz structure is inferred. One therefore asks the question: What in fused quartz will chemically react with molecular hydrogen? Well, the very thing that characterizes fused quartz from glass is its purity so that, other than a few hundred ppm metallic impurities and hydroxyl, there is nothing but silicon and oxygen. The amounts of dissolved hydrogen, however, though large on a mass spectrometric scale are also low, in the ppm range. Therefore, both types of impurities (1) metallic ions and (2) hydroxyl - as well as the SiO_2 network itself - become suspect as the chemical reactants.

Of these, a two fold variation in metallic ion content produced no measurable variation in diffusion results; however, a very great difference occurs with a variation in hydroxyl content - in exactly the wrong direction. That is,

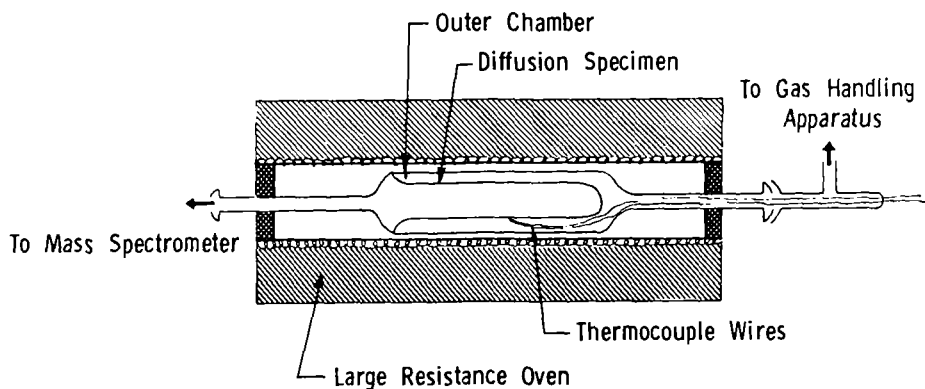


Fig. 1. Sample system.

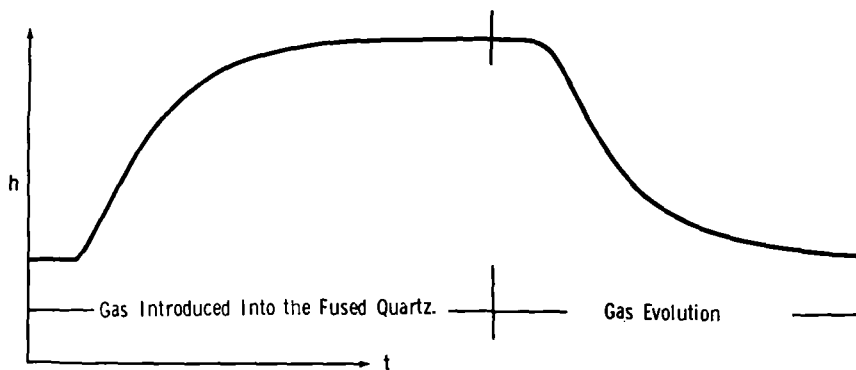


Fig. 2. Mass spectrometer strip chart recording (h) for input and decay of hydrogen (or deuterium) in fused quartz. t = time.

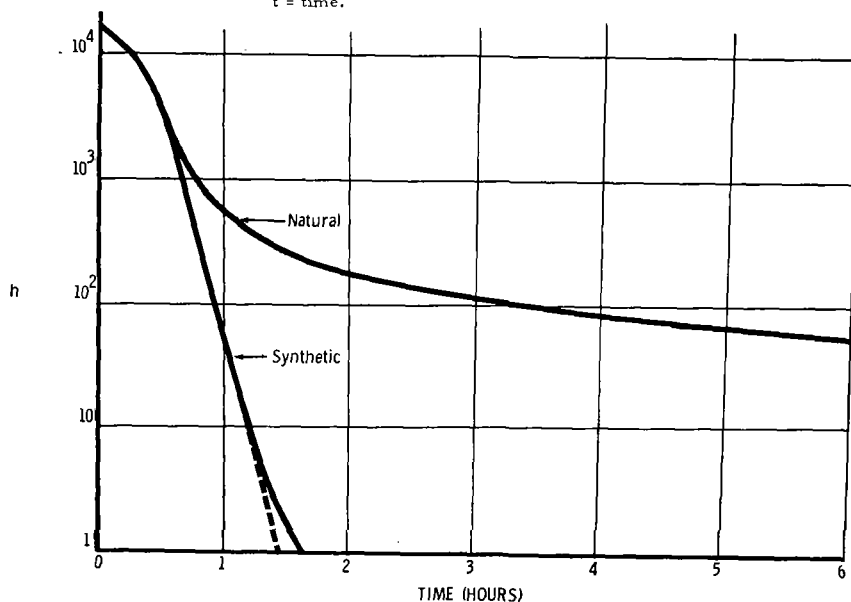


Fig. 4. Hydrogen evolution from natural and synthetic fused quartz. h = mass spectrometer peak height.

intuitively one would expect a greater chemical interaction the higher the hydroxyl level, but just the opposite seems to occur as shown in Fig. 4.

The high temperature hydrogen evolution from natural fused quartz of the type previously studied shows, as before, the anomalous curvature. However, synthetic fused quartz with over two hundred times more hydroxyl hardly deviates from simple diffusion theory. This would seem to imply that the higher the hydroxyl the less the anomaly. But before jumping to conclusions, I will define natural and synthetic fused quartz as follows: Natural fused quartz is made by melting fine grains of pure rock quartz crystal and normally contains about 200 ppm of metallic impurities and as low as 5 or 10 ppm hydroxyl. Synthetic, on the other hand, is manufactured from pure chemicals, e.g. by flame fusion of silicon tetrachloride, and can be produced with essentially no metallic impurities but at the price of introducing high concentrations of hydroxyl. Therefore, the differences between the two are both hydroxyl and metallic impurity contents.

We seem no nearer to the solution of the problem at this point than at the outset except for one bit of information which provided the breakthrough. During much of the diffusion work we often performed a deuterium run following one of hydrogen and vice versa. Above about 600°C this resulted in the release of large quantities of residual gas in the form of HD and H₂ during the introduction of D₂. This observation was what prompted infrared absorption experiments which identified hydroxyl as the trapped form of the gas.

Once again hydroxyl is suggested as the source of the anomaly in spite of my previous remarks. The significant difference, however, is that it now becomes a matter of quality rather than quantity. I.e., there appears to be metastable hydroxyl in natural fused quartz which does not exist in the synthetic variety. This is illustrated in Fig. 5a. The lower dashed line represents the permanent hydroxyl at a level of about 5 ppm. This type of OH is formed during manufacture and is stable at all temperatures investigated - up to and including 1100°C. At temperatures above about 500°C, however, a less stable hydroxyl is added during hydrogen loading. This level is shown as the upper dashed line in Fig. 5a. Upon evacuation of the molecular hydrogen only a portion of this added hydroxyl remains stable. This is labeled residual OH in the figure and drawn as the solid line.

These types of hydroxyl relate to the diffusion anomaly as follows: Consider the typical high temperature hydrogen evolution from natural fused quartz as shown in Fig. 5b. When the input gas is evacuated, the normal quantity of interstitially dissolved molecular hydrogen diffuses out quickly as represented by the initial linear portion. After a short time, however, the rate of decay decreases as the unstable added hydroxyl converts to molecular hydrogen. This provides an internal source of diffusible hydrogen which evolves at a rate characteristic of the conversion rather than that of the hydrogen diffusion. The quantity of gas representative of the difference between the added hydroxyl level and the residual level is therefore the source of this excess hydrogen evolution earlier referred to as the diffusion anomaly.

This model for the diffusion of hydrogen in natural fused quartz is consistent with the results for the synthetic variety since hydrogen exchange with permanent hydroxyl leaves the system unchanged and only permanent hydroxyl appears to exist in synthetic fused quartz. The remaining question is: How and why does hydroxyl add to natural and not to synthetic fused quartz? To get at this question we will consider the structure of fused quartz in some detail.

Figure 6a is a two-dimensional schematic of the basic fused silica or fused quartz structure. The silicon atoms shown as the solid circles are bonded to four oxygen atoms forming what is called the basic tetrahedra of the structure. (Actually only three oxygens are shown in this two-dimensional

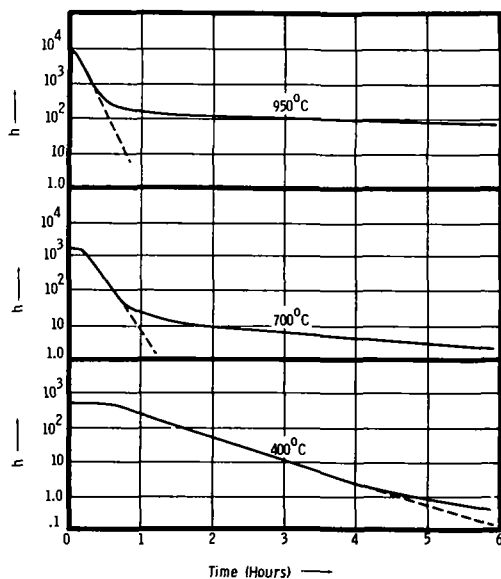


Fig. 3. Logarithmic plots of mass spectrometer strip chart recordings (h) during evolution (decay) of hydrogen from fused quartz.

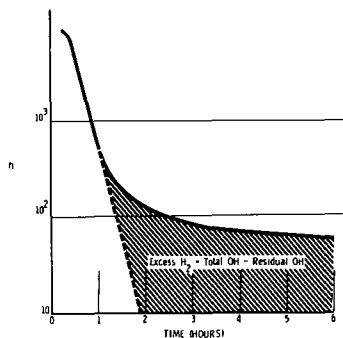
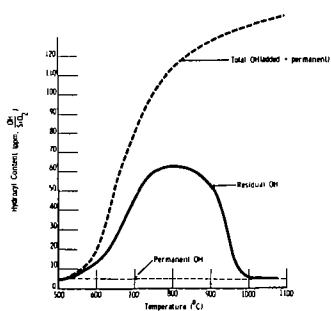


Fig. 5. (a) Temperature dependence of hydroxyl in natural fused quartz.
(b) Typical high temperature hydrogen evolution from natural fused quartz. h = mass spectrometer peak height.

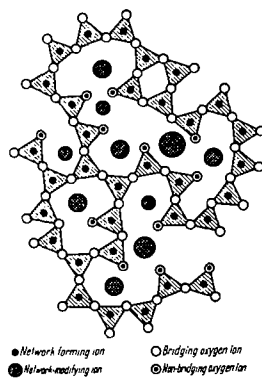
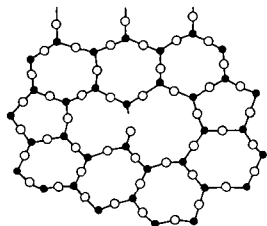


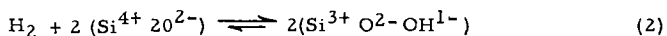
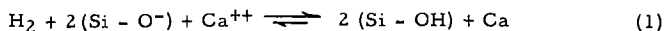
Fig. 6. (a) Two-dimensional schematic representation of the structure of fused silica after Oberlies and Dietzel¹.
(b) Two-dimensional schematic representation of an oxide glass after Zachariasen².

schematic). The broken silicon-oxygen bond in about the center of the drawing provides a non-bridging oxygen ion, the existence of which has been suggested by x-ray diffraction¹.

The incorporation of metallic ions in this basic silicon-oxygen structure is shown in Fig. 6b. Some ions like B and Al can replace silicon as network formers while others like Ca and Na occupy interstitial positions as networks modifying ions as represented by the crosshatched circles. Again the non-bridging oxygen ions shown as the dot-centered circles are required near the impurity cations to preserve charge neutrality.

A very dilute dispersion of the glassy structure (Fig. 6b) in the basic structure (Fig. 6a) represents a well documented model of fused quartz with the exception of the very thing I have blamed for the diffusion anomaly - namely, hydroxyl.

The permanent, strongly bound, hydroxyl which is incorporated in fused quartz during manufacture is almost certainly formed by the attachment of hydrogen atoms to isolated non-bridging oxygen ions of the sort shown in Fig. 6a. The more interesting hydroxyl from the standpoint of hydrogen diffusion is what I have called "added" hydroxyl. Two possible reactions by which this relatively unstable hydroxyl may be added to and removed from the fused quartz structure are the following:



Equation (1) requires the presence of metallic impurities as in natural fused quartz whereas equation (2) implies a silicon valence change coincident with the breaking of silicon-oxygen bonds. We are currently trying to establish which of these or other reactions are operative and why the second reaction, if valid, does not occur to the extent in synthetic fused quartz that it does in the natural fused quartz. At the moment it is an open question.

I have not presented the quantitative diffusivity and permeability results which came from this study since these are available in the literature^{3,4}. Rather, I have stressed what to me was the interesting aspect of the work - namely, the diffusion anomaly and its dependence upon the addition and removal of a metastable hydroxyl in fused quartz.

References

1. F. Oberlies and A. Dietzel, Glastechn. Ber. **30**, 37 (1957).
2. W. H. Zachariasen, J. Amer. Chem. Soc. **54**, 3841 (1932) and J. Chem. Phys. **3**, 162 (1935).
3. R. W. Lee, R. C. Frank, and D. E. Swets, J. Chem. Phys. **36**, 1062 (1962).
4. R. W. Lee, J. Chem. Phys. **38**, 448 (1963).

DETERMINATION OF GAS CONTENT OF METALS WITH SPARK SOURCE MASS SPECTROGRAPH

by
John Roboz
General Telephone & Electronics Laboratories, Inc.
Bayside 60, New York

Due to the known limitations of the vacuum fusion and extraction techniques for many metal systems, particularly refractories, there exists a need for a direct method for the analysis of gases in metals. In metallurgy the knowledge of the gas content in adjacent layers is frequently desired and so is information on gradients in moving from surfaces towards the cores of materials. The objective of this work was to explore the possibility of determining gases in metals by means of a CEC spark source mass spectrograph. The present paper is intended to summarize initial results, dealing mostly with the determination of nitrogen in Fe, Ti and Mo. Our investigations on the determination of hydrogen and oxygen are only at a preliminary stage at this time.

Hydrogen, oxygen and nitrogen, together with carbon, are perhaps the most difficult elements encountered in solids mass spectrography because they are also present in the background vacuum of the instrument. Since the mass spectrum is essentially atomic in nature, these elements will be detected as if they were present in the sample. In addition, as it was suggested by Craig and Brown, relative sensitivities for these gases may be excessively high because of a high probability of their return to the spark region several times before finally being pumped away or adsorbed on surrounding surfaces. The problem of surface contamination during the cleaning procedure is also a serious one. Several possible solutions have, however, been suggested by various authors. In the present work the samples were "pre-sparked" in order to remove surface contaminations.

As it is well known, metals with standard or known gas content are difficult to obtain. The first slide (1) shows the four NBS standards selected for our initial studies. In addition to the fact that there are very few samples to choose from, our reasons for choosing these samples were as follows: With the iron samples we wanted to establish the smallest amount of nitrogen that can be evaluated with some confidence. Also the presence of the heavy lines of $^{56}\text{Fe}^{+4}$ and $^{28}\text{Si}^{+2}$, only 19 and 25 milli-mass units away from the $^{14}\text{N}^{+}$ line, presented an interesting case to utilize the high resolution of the instrument. We were also planning to investigate our ability to evaluate the oxygen content of the 1043 iron sample in the presence of the large amount of sulfur. I might mention at this time that we have not had much luck in determining oxygen in the presence of sulfur, but there may still be some possibility of success.

The titanium samples were selected in order to develop a method of determining nitrogen in refractories, and also to test our ability to distinguish between samples differing in nitrogen content by a factor of only 1.5.

Operating procedures for the mass spectrograph were relatively standard. All the NBS samples are supplied in the form of small millings from which the largest pieces were selected. Approximate sample size was 1/8 of an inch in length and 20 mils in width. Determinations were made at both high and low dispersion; analysis was possible under both conditions, and the results were not noticeably different. A single batch of Ilford Q-2 photoplates was used throughout this work. Each plate was individually calibrated using a series of short exposures, and all calibration curves were in agreement within approximately 15%. The evaluation of the analytical results was made by using a microphotometric method similar to that originally proposed by Craig, Errock, and Waldron. Efforts were made to place the mass 14 area at that section of the plates for which mass resolution is highest, and also to place the lines used for calibration in the same position in order to provide the sharpest lines and also to minimize effects due to energy and path differences. In cases where this was not done, corrections were applied.

NBS STANDARD SAMPLES SELECTED
FOR NITROGEN DETERMINATIONS

Sample	Type	Composition, weight %				Nitrogen, ppm	
		O	S	Si	Fe	Weight	Atomic
1043	Steel (low carbon)	.002	.030	.090	--	50	200
33C	Steel	--	.030	.280	--	30	120
173	Ti-alloy (6 Al - 4 V)	--	--	.045	.160	180	610
174	Ti-alloy (4 Al - 4 Mn)	--	--	.015	.170	120	410

Slide 1.

DETERMINATION OF NITROGEN IN NBS STEEL SAMPLES

Sample	Si content, ppm atomic	N content, ppm atomic		
		Certified	Found	Range
1043	1800	200	380*	300-400
33C	4800	120	Unsuccessful	

* Average of 6 determinations (area correction applied)

Slide 2.

DETERMINATION OF NITROGEN IN NBS TITANIUM SAMPLES

Sample	N content, ppm atomic			Ratio	
	Certified	Found*	Range	Certified	Found
173	610	470	320-550	1.5	1.8
174	410	260	240-320		

* Average of 5 determinations

Slide 5.

At the present state of the art it is generally accepted that the analytical accuracy of the spark machines in routine measurements is approximately within a factor of two. Since our primary objective was to explore the feasibility of determining gases in metals, we did not intend to pay particular attention to absolute values. Moreover, the certification of the gas content of the available standards does not necessarily apply to the small sample quantities consumed by this instrument. Therefore, a more rigorous method of plate evaluation was hardly justified.

In order to determine the nitrogen background, several of the highest purity materials available were analyzed. It was found that a particular type of silver, ASARCO A-59, gave the lowest value for nitrogen, and, incidentally, for oxygen as well. This it should be noted, is in agreement with theoretical expectations based on gas solubilities. The instrument background for nitrogen, and also for oxygen, as estimated on the basis of these measurements, is approximately 10 ppm. This clearly indicates that the background was insignificant in the determinations we intended to make. In order to detect possible changes in the background, exposures using this silver sample were frequently included on plates run for these analyses. As long as operating conditions remained normal, the values were stable within a factor of two or three.

Since no information was available on the relative intensities of the atomic and molecular nitrogen lines as they are formed in the vacuum spark during decomposition of nitrides, an experiment was made to determine whether any correction for this effect was necessary. A boron nitride sample was used for this purpose, and no significant N_2 formation was found. Also, incidentally, no oxygen line was detected at mass 32, although the oxygen content of the sample was relatively high.

Experimental results are shown on the next slide (2) for the determination of nitrogen in iron. While the average value shown is within a factor of two of the certified value, it is also seen that all determinations resulted in higher values. This may suggest a somewhat higher sensitivity to nitrogen as compared to iron. Attempts to determine the nitrogen content of sample #33C were unsuccessful. This can be understood from the next slide (3), which shows microphotometer tracings at mass 14 for both iron samples. The high silicon content of sample #33C makes the evaluation of the nitrogen content highly inaccurate.

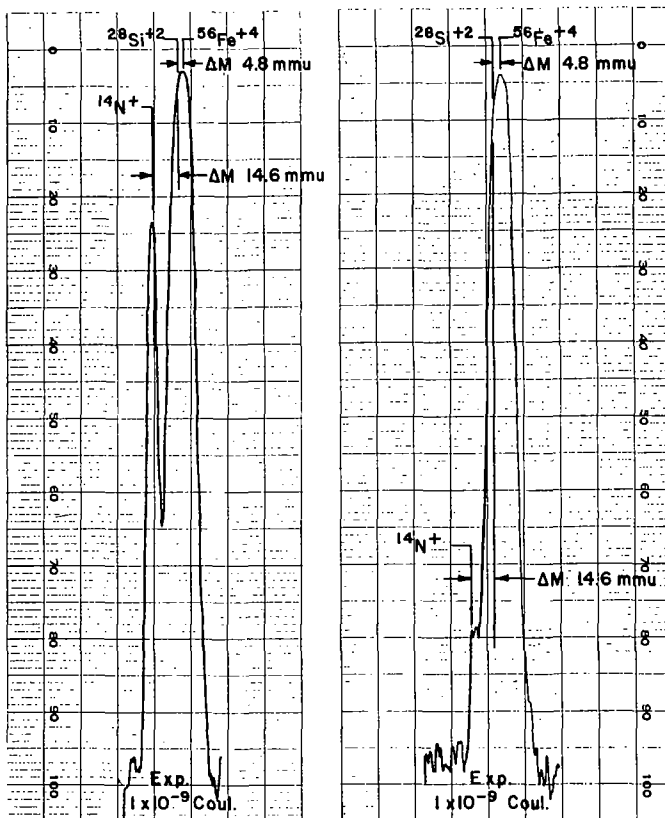
The next slide (4) shows curves of a typical analysis for the determination of the nitrogen content of the titanium samples. It is seen that the lines for the nitrogen in both samples are essentially parallel to the lines of the titanium isotopes.

Experimental results are shown on the next slide (5). As previously, the average value again lies within a factor of two of the certified values. In the case of titanium, the values appear to be lower than expected. This may suggest a sensitivity value for nitrogen with respect to titanium somewhat smaller than unity. The explanation may very well lie in the gettering properties of titanium. It appears significant that in all the analyses we have made, not a single instance of an inverted ratio was encountered in the titanium samples.

A very important application of the determination of gases in metals is to discern small concentration differences in adjacent layers. A particular case concerned the nitrogen content in a diffusion-strengthened Mo alloy specimen wherein the metallurgical properties of the core were markedly different from those observed in the rest of the sample. The problem was attacked by using milliprobe techniques. Details of this method were given in a previous paper, and now I would only like to comment on the analytical aspects. The analysis desired for this particular specimen specified carbon, nitrogen and oxygen.

The next slide (6) shows a portion of the spectrum in the vicinity of these elements. Naturally, reduced magnetic field was applied, covering the

MICROPHOTOMETER TRACINGS at MASS 14

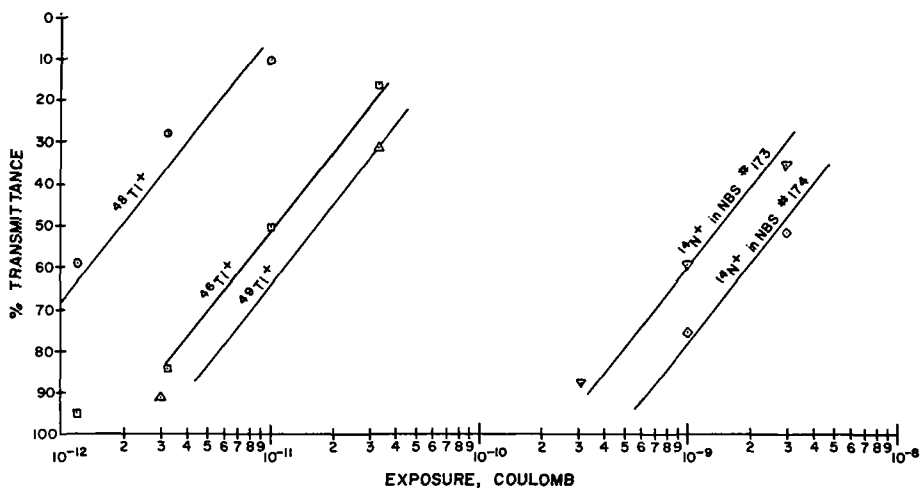


MEDIUM SI CONTENT

HIGH SI CONTENT

Slide 3.

LINE DENSITY vs EXPOSURE FOR N IN Ti



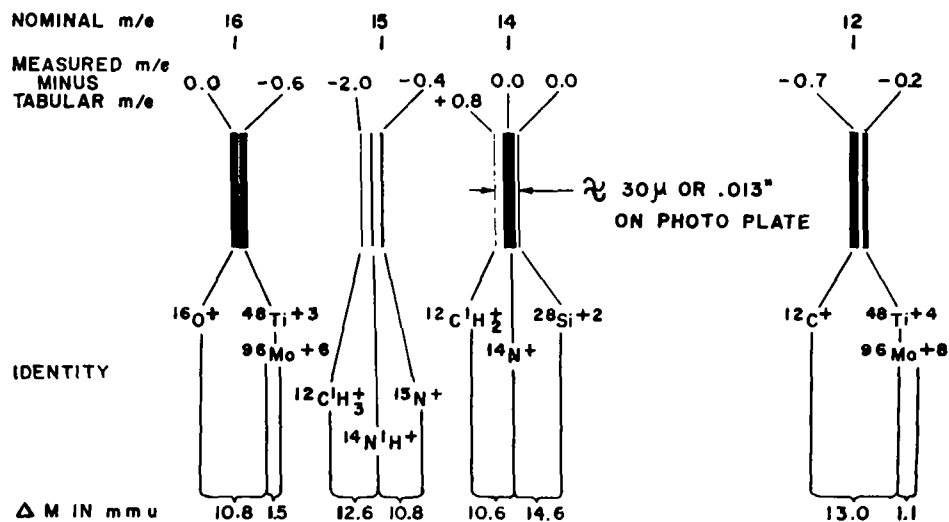
Slide 4.

mass range from 1 to about 26. The figures below the nominal masses show the differences in millimass units between our measured mass for the lines as calculated from line position measurements on the plate and the published isotopic masses.

The next slide (7) shows one of the craters inside the zone of interest. Its size is about 10 mils in diameter and 5 mils in depth. The results of the analysis indicated that the nitrogen content outside the zone was about 3 1/2 times larger than that inside the zone. These results confirmed the predictions of the metallurgists, based on observed differences in properties and theoretical aspektations. Incidentally, no differences were found for the carbon content, and only a slight effect was noted for oxygen, the larger amount again being outside the zone.

In summarizing, the feasibility of the application of the spark source mass spectrograph to determine the nitrogen content of metals has been illustrated; experiments showed that the nitrogen content of iron and titanium samples with known gas concentration could be determined with essentially the same accuracy and precision as those for other elements.

CARBON NITROGEN OXYGEN SECTION OF LOW MASS SPECTRUM (m/e 0-26), MILLIPROBE WORK



Slide 6.



Slide 7.

A MASS SCALE BASED ON $\text{CH}_2=14.0000$ FOR
HIGH RESOLUTION MASS SPECTROMETRY OF ORGANIC COMPOUNDS

E. Kendrick
Analytical Research Division
Esso Research and Engineering Company
Linden, New Jersey

ABSTRACT

The problems of computing, storing, and retrieving precise masses of the many combinations of elements likely to occur in the mass spectra of organic compounds can be significantly reduced by the adoption of a mass scale in which the mass of the CH_2 radical is taken as 14.0000 mass units.

The advantage of this scale is that ions differing by one or more CH_2 groups have the same mass defect. The precise masses of a series of alkyl naphthalene parent peaks, for example, are 127.9195, 141.9195, 155.9195, etc. Because of the identical mass defects, the similar origin of these peaks is recognisable without reference to tables of masses.

Mass defects on this scale consist of two components, one of which is directly associated with the mass number and the other with the basic combination of elements. By this means, two tables with a total of about 850 numbers are sufficient to cover the mass defects of $1\frac{1}{2}$ million combinations of hydrogen, carbon, nitrogen, oxygen, and sulfur in the mass range from 12 to 600.

Double focussing mass spectrometers with resolutions of one part in 5,000 or better are now coming into use as analytical instruments. Commercial instruments after the original design by Mattauch and Herzog (1,2,3) have been described by Voorhies and coworkers (4) and by Craig and coworkers (5). Another instrument based on a design by Nier and Roberts (6,7,8,9) has been described by Craig and Errock (10). Beynon (11) has pioneered the application of high resolution mass spectrometers to organic chemistry.

The high resolution of these instruments makes possible precise mass measurement to a few parts in 10^5 or better. This is sufficient to distinguish between ions having the same mass number, but different chemical composition. The precise mass of an ion is the sum of the masses of its constituent elements and the empirical formula can usually be found from the mass determination. This ability to determine the chemical composition of an ion from a measurement of its mass gives mass spectrometry a new dimension.

With the advent of the high resolution mass spectrometer have come the problems of computing, storing, and comparing large amounts of mass data. The masses of the isotopes of most elements are known to very high accuracy, but the number of combinations of these elements in organic chemistry is extremely large. Published tables cover only a fraction of the combinations.

The table of precise masses most widely used at present is by Beynon (11). This table, which is based on $^{16}\text{O}=16.00000$, covers combinations of elements up to a mass number of 250, and is limited to those containing no more than four oxygen atoms, four nitrogen atoms, and a total of no more than six atoms other than carbon and hydrogen. Beynon's table has about 6,000 entries. Extension of the table to higher mass numbers and the inclusion of sulfur (^{32}S and ^{34}S isotopes) and ^{13}C would increase the size of the table enormously. Over one and a half million entries would be required to cover the ions up to mass 600.

A mass scale with $^{12}\text{CH}_2=14.00000$ enables the same data (i.e., up to mass 600) to be expressed in less than 100,000 entries. This reduction is a consequence of the same defect being repeated at intervals of fourteen mass units, i.e., one (CH_2) group. Restrictions similar to those imposed by Beynon have been used for these tables. These restrictions are as follows:

- o The number of oxygen atoms in any combination is not greater than four.
- o The number of nitrogen atoms in any combination is not greater than four.
- o The number of sulfur atoms in any combination is not greater than four.
- o The number of ^{34}S atoms in any combination is not greater than two.
- o The number of ^{13}C atoms in any combination is not greater than four.
- o The total number of nitrogen, oxygen, and sulfur atoms in any combination is not greater than six.

Figure 1
MULTIPLY AT MASS 142

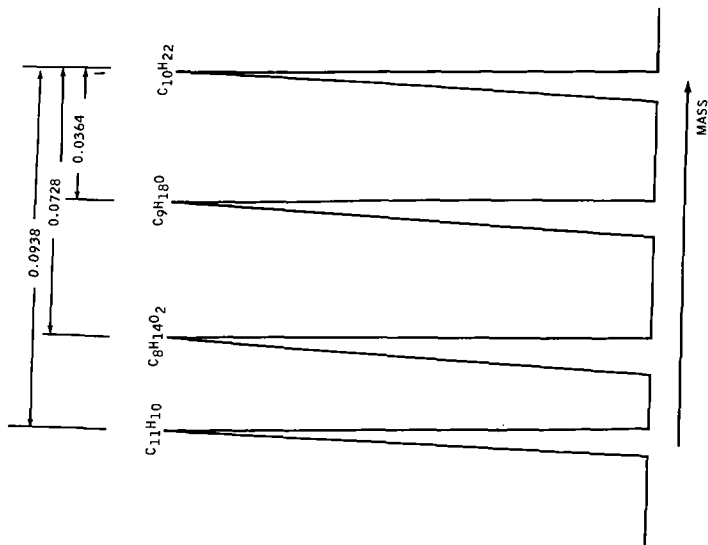
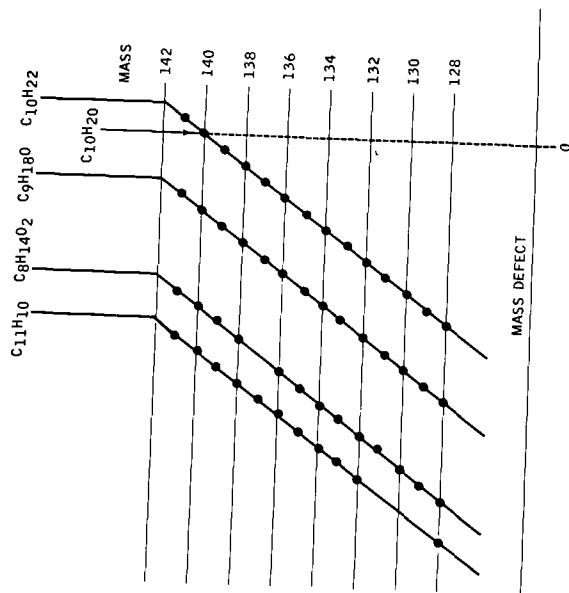


Figure 2

MASS DEFECTS m/e 128 TO m/e 142



Masses on the ^{16}O scale can be converted to the CH_2 scale by dividing by 1.0014361.

The Basis of the CH_2 Mass Scale

The basis of the CH_2 scale is best appreciated by considering a multiplet which could arise at a particular mass. Figure 1 shows such a multiplet at m/e 142. These peaks could be the parent ions of methyl naphthalene, a C_8 diketone, a C_9 ketone, and decane. The pattern presented by the peaks will be repeated at m/e 156 for compounds one carbon number high in each series, i.e., for dimethyl naphthalene, a C_9 diketone, a C_{10} ketone, and undecane.

The same pattern will appear at intermediate or lower masses if the same number of protons is stripped from each of the molecules. Thus, at mass 140, we may find the same pattern for ions with the formulae C_{11}H_8 , $\text{C}_9\text{H}_{12}\text{O}_2$, $\text{C}_9\text{H}_{16}\text{O}$, and $\text{C}_{10}\text{H}_{20}$. The spacings between the peaks are exactly the same as those in the other two cases. The mass defects for ions of these species at different mass numbers vary as the numbers of hydrogen atoms vary, but the differences between the defects for the different species remain constant.

Figure 2 is a representation of the mass defects of ions of the types previously considered containing carbon, hydrogen, and one or two atoms of oxygen. This diagram covers the mass numbers from 128 to 142. It can now be made to cover an infinite number of mass numbers by defining the mass scale as $\text{CH}_2=14.0000$. Because with $\text{CH}_2=14.0000$ the defect of the combination $(\text{CH}_2)_n$ is always zero, e.g., $\text{C}_{10}\text{H}_{20}=140.0000$ and $\text{C}_9\text{H}_{18}=126.0000$, the defects for other combinations apply at any carbon number. Figure 3 shows the manner in which the pattern is repeated.

Now that the zero of the mass defect scale has been fixed and with it the units in which the defects are measured, the defects for ions containing say one oxygen atom can be read off. At 140, for example, the $\text{C}_9\text{H}_{16}\text{O}$ ions would have a defect of 36.4×10^{-3} mass units. At 126, the ions of formula $\text{C}_8\text{H}_{14}\text{O}$ would have the same defect. The difference in composition between the two examples is (CH_2) , which has zero defect by definition.

As an alternative to reading a chart, the defects can be found from tables. It is convenient to consider the defect as the sum of contributions from the hydrocarbon ion and from the separation of the peak from the hydrocarbon peak. In the two examples previously considered this doublet separation is 36.4×10^{-3} mass units. The hydrocarbon contributions are zero because in both cases the hydrocarbon was of the C_nH_{2n} type.

Figure 4 shows these two contributions in the general case. "A" is the separation of the peak from the corresponding hydrocarbon, and "B" is the contribution from the hydrocarbon.

Advantages of the CH_2 Mass Scale

- (1) The number of precise masses to be calculated, stored, and compared with data from a sample is very greatly reduced.
- (2) A further advantage of the CH_2 mass scale is that the identification of ions is simplified. Ions having masses fourteen units apart and having similar defects could be assumed to have similar structures and to differ only in the number of CH_2 units. Averaging these defects gives a more accurate value for comparison with the tables.
- (3) Still another advantage of the CH_2 scale is that the same defects apply in the higher mass ranges. Above about 500 mass units the defects calculated do not cover all possibilities. The proportion covered decreases with the mass number, but those combinations not included are unlikely combinations with large numbers of carbon atoms and relatively few hydrogen atoms.

An example of the value of the CH_2 mass scale is given in Table I in which the masses of series of paraffins, alkyl naphthalenes and aliphatic ketones, which have parent peaks at the same nominal masses, are compared.

Table I
COMPARISON OF THE MASSES OF
SOME ORGANIC IONS ON THE TWO SCALES

	Mass Scale	
	$^{16}\text{O} = 16.0000$	$^{12}\text{CH}_2 = 14.0000$
	(11)	
Naphthalenes	128.1036	127.9196
	142.1237	141.9196
	156.1439	155.9196
	170.1640 etc.	169.9196 etc.

Figure 3
REPETITION OF DEFECTS ON CH₂ MASS SCALE

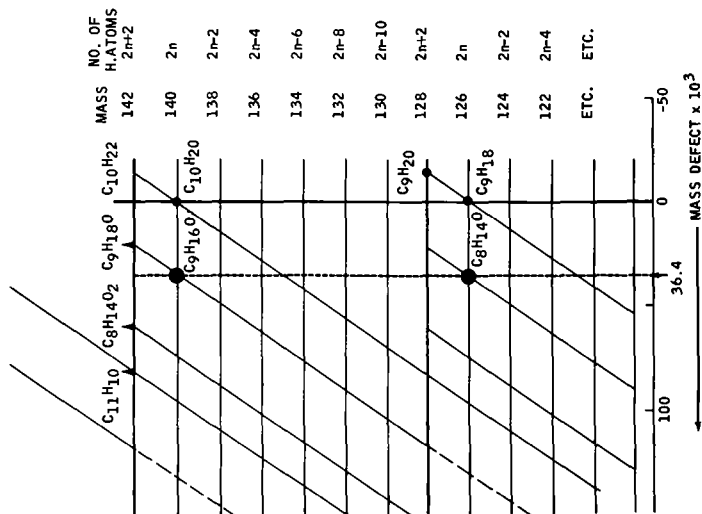


Figure 4
COMPONENTS OF A MASS DEFECT

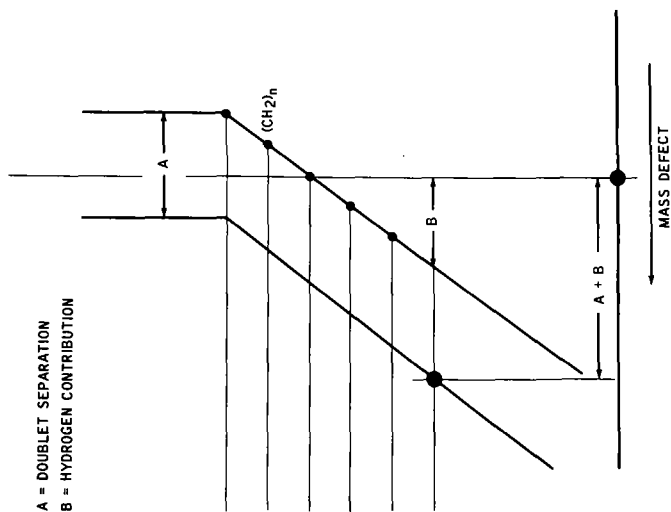


Table I (Cont'd.)

	----- 160 = 16.0000 (11) -----	Mass Scale----- 12CH ₂ = 14.0000 -----
Paraffins	128.1975 142.2176 156.2378 170.2579 etc.	128.0134 142.0134 156.0134 170.0134 etc.
C _n H _{2n} O	128.1611 142.1812 156.2013 170.2214 etc.	127.9770 141.9770 155.9770 169.9770 etc.

The mass defects for all the naphthalenes are the same, and obviously different from those for paraffins or ketones. Ions having one less hydrogen atom than each of the examples given have mass defects which are larger by 0.0067. They therefore give sets of values similar to those presented in Table I.

Presentation of the CH₂ Mass Tables

It will be appreciated that the data in Table I on naphthalenes, paraffins, and ketones would be better expressed in terms of the defects, i.e., naphthalenes: 0.0804, paraffins: -0.0134, and ketones: 0.0230. The negative defect of paraffin parent peaks is an exception to the general rule.

The most useful way of having these data available would be in the form of tables each of which would relate to a particular kind of empirical formula, e.g., the formula C_nH_m, where (2n+2) < m < (2n-11) would cover the parent peaks of all the simpler hydrocarbons including paraffins, olefins, cycloparaffins, alkylbenzenes, styrenes, tetralins and indanes and indenenes. For a given mass number, the values of "n" and "m" may be obtained from Fig. 5. The same empirical formula with a lower value of "m" would cover most cases of ions formed when several hydrogen atoms are stripped off the paraffins, olefins, and cycloparaffins. A paraffin with fourteen hydrogen atoms stripped off is indistinguishable from a naphthalene of the same carbon number, and the defects for paraffin ions with between fourteen and twenty-eight missing hydrogen atoms may be found, therefore, from the table of defects for the parent and fragment peaks of naphthalenes and other condensed aromatics. To preserve the values of "n" and "m" as those obtained from Fig. 5, the empirical formula for naphthalenes may be written as C_{n+1}H_{m-12}, where m=2n+2, instead of the usual formula C_nH_{2n-12}. It will be seen from Fig. 5 that for a mass number of 128, "n"=9 and "m"=2n+2=20. The formula thus gives the usual formula, C₁₀H₈. The number "n" might be described as the "equivalent carbon number" because it is in fact the number of carbon atoms in the simplest hydrocarbon ion which could be found at a particular mass number.

Ions containing oxygen, nitrogen, or sulfur can have their empirical formulae expressed in a similar manner; for example, the ions containing one oxygen atom and having a nominal mass of 128 would have the empirical formula C_{n-1}H_{m-4}O where "m" is again equal to (2n+2).

Peaks from ions containing one ¹³C atom can only be separated from the normal hydrocarbon peak at the same nominal mass when the mass number is fairly low (below about 50). Further instrumental developments will, however, make it necessary to distinguish between these peaks and precise masses of the ions will be required. Provision has been made for these data in the tables.

Table II gives the mass defects of the ions with the formulae ¹²C_nH_m, where "m" lies in the range from (2n+2) to (2n-11). Below these are the defects for the first four isotope peaks which could occur at the same mass number.

Substituting an oxygen atom for a carbon and four hydrogen atoms will give a peak at the same mass number, but a mass defect which is larger by 36.4 millimass units, the spacing of the doublet CH₄-O. Thus for an empirical formula of C_{n-1}H_{m-4}O we have a table similar to Table II, but with each entry increased by 36.4 millimass units. Similar tables can be prepared for other empirical formulae involving oxygen, nitrogen, sulfur, etc. In practice, Table II is the basic table and the subsidiary tables are prepared by adding to each defect a mass defect which is the spacing of the doublet formed by the peak with which we are concerned and the simple hydrocarbon ion.

To avoid listing in full each of the tables of defects, tables have been prepared in which the general formula of the combination of atoms and the appropriate doublet spacing have been listed. Figs. 6, 7 and 8 are portions of the table for combinations of oxygen, nitrogen and sulfur with the limitations which were discussed previously.

Table II

MASS DEFECTS OF HYDROCARBON IONS C_nH_{2n+2} TO C_nH_{2n-11}

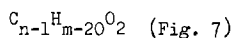
Empirical Formula	mass units x 10 ³														
	2n+2	2n+1	2n	2n-1	2n-2	2n-3	2n-4	2n-5	2n-6	2n-7	2n-8	2n-9	2n-10	2n-11	
¹² C _n H _m	-13.4	-6.7	0.0	6.7	13.4	20.1	26.8	33.5	40.2	46.9	53.6	60.3	67.0	73.7	
¹³ ₁ ¹² C _{n-1} H _{m-1}	- 8.9	-2.2	4.5	11.2	17.9	24.6	31.3	38.0	44.7	51.4	58.1	64.8	71.5	78.2	
¹³ ₂ ¹² C _{n-2} H _{m-2}	- 4.5	2.2	8.9	15.6	22.3	28.9	35.6	42.4	49.1	55.8	62.5	69.2	75.9	82.6	
¹³ ₃ ¹² C _{n-3} H _{m-3}	0.0	6.7	13.4	20.1	26.8	33.5	40.2	46.9	53.6	60.3	67.0	73.7	80.4	87.1	
¹³ ₄ ¹² C _{n-4} H _{m-4}	4.4	11.1	17.8	24.5	31.2	37.9	44.6	51.3	58.0	64.7	71.4	78.1	84.8	91.5	
											2n+6	2n+5	2n+4	2n+3	
¹³ ₁ ¹² C _{n-1} H _{m-1}													-17.9	-11.2	
¹³ ₂ ¹² C _{n-2} H _{m-2}												-20.1	-13.4	- 6.7	
¹³ ₃ ¹² C _{n-3} H _{m-3}											-22.4	-15.7	- 9.0	- 2.3	
¹³ ₄ ¹² C _{n-4} H _{m-4}															
														-15.6	

A hypothetical example of the use of the tables in the interpretation of precise mass measurements is given in Table III. This table shows the initial separation of the precise mass into a mass number with its corresponding "n" and "m" values, and a mass defect (mass number-precise mass).

Table III
ASSIGNMENT OF MASSES ON THE CH₂ SCALE

Mass No.	Precise Mass	Mass Defect	From Fig. 5		---Analysis of Defect----	Residual	Assignment*
			n	m	H Contribution (From Table II)		
351	350.8402	159.8	25	2n+1	- 6.7	166.5	C ₂₄ H ₃₁ O ₂
352	351.8469	153.1	25	2n+2	-13.4	166.5	C ₂₄ H ₃₂ O ₂
353	352.8535	146.5	26	2n-11	73.7	72.8	C ₂₄ H ₃₃ O ₂
354	353.8602	139.8	26	2n-10	67.0	72.8	C ₂₄ H ₃₄ O ₂
365	364.8402	159.8	26	2n+1	- 6.7	166.5	C ₂₅ H ₃₃ O ₂
366	365.8469	153.1	26	2n+2	-13.4	166.5	C ₂₅ H ₃₄ O ₂
367	366.8535	146.5	27	2n-11	73.7	72.8	C ₂₅ H ₃₅ O ₂
368	367.8602	139.8	27	2n-10	67.0	72.8	C ₂₅ H ₃₆ O ₂
369	368.8624	137.6	27	2n-9	64.8	72.8	¹³ CC ₂₄ H ₃₆ O ₂
370	369.8647	135.3	27	2n-8	62.5	72.8	¹³ C ₂ C ₂₃ H ₃₆ O ₂
379	378.8402	159.8	27	2n+1	- 6.7	166.5	C ₂₆ H ₃₅ O ₂
380	379.8469	153.1	27	2n+2	-13.4	166.5	C ₂₆ H ₃₆ O ₂
381	380.8535	146.5	28	2n-11	73.7	72.8	C ₂₆ H ₃₇ O ₂

* Residual defects of 166.5 and 72.8 millimass units correspond to the formulae



Hence for n=25 and m=2n+1, we have C₂₄H₃₁O₂, etc.

The hydrocarbon ion with the same value of "m" has a mass defect (found from Table II) which is listed in the sixth column. Subtracting this defect from the observed defect gives a residual corresponding to one of the formulae in Figs. 6, 7 and 8. This formula is a general empirical formula for the unknown ion. It may be converted into a specific formula by substituting the appropriate values of "n" and "m".

Conclusions

The main advantages of the CH₂ scale can be summarized as:

(1) A reduction by a factor of about thirty times in the amount of data to be calculated, stored and subsequently compared with precise mass determinations.

(2) The mass defects found from high resolution spectra can be compared directly and associated peaks can be recognized immediately.

FIGURE 5

MASS NUMBERS FOR DIFFERENT VALUES OF "n" AND "m"

n	2n+2	2n+1	2n	2n-1	2n-2	2n-3	2n-4	2n-5	2n-6	2n-7	2n-8	2n-9	2n-10	2n-11
2	30	29	28	27	26	25	24							
3	44	43	42	41	40	39	38	37	36	35	34	33	32	31
4	58	57	56	55	54	53	52	51	50	49	48	47	46	45
5	72	71	70	69	68	67	66	65	64	63	62	61	60	59
6	86	85	84	83	82	81	80	79	78	77	76	75	74	73
7	100	99	98	97	96	95	94	93	92	91	90	89	88	87
8	114	113	112	111	110	109	108	107	106	105	104	103	102	101
9	128	127	126	125	124	123	122	121	120	119	118	117	116	115
10	142	141	140	139	138	137	136	135	134	133	132	131	130	129
11	156	155	154	153	152	151	150	149	148	147	146	145	144	143
12	170	169	168	167	166	165	164	163	162	161	160	159	158	157
13	184	183	182	181	180	179	178	177	176	175	174	173	172	171
14	198	197	196	195	194	193	192	191	190	189	188	187	186	185
15	212	211	210	209	208	207	206	205	204	203	202	201	200	199
16	226	225	224	223	222	221	220	219	218	217	216	215	214	213
17	240	239	238	237	236	235	234	233	232	231	230	229	228	227
18	254	253	252	251	250	249	248	247	246	245	244	243	242	241
19	268	267	266	265	264	263	262	261	260	259	258	257	256	255
20	282	281	280	279	278	277	276	275	274	273	272	271	270	269
21	296	295	294	293	292	291	290	289	288	287	286	285	284	283
22	310	309	308	307	306	305	304	303	302	301	300	299	298	297
23	324	323	322	321	320	319	318	317	316	315	314	313	312	311
24	338	337	336	335	334	333	332	331	330	329	328	327	326	325
25	352	351	350	349	348	347	346	345	344	343	342	341	340	339
26	366	365	364	363	362	361	360	359	358	357	356	355	354	353
27	380	379	378	377	376	375	374	373	372	371	370	369	368	367
28	394	393	392	391	390	389	388	387	386	385	384	383	382	381
29	408	407	406	405	404	403	402	401	400	399	398	397	396	395
30	422	421	420	419	418	417	416	415	414	413	412	411	410	409
31	436	435	434	433	432	431	430	429	428	427	426	425	424	423
32	450	449	448	447	446	445	444	443	442	441	440	439	438	437
33	464	463	462	461	460	459	458	457	456	455	454	453	452	451
34	478	477	476	475	474	473	472	471	470	469	468	467	466	465
35	492	491	490	489	488	487	486	485	484	483	482	481	480	479
36	506	505	504	503	502	501	500	499	498	497	496	495	494	493
37	520	519	518	517	516	515	514	513	512	511	510	509	508	507
38	534	533	532	531	530	529	528	527	526	525	524	523	522	521
39	548	547	546	545	544	543	542	541	540	539	538	537	536	535
40	562	561	560	559	558	557	556	555	554	553	552	551	550	549
41	576	575	574	573	572	571	570	569	568	567	566	565	564	563
42	590	589	588	587	586	585	584	583	582	581	580	579	578	577
43	604	603	602	601	600	599	598	597	596	595	594	593	592	591
44	618	617	616	615	614	613	612	611	610	609	608	607	606	605
45	632	631	630	629	628	627	626	625	624	623	622	621	620	619
46	646	645	644	643	642	641	640	639	638	637	636	635	634	633
47	660	659	658	657	656	655	654	653	652	651	650	649	648	647
48	674	673	672	671	670	669	668	667	666	665	664	663	662	661
49	688	687	686	685	684	683	682	681	680	679	678	677	676	675
50	702	701	700	699	698	697	696	695	694	693	692	691	690	689

FIGURE 6

MASS DEFECTS FOR BASIC COMBINATIONS OF CARBON, HYDROGEN, SULFUR, NITROGEN, AND OXYGEN

Formula	Mass Defect x 10 ³	Formula	Mass Defect x 10 ³	Formula
C ₂ H ₄ N ₂ O	50.0-59.9	C ₂ H ₄ N ₂ O	50.0-59.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	51.7	C ₂ H ₄ N ₂ O	51.7	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	52.9	C ₂ H ₄ N ₂ O	52.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	53.9	C ₂ H ₄ N ₂ O	53.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	58.0	C ₂ H ₄ N ₂ O	58.0	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	60.0-69.9	C ₂ H ₄ N ₂ O	60.0-69.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	61.3	C ₂ H ₄ N ₂ O	61.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	64.3	C ₂ H ₄ N ₂ O	64.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	66.4	C ₂ H ₄ N ₂ O	66.4	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	69.4	C ₂ H ₄ N ₂ O	69.4	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	70.0-79.9	C ₂ H ₄ N ₂ O	70.0-79.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	70.4	C ₂ H ₄ N ₂ O	70.4	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	72.7	C ₂ H ₄ N ₂ O	72.7	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	73.8	C ₂ H ₄ N ₂ O	73.8	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	76.8	C ₂ H ₄ N ₂ O	76.8	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	77.8	C ₂ H ₄ N ₂ O	77.8	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	80.0-89.9	C ₂ H ₄ N ₂ O	80.0-89.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	81.8	C ₂ H ₄ N ₂ O	81.8	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	82.9	C ₂ H ₄ N ₂ O	82.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	85.2	C ₂ H ₄ N ₂ O	85.2	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	86.3	C ₂ H ₄ N ₂ O	86.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	87.1	C ₂ H ₄ N ₂ O	87.1	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	89.2	C ₂ H ₄ N ₂ O	89.2	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	90.0-99.9	C ₂ H ₄ N ₂ O	90.0-99.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	90.3	C ₂ H ₄ N ₂ O	90.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	91.3	C ₂ H ₄ N ₂ O	91.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	94.3	C ₂ H ₄ N ₂ O	94.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	97.6	C ₂ H ₄ N ₂ O	97.6	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	99.6	C ₂ H ₄ N ₂ O	99.6	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	100.0-109.9	C ₂ H ₄ N ₂ O	100.0-109.9	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	101.7	C ₂ H ₄ N ₂ O	101.7	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	103.8	C ₂ H ₄ N ₂ O	103.8	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	105.7	C ₂ H ₄ N ₂ O	105.7	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	106.3	C ₂ H ₄ N ₂ O	106.3	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	107.0	C ₂ H ₄ N ₂ O	107.0	C ₂ H ₄ N ₂ O
C ₂ H ₄ N ₂ O	109.1	C ₂ H ₄ N ₂ O	109.1	C ₂ H ₄ N ₂ O

References

- (1) Mattauch, J., Herzog, R., Z. Phys. 89, 786 (1934).
- (2) Mattauch, J., Phys. Rev. 50, 617 (1936).
- (3) Mattauch, J., Phys. Rev. 50, 1089 (1936).
- (4) Voorhies, H.G., Robinson, C.F., Hall, L.G., Boubaker, W.M., and Berry, C.E., "Advances in Mass Spectrometry", Pergamon Press, London, 1959.
- (5) Craig, R.D., Errock, G.A., Waldron, J.D., "Advances in Mass Spectrometry", Pergamon Press, London, 1959.
- (6) Collins, T.L., Johnson, W.H., Nier, A.O., Phys. Rev. 94, 398 (1954).
- (7) Nier, A.O., Roberts, T.R., Franklin, E.G., Phys. Rev. 75, 346 (1949).
- (8) Nier, A.O., Roberts, T.F., Phys. Rev. 81, 507 (1951).
- (9) Nier, A.O., Natl. Bur. Standards Proc. 522, 29 (1953).
- (10) Craig, R.D., Errock, G.A., "Advances in Mass Spectrometry", Pergamon Press, London, 1959.
- (11) Beynon, J.H., "Mass Spectrometry and its Application to Organic Chemistry", Elsevier Pub. Co., (1960).

FIGURE 7

TABLE 8

Mass Defect $\times 10^3$	Formula	Mass Defect $\times 10^3$	Formula	Mass Defect $\times 10^3$	Formula
110.0-110.9	Cn-5Hm-14H ₂ O ₂	140.0-149.9	Cn-9Hm-6H ₂ S ₂ M ₂ O	170.0-179.9	Cn-6Hm-20H ₂ O ₄
111.0	Cn-2Hm-10H ₂ O ₃	140.0	Cn-6Hm-16H ₂ SN ₄	170.0	Cn-5Hm-14H ₂ SN ₂ O
111.3	Cn-7Hm-8H ₂ SN ₂	140.4	Cn-9Hm-11H ₂ SN ₄	171.6	Cn-8Hm-14H ₂ SN ₂ O
112.1	Cn-7Hm-8H ₂ SN ₂	142.1	Cn-9Hm-8H ₂ SN ₄ O ₃	171.7	Cn-8Hm-14H ₂ SN ₂ O
112.5	Cn-4Hm-12H ₂ SN ₂ O ₂	142.1	Cn-9Hm-8H ₂ SN ₄ O ₃	172.2	Cn-10Hm-13H ₂ S ₂ NO
112.8	Cn-4Hm-12H ₂ SN ₂ O ₂	142.6	Cn-1Hm-18H ₂ S ₂ M ₂ O	173.2	Cn-10Hm-13H ₂ S ₂ NO
113.2	Cn-9Hm-16H ₂ SN ₂	143.7	Cn-8Hm-20H ₂ SN ₄ O	174.2	Cn-8Hm-16H ₂ SN ₄ O
113.8	Cn-9Hm-16H ₂ SN ₂	143.7	Cn-8Hm-20H ₂ SN ₄ O	174.2	Cn-8Hm-16H ₂ SN ₄ O
118.2	Cn-13Hm-16H ₂ SN ₂	144.4	Cn-9Hm-12H ₂ S ₂ SN ₂ O	175.6	Cn-7Hm-16H ₂ SN ₄ O
118.8	Cn-13Hm-16H ₂ SN ₂	145.1	Cn-11Hm-8H ₂ S ₂ SN ₂ O	175.6	Cn-7Hm-16H ₂ SN ₄ O
119.4	Cn-6Hm-8H ₂ S ₂ SN ₂ O	145.4	Cn-4Hm-16H ₂ O ₄	176.7	Cn-9Hm-16H ₂ SN ₄ O
120.0-120.9	Cn-10Hm-8H ₂ SN ₂ O ₂	146.5	Cn-6Hm-18H ₂ O ₃	176.7	Cn-9Hm-16H ₂ SN ₄ O
121.6	Cn-10Hm-8H ₂ SN ₂ O ₂	146.7	Cn-3Hm-14H ₂ SN ₄ O	177.6	Cn-9Hm-16H ₂ SN ₄ O
122.2	Cn-6Hm-16H ₂ SN ₂ O ₃	147.7	Cn-5Hm-12H ₂ SN ₂ O ₃	177.6	Cn-9Hm-16H ₂ SN ₄ O
122.6	Cn-6Hm-16H ₂ SN ₂ O ₃	148.4	Cn-10Hm-12H ₂ S ₂ SN ₂ O	178.7	Cn-7Hm-12H ₂ S ₂ O ₄
122.8	Cn-3Hm-12H ₂ SN ₂ O	150.0-159.9	Cn-8Hm-14H ₂ SN ₂ O ₃	178.7	Cn-7Hm-12H ₂ S ₂ O ₄
123.5	Cn-6Hm-8H ₂ SN ₂ O	150.5	Cn-8Hm-14H ₂ SN ₂ O ₃	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
123.5	Cn-6Hm-8H ₂ SN ₂ O	151.8	Cn-8Hm-16H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
123.6	Cn-8Hm-10H ₂ SN ₂ O	151.8	Cn-8Hm-16H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
126.7	Cn-6Hm-12H ₂ SN ₂ O ₂	151.8	Cn-8Hm-16H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
126.8	Cn-5Hm-8H ₂ SN ₂ O	154.6	Cn-10Hm-12H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
126.8	Cn-5Hm-8H ₂ SN ₂ O	154.6	Cn-10Hm-12H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
127.9	Cn-5Hm-12H ₂ SN ₂ O	154.6	Cn-10Hm-12H ₂ SN ₂ O	179.5	Cn-7Hm-12H ₂ S ₂ O ₄
130.0-130.9	Cn-8Hm-16H ₂ SN ₂ O ₃	155.1	Cn-2Hm-20H ₂ O	180.0-189.9	Cn-4Hm-24H ₂ O
130.1	Cn-8Hm-16H ₂ SN ₂ O ₃	155.1	Cn-2Hm-20H ₂ O	180.0	Cn-4Hm-24H ₂ O
131.1	Cn-8Hm-16H ₂ SN ₂ O ₃	155.8	Cn-7Hm-12H ₂ S ₂ SN ₂ O	180.8	Cn-9Hm-18H ₂ S ₂ SN ₂ O
131.2	Cn-8Hm-16H ₂ SN ₂ O ₃	156.5	Cn-10Hm-12H ₂ S ₂ SN ₂ O	181.6	Cn-9Hm-18H ₂ S ₂ SN ₂ O
131.2	Cn-8Hm-16H ₂ SN ₂ O ₃	156.5	Cn-10Hm-12H ₂ S ₂ SN ₂ O	181.6	Cn-9Hm-18H ₂ S ₂ SN ₂ O
131.9	Cn-7Hm-10H ₂ S ₂ SN ₂ O	158.2	Cn-9Hm-14H ₂ S ₂ SN ₂ O	184.1	Cn-6Hm-20H ₂ SN ₄ O
132.0	Cn-7Hm-10H ₂ S ₂ SN ₂ O	158.2	Cn-9Hm-14H ₂ S ₂ SN ₂ O	184.1	Cn-6Hm-20H ₂ SN ₄ O
134.0	Cn-5Hm-16H ₂ SN ₂ O	159.1	Cn-10Hm-12H ₂ S ₂ SN ₂ O	184.8	Cn-11Hm-13H ₂ S ₂ SN ₂ O
134.0	Cn-5Hm-16H ₂ SN ₂ O	159.1	Cn-10Hm-12H ₂ S ₂ SN ₂ O	184.8	Cn-11Hm-13H ₂ S ₂ SN ₂ O
134.7	Cn-10Hm-8H ₂ S ₂ SN ₂ O ₃	159.8	Cn-9Hm-8H ₂ S ₂ SN ₂ O	186.7	Cn-2Hm-24H ₂ S ₂ M ₂ O
134.7	Cn-10Hm-8H ₂ S ₂ SN ₂ O ₃	159.8	Cn-9Hm-8H ₂ S ₂ SN ₂ O	186.7	Cn-2Hm-24H ₂ S ₂ M ₂ O
135.3	Cn-4Hm-14H ₂ SN ₂ O	160.0-169.9	Cn-6Hm-18H ₂ SN ₄ O	187.6	Cn-11Hm-10H ₂ S ₂ SN ₂ O
135.3	Cn-4Hm-14H ₂ SN ₂ O	160.2	Cn-6Hm-18H ₂ SN ₄ O	187.6	Cn-11Hm-10H ₂ S ₂ SN ₂ O
135.9	Cn-9Hm-6H ₂ S ₂ S ₂ NO	160.2	Cn-6Hm-18H ₂ SN ₄ O	188.1	Cn-6Hm-20H ₂ SN ₄ O
136.0	Cn-7Hm-10H ₂ SN ₂ O	160.9	Cn-9Hm-14H ₂ S ₂ SN ₂ O	188.1	Cn-6Hm-20H ₂ SN ₄ O
136.1	Cn-7Hm-10H ₂ SN ₂ O	161.9	Cn-7Hm-14H ₂ SN ₄ O	188.8	C ₁₁ Hm-12H ₂ S ₂ S ₂ SN ₂ O
136.3	Cn-10Hm-8H ₂ S ₂ NO	163.2	Cn-4Hm-16H ₂ SN ₄ O	188.8	C ₁₁ Hm-12H ₂ S ₂ S ₂ SN ₂ O
163.2	Cn-4Hm-16H ₂ SN ₄ O	163.2	Cn-4Hm-16H ₂ SN ₄ O		
164.2	Cn-8Hm-14H ₂ SN ₄ O	164.2	Cn-8Hm-14H ₂ SN ₄ O		
164.3	Cn-8Hm-14H ₂ SN ₄ O	164.3	Cn-8Hm-14H ₂ SN ₄ O		
166.3	Cn-11Hm-10H ₂ S ₂ S ₂ SN ₂ O	166.3	Cn-11Hm-10H ₂ S ₂ S ₂ SN ₂ O		
166.5	Cn-3Hm-22H ₂ NO	166.5	Cn-3Hm-22H ₂ NO		
167.6	Cn-8Hm-14H ₂ S ₂ SN ₂ O	167.6	Cn-8Hm-14H ₂ S ₂ SN ₂ O		
168.3	Cn-8Hm-14H ₂ S ₂ SN ₂ O	168.3	Cn-8Hm-14H ₂ S ₂ SN ₂ O		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S ₂ NO		
169.0	Cn-11Hm-10H ₂ S ₂ NO	169.0	Cn-11Hm-10H ₂ S		

PHOTOGRAPHIC INDEXING TECHNIQUE FOR EVALUATING EMULSION UNIFORMITY OF SPECTROGRAPHIC PLATES

J. M. McCrea
Applied Research Laboratory
U. S. Steel Corporation
Monroeville, Pennsylvania

Abstract

Emulsion variations on special-purpose spectrographic plates for detection of ions or invisible radiation greatly complicate use of these plates in quantitative analysis. In the conventional graded exposure technique for spark-source mass spectrography, different source-performance and emulsion-response factors may affect each exposure. Because magnet gaps are much less than plate widths, a simultaneous calibration for ion exposure cannot be obtained over the full width of a plate. As a result, "across-the-plate" emulsion variations are best studied by an independent method.

Control indexing of plates by visible light is a useful technique for investigating emulsions and for improving precision of quantitative analysis. A convenient apparatus has been constructed for exposing arbitrary 1- to 40-mm bands of full plate width to light under controlled conditions. These index bands may be applied either before or after the plate is used as an ion detector, and in such a manner that they do not overlap mass spectral lines.

Photographic index bands or lines on mass spectrographic plates serve several important functions. They provide a permanent record of emulsion and processing uniformity, permit "in-batch" and "batch-to-batch" comparisons of plates on a common basis, and aid in comparison of processing techniques. Plates with major emulsion irregularities, such as severe across-the-plate variation in conjunction with relative uniformity along the plate, can be rejected by careful darkroom inspection prior to use, but index bands can be used to identify plates with variations not noticed during inspection. Until the incidence of rejectable plates in fresh batches is substantially reduced, all mass spectrograph plates used for quantitative purposes should bear index bands for recording evidence of emulsion uniformity.

Introduction

Mass spectrometers employing both the spark source for excitation of solids and the double focussing geometry developed by Mattauch and Hertzog were applied to analytical problems during the 1950's.^{1,2)} The detector chosen for both instruments was the ion-sensitive photographic plate. A similar choice of detector was made for the commercial instrument now installed at U. S. Steel's Applied Research Laboratory.³⁾ The spectrographic system with photographic plate was chosen because a plate can act as an integrating detector for each of the ion species individually but simultaneously over a specific mass (m/e) range covering virtually the entire periodic table. Simultaneous data integration for all ions from Li^+ (m/e 6 and 7) to transuranic ions in the region of m/e 250 is most desirable when the source of those ions is as variable and temperamental as the radio frequency pulsed spark. An alternative electrical readout for the spark-source instrument was reported in 1952, but research on and commercial development of this system has been very slow.⁴⁾

Photographic plates were used as ion detectors by J. J. Thomson and others in research of the 1900 era.⁵⁾ Aston and Messrs. Ilford, Ltd., were responsible for introduction of the Type Q plates.⁶⁾ Although a development of the 1930's, the Q-2 plate is still the most widely used ion detector in the spark-source mass spectrographs of the 1960's.^{1,2,3)} For nearly 20 years there was little research activity with mass spectrometers using photographic ion detectors. Emulsion making and coating are accomplished and easily lost arts, and this hiatus in research is undoubtedly the cause of some current problems in spark-source mass spectrometry. Since 1960, interest in these photographic ion detectors has increased rapidly; separate investigations by Owens and by Rudloff have yielded current data on the sensitivity of photographic emulsions to ions.^{7,8)}

In their description of a spark-source instrument, Craig, Errock, and Waldron mention that the Type Q emulsion is known to be more variable than other photographic emulsions.⁹⁾ Special plates used for ultraviolet emission spectrography have also exhibited a gradation of sensitivity across a plate, particularly near the edges.¹⁰⁾ The present work on photographic indexing was initiated shortly after plates with obviously uneven emulsions were noticed during normal plate loading operations.

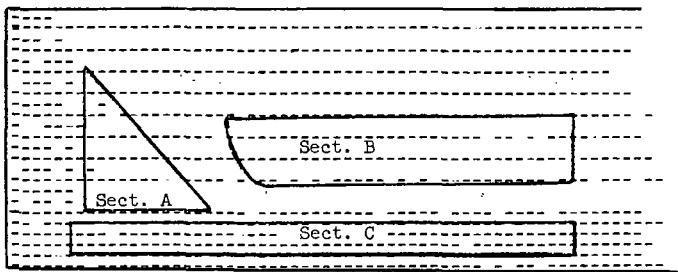
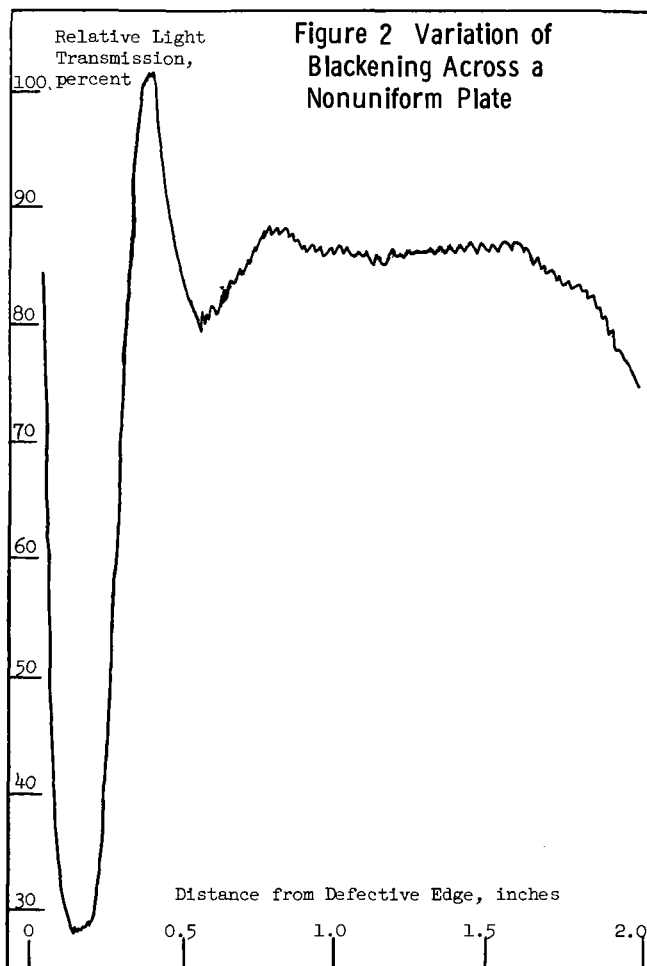


Figure 1 Sections at Corner of Uneven Plate

Section	<u>Analytical Data</u>	
	Silver Concentration	
A	0.139 mg/sq cm	
B	0.122	
C	0.160	



Systematic inspection of all plates for mass spectrographic use was adopted as standard practice while photographic indexing techniques were being developed, and inspection is now used in conjunction with indexing.

At RCA Laboratories, too, it is the rule that all ion-detector plates shall be inspected prior to use in the mass spectrometer, although by a somewhat different technique.¹¹⁾ R. D. Craig has reported that another emulsion problem was encountered by European users of Type Q-2 plates, emulsions with limited maximum blackness and poor contrast.¹²⁾ About the end of 1961 these users met with Messrs. Ilford, Ltd., and it was decided to alter the Type Q-2 emulsion to give higher contrast; according to Craig this change cut the ion sensitivity of the Q-2 emulsion approximately in half. With at least two laboratories in the United States routinely inspecting all ion-detector plates, and because a deliberate alteration in emulsion manufacturing practices has occurred, a study of emulsion characteristics and uniformity is important to every laboratory engaged in quantitative or even semiquantitative analysis based on ion-sensitive plates.

Visual Plate Inspection

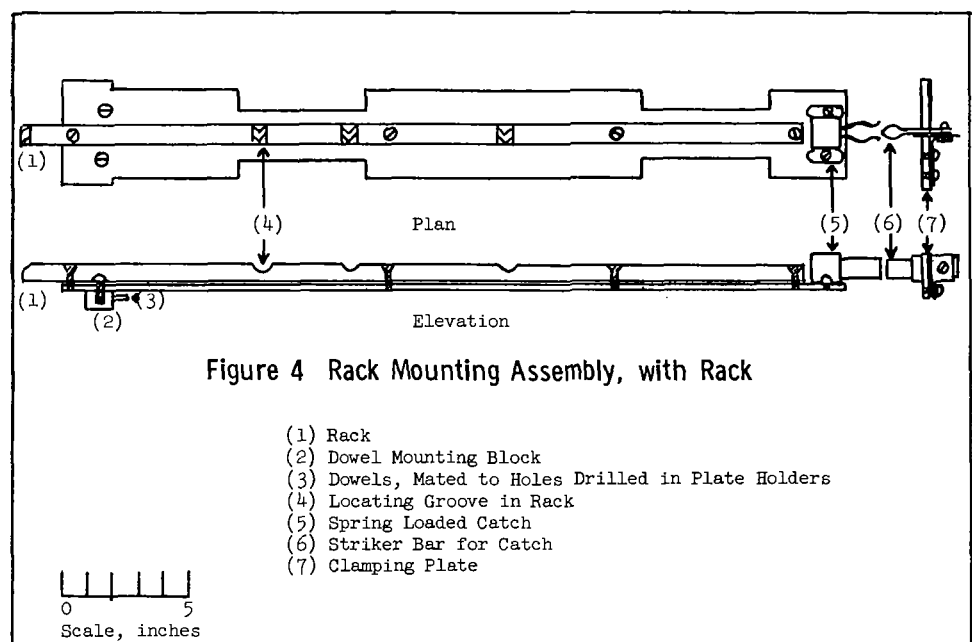
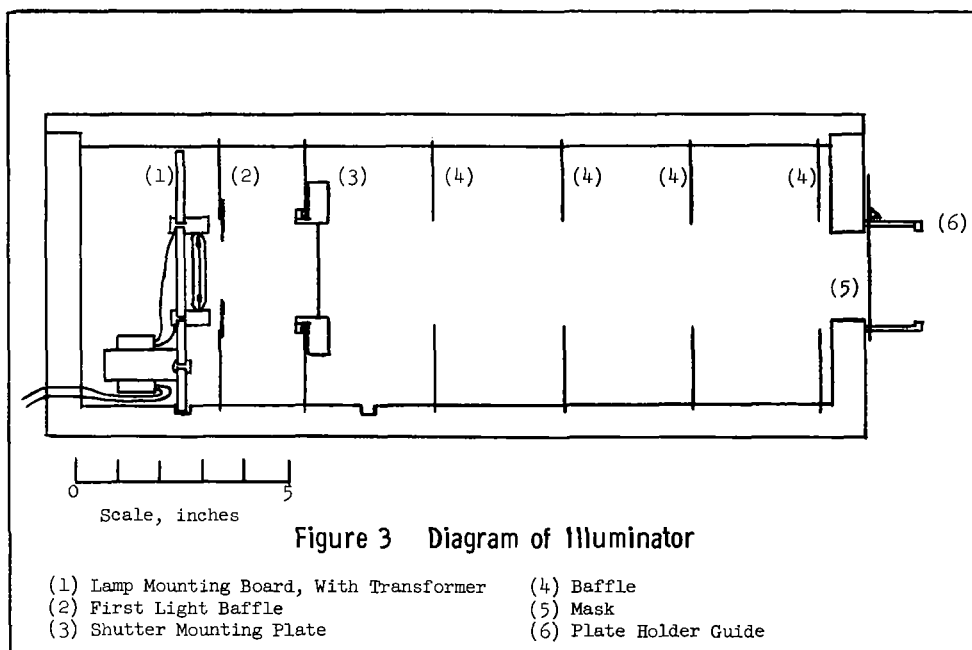
Originally an auxiliary darkroom near the solids mass spectrometer laboratory was used for loading and processing ion-detector plates. This arrangement proved to be unsatisfactory; the safelighting required by others using the darkroom was inconsistent with the high photographic sensitivity of Ilford Type Q-2 plates, and abrasion marks on plates caused by transportation of the loaded plate holder were undesirably frequent. In addition, fibers from the black cloth sleeve used to exclude light during transit between spectrometer and darkroom caught occasionally in the O-ring seal of the instrument plate chamber door and caused poor vacuum. These difficulties were overcome by light-proofing the mass spectrometer laboratory for darkroom use. An Ilford Type 904 Safelight was evaluated; to avoid safelight fogging of the sensitive Type Q-3 plates, a 7-1/2 watt bulb was required instead of the normal 15-watt safelight bulb.

Unexposed plates are held at least 3 feet from the safelight and inspected by transmitted light. An eye accommodation interval of at least 10 minutes is necessary before effective inspection work can be done. Emulsion nonuniformities of various types have been observed under these conditions and subsequently confirmed under normal lighting. Random unevenness may consist of scratch marks, uncoated pin holes, emulsion splatter on reverse side of plate, clear spots where there is no photosensitive material in the gelatin, and opaque spots containing either foreign matter or excess photosensitive material. The last two defects originate in emulsion mixing operations. Four defects that are direction-correlated with plate edges are emulsion on edges, uncoated areas at a corner, an uneven bar along the end of a plate, and an uneven bar along the side. Uneven bars of emulsion along the side are the most significant defects; up to half the working area of a plate may be affected. An unexposed plate with bar defects along one end and one side was dissected with a glass knife into sections of heavy opaque, normal, and semitransparent emulsion. To establish quantitative data on variations for this plate, total silver was determined chemically on each section. Chemical analysis and visual inspection concur; the map of the sections given in Figure 1 shows that the plate was nonuniform. When a plate with bar unevenness is exposed to light and processed, the blackening of the plate is greatest on the densest part of the bar. Relative light transmission across a plate with a narrow bar is shown in Figure 2. The microphotometer slit was aligned parallel to the bar so that the plate was scanned in the direction of greatest variation.

Bar unevenness is an edge effect caused by surface tension at the edge of large glass sheets during coating. Side bars affected 4 to 5 plates in a box of a dozen, that is, about 40 percent of all plates. Arrangements were made with Ilford, Ltd., to alter cutting procedure so that at least an inch of outside edge on the large coated sheets was cropped prior to plate cutting. Plates of emulsion number S4143 (Q-2) and S4152 (Q-3), supplied on special order to this specification, have exhibited no barring. Exclusive use of specially cropped plates for mass spectrography is highly desirable.*

The longitudinal bar is very deceptive; there is frequently no evidence of it on processed plates when the plates have been handled properly both in the mass spectrometer and in processing. If background fog is produced by careless handling, the bars appear as bands of darker background. The graded ion exposures taken across a plate that impinge on a longitudinal bar strike a region of different response characteristics. Should the bar not be identified, erroneous data must result.

* Spot checking of regular plates of emulsion number S4140 and higher has shown a like uniformity of coating.



Solids mass spectrometers have a limited line length as a result of the geometrical restrictions of the magnet pole pieces, and any attempt to establish uniform ion exposure across the plate width requires the assumption of source, analyzer, and vacuum stability over the interval in which successive exposures are taken. Consequently, appropriate apparatus was developed for exposing selected bands across the mass spectrographic plates to uniform visible light.

Illuminator for Photographic Indexing

An illuminator to produce uniform illumination over a 2- by 2-inch maximum area requires more design features than might be expected. A diagram of a lensless illuminator for this purpose is shown in Figure 3. Although a lensless system eliminates focussing problems and some scattering effects, a baffling system and complete black finishing inside are needed to hold scattered light at an acceptable low level. A linear filament, tubular envelope automotive lamp (Lucas 256 or Sears 28VA58517, selected for straight filament), operated well below rated voltage, was chosen as a light source. This lamp is oriented parallel to the plate width or racking direction to give geometrical averaging over the filament in the most significant direction; preferential effects resulting from angularly correlated variation of the glass envelope are eliminated in this manner. The lamp is energized continuously while the illuminator is in use, and exposure times are controlled by the externally activated shutter; this procedure results in steady state thermal gradients about the lamp and more uniform lamp intensity. The mounting board for the lamp may be located in either of two positions; in one, the lamp is 15.75 inches from the plate, in the other, 11.25 inches. Since these positions were selected close to the distance ratio $\sqrt{2}:1$, light intensity at the plate from the closer position is approximately twice that from the more remote as a result of the inverse square law.

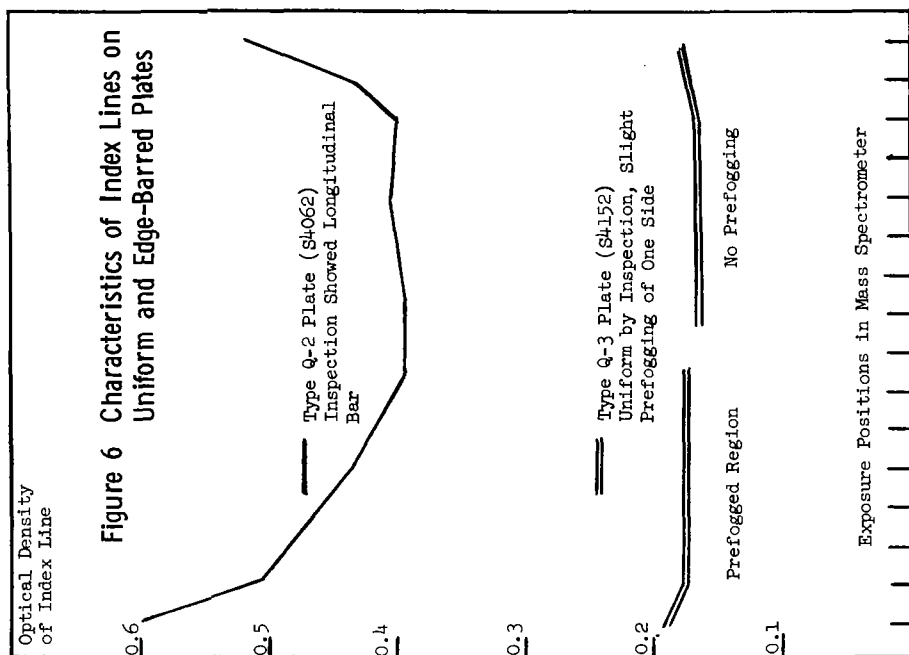
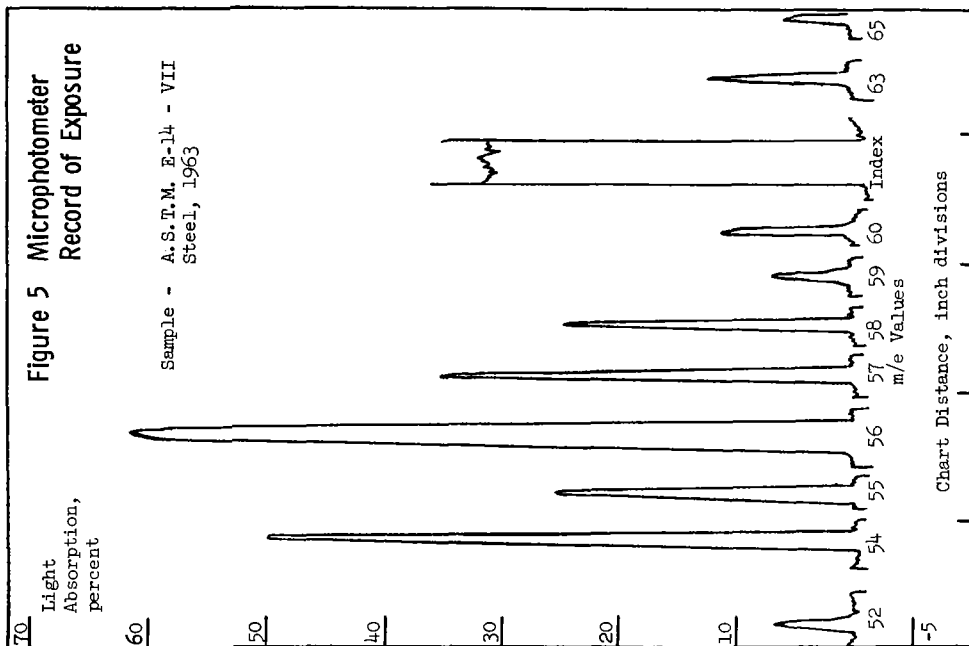
The machined channel mounted at the end of the illuminator acts as a guide for standard mass spectrometer plate holders. A 2-inch-wide section cut from the middle portion of the channel provides a light path to the plate. Masks can be inserted into grooves at the edges of the open section. Thus a narrow light band, a wide light band, geometrical figures, or printing may be projected on the portion of the plate behind a mask.

Plate Locating Accessories

If a light band were haphazardly applied to a plate as a quality index for emulsion uniformity, in many cases the band would interfere with important features of the mass spectrum obtained later. Accordingly, the plate should be accurately positioned in the illuminator for the light exposure. This operation and the subsequent handling of the plate holder until the plate is located in the mass spectrometer plate chamber must be done in such a way that neither light fog nor abrasion marks are produced on the emulsion. In addition, any modification to the plate holder for locating in the illuminator must also be compatible with mechanical arrangements for locating the plate holder in the mass spectrometer.

The rack and mounting assembly shown in Figure 4 was designed to attach to the rear of plate holders by means of two locating dowels at one end and a spring-loaded catch plate at the other. This rack mounting assembly can easily be removed from a plate holder under safelight conditions. Two locating holes matching the dowels must be drilled in the end of the plate holders, but no other modification to the plate holder is required. On the illuminator, the plate guide channel is fitted with a spring-loaded positioning roller to complete means for locating the plate holder with respect to the illuminator. To ensure consistency of the index marks with mass spectra, the plate holder must also be firmly located against one of the stops in the mass spectrometer plate chamber during the loading of the holder.

A variety of sample and instrument conditions makes use of a single positioning rack unworkable. Wood blanks, cut to standard dimensions, can be transformed in a few minutes into locating racks to fit any specific purpose. A knowledge of where notches are required in the rack and a round file are all that are necessary to convert a blank into a suitable rack. The roller positioner operates precisely in locating the rack by one of its grooves. With masks carefully set in the grooves of the open section of the guide channel to eliminate the effects of play there, the position of index marks in relation to mass spectra can be reproduced from plate to plate with a precision better than 0.5 millimeter, a precision usually adequate for use of index marks as mass marks.



Applications of Photographic Indexing

The original purpose of the apparatus described was that of applying quality control marks on all plates intended for mass spectrographic use. The versatility needed to do this so that there would be minimal interference with mass spectral lines has made the apparatus suitable for a wide variety of uses connected with spark-source mass spectrography. Such uses are

1. Application of uniformly exposed light bands on a plate as a record of emulsion and processing uniformity.
2. Application of mass marks at selected m/e values for given magnetic field conditions.
3. Application of plate and sample identification data on unused portions of a plate.
4. Studies of photographic light prefogging in relation to response of plates to ion exposures.
5. Determination of light sensitivity curves for various plate shipments as a quality control measure.
6. Evaluation of various emulsion types.
7. Evaluation of various processing chemicals and techniques.
8. Evaluation of backing materials for plate holders.

Example Applications

Some aspects of photographic indexing techniques merit additional discussion. All plates considered here were indexed in the illuminator described and were processed in an apparatus similar to that of Owens but based on a standard thermostatic bath.^{13,14)} A Consolidated Type 21-110 mass spectrometer was used to make ion exposures on plates, and a Jarrell-Ash Type JA-203 microphotometer was used to obtain light absorption data. Handling data are summarized in Table I. Processing was carried out at a higher temperature, but for a shorter time, than recommended for normal use.¹⁵⁾

Table I
Test Plate Handling Data

<u>Ion Exposure</u>	
Number	up to 16
Sample	1963 ASTM E-14
	Subcom. VII Steel
Monitor	0.92 x 10 ⁻¹¹ coulombs
(Target Value)	
Spark Pulsing Rate	30 per sec
Accelerating Voltage	17.2 kv
<u>Processing</u>	
Developer	Ilford ID-19
Fixer	Kodafix
Concentration of	Standard
Chemicals	
Temperature of	25 C
Bath	
Reciprocation	10 per min, 2.5 in stroke

Figure 5 shows a microphotometer record of various spectral lines in one exposure along with an index mark located between m/e 60 and 63. To shorten recording time, scanning speed between lines was increased tenfold and background scanned at the faster speed is not shown. Narrow dark edges on the magnified image of the index mark in the microphotometer correspond to the spikes on the chart record. The spikes are edge effects, and their widths of 0.03 millimeter correspond to the widths of first diffraction maxima calculated from the Cornu spiral for the geometry involved.¹⁶⁾ Type Q plates are not color-sensitized and are naturally more sensitive to blue radiation. Hence the averaging effect of incandescent light on diffraction phenomena is suppressed during plate sensitization. The diffraction spikes are not appreciably affected by photographic adjacency phenomena, such as Mackie lines and the Eberhard effect, at the low coating weight and reduced gelatin content of Type Q plates.¹⁷⁾

Characteristics of index line blackening across plates are illustrated in Figure 6. Plates showing longitudinal barring on darkroom inspection show much less uniform blackening than plates judged to be uniform by inspection. Penetration of light through the emulsion was investigated because large absorption of light by the front layers of emulsion would largely shield the rear layers from exposure and considerably reduce effectiveness of the indexing technique for detection of emulsion unevenness.

Penetration experiments were coupled with a study on reflectivity of backings by inserting a multilayer sandwich consisting of plate, spacing strips, second plate, and backing materials mounted on a black background in a plate holder for indexing exposures. The data in Table II for the processed plates clearly establish that light penetrated to the rear of the second plate and reflected off reflective backing materials. To prevent different reflectivities of the plate holder springs and body from interfering with uniformity of index marks, plates should be uniformly backed during indexing.

Table II
Effect of Backing on Optical Density

Backing Material (For 62.5 sec Exposure)	Density of Developed Q-3 Plate Section		
	Single Plate	Sandwiched Plates	
		Front	Rear
Aluminum Foil (bright side)	0.55	0.52	0.38
Aluminum Plate Holder	0.51	0.49	0.34
Stainless Steel Shimstock	0.51	0.47	0.31
Brass Shimstock (polished)	0.49	0.50	0.30
Copper Shimstock (polished)	0.48	0.47	0.30
Copper Shimstock (dull)	0.48	0.52	0.27
Black Paper (flat finish)	0.45	0.48	0.28

Spark-source mass spectrometers are frequently used for trace analysis, and any technique for improving detection capabilities merits serious evaluation. Ion response curves published for Type Q emulsions show threshold behavior at low exposure similar to that for photon exposure.^{8,15} Incremental response of a plate to photons can be improved by prefogging, to bring the emulsion to a more favorable portion of the response curve. If there is adequate reciprocity between ion and photon exposure, a similar increase in sensitivity to ions should be attained by giving a plate a pre-fogging with controlled light. The illuminator was used to determine photon response characteristics for Type Q-3 plates, and exposure levels for photon prefogging were selected from these data. Photon prefogging was applied to plates in the m/e 50-60 range over half the plate width; for comparison purposes the rest of the plate was left unfogged. Microphotometer data from the plates showed clearly that reciprocity does not hold between photon and ion exposures. While a plate region prefogged to 0.016 density showed a rather slight increase in sensitivity, the associated increase in noise level in the prefogged region was great enough to decrease substantially the sensitivity-to-noise ratio. As may be seen from Table III, prefogging to a higher density is even more undesirable, as both sensitivity and noise factors detract from detection capability of the Q-3 plate for ions. Photon prefogging of Q-3 plates should be avoided.

Table III
Relative Detection Capability of Prefogged Q-3 Plates

Density of Prefog	Relative Ion Sensitivity (Nonfogged = 1.00)	Density Units of Noise	Detection Capability
			Relative Sensitivity ($\frac{\text{Relative Sensitivity}}{\text{Noise}}$)
0.000	1.00	0.007	140
0.016	1.10	0.011	100
0.14	0.46	0.011	41

Summary

The foregoing examples show the usefulness of a versatile illuminator for indexing photographic plates in conjunction with mass spectrographic work. Many quality control functions can be performed with the illuminator described, and variants of handling technique can be evaluated positively and quickly. As a result, photographic indexing techniques can be a continuing aid to research in the field of solids mass spectrometry whenever ion-sensitive emulsions are used as detectors.

The variations in emulsion homogeneity and coating encountered during this research demonstrate without question that the mass spectroscopist may not tacitly assume that plates are satisfactory for quantitative purposes. All mass spectrographic plates should be inspected prior to use and should bear index bands as a permanent record of emulsion uniformity.

References

1. N. B. Hannay and A. J. Ahearn, *Anal. Chem.*, **26**, 1056 (1954).
2. R. D. Craig, G. A. Errock, and J. D. Waldron in "Advances in Mass Spectrometry," J. D. Waldron, Ed., Pergamon Press, New York, pp. 136-156 (1959).
3. Bulletin 21110, "Type 21-110 Mass Spectrometer," Analytical and Control Division, Consolidated Electrodynamics Corporation, Pasadena, Calif. (1960).
4. J. G. Gorman, E. J. Jones, and J. A. Hipple, *Anal. Chem.*, **23**, 438 (1951).
5. J. J. Thomson, "Rays of Positive Electricity," Longmans, Green & Co., London (1913).
6. F. W. Aston, "Mass Spectra and Isotopes," 2nd ed., Edward Arnold Ltd., London (1940).
7. E. B. Owens, *Applied Spectroscopy*, **16**, 148 (1962).
8. W. Rudloff, *Z. Naturforschung*, **17a**, 414 (1962).
9. R. D. Craig, G. A. Errock, and J. D. Waldron, *op. cit.*, p. 146.
10. British Iron and Steel Research Association Special Report No. 47, The Iron and Steel Institute, London (1952), p. 25.
11. J. R. Woolston, R.C.A. Laboratories, Princeton, N. J., private communication.
12. R. D. Craig, Regional Symposium on A.E.I. M.S. 7 Mass Spectrograph, sponsored by Picker X-Ray Corp., Pittsburgh, Pa., Dec. 12, 1962.
13. E. B. Owens, *Rev. Sci. Inst.*, **32**, 1420 (1961).
14. Catalog No. 74893, Precision Scientific Co., Chicago, designed to meet specifications for water bath, ASTM D323-58, Test for Vapor Pressure of Petroleum Products (Reid Method).
15. "Ilford Q Plates," Technical Information Sheet B524, Issue 1, Ilford Ltd., Ilford (1953).
16. M. Born and E. Wolf, "Principles of Optics - Electromagnetic Theory of Propagation, Interference and Diffraction of Light," Pergamon Press, New York (1959), pp. 431-433.
17. "Kodak Plates and Films for Science and Industry," 1st ed., Eastman Kodak Company, Rochester (1962), pp. 14-17.

THE ENERGY DISTRIBUTION OF IONS FORMED IN THE RF SPARK SOURCE

J. Rogers Woolston and Richard E. Honig
RCA Laboratories
Princeton, New Jersey

INTRODUCTION

The RF spark source, developed some 30 years ago by Dempster⁽¹⁾, is widely used today to produce ions for the study and trace analysis of solids by mass spectrometry. While there have been recent technological advances in spark source circuitry^(2,3,4), the physical processes leading to ion production are not yet clearly understood. Even the wide energy distribution, which necessitates the use of a double-focussing mass spectrograph, has not been systematically investigated, although rough estimates of the energy spread have been quoted⁽⁵⁾.

The present study was undertaken to determine the shape of the energy distribution curve for ions formed in the spark, as a function of spark conditions (RF voltage, pulse length, repetition rate, gap width, etc.), electrode material, and other parameters. While double-focussing mass spectrographs in principle accept ions of any initial energy, practical considerations will limit the energy pass-band to about 600 ev. Therefore, if different elements have dissimilar energy distributions which are significantly wider than this pass-band, ions of one element may be largely rejected while those of another are mostly transmitted. It will be shown below that energy distributions do indeed differ widely, but that the results obtained can lead to reliable analyses with the mass spectrograph. While this paper was being prepared, a parallel study was published by Franzen and Hintenberger⁽⁶⁾ which deals with the same topic, but uses a somewhat different experimental approach.

THEORETICAL CONSIDERATIONS

Hintenberger et al⁽⁷⁾ have shown that the ion trajectory after deflection in a radial electrostatic field can be expressed as a power series expansion of α and β , where α is the entrance angle of an ion into the field, as shown in Fig. 1, and $\beta = \Delta v/v_0$. Here, Δv is the velocity deviation, and v_0 the normal velocity of that ion. To simplify the discussion, this paper will consider singly-charged ions only, which permits voltage V (volts) to be used interchangeably with energy E (electron-volts). When the normal ion accelerating voltage V_A is applied to the system, Δv is equivalent to the initial velocity of the ion. If fringing field effects are neglected and the expansion is limited to second-order terms, the following relation holds for the central plane of the system:

$$y = r(K_1\alpha + K_2\beta + K_{11}\alpha^2 + K_{12}\alpha\beta + K_{22}\beta^2) + x(L_1\alpha + L_2\beta + L_{11}\alpha^2 + L_{12}\alpha\beta + L_{22}\beta^2) \quad (1)$$

where

- x = the axial distance, in cm, measured from the exit boundary of the field
- y = the corresponding ion position, in cm, measured from the axis
- r = the radius of curvature, in cm, of the median equipotential of the electrostatic field

K_1, L_1 = parameters dependent upon the geometry of the system. Numerical values for quantities K_1 and L_1 are given in Table I.

TABLE I

NUMERICAL VALUES OF THE CONSTANTS OF EQUATION (1)
FOR ANY INSTRUMENT WITH MATTAUCH-HERZOG GEOMETRY AND $\sqrt{2} \phi_e = 45^\circ$

$K_1 = 1$	$L_1 = 0$
$K_2 = 0.2929320$	$L_2 = 1$
$K_{11} = -0.10774109$	$L_{11} = -1.4166666$
$K_{12} = 1.2357024$	$L_{12} = 3.2189513$
$K_{22} = -0.33925567$	$L_{22} = -1.1094758$
ϕ_e = the deflection angle of the electrostatic field	

If the maximum value of α is made negligibly small by suitably reducing the widths of the collimating slits S_3 and S_9 , Eq. (1) reduces to

$$y = r(K_2\beta + K_{22}\beta^2) + x(L_2\beta + L_{22}\beta^2) \quad (2)$$

Since $\beta^2 \ll \beta$, y is a nearly linear function of β .

If a photoplate is positioned at the exit boundary of the electrostatic field, or at any distance x beyond, it intercepts the ion beam and will graphically display this function. The photographic density of any area on the

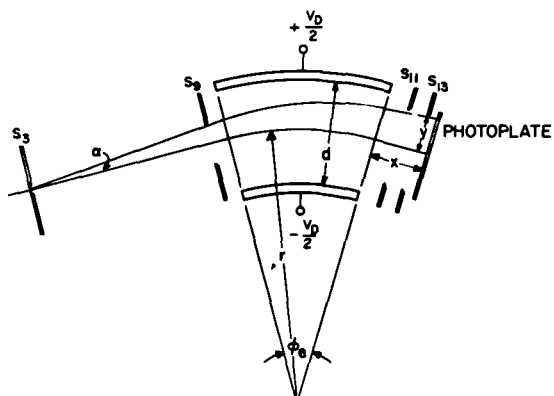


FIG.1. GEOMETRY OF ELECTROSTATIC FIELD

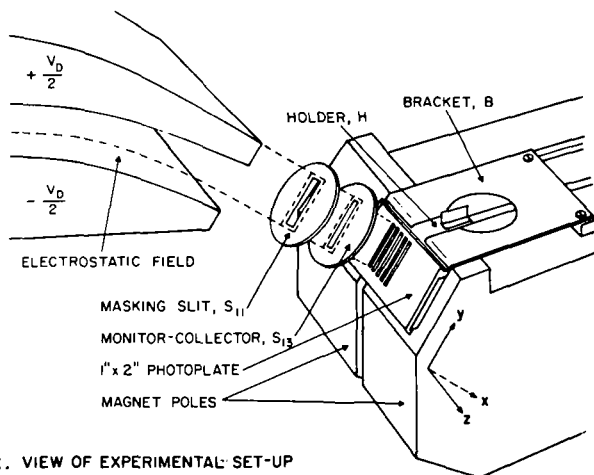


FIG.2. VIEW OF EXPERIMENTAL SET-UP

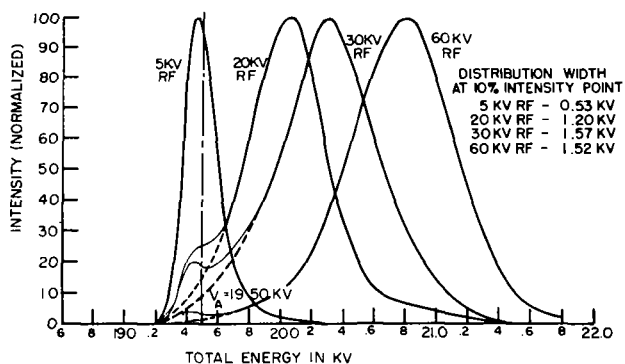


FIG.5. EFFECT OF RF SPARK VOLTAGE ON ENERGY DISTRIBUTION - NARROW SPARK GAP-Au IONS

plate can be converted to an ion density by means of an emulsion calibration curve. Thus this photoplate provides a "picture" of the energy distribution of ions leaving the ion source of the instrument. The energy range which will be recorded by the photoplate is directly proportional to the ion-accelerating voltage V_A , and is restricted by the size of the photoplate, limiting slit S_{11} or S_{13} ahead of the photoplate, or the spacing of the deflection plates of the electrostatic field. The smallest increment of energy resolvable is also directly proportional to V_A and depends principally on the residual value of α after S_3 and S_9 have been reduced in width as far as practical. The theoretical increment may be calculated by first determining the residual α from the geometry and using Eq. (1), setting y equal to zero. The equivalent β can be converted to an energy increment by the following relation:

$$\Delta V = 2 \beta V_A \text{ volts} \quad (3)$$

The incremental resolution also depends on the stability, including hum, of the accelerating and electrostatic field voltages.

The electrostatic field voltage V_D is related to V_A by

$$V_D = \frac{2 d V_A}{r} \quad (4)$$

where d = spacing between electrostatic plates, in cm

r = median radius of curvature, in cm.

Ion energy can be calibrated in terms of line location on the photoplate in a convenient manner. Thermal ions from a hot filament have a small energy spread, typical of the temperature of the emitting surface (~ 0.5 eV for a temperature of 1200°K). When such ions are accelerated by the normal accelerating voltage V_A , they follow the median equipotential of the electrostatic field and produce a sharp line at the middle of the photoplate. The center of this line indicates the location for ions with zero pre-acceleration energy, while the width of this line measures directly the smallest energy increment that can be resolved. If these thermal ions are then accelerated by a series of voltages that differ from V_A by convenient increments and cover the entire energy range included on the photoplate, a direct energy scale is obtained on the photoplate, which should agree with that predicted from Eq. (2).

EXPERIMENTAL

The source and electrostatic field section of a double-focussing mass spectrograph (AEI type MS7) was used for this study. The following modifications were made to the y-dimension of various slits: 1) source exit slit S_3 was reduced from 0.005" to 0.001"; 2) entrance slit S_9 of the electrostatic field was reduced from 0.080" to 0.001"; 3) grounded masking slit S_{11} just ahead of the monitor collector was increased from 0.120" to 0.700"; and 4) monitor collector slit S_{13} was increased from 0.120" to 0.500".

The two 0.001" slits give rise to a residual α of 0.00011. This corresponds to a calculated incremental energy resolution of 18.2 volts for $V_A = 20$ kv, which is in reasonable agreement with the measured resolution of 15 volts. For $V_A = 20$ kv, the 0.500" slit of the monitor collector permitted ions with total energies between 18.77 and 21.97 kv to be recorded on the photoplate. The center of the monitor slit corresponded to $V_A = 20.30$ kv as read on a calibrated digital voltmeter.

For all measurements made on ions formed by the RF spark, the electrostatic field voltage V_D was held constant at 2000 volts, as read on a voltmeter of one percent accuracy. Some thermal ion calibration runs were made with $V_D = 500$ and 1000 volts, to which correspond nominal accelerating voltages of 5.00 and 10.00 kv respectively. Table II summarizes the calculated and observed energy ranges and incremental energy resolutions obtainable at $V_A = 5, 10, \text{ and } 20$ kv.

TABLE II

Nominal V_A (kv)	Energy Range (kv)		Incremental Energy Resolution (V)	
	Calculated	Observed	Calculated	Observed
5	4.62-5.42	4.75-5.55		
	0.80	0.80	4.5	3.5
10	9.24-10.84	9.60-11.20		
	1.60	1.60	9.1	8
20	18.47-21.67	18.77-21.97		
	3.20	3.20	18.2	15

It should be noted that in any nominal range, the exact value of V_A may be shifted at will. For much of this work, V_A was selected so that ions with pre-acceleration energies from -1.00 to +2.00 kv could be displayed, as it was expected that most ions would have positive values of β . A 1" by 2" piece of an Ilford Q2 photoplate was mounted close to the entrance boundary of the

PLATE I AND DATA

BAND	MATERIAL	RF SPARK VOLTAGE (IN kV)	GAP WIDTH(n)	REMARKS
1	thermal-ion energy calibration			
2	Au(1)	5	n	20 kv range
3	"	20	"	"
4	"	30	"	"
5	"	40	"	"
6	"	50	"	"
7	"	60	"	"
8	"	60	"	"
9	"	60	"	"
10	"	20	"	magnet on
11	"	20	"	"
12	"	20	"	(c)
13	10 Ω cm Si(b)	20	"	(c)
14	"	20	"	"
15	"	20	"	"
16	"	20	"	"
17	"	30	"	"
18	"	30	"	"
19	"	30	"	"
20	"	30	"	"
21	"	60	"	"
22	"	60	"	"
23	"	30	"	magnet on
24	"	20	"	"
25	thermal-ion energy calibration			20 kv range
26	"			10 kv range
27	thermal-ion spectrum, $V_A = 19.00$ kv			magnet on

- (a) For Au bands 2-17, repetition rates of 50-100 pulses/sec were used with a pulse width of 50 μ sec.
- (b) For Si bands 19-24, repetition rates of 100-300 pulses/sec were used with a pulse width of 50 μ sec.
- (c) Potential of $S_1 = -180$ v with respect to the sample electrode.
- (d) RF spark voltages are estimated peak-to-peak values.
- (e) n - narrow spark gap, not quite abraded.
- * - wide spark gap, barely sustaining a spark.

FIGURE 1

PLATE II AND DATA

BAND	MATERIAL	RF SPARK VOLTAGE (IN kV)	CAPACIT	REMARKS
1	Au(1)	5	"	
2	"	10	"	
3	"	20	"	
4	"	30	"	
5	"	40	"	
6	"	50	"	
7	"	60	"	
8	thermal-ion energy calibration			2.5 kv range
9	"			5 kv range
10	"			20 kv range
11	Au(1)	5	"	
12	"	20	"	
13	Al	5	"	
14	"	30	variable	
15	"	30	variable	
16	"	60	variable	
17	.001 Ω cm Ge	10	"	
18	crystalline AgBr	10	"	

Bands 1-7 were produced by ions formed in a Triggered Low Voltage Arc Discharge ion source, to be described in a separate paper.

- (a) For bands 8-14 and 16-25, repetition rates of 50-5000 pulses/sec were used with pulse widths of 50-100 μ sec.
- (b) RF spark voltages are estimated peak-to-peak values.
- (c) * - wide spark gap, barely sustaining a spark.

FIGURE 4

magnetic analyzer as shown in Fig. 2. The position of the emulsion of this photoplate corresponded to $x = 7.40$ cm. The stainless steel bracket, B, was mounted from the low-mass end of the MS7 photoplate racking carriage. Thus, the 1" x 2" photoplate could be moved in the z-direction over the full range of lateral motion afforded by the racking mechanism, which allowed up to 31 exposures to be made on each plate. To install the photoplate, the instrument was vented, and the plate with its holder H inserted, under a safelight, through an opening in the top of the magnetic analyzer housing. To calibrate with thermal ions, *spodumene* (an alkali ion emitter) was coated on a tungsten filament and heated with about 12 watts of a-c power. Both the center-tap of the heater transformer and the first slit in the ion source were connected to V_A . Ion currents of 10^{-9} amp were readily obtainable from this source, though currents of 10^{-14} to 10^{-13} amp were sufficient for the exposures required. These currents are measured by an electrometer amplifier connected to the monitor-collector slit S_{13} . Masking slit S_{11} is so designed that S_{13} intercepts a fixed fraction of the total ion beam regardless of position or breadth of the beam in the y direction. An integrator, connected to the electrometer output, provides a direct measure of exposure in terms of charge in coulombs. $2 \cdot 10^{-14}$ coulomb was chosen for the calibration exposures in the 20 kv range. For accelerating voltages in the 5 kv and 10 kv ranges longer exposures, $1 \cdot 10^{-13}$ and $5 \cdot 10^{-14}$ coulomb respectively, were required to compensate for the decrease in response of the photoplate to ions of lower energy⁽⁸⁾. For the 20 kv range, exposures were made between 18.75 and 20.75 kv (the upper limit of the power supply), the accelerating voltage being increased in steps of 250 volts. To identify the voltage scale, exposures were also made at 19.90 and 20.10 kv. A similar procedure was used for the 5 kv and 10 kv ranges. To avoid line broadening and displacement by any residual magnetic field, the magnetic analyzer and all surrounding iron was thoroughly demagnetized with a color TV degaussing coil.

After the voltage calibration, the thermal ion source was replaced by pairs of bar-shaped samples which were sparked by the RF source under various spark conditions. Exposures of $1.5 \cdot 10^{-11}$ coulomb were found to be most satisfactory. When 31 exposures had been made on the photoplate, it was removed from the instrument and developed for three minutes in D19 at 20°C.

THE ENERGY DISTRIBUTIONS

Data were obtained for ions formed by the RF spark for the following materials: Au, high-resistivity Si, low-resistivity Ge, Al, and AgBr. For some of these substances, data were obtained for RF voltages ranging from 5 to 60 kv, with wide as well as narrow spark gaps. Fig. 3 is a reproduction of one of the 1" by 2" photoplates made which contains 27 separate bands. The essential data are entered opposite each individual band. Several qualitative observations may be made from Fig. 3. As a group, the energy distributions for Au ions (bands 2-12) are much narrower than those for Si (bands 13-24). Reasonably good reproducibility is obtained as can be seen in bands 3, 4, and 5 which were produced under identical conditions. For a narrow spark gap, the distribution maximum shifts to higher energies with increasing RF spark voltage (bands 2, 3, 6, and 8 corresponding to 5, 20, 30, and 60 kv spark voltage). It is also apparent that these effects are much more pronounced with Au than with the high-resistivity Si. The effect of the fringing field of the magnetic analyzer appears in bands 10, 23, and 27. The entire image is displaced a small amount to the left for the Au ions (band 10) and a greater amount for the lighter Si ions (band 23). In band 27 the thermal ion beam is split into a small mass spectrum.

A second plate is shown in Fig. 4. Again, a few qualitative observations may be made directly from Fig. 4. For a wide gap, increasing RF spark voltages produce a shift of the distribution maximum toward values lower than the applied voltage, and the distribution broadens (bands 8-14). Under the same conditions, both metals, Au and Al, appear very similar (bands 18 and 20). During a typical analysis, sparking occurs with a variable width gap, which produces a very broad distribution even for a metal (bands 21-23). The low-resistivity Ge is markedly different from high-resistivity Si (band 24 in Fig. 4 as contrasted with bands 13-24 in Fig. 3). AgBr has an anomalously narrow distribution unlike any of the others, and warrants further study (band 25).

All the bands on these photoplates were scanned with a recording micro-densitometer. The percent transmission-vs-distance tracings thus obtained were replotted, after percent transmission had been converted into ion density by means of an emulsion calibration curve. The thermal-ion energy calibration bands provided the energy abscissa for these plots. Several of these plots are reproduced in Figures 5, 6, and 8 and quantitatively show the effects of various parameters on the energy distributions. The widths of the distribu-

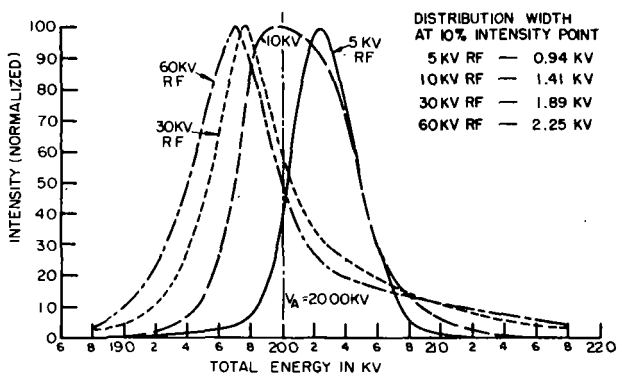


FIG. 6. EFFECT OF RF SPARK VOLTAGE ON ENERGY DISTRIBUTION-WIDE SPARK GAP-Au IONS

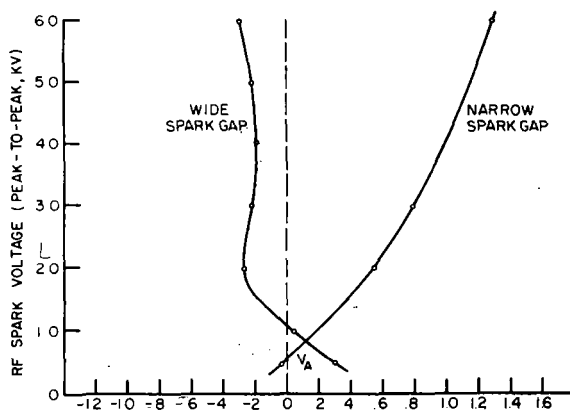


FIG. 7. DISPLACEMENT OF ENERGY DISTRIBUTION MAXIMUM FROM V_A IN KEV

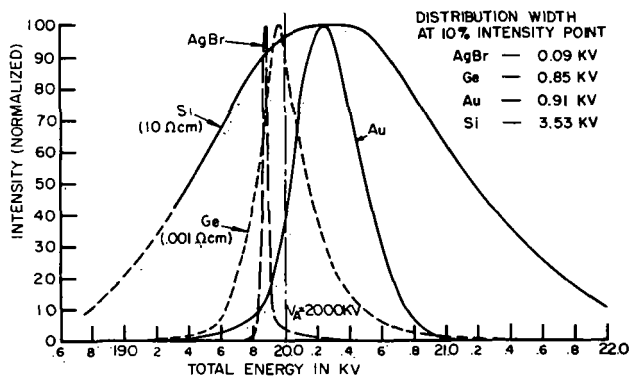


FIG. 8. ENERGY DISTRIBUTIONS OF IONS OF VARIOUS MATERIALS-WIDE SPARK GAP-LOW RF VOLTAGE

tions, measured at 10% intensity, are shown on the Figures.

Fig. 5 shows the effect of the RF spark voltage for Au ions with a narrow spark gap. Fig. 6 displays the same function for a wide spark gap. In Fig. 7 the energies corresponding to the distribution maxima are plotted for the distributions shown in Figures 5 and 6. They bring out clearly the unexpected and extreme dependence of the distribution shape and the position of the maximum on spark gap width. Since during an analysis it is practically impossible to maintain a fixed gap width, the energy distribution is likely to vary continuously. Fig. 8 shows for five different materials the energy distributions of the ions produced under similar source conditions, except for the high-resistivity Si which had to be run at a higher RF voltage. The two semiconductors, $10\ \Omega\text{-cm}$ Si and $0.001\ \Omega\text{-cm}$ Ge, differ markedly which suggests a dependence of the energy distribution upon sample resistivity. Indeed, the low resistivity Ge behaves very much like the metals. The AgBr is in a class by itself.

DISCUSSION

The curves shown in Figures 5, 6, and 8 are the energy distributions of the unresolved ion beam (including all multiply-charged, polyatomic, molecular, and impurity ions) for relatively pure materials. These curves are equivalent to the ion beam profile in the y-direction at the monitor-collector for the special condition of the near-zero α . Under normal analytical conditions, the ion beam is considerably broadened by the large α customarily employed. This has the effect of broadening the energy distributions, thus lessening the effect of differences between the distributions of various materials.

Nevertheless, energy distributions may well be important in their effect on RF spark-source analyses. Any instrument of Mattauch-Herzog geometry contains a physical limit in the y-direction of the ion beam in the space between the electrostatic and magnetic fields. This is usually in the form of a wide slit and is often erroneously referred to as a beta-stop or beta slit. The actual energy pass-band of this slit depends not only on its y-dimension, but also on the magnitude of α . In most instruments, however, the energy pass-band will be appreciably smaller than the distribution widths shown in Figure 9 (except for the peculiar case of AgBr). This can lead to serious discrimination effects.

Attempts to explain the shape of the various observed energy distributions are beyond the scope of this paper and will not be included here. It is to be noted, however, that it is difficult to explain the appearance of ions with "negative initial energies", e.g. ions with total energies appreciably less than the accelerating voltage. Whether the ions of impurities in a matrix have energy distributions different from each other or from the matrix ions is a point that has not been established in the present study, but should be pursued further.

CONCLUSIONS

Four general conclusions can be drawn from this work:

- 1) Various matrix materials exhibit rather different ion energy distributions under equivalent conditions.
- 2) These distributions are greatly affected by ion source parameters, such as spark-gap width and RF spark voltage.
- 3) Care must be taken in the geometrical design of an ion beam monitor-collector, located between the electrostatic and magnetic fields, to ensure that the ratio of beam collected-to-beam transmitted is constant under all conditions, i.e., for any energy distribution, for any accelerating voltage.
- 4) The accelerating voltage must be well regulated and resettable to a given value with good precision.

FUTURE WORK

It has been established that various matrix materials give rise to markedly different ion energy distributions. It remains now to determine the extent to which such materials retain these characteristics when they are themselves an impurity in another matrix since this may affect the analysis of trace impurities. This can only be accomplished by examining the energy distributions of the various ionic species after mass separation. Of further interest will be the distributions of the various multiply-charged and polyatomic ions as compared to singly-charged, monoatomic ions.

ACKNOWLEDGMENT

The authors gratefully acknowledge the competent technical assistance rendered by E. M. Botnick.

REFERENCES

1. A. J. Dempster, Rev. Sci. Instr. 7, 46 (1936)
2. N. B. Hannay, Rev. Sci. Instr. 25, 644-8 (July 1954)
3. R. D. Craig, G. A. Errock, and J. D. Waldron, "Advances in Mass Spectrometry," (J. D. Waldron, Ed.), Pergamon Press, London, 1959, pp. 136-156
4. C. F. Robinson, G. D. Perkins, and N. W. Bell, "Proceedings, 5th International Instruments and Measurements Conference," Stockholm, Sweden, Sept. 1960
5. H. E. Duckworth, "Mass Spectroscopy," Cambridge University Press, 1958, p. 41
6. J. Franzen and H. Hintenberger, Z. Naturf., 18A, 397-409 (1963)
7. H. Hintenberger and L. A. Konig, "Advances in Mass Spectrometry," (J. D. Waldron, Ed.), Pergamon Press, London, 1959, pp. 16-35
8. E. B. Owens, Appl. Spectr., 16, 148 (1962)
9. R. E. Honig, S. Glass, and J. R. Woolston, to be presented at the 6th International Conference on Ionization Phenomena in Gases, Paris, July 1963

Bibliography of Published and Unpublished Papers on Mass Spectrometry
for 1962

The following pages were prepared by Subcommittees II, III, and V as part of the Annual Report of Subcommittees, covering activities in their fields of interest. As was done last year, these bibliographies are included with the papers to provide a broader and more useful distribution of such information. In the present list, no specific attempt has been made to avoid multiple listings of papers of interest in several fields.

1962 Bibliography

Theoretical and Fundamental Aspects of Mass Spectrometry

Prepared by Subcommittee II

H. M. Rosenstock, National Bureau of Standards, Chairman
E. J. Catanzaro, U. S. Geological Survey
V. H. Dibeler, National Bureau of Standards
F. H. Field, Humble Oil and Refining Co.
J. T. Herron, National Bureau of Standards
R. W. Kiser, Kansas State University
M. Krauss, National Bureau of Standards
R. M. Reese, National Bureau of Standards
B. W. Steiner, National Bureau of Standards
A. L. Wahrhaftig, University of Utah
N. Wells, National Bureau of Standards

Preface

In view of the explosive growth of the number of papers bearing on the topic of this report, it was decided to restrict this report to a bibliography. One contributor, nevertheless, provided a very useful discussion, which is included. A serious attempt was made to include references which, though not considered mass spectrometry in the narrow sense, do give methods, discussions, results or applications which are very closely related. Some references published in 1963 are included, to narrow the gap between the cut-off date and the date where this bibliography will reach the intended users. There is some duplication of references. Evidently various people felt that a given paper was relevant to their area of coverage. The sections of this report are as follows:

1. Ionization and appearance potentials
2. Photoionization and related studies
3. Fundamental charged particle phenomena
4. Ion-molecule reactions
5. Free radicals and chemical kinetics
6. Quasi-equilibrium theory of mass spectra
7. Isotopic abundance and atomic weight
8. Miscellaneous

I. Ionization and Appearance Potentials

Bibliography

R. W. Kiser

1. D. A. Ansdell and F. M. Page, "DETERMINATION OF ELECTRON AFFINITIES. IV. ELECTRON AFFINITIES OF THE SULPHYDRYL RADICAL AND THE SULPHUR ATOM," Trans. Faraday Soc., 58, 1084 (1962).
2. M. Batley and L. E. Lyons, "ELECTRON AFFINITIES OF ORGANIC MOLECULES" Nature, 196, 573 (1962).
3. J. Berkowitz, "HEAT OF FORMATION OF THE CN RADICAL," J. Chem. Phys. 36, 2533 (1962).
4. J. Berkowitz and J. R. Marquat, "MASS SPECTROMETRIC STUDY OF THE MAGNESIUM HALIDES," J. Chem. Phys., 37, 1853 (1962).
5. J. Berkowitz and S. Wexler, "ON THE IONIZATION POTENTIAL OF THE CH_2 RADICAL," J. Chem. Phys. 37, 1476 (1962).
6. R. P. Burns, G. DeMaria, J. Drowart and M. G. Inghram, "MASS SPECTROMETRIC INVESTIGATION OF THE VAPORIZATION OF In_2O_3 ," J. Chem. Phys., 38, 1035 (1963).
7. R. Colin and J. Drowart, "THERMODYNAMIC STUDY OF TIN SULFIDE AND LEAD SULFIDE USING A MASS SPECTROMETER," J. Chem. Phys., 37, 1120 (1962).
8. J. E. Collin, "IONIZATION POTENTIAL OF NO_2 ," Nature, 196, 373 (1962).
9. G. F. Crable and G. L. Kearns, "EFFECT OF SUBSTITUENT GROUPS ON THE IONIZATION POTENTIALS OF BENZENES," J. Phys. Chem., 66, 436 (1962).
10. W. R. Cullen and D. C. Frost, "IONIZATION POTENTIALS OF SOME PERFLUOROALKYL ARSINES," Can. J. Chem., 40, 390 (1962).
11. R. K. Curran, "NEGATIVE ION FORMATION IN VARIOUS GASES AT PRESSURES UP TO 0.5 mm OF Hg," ASTM Committee E-14 on Mass Spectrometry, 10th Annual Meeting, New Orleans, La., June 3-8, 1962.
12. R. K. Curran, "FORMATION OF NO_2^- BY CHARGE TRANSFER AT VERY LOW ENERGIES," Phys. Rev., 125, 910 (1962).
13. S. Ehrenson, "A CLOSED FORM ANALYSIS OF THE LCAO-MO ω -TECHNIQUE. I. IONIZATION POTENTIALS AND ELECTRON AFFINITIES," J. Phys. Chem., 66, 706 (1962).
14. S. Ehrenson, "A CLOSED FORM ANALYSIS OF THE LCAO-MO ω -TECHNIQUE. II. MECHANICS OF THE TECHNIQUE," J. Phys. Chem., 66, 712 (1962).
15. F. A. Elder, C. Giese, B. Steiner and M. Inghram, "PHOTOIONIZATION OF ALKYL FREE RADICALS," J. Chem. Phys., 36, 3292 (1962).
16. S. N. Foner and R. L. Hudson, "IONIZATION AND DISSOCIATION OF HYDROGEN PEROXIDE BY ELECTRON IMPACT," J. Chem. Phys., 36, 2676 (1962).
17. S. N. Foner and R. L. Hudson, "MASS SPECTROMETRY OF THE HO_2 FREE RADICAL," J. Chem. Phys., 36, 2681 (1962).
18. S. N. Foner and R. L. Hudson, "MASS SPECTROMETRIC STUDIES OF METASTABLE NITROGEN ATOMS AND MOLECULES IN ACTIVE NITROGEN," J. Chem. Phys., 37, 1662 (1962).
19. D. C. Frost, D. Mak and C. A. McDowell, "PHOTOIONIZATION PROCESSES STUDIED BY MASS SPECTROMETRY," ASTM Committee E-14 on Mass Spectrometry, 10th Annual Meeting, New Orleans, La., June 3-8, 1962.

20. E. J. Gallegos and R. W. Kiser, "ELECTRON IMPACT SPECTROSCOPY OF THE FOUR- AND FIVE-MEMBERED, SATURATED HETEROCYCLIC COMPOUNDS CONTAINING NITROGEN, OXYGEN, AND SULFUR," J. Phys. Chem., 66, 136 (1962).
21. E. W. Godbole and P. Kebarle, "IONIZATION AND DISSOCIATION OF DEUTERATED ETHYL AND ISOPROPYL ACETATES AND ETHYL FORMATE UNDER ELECTRON IMPACT," Trans. Faraday Soc., 58, 1897 (1962).
22. B. G. Gowenlock, R. M. Haynes and J. R. Majer, "ELECTRON IMPACT MEASUREMENTS ON SOME ORGANOMERCURY COMPOUNDS," Trans. Faraday Soc., 58, 1905 (1962).
23. B. G. Gowenlock, J. R. Majer and D. R. Snelling, "BOND DISSOCIATION ENERGIES IN SOME AZO COMPOUNDS," Trans. Faraday Soc., 58, 670 (1962).
24. A. G. Harrison and T. W. Shannon, "AN ELECTRON IMPACT STUDY OF CHLOROMETHYL AND DICHLOROMETHYL DERIVATIVES," Can. J. Chem., 40, 1730 (1962).
25. J. B. Hasted and A. Y. J. Chong, "ELECTRON CAPTURE PROCESSES FOR MULTIPLY CHARGED IONS," Proc. Phys. Soc. (London), 80, 441 (1962).
26. B. G. Hobrock and R. W. Kiser, "ELECTRON IMPACT SPECTROSCOPY OF TETRAMETHYLGERMANIUM, TRIMETHYLSILANE, AND DIMETHYLMERCURY," J. Phys. Chem., 66, 155 (1962).
27. B. G. Hobrock and R. W. Kiser, "ELECTRON IMPACT SPECTROSCOPY OF PROPYLENE SULFIDE," J. Phys. Chem., 66, 1551 (1962).
28. B. G. Hobrock and R. W. Kiser, "ELECTRON IMPACT SPECTROSCOPY OF SULFUR COMPOUNDS. I. 2-THIABUTANE, 2-THIAPENTANE AND 2,3-DITHIABUTANE," J. Phys. Chem., 66, 1648 (1962).
29. B. G. Hobrock and R. W. Kiser, "ELECTRON IMPACT INVESTIGATIONS OF SULFUR COMPOUNDS. II. 3-METHYL-2-THIABUTANE, 4-THIA-1-PENTENE, AND 3,4-DITHIAHEXANE," J. Phys. Chem., 67, 648 (1963).
30. J. R. Hoyland and L. Goodman, "CHARGE DISTRIBUTION IN NEGATIVE IONS AND THE ELECTRON AFFINITIES OF CONJUGATED HYDROCARBONS," J. Chem. Phys., 36, 21 (1962).
31. M. Inokuti, "IONIZATION OF THE METHANE MOLECULE BY ELECTRON IMPACT," J. Chem. Phys., 37, 2387 (1962).
32. J. J. Kaufman, "THE EFFECT OF SUBSTITUTION ON THE IONIZATION POTENTIALS OF FREE RADICALS AND MOLECULES. III. ESTIMATION OF THE IONIZATION POTENTIALS OF CYCLOALKYL RADICALS AND CYCLIC AMINES BY σ_K VALUES," J. Am. Chem. Soc., 84, 4393 (1962).
33. J. J. Kaufman, "THE EFFECT OF SUBSTITUTION ON THE IONIZATION POTENTIALS OF FREE RADICALS AND MOLECULES. IV. σ_K VALUES FOR ALCOHOLS, ETHERS, THIOLS AND SULFIDES," J. Phys. Chem., 66, 2269 (1962).
34. J. J. Kaufman, W. S. Koski, L. J. Kuhns and R. W. Law, "APPEARANCE AND IONIZATION POTENTIALS OF SELECTED FRAGMENTS FROM DECABORANE, $B_{10}H_{14}$," J. Am. Chem. Soc., 84, 4198 (1962).
35. R. W. Kiser, "STUDIES OF THE SHAPES OF IONIZATION-EFFICIENCY CURVES OF MULTIPLY-CHARGED MONATOMIC IONS. I. INSTRUMENTATION AND RELATIVE ELECTRONIC-TRANSITION PROBABILITIES FOR KRYPTON AND XENON IONS," J. Chem. Phys., 36, 2964 (1962).
36. R. W. Kiser and E. J. Gallegos, "A TECHNIQUE FOR THE RAPID DETERMINATION OF IONIZATION AND APPEARANCE POTENTIALS," J. Phys. Chem., 66, 947 (1962).
37. R. W. Kiser and B. G. Hobrock, "THE IONIZATION POTENTIALS OF CYCLOPROPYL RADICAL AND CYCLOPROPYL CYANIDE," J. Phys. Chem., 66, 957 (1962).

38. R. W. Kiser and B. G. Hobrock, "THE IONIZATION POTENTIAL OF HYDROGEN DISULFIDE (H_2S_2)," J. Phys. Chem., 66, 1214 (1962).
39. W. F. Kuhn, C. J. Varsel and W. A. Powell, "MASS SPECTRA CORRELATIONS AND APPEARANCE POTENTIALS OF THE MAJOR TOBACCO ALKALOIDS," ASTM COMMITTEE E-14 ON MASS SPECTROMETRY, 10th ANNUAL MEETING, NEW ORLEANS, LA., JUNE 3-8, 1962.
40. A. Kuppermann and L. M. Raff, "DETERMINATION OF ELECTRONIC ENERGY LEVELS OF MOLECULES BY LOW-ENERGY ELECTRON IMPACT SPECTROSCOPY," J. Chem. Phys., 37, 2497 (1962).
41. C. Lifshitz and F. A. Long, "APPEARANCE POTENTIALS AND THE MASS SPECTRA OF FLUORINATED OLEFINS," ASTM Committee E-14 on Mass Spectrometry, 10th Annual Meeting, New Orleans, La., June 3-8, 1962.
42. J. R. Majer and C. R. Patrick, "ELECTRON IMPACT ON SOME HALOGENATED COMPOUNDS," Trans. Faraday Soc., 58, 17 (1962).
43. W. McGowan and L. Kerwin, "ON THE APPLICATION OF ASTON BANDS AND APPEARANCE POTENTIAL MEASUREMENTS TO ION COLLISION STUDIES," Can. J. Phys., 41, 316 (1963).
44. C. E. Melton, "IONIZATION AND EXCITATION PROCESSES IN ARGON, KRYPTON AND THE C_2 HYDROCARBONS PRODUCED BY VARIOUS MEANS," J. Chem. Phys., 37, 562 (1962).
45. P. Natalis, "BEHAVIOR OF CIS AND TRANS ISOMERS OF DECALINE UNDER ELECTRON IMPACT," Nature, 197, 284 (1963).
46. C. W. Nutt and A. J. Biddlestone, "THEORY AND APPLICATIONS OF MOLECULAR-BEAM TECHNIQUES FOR THE DESIGN OF COLLISION-FREE SAMPLING SYSTEMS. IV. APPEARANCE POTENTIAL AND SCATTERING CROSS SECTION OF OXYGEN ATOMS FROM AND R. F. DISCHARGE (10 MCSEC)," Trans. Faraday Soc., 58, 1368 (1962).
47. T. J. Palmer and F. P. Lossing, "FREE RADICALS BY MASS SPECTROMETRY. XXVIII. THE HS , CH_3S , AND PHENYL-S RADICALS; IONIZATION POTENTIALS AND HEATS OF FORMATION," J. Am. Chem. Soc., 84, 4661 (1962).
48. R. F. Pottie and F. P. Lossing, "FREE RADICALS BY MASS SPECTROMETRY. XXIX. IONIZATION POTENTIALS OF SUBSTITUTED CYCLOPENTADIENYL RADICALS," J. Am. Chem. Soc., 85, 269 (1963).
49. W. C. Price, P. V. Harris and T. R. Passmore, "THE IONIZATION AND DISSOCIATION ENERGIES OF MOLECULES AND RADICALS," J. Quant. Spectrosc. Radn. Transfer, 2, 327 (1962).
50. F. E. Saalfeld and H. J. Svec, "THE MASS SPECTRA OF VOLATILE HYDRIDES. I. THE MONOELEMENTAL HYDRIDES OF THE GROUP IVB AND VB ELEMENTS," Inorg. Chem., 2, 46 (1963).
51. F. E. Saalfeld and H. J. Svec, "THE MASS SPECTRA OF VOLATILE HYDRIDES. II. SOME HIGHER HYDRIDES OF THE GROUP IVB AND VB ELEMENTS," Inorg. Chem., 2, 50 (1963).
52. A. A. Sandoval, H. C. Moser and R. W. Kiser, "IONIZATION AND DISSOCIATION PROCESSES IN PHOSPHORUS TRICHLORIDE AND DIPHOSPHORUS TETRACHLORIDE," J. Phys. Chem., 67, 124 (1963).
53. R. I. Schoen, "ABSORPTION, IONIZATION AND ION-FRAGMENTATION CROSS SECTIONS OF HYDROCARBON VAPORS UNDER VACUUM-ULTRAVIOLET RADIATION," J. Chem. Phys., 37, 3032 (1962).
54. G. J. Schulz, "CROSS SECTIONS AND ELECTRON AFFINITY FOR O^- IONS FROM O_2 , CO , AND CO_2 BY ELECTRON IMPACT," Phys. Rev., 128, 178 (1962).

55. G. J. Schulz and J. T. Dowell, "EXCITATION OF VIBRATIONAL AND ELECTRONIC LEVELS IN O₂ BY ELECTRON IMPACT," *Phys. Rev.*, 128, 174 (1962).
56. M. L. Seman and L. M. Branscomb, "STRUCTURE AND PHOTODETACHMENT SPECTRUM OF THE ATOMIC CARBON NEGATIVE ION," *Phys. Rev.*, 125, 1602 (1962).
57. R. C. Shenkel, B. G. Hobrock and R. W. Kiser, "THE IONIZATION POTENTIAL OF (ISO)THIOCYANIC ACID," *J. Phys. Chem.*, 66, 2074 (1962).
58. W. C. Steele and F. G. A. Stone, "AN ELECTRON IMPACT STUDY OF 1,1,1-TRIFLUOROETHANE, 1,1,1-TRIFLUOROPROPANE AND 3,3,3-TRIFLUOROPROPENE," *J. Am. Chem. Soc.*, 84, 3450 (1962).
59. W. C. Steele and F. G. A. Stone, "SILICON-SILICON BOND DISSOCIATION ENERGIES IN DISILANE AND HEXACHLORODISILANE," *J. Am. Chem. Soc.*, 84, 3599 (1962).
60. W. C. Steele, L. D. Nichols and F. G. A. Stone, "AN ELECTRON IMPACT INVESTIGATION OF SOME ORGANOBORON DIFLUORIDES," *J. Am. Chem. Soc.*, 84, 1154 (1962).
61. W. C. Steele, L. D. Nichols and F. G. A. Stone, "THE DETERMINATION OF SILICON-CARBON AND SILICON-HYDROGEN BOND DISSOCIATION ENERGIES BY ELECTRON IMPACT," *J. Am. Chem. Soc.*, 84, 4441 (1962).
62. B. Steiner, M. L. Seman and L. M. Branscomb, "ELECTRON AFFINITY OF ATOMIC IODINE," *J. Chem. Phys.*, 37, 1200 (1962).
63. D. P. Stevenson and D. O. Schissler, "MASS SPECTROMETRY AND RADIATION CHEMISTRY," in *Actions Chimiques et Biologiques des Radiations*, Vol. 5, Edited by M. Haissinsky, Masson et Cie, Paris, 1961. pp. 167-271.
64. A. Streitwieser, Jr., "A MOLECULAR ORBITAL STUDY OF THE EFFECT OF METHYL GROUPS ON IONIZATION POTENTIALS," *J. Phys. Chem.*, 66, 368 (1962).
65. Y. Tanaka and A. S. Jursa, "HIGHER IONIZATION POTENTIALS OF NO₂," *J. Chem. Phys.*, 36, 2493 (1962).
66. R. Taubert and F. P. Lossing, "FREE RADICALS BY MASS SPECTROMETRY. XXVII. IONIZATION POTENTIALS OF FOUR PENTYL RADICALS," *J. Am. Chem. Soc.*, 84, 1523 (1962).
67. D. W. Turner and M. I. Al Jobory, "DETERMINATION OF IONIZATION POTENTIALS BY PHOTOELECTRON ENERGY MEASUREMENT," *J. Chem. Phys.*, 37, 3007 (1962).
68. G. Verhaegen, F. E. Stafford, M. Ackerman and J. Drowart, "MASS SPECTROMETRIC INVESTIGATION OF GASEOUS SPECIES IN THE SYSTEM BORON-CARBON," *Nature*, 193, 1280 (1962).
69. Y. Wada and R. W. Kiser, "ELECTRON IMPACT SPECTROSCOPY OF SOME SUBSTITUTED OXIRANES," *J. Phys. Chem.*, 66, 1652 (1962).
70. K. Watanabe, T. Nakayama and J. Mottl, "IONIZATION POTENTIALS OF SOME MOLECULES," *J. Quant. Spectrosc. Radn. Transfer*, 2, 369 (1962).
71. G. L. Weissler, "CROSS SECTION MEASUREMENTS FOR SOME PHOTON-GAS INTERACTION PROCESSES," *J. Quant. Spectrosc. Radn. Transfer*, 2, 383 (1962).
72. P. Wilmenius and E. Lindholm, "DISSOCIATION OF METHANOL MOLECULE IONS FORMED IN CHARGE EXCHANGE COLLISIONS WITH POSITIVE IONS," *Arkiv Fys.*, 21, 97 (1962).
73. E. G. Wilson, J. Jortner and S. A. Rice, "A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON DIFLUORIDE," *J. Am. Chem. Soc.*, 85, 813 (1963).

II. Photoionization and Related Studies

R. M. Reese and V. H. Dibeler

1. Back, R. A. and Walker, D. C., J. Chem. Phys. 37, 2348 (1962). PHOTOCHEMISTRY IN THE PHOTO-IONIZATION REGION. I. APPARATUS AND TECHNIQUES.
2. Balloffet, G., Romand, J. and Kieffer, J., Spectrochimica Acta 18, 791 (1962). EMISSION SOURCE WITH CONTINUOUS SPECTRUM FROM THE VISIBLE TO THE X-RAY REGION.
3. Bayer, K. D., Becker, K. H., Welge, K. H., Z. Naturforsch. 17a, 676 (1962), FLASH PHOTOLYSIS OF NH_3 IN THE VACUUM ULTRAVIOLET.
4. Biberman, L. M., Norman, G. E., Ul'yanov, K. N., Astron. Zh. 39, 107 (1962). THE PHOTOIONIZATION OF EXCITED COMPLEX ATOMS AND IONS.
5. Black, G., Porter, G., Proc. Royal Soc. 266, 185 (1962), VACUUM ULTRAVIOLET FLASH PHOTOLYSIS OF WATER VAPOR.
6. Branscomb, L. M., Pure Appl. Phys. 13, 100 (1962), PHOTODETACHMENT.
7. Comes, F. J. and Lessman, W., Z. Naturforsch. 17a, 704 (1962). ION FORMATION IN NITROGEN.
8. COMMISSION ON STANDARDS OF WAVE-LENGTHS AND TABLES OF SPECTRA, Trans. Int. Astron. Union XIA, 97 (1962).
9. Cooper, J. W., Phys. Rev. 128, 681 (1962), PHOTOIONIZATION FROM OUTER ATOMIC SUBSHELLS. A MODEL STUDY.
10. Ditchburn, R. W., Pure Appl. Phys. 13, 79 (1962), PHOTOIONIZATION PROCESSES.
11. Doering, J. P. and Mahan, D. H., J. Chem. Phys. 36, 669 (1962), PHOTOIONIZATION OF NITRIC OXIDE.
12. Ehrenson, S., J. Chem. Phys. 37, 455 (1962), PHOTO- AND SPECTROSCOPIC IONIZATION POTENTIALS IN THE ω -TECHNIQUE FRAMEWORK.
13. Elder, F. A., Giese, C., Steiner, B., and Inghram, M. G., J. Chem. Phys. 36, 3292 (1962). PHOTOIONIZATION OF ALKYL FREE RADICALS.
14. Feates, F. S., Knight, B., and Richards, E. W. T., Spectrochim. Acta 18, 485 (1962), HIGH INTENSITY VACUUM ULTRAVIOLET SOURCE.
15. Frost, D. C., Mak, D. and McDowell, C. A., Can. J. Chem. 40, 1064 (1962), THE PHOTOIONIZATION OF NO_2 .
16. Garron, R., Compt. Rend. 254, 243 (1962), PHOTOELECTRIC YIELD OF THIN ALUMINUM LAYERS.
17. Golomb, D., Watanabe, K., Marmo, F. F., J. Chem. Phys. 36, 958 (1962), ABSORPTION COEFFICIENTS OF SULFUR DIOXIDE IN THE VACUUM ULTRAVIOLET.
18. Harteck, P., Reeves, R. R., Angew. Chem. 74, 1 (1962). CHEMICAL REACTIONS IN THE ATMOSPHERE.
19. Hartman, P. L., Rev. Sci. Instr. 33, 1082 (1962), VACUUM ULTRAVIOLET MONOCHROMATOR.
20. Heroux, L. and Hinteregger, H. E., Appl. Opts. 1, 701 (1962), PHOTOELECTRON ENERGY DISTRIBUTION MEASUREMENTS FOR 10 TO 50 ev PHOTONS WITH A PLANAR ANALYSER AND ELECTRON MULTIPLIER.

21. Hinteregger, H. E., J. Atmospheric Sci. 19, 351 (1962), ABSORPTION SPECTROMETRIC ANALYSIS OF THE UPPER ATMOSPHERE IN THE EXTREME ULTRAVIOLET REGION.
22. Huffman, R. E., Tanaka, Y., Larrabee, J. C., J. Opt. Soc. Am. 52 851 (1962), NEW VACUUM ULTRAVIOLET EMISSION CONTINUA OF HELIUM PRODUCED IN HIGH-PRESSURE DISCHARGES.
23. Jackson, W. N., and McNesby, J. R., J. Am. Chem. Soc., 83, 84 (1962), PHOTOLYSIS OF HEXADEUTEROACETONE IN THE PRESENCE OF 2,2-DIDEUTERO PROPANE DECOMPOSITION OF THE N-PROPYL RADICAL.
24. Jeppesen, M. A., J. Opt. Soc. Am. 52 1081 (1962), PHOTOELECTRIC EMITTANCE FROM GOLD FILMS AS A FUNCTION OF FILM THICKNESS.
25. Kato, R., J. Phys. Soc. Japan 17, 413 (1962), OPTICAL PROPERTIES OF LITHIUM FLUORIDE IN THE EXTREME ULTRAVIOLET.
26. Kay, J. G., Kuebler, N. A., Nelson, L. S., Nature 194, 671 (1962), VACUUM ULTRAVIOLET ABSORPTION SPECTRA OF FLASH-HEATED LEAD REACTING WITH VARIOUS GASES.
27. King, G. W., Moule, D., Can. J. Chem. 40, 2057 (1962), THE ULTRAVIOLET ABSORPTION SPECTRUM OF NITROUS ACID IN THE VAPOR STATE.
28. Kulikov, S. A., Optika i Spektroskopiya 13, 754 (1962), CONFERENCE ON INSTRUMENTS AND METHODS FOR THE INVESTIGATION IN VACUUM OF THE ULTRAVIOLET REGION OF THE SPECTRUM.
29. Lincke, R., Wilkerson, T. D., Rev. Sci. Instr. 33, 911 (1962), NEW DETECTOR FOR THE VACUUM ULTRAVIOLET.
30. McNesby, J. R., Tanaka, I., and Okabe, H., J. Chem. Phys. 36, 605 (1962), VACUUM ULTRAVIOLET PHOTOCHEMISTRY, III. PRIMARY PROCESSES IN THE VACUUM ULTRAVIOLET PHOTOLYSIS OF WATER AND AMMONIA.
31. Mahan, B. H. and Mandel, R., J. Chem. Phys. 37, 207 (1962). VACUUM ULTRAVIOLET PHOTOLYSIS OF METHANE.
32. Milazzo, G., Pure Appl. Chem. 4, 135 (1962), VACUUM ULTRAVIOLET SPECTROSCOPY.
33. Milazzo, G., Sci. Rept. Inst. Super. Sanita 2, 13 (1962), MOLECULAR SPECTROSCOPY IN THE VACUUM ULTRAVIOLET.
34. Milgram, A., Givens, M. P., Phys. Rev. 125, 1506 (1962), EXTREME ULTRAVIOLET ABSORPTION BY LITHIUM FLUORIDE.
35. Mohler, F. L., U. S. Dept. Comm., Office Tech. Serv. P. B. Rept. 161,632 (1962), PHOTOIONIZATION OF ATOMS AND MOLECULES.
36. Moore, C. E., NBS Circular No. 488, Sects. 3, 4, and 5. (1962), AN ULTRAVIOLET MULTIPLE TABLE.
37. Newburgh, R. G., Heroux, J., Hinteregger, H. E., Applied Optics 1, 733 (1962). TWO LIGHT SOURCES FOR USE IN THE EXTREME ULTRAVIOLET.
38. Ogawa, M. and Tanaka Y., Can. J. Phys. 40, 1593 (1962), RYDBERG ABSORPTION SERIES OF N_2 .
39. Okabe, H. and McNesby, J. R., J. Chem. Phys. 36, 601 (1962). VACUUM ULTRAVIOLET PHOTOCHEMISTRY. II. PHOTOLYSIS OF ETHYLENE.
40. Okabe, H. and McNesby, J. R., J. Chem. Phys. 37, 1340 (1962). VACUUM ULTRAVIOLET PHOTOCHEMISTRY. IV. PHOTOLYSIS OF PROPANE.
41. Patterson, D. A. and Vaughan, W. H., Rept. NRL. Prog. 1962, OPTICAL PROPERTIES OF LiF IN THE VACUUM ULTRAVIOLET.

42. Pisimenny, V. D., Podgorny, I. M., Sukever, S., Zh. Eksper. Theor. Fiz. 43, 2008 (1962), INVESTIGATION OF VACUUM ULTRAVIOLET RAYS FROM A POWERFUL PULSED DISCHARGE.
43. PROCEEDINGS OF THE FIRST INTERNATIONAL CONFERENCE ON VACUUM ULTRAVIOLET RADIATION PHYSICS, J. Quantitative Spectroscopy and Radiative Transfer, Oct./ Dec. 1962, Pergamon Press.
44. Reed, R. I., Academic Press, London, (1962), ION PRODUCTION BY ELECTRON IMPACT.
45. Reese, R. M., Anal. Chem. 34, 243R (1962), MASS SPECTROMETRY.
46. Sampson, J. A. R. and Liebl, H., Rev. Sci. Instr. 33, 1340 (1962), DUOPLASMATRON AS A VACUUM ULTRAVIOLET LIGHT SOURCE.
47. Sampson, J. A. R., Marmo, F. F. and Watanabe, K., J. Chem. Phys. 36, 783 (1962), ABSORPTION AND PHOTOIONIZATION COEFFICIENTS OF PROPYLENE AND BUTENE-1 IN THE VACUUM ULTRAVIOLET.
48. Scheer, M. D., McNesby, J. R. and Okabe, H., J. Chem. Phys. 36, 3504 (1962). VACUUM ULTRAVIOLET PHOTOLYSIS OF SOLID ETHANE AT 77°K.
49. Schoen, R. I., J. Chem. Phys. 37, 2032 (1962), ABSORPTION, IONIZATION AND ION-FRAGMENTATION CROSS SECTIONS OF HYDROCARBON VAPORS UNDER VACUUM ULTRAVIOLET.
50. Timusk, T., Dissert, Abs. 22, 4060 (1962), LUMINESCENCE STUDY OF ALKALI HALIDES IN THE VACUUM ULTRAVIOLET.
51. Tousey, R., Appl. Opt. 1, 679 (1962), EXTREME ULTRAVIOLET: PAST AND FUTURE.
52. Turner, D. W. and Al Jobory, M. I., J. Chem. Phys. 37, 3007 (1962). DETERMINATION OF IONIZATION POTENTIALS BY PHOTO-ELECTRON ENERGY MEASUREMENTS.
53. Vilesov, F. I., Akopyan, M. E., Prib. i Tekh. Eksp. 7, 145 (1962), PHOTOIONIZATION AND ITS APPLICATION IN ANALYTIC MASS SPECTROSCOPY.
54. Walker, W. C., J. Opt. Soc. Am. 52, 223 (1962). EXTREME ULTRAVIOLET REFLECTION SPECTRUM OF LiF.
55. Watanabe, K., Hinteregger, H. E., J. Geophys. Res. 67, 999 (1962), PHOTOIONIZATION RATES IN THE E AND F REGIONS.
56. Wilkinson, P. G. and Angel, D. W., J. Opt. Soc. Am. 52, 1120 (1962). EVALUATION OF A SPECIALLY COATED CONCAVE DIFFRACTION GRATING IN THE VACUUM ULTRAVIOLET.
57. Zhirnov, V. A., Zh. Eksp. i Teor. Fiz. 42, 1097 (1962). EFFECTIVE CROSS-SECTIONS FOR PHOTOIONIZATION OF Li IONS.

III. FUNDAMENTAL CHARGED PARTICLE PHENOMENA

Bruce Steiner
Nikita Wells

Charge Exchange

1. Afrosimov, V.V., Il'in, R.N., Oparin, V.A., Solov'ev, E.S., and Fedorenko, N.V., Soviet Phys.-JETP, 14, 747. IONIZATION OF ARGON BY ATOMS, AND SINGLY OR DOUBLY CHARGED IONS OF NEON AND ARGON.
2. Bates, D.R., and Boyd, Anne. H., Proc. Phys. Soc. (London) 80, 1301. EFFECT ON SYMMETRICAL RESONANCE CHARGE TRANSFER CROSS SECTIONS OF CHANGE IN RELATIVE MOTION DURING ENCOUNTER.
3. Boelrijk, N., and Hamill, W.H., J. Am. Chem. Soc., 84, 730. EFFECTS OF RELATIVE VELOCITY UPON GASEOUS ION-MOLECULE REACTIONS; CHARGE TRANSFER TO THE NEOPENTANE MOLECULE.
4. Bourdeau, R.E., Whipple, E.C., Jr., Donley, J.L., and Bauer, S.J., J. Geophys. Res., 67, 467. EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF HELIUM IONS BASED ON EXPLORER VIII SATELLITE DATA.
5. Crable, George F., and Kearns, Gerard L., J. Chem. Phys., 36, 558. CHARGE-EXCHANGE PHENOMENA IN A MASS SPECTROMETER.
6. Curran, R.K., Phys. Rev., 125, 910. FORMATION OF NO_2^- BY CHARGE TRANSFER AT VERY LOW ENERGIES.
7. Dahler, J.S., Franklin, J.L., Munson, M.S.B., and Field, E.H., J. Chem. Phys., 36, 3332. RARE-GAS MOLECULE-ION FORMATION BY MASS SPECTROMETRY. KINETICS OF Ar_2^+ , Ne_2^+ , and He_2^+ FORMATION BY SECOND-AND THIRD-ORDER PROCESSES.
8. Dehmeit, H.G., and Major, F.G., Phys. Rev. Letters, 8, 213. ORIENTATION OF $(\text{He } 4^+)$ IONS BY EXCHANGE COLLISIONS WITH CESIUM ATOMS.
9. Dmitriev, T.S., Nikolaev, V.S., Fateeva, L.N., and Teplove, Ya. A., Soviet Phys.-JETP, 15, 11. EXPERIMENTAL STUDY OF ELECTRON LOSS BY MULTIPLY CHARGED IONS IN GASES.
10. Dmitriev, I.S., Nikolaev, V.S., Fateeva, L.N., and Teplova, Ya. A., Soviet Phys.-JETP, 16, 259. INVESTIGATION OF THE LOSS OF SEVERAL ELECTRONS BY FAST MULTIPLY CHARGED IONS.
11. Field, F.H., Head, Harlan N., and Franklin, J.L., J. Am. Chem. Soc., 84, 1118. REACTIONS OF GASEOUS IONS. XI. IONIC REACTIONS IN KRYPTON-METHANE AND ARGON-METHANE MIXTURES.
12. Filippenko, L.G., Soviet Phys.-Tech. Phys., 7, 254. FEATURES OF THE IONIZATION PROCESSES IN HEAVY ATOMS AND IONS.
13. Fite, W.L., Rutherford, J.A., Snow, W.R., and van Lint, V.A.J., Discussions of Faraday Soc., 33, 264. ION-NEUTRAL COLLISIONS IN AFTERGLOWS.
14. Fite, W.L., Smith, A.C.H., and Stebbings, R.F., Proc. Roy. Soc. (London)A 268, 527. CHARGE TRANSFER IN COLLISIONS INVOLVING SYMMETRIC AND ASYMMETRIC RESONANCE.
15. Flaks, I.P., Ogurtsov, G.N., and Fedorenko, N.V., Soviet Phys.-JETP, 14, 781. SLOW-IONS PRODUCED IN GASES UPON PASSAGE OF FAST ATOM AND ION BEAMS.
16. Flaks, I.P., Ogurtsov, G.N., and Fedorenko, N.V., Soviet Phys.-JETP, 14, 1027. IONIZATION IN THE COLLISIONS OF Ne^{n+} with Xe ATOMS AND OF Xe^{n+} with Ne ATOMS ($n = 0, 1, 2, 3, 4$)
17. Gerasimenko, V.I., Soviet Phys.-JETP, 14, 789. TWO-ELECTRON CHARGE EXCHANGE OF PROTONS IN HELIUM DURING FAST COLLISIONS.

18. Hanson, W.B., J. Geophys. Res., 67, 183. UPPER-ATMOSPHERE HELIUM IONS.
19. Hasted, J.B., and Lee, A.R., Proc. Phys. Soc. (London), 79, 702. THE NEAR-ADIABATIC CRITERION IN CHARGE TRANSFER COLLISIONS.
20. Hasted, J.B., and Chong, A.Y.J., Proc. Phys. Soc. (London), 80, 441. ELECTRON CAPTURE PROCESSES FOR MULTIPLY CHARGED IONS.
21. Henglein, A., and Muccini, G.A., Z. Naturforsch., 17a, 452. MASS SPECTROMETRIC OBSERVATIONS OF ELECTRON AND PROTON TRANSFER REACTIONS BETWEEN POSITIVE IONS AND NEUTRAL MOLECULES.
22. Heberman, M.N., Phys. Rev., 127, 799. PARTIAL IONIC STOPPING POWER AND THE ENERGY EXPENDED IN ELECTRON CAPTURE AND LOSS COLLISIONS OF PROTONS IN HYDROGEN GAS. II
23. Islam, M., Hasted, J.B., Gilbody, H. B., and Ireland, J.V., Proc. Phys. Soc., (London), 79, 1118. CHARGE TRANSFER REACTIONS OF DOUBLY CHARGED IONS.
24. Johnson, B.L., J. Appl. Phys., 33, 739. CHARGE TRANSFER SCATTERING IN HIGH-VELOCITY NEUTRAL PARTICLE PRODUCTION.
25. Lockwood, Grant J., and Everhart, Edgar, Phys. Rev., 125, 567. RESONANT ELECTRON CAPTURE IN VIOLENT PROTON-HYDROGEN ATOM COLLISIONS.
26. Mapleton, R.A., Phys. Rev., 126, 1477. ELECTRON CAPTURE FROM ATOMIC HYDROGEN BY PROTONS.
27. Marino, L.L., Smith, A.C.H., and Carplinger, E., Phys. Rev., 128, 2243. CHARGE TRANSFER BETWEEN POSITIVE CESIUM IONS AND CESIUM ATOMS.
28. Marmet, P., and Morrison, J.D., J. Chem. Phys., 36, 1238. SECONDARY REACTIONS IN THE ION CHAMBER OF A MASS SPECTROMETER.
29. Murakhver, Yu. E., Soviet Phys.-JETP., 15, 859. RESONANCE CHARGE EXCHANGE IN ATOMIC HYDROGEN.
30. Nikolaev, S., Fateeva, L.N., Dmitriev, I.S., and Teplova, Ya. A., Soviet Phys.-JETP, 14, 67. CAPTURE OF SEVERAL ELECTRONS BY FAST MULTICHARGED IONS.
31. Ogurtsov, G.N., and Flaks, I.P., Soviet Phys.-JETP, 15, 502. CHARGE EXCHANGE OF Xe^{3+} AND Xe^{4+} IN NEON.
32. Pivovarov, L.I., Tubaev, V.M., and Novikov, M.T., Soviet Phys.-JETP, 14, 20. ELECTRON LOSS AND CAPTURE BY 200-1500 keV HELIUM IONS IN VARIOUS GASES.
33. Pivovarov, L.I., Novikov, M.T., and Tubaev, V.M., Soviet Phys.-JETP, 15, 1035. ELECTRON CAPTURE BY HELIUM IONS IN VARIOUS GASES IN THE 300-1500 keV ENERGY RANGE.
34. Rapp, D., and Francis, W.E., J. Chem. Phys., 37, 2631. CHARGE EXCHANGE BETWEEN GASEOUS IONS AND ATOMS.
35. Smirnov, B.M., Soviet Phys.-JETP, 16, 81. INELASTIC COLLISIONS OF LIGHT ATOMS IN THE ADIABATIC APPROXIMATION.
36. Solov'ev, E.S., Il'in, R.N., Oparin, V.A., and Fedorenko, N.V., Soviet Phys.-JETP, 15, 459. IONIZATION OF GASES BY FAST HYDROGEN ATOMS AND BY PROTONS.
37. Teplova, Ya. A., Nikolaev, V.S., Dmitriev, I.S., and Fateeva, L.N., Soviet Phys.-JETP, 15, 31. SLOWING DOWN OF MULTICHARGED IONS IN SOLIDS AND GASES.
38. Walther, V., and Hintenberger, H., Angew. Chem., 74, 159. REFLEXION VON EGELGAS-IONEN AN METALLOBERFLACHEN UND DIE EMISSION VON SEKUNDAR-IONEN.
39. Walther, V., and Hintenberger, H., Angew. Chem. Int. Ed., 1, 164. REFLECTION OF NOBLE GAS IONS AT METAL SURFACES AND THE EMISSION OF SECONDARY IONS.

40. Wilmenius, P., and Lindholm, E., Arkiv Fysik, 21, 97. DISSOCIATION OF METHANOL MOLECULE IONS FORMED IN CHARGE EXCHANGE COLLISIONS WITH POSITIVE IONS. ION-MOLECULE REACTIONS OF METHANOL WITH VERY SLOW POSITIVE IONS.

ELASTIC SCATTERING

1. Baker, C.E., McGuire, J.M., and Muschlitz, E.E., J. Chem. Phys., 37, 2571. LOW ENERGY COLLISION CROSS SECTIONS OF H⁺ and OH⁻ IONS IN OXYGEN.
2. Bayes, K.D., Kivelson, D., and Wong, S.C., J. Chem. Phys., 37, 1217. MEASUREMENT BY CYCLOTRON RESONANCE OF MOLECULAR CROSS SECTIONS FOR ELASTIC COLLISIONS WITH 295°K ELECTRONS.
3. Bernstein, M.J., Phys. Rev., 127, 335. ELECTRON DRIFT AND DIFFUSION MEASUREMENTS IN H₂ AND D₂ WITH CROSSED ELECTRIC AND STRONG MAGNETIC FIELDS.
4. Bernstein, M.J., Phys. Rev., 127, 342. TOWNSEND IONIZATION COEFFICIENT FOR HYDROGEN IN A TRANSVERSE STRONG MAGNETIC FIELD.
5. Boersch, H., and Forst, G., Z. Physik, 169, 239. BEUGUNG VON Li⁺ - IONEN AN CCl₄. ABWEICHUNG VON DER DEBYE-EHRENFESTSCHEN STREUTHEORIE.
6. Bransden, B.H., Proc. Phys. Soc. (London), 79, 190. THE LOW ENERGY SCATTERING OF POSITIONS BY HYDROGEN ATOMS.
7. Burge, R.E., and Smith, G.H., Proc. Phys. Soc. (London), 79, 673. A NEW CALCULATION OF ELECTRON SCATTERING CROSS SECTIONS AND A THEORETICAL DISCUSSION OF IMAGE CONTRAST IN THE ELECTRON MICROSCOPE.
8. Burke, Philip G., and Schey, Harry M., Phys. Rev., 126, 147. ELASTIC SCATTERING OF LOW-ENERGY ELECTRONS BY ATOMIC HYDROGEN.
9. Burke, P. G., and Schey, H.M., Phys. Rev., 126, 163. POLARIZATION AND CORRELATION OF ELECTRON SPIN IN LOW-ENERGY ELASTIC ELECTRON-HYDROGEN COLLISIONS.
10. Burke, P.G., Burke, V.M., Percival, I.C., and McCarroll, R., Proc. Phys. Soc., (London), 80, 413. ELECTRON SCATTERING BY ATOMIC HYDROGEN IN THE 1s, 2s, or 2p STATE: I
11. Burke, P.G., and Smith, Kenneth, Revs. Modern Phys., 34, 458. THE LOW-ENERGY SCATTERING OF ELECTRONS AND POSITRONS BY HYDROGEN ATOMS.
12. Burke, V.M., and McCarroll, Proc. Phys. Soc., (London), 80, 422. ELECTRON SCATTERING BY ATOMIC HYDROGEN IN THE 1s, 2s, or 2p STATE: II.
13. Carleton, N.P., and Megill, L.R., Phys. Rev., 126, 2089. ELECTRON ENERGY DISTRIBUTION IN SLIGHTLY IONIZED AIR UNDER THE INFLUENCE OF ELECTRIC AND MAGNETIC FIELDS.
14. Chen, C.L., and Raether, M., Phys. Rev., 128, 2679. COLLISION CROSS SECTION OF SLOW ELECTRONS AND IONS WITH CESIUM ATOMS.
15. Cloney, R.D., Mason, E. A., and Vanderslice, J.T., J. Chem. Phys., 36, 1103. BINDING ENERGY OF Ar₂⁺ FROM ION SCATTERING DATA.
16. Cloney, R.D., and Vanderslice, J.T., J. Chem. Phys., 36, 1866. INTERACTION ENERGIES FROM SCATTERING CROSS SECTIONS OF HYDROGEN IONS IN CH₄, CF₄, C₂H₆, and C₂F₆.
17. Cochran, L.W., and Forester, D.W., Phys. Rev., 126, 1785. DIFFUSION OF SLOW ELECTRONS IN GASES.
18. Cooper, John W., and Martin, Jerry B., Phys. Rev., 126, 1482. ELECTRON PHOTO-DETACHMENT FROM IONS AND ELASTIC COLLISION CROSS SECTIONS FOR O, C, Cl, and F.
19. De., M.L., Naturwissenschaften, 49, 228. ON THE DEPENDENCE OF ELECTRON SCATTERING CROSS-SECTION OF ATOMS ON THEIR ATOMIC NUMBER.

20. Damburg, R., and Peterkop, R., Proc. Phys. Soc., (London), 80, 1073. APPLICATION OF THE MULTICHANNEL EFFECTIVE RANGE THEORY TO ELECTRON-HYDROGEN SCATTERING.
21. Damburg, R. Ya., and Peterkop, R.K., Optics and Spectroscopy, 13, 338. STRONG BOND AND EXCHANGE TAKEN INTO ACCOUNT IN THE COLLISION OF ELECTRON WITH HYDROGEN ATOMS.
22. Falckenberg, H.R., and Schumaker, B.W., Can. J. Phys., 40, 1521. THE POSSIBILITIES FOR GAS DENSITY GAUGING BY SINGLE SCATTERING OF ELECTRONS.
23. Frost, L.S., and Phelps, A.V., Phys. Rev., 127, 1621. ROTATIONAL EXCITATION AND MOMENTUM TRANSFER CROSS SECTIONS FOR ELECTRONS IN H_2 AND N_2 FROM TRANSPORT COEFFICIENTS.
24. Gerjuoy, E., and Krall, N.A., Phys. Rev., 127, 2105. DISPERSION RELATIONS FOR ELECTRON SCATTERING FROM ATOMIC HELIUM.
25. Gorshanova, A.F., and Damburg, R. Ya., Optics and Spectroscopy, 12, 55. CONSIDERATION OF STRONG COUPLING IN COLLISIONS OF ELECTRONS WITH HYDROGEN ATOMS.
26. Harada, J., and Kashiwase, Y., J.Phys. Soc. (Japan), 17, 829. ATOMIC SCATTERING FACTOR FOR ELECTRONS OF ATOMS WITH ASPHERICAL CHARGE DISTRIBUTION.
27. Heylen, A.E.D., Proc. Phys. Soc., (London), 79, 284. CALCULATED ELECTRON MOBILITY IN NITROGEN, OXYGEN, AND AIR FOR $0.1 \leq E/p \leq 100 \text{ V cm}^{-1} \text{ mm Hg}^{-1}$.
28. Heylen, A.E.D., Proc. Phys. Soc., (London), 80, 1109. THE INFLUENCE OF THE TOWNSEND-RAMSAUER EFFECT ON THE ELECTRON TRANSPORT COEFFICIENTS OF MOLECULAR GASES.
29. Hurst, G.S., O'Kelly, L.B., and Stockdale, J.A., Nature, 195, 66. QUASI-TRAPPING OF LOW-ENERGY ELECTRONS IN WATER VAPOR.
30. Kamenetskii, V.P., Optics and Spectroscopy, 12, 366. THE COLLISION OF SLOW ELECTRONS WITH HYDROGEN ATOM.
31. Kolesnikov, V.N., and Obukhov-Denisov, V.V., Soviet Phys.-JETP, 15, 692. THE EFFECTIVE CROSS SECTION FOR ELASTIC SCATTERING OF SLOW ELECTRONS BY HYDROGEN ATOMS.
32. Kevine, J., and Sanders, T.M., Phys. Rev. Letters, 8, 159. ANOMALOUS ELECTRON MOBILITY AND COMPLEX NEGATIVE ION FORMATION IN LOW-TEMPERATURE HELIUM VAPOR.
33. Lippert, W., Naturwissenschaften, 49, 534. ZUR BRAUCHBARKEIT DER BORNSCHEN NAHRUNG BEI DER BERECHNUNG DER ELEKTRONENSTREUUNG FÜR DEN BEREICH DER ELEKTRONENMIKROSKOPIE.
34. Mirlin, D.N., Pikus, G.E., and Yur'ev, V.G., Soviet Phys.-Tech. Phys., 7, 559. DETERMINATION OF ELECTRON SCATTERING CROSS SECTION BY THE ELECTRICAL CONDUCTIVITY OF WEAKLY IONIZED GAS.
35. Mittleman, M.H., Phys. Rev. Letters, 9, 495. SPIN EXCHANGE IN ELECTRON-HYDROGEN COLLISIONS.
36. Moiseiwitsch, B.L., Proc. Phys. Soc. (London), 79, 1166. ON THE RELATION BETWEEN PHASE SHIFT AND QUANTUM DEFECT.
37. Morgulis, N.D., and Korchevoi, Yu. P., Soviet Phys.-Tech. Phys., 7, 655. MOBILITY AND SCATTERING CROSS SECTION OF ELECTRONS IN WEAKLY IONIZED PLASMA.
38. Müller, K. G., Z. Physik, 169, 432. DIE ELEKTRONENBEWEGUNG IM NEUTRAL-GAS BEI HOHEN ELEKTRISCHEN FELDERN.
39. O'Malley, T.F., Rosenberg, L., and Spruch, L., Phys. Rev., 125, 1300. LOW-ENERGY SCATTERING OF A CHARGED PARTICLE BY A NEUTRAL POLARIZABLE SYSTEM.

40. Pack, J.L., Voshell, R.E., and Phelps, A.V., Phys. Rev., 127, 2084. DRIFT VELOCITIES OF SLOW ELECTRONS IN KRYPTON, XENON, DEUTERIUM, CARBON MONOXIDE, CARBON DIOXIDE, WATER VAPOR, NITROUS OXIDE, AND AMMONIA.
41. Parzen, P., J. Appl. Phys., 33, 2062. SCATTERING OF AN ELECTRON BEAM BY A NEUTRAL GAS.
42. Perel, Julius, Englander, Paula, and Bederson, Benjamin, Phys. Rev. 128, 1148 MEASUREMENT OF TOTAL CROSS SECTIONS FOR THE SCATTERING OF LOW-ENERGY ELECTRONS BY LITHIUM, SODIUM, AND POTASSIUM.
43. Peterkop, R.K., Optics and Spectroscopy, 13, 87. THE WAVE FUNCTION OF THE e-H COLLISION.
44. Robinson, Lawrence Baylor, Phys. Rev., 127, 2076. THEORETICAL ELASTIC COLLISION FREQUENCY BETWEEN ELECTRONS AND NEUTRAL ATOMS IN A CESIUM PLASMA.
45. Romanov, V.E., Optics and Spectroscopy, 12, 54. CALCULATION OF THE CROSS SECTION FOR FREE-FREE TRANSITIONS OF AN ELECTRON IN THE FIELD OF A NEUTRAL HYDROGEN ATOM.
46. Saraph, H.E., and Seaton, M.J., Proc. Phys. Soc., (London), 80, 1057. AN ITERATION-VARIATION METHOD FOR ATOMIC SCATTERING PROBLEMS.
47. Schwartz, Charles, Phys. Rev., 126, 1015. IMPORTANCE OF ANGULAR CORRELATIONS BETWEEN ATOMIC ELECTRONS.
48. Smith, Kenneth, McEachran, Robert P., and Fraser, Peter A., Phys. Rev., 125, 553. EFFECT OF VIRTUAL EXCITATION OF THE 2s STATE ON THE ELASTIC SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN.
49. Temkin, A., Phys. Rev., 126, 130. NONADIABATIC THEORY OF ELECTRON-HYDROGEN SCATTERING.
50. Temkin, A., Proc. Phys. Soc., (London), 80, 1277. POSITION-HYDROGEN SCATTERING.
51. Teplova, Ya. A., Nikolaev, V.S., Dmitriev, I.S., and Fateeva, L.N., Soviet Phys.-JETP, 13, 31. SLOWING DOWN OF MULTICHARGED IONS IN SOLIDS AND GASES.
52. Twiss, R.Q., Astrophys. J., 136, 438. ON NEGATIVE ABSORPTION IN AN ELECTRON-ION PLASMA WHEN RADIATION TAKES PLACE BY FREE-FREE TRANSITIONS.

C. Other Charged Particle Collisions

1. Charged-charged

1. Albrecht, G., and Ecker, G., Z. Naturforsch., 17a, 848. THEORIE DER NICHT-KONTRAHIERTEN POSITIVEN SAULE UNTER DEM EINFLUSS NEGATIVER IONEN.
2. Albrecht, G., Ecker, G., and Muller, K.G., Z. Naturforsch., 17a, 854. THEORIE DER KONTRAKTION DER POSITIVEN SAULE.
3. Bates, D.R., and Boyd, Anne H., Proc. Phys. Soc. (London), 79, 710. EFFECT OF COULOMB REPULSION BETWEEN CHARGED ATOMIC SYSTEMS ON EXCITATION AND IONIZATION CROSS SECTIONS.
4. Bates, D.R., Kinston, A.E., and McWhirter, R.W.P., Proc. Roy. Soc. (London)A, 267, 297. RECOMBINATION BETWEEN ELECTRONS AND ATOMIC IONS I.
5. Bates, D.R., Kingston, A.E., and McWhirter, R.W.P., Proc. Roy. Soc. (London)A, 270, 155. RECOMBINATION BETWEEN ELECTRONS AND ATOMIC IONS II. OPTICALLY THICK PLASMAS.
6. Berg, H.F., Ali, A.W., Lincke, R., and Griem, H.R., Phys. Rev., 125, 199. MEASUREMENT OF STARK PROFILES OF NEUTRAL AND IONIZED HELIUM AND HYDROGEN LINES FROM SHOCK-HEATED PLASMAS IN ELECTROMAGNETIC T TUBES.
7. Bourdeau, R.E., Whipple, E.C., Jr., Donley, J.L., and Bauer, S.J., J. Geophys. Res., 67, 467. EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF HELIUM IONS BASED ON EXPLORER VIII SATELLITE DATA.

8. Butler, S.T., and Buckingham, M.J., Phys. Rev., 126, 1. ENERGY LOSS OF A FAST ION IN A PLASMA.
9. Byron, Stanley, Stabler, R.C., and Bortz, P.I., Phys. Rev. Letters, 8, 376, Erratum: 8, 497. ELECTRON-ION RECOMBINATION BY COLLISIONAL AND RADIATIVE PROCESSES.
10. Doering, John P., and Mahah, Bruce H., J. Chem. Phys., 36, 669. PHOTOIONIZATION OF NITRIC OXIDE.
11. Elkomoss, S.G., and Magee, J.L., J. Chem. Phys., 36, 256. PARENT-ION RECAPTURE IN GASES.
12. Griem, Hans R., Phys. Rev., 128, 515. STARK BROADENING OF ISOLATED SPECTRAL LINES FROM HEAVY ELEMENTS IN A PLASMA.
13. Guidini, Joseph, Jeudon, Andre, Manus, Claude, and Sinda, Theo., Compt. rend., 254, 3081. REACTIONS PRODUITES PAR LE PASSAGE D'UN FAISCEAU D'IONS HYDROGENE MOLECULAIRES A TRAVERS UN MILIEU IONISE.
14. Hinnov, Einar, and Hirschberg, Jos. G., Phys. Rev., 125, 795. ELECTRON-ION RECOMBINATION IN DENSE PLASMAS.
15. Kenty, Carl, Phys. Rev., 126, 1235. VOLUME RECOMBINATION, CONSTRICTION, AND VOLT-AMPERE CHARACTERISTICS OF THE POSITIVE COLUMN.
16. King, I. R., J. Chem. Phys., 36, 553. RECOMBINATION RATES OF ALKALI METAL IONS.
17. King, I.R., J. Chem. Phys., 37, 74. RECOMBINATION OF IONS IN FLAMES.
18. Liberman, L.M., Toropkin, Yu. N., and Ul'yanov, K.N., Soviet Phys., Tech. Phys. 7, 605. THE THEORY OF MULTISTAGE IONIZATION AND RECOMBINATION.
19. Pitaevskii, L.P., Soviet Phys., JETP, 15, 919. ELECTRON RECOMBINATION IN A MONATOMIC GAS.
20. Tavendale, A.J., Proc. Phys. Soc. (London), 79, 652. COLUMNAR RECOMBINATION LUMINESCENCE IN ARGON-NITROGEN MIXTURES.
21. Twiss, R.Q., Astrophys. J., 136, 438. ON NEGATIVE ABSORPTION IN AN ELECTRON-ION PLASMA WHEN RADIATION TAKES PLACE BY FREE-FREE TRANSITIONS.
22. Zirin, Harold, Astrophys. J., 135, 521. PHYSICAL CONDITIONS IN LIMB FLARES AND ACTIVE PROMINENCES. V. EXCITATION AND IONIZATION OF HELIUM AND METALS.

2. Charged-Uncharged, other than conventional mass spectrometry
and negative ion work

1. Afrosimov, V.V., Il'in, R.N., Oparin, V.A., Solov'ev, E.S., and Fedorenko, N.V., Soviet Phys.-JETP, 14, 747. IONIZATION OF ARGON BY ATOMS, AND SINGLY OR DOUBLY CHARGED IONS OF NEON AND ARGON.
2. Barker, R., Nature, 196, 826. ROLE OF ION-MOLECULE REACTIONS IN THE RADIOLYSIS OF HYDROCARBONS.
3. Bell, R.J., and Skinner, B.G., Proc. Phys. Soc. (London), 80, 404. EXCITATION OF THE 1s-2p TRANSITION IN HYDROGEN AND THE 3s-3p TRANSITION IN SODIUM BY NUCLEI.
4. Bely, Oleg, Compt. rend., 254, 3075. CALCUL DE SECTIONS D'EXCITATION PAR CHOCS ELECTRONIQUES DANS O VI.
5. Berg, H.F., Ali, A.W., Lincke, R., and Griem, H.R., Phys. Rev., 125, 199. MEASUREMENT OF STARK PROFILES OF NEUTRAL AND IONIZED HELIUM AND HYDROGEN LINES FROM SHOCK-HEATED PLASMAS IN ELECTROMAGNETIC T TUBES.
6. Bernstein, Melvin J., Phys. Rev., 127, 342. TOWNSEND IONIZATION COEFFICIENT FOR HYDROGEN IN A TRANSVERSE STRONG MAGNETIC FIELD.
7. Berry, H.W., Phys. Rev., 127, 1634. ENERGY DISTRIBUTION OF ELECTRONS FROM IONIZING COLLISIONS OF ATOMS AND IONS.

8. Biberman, L.M., Torokin, Yu. N., and Ul'yanov, K.N., Soviet Phys.-Tech. Phys., 7, 605. THE THEORY OF MULTISTAGE IONIZATION AND RECOMBINATION.
9. Bigl, F., Kernenergie, 5, 411. UBER DIE BILDUNG DER IONEN H_3^+ , H_2D^+ , und D_3^+ IN ELEKTROSTOSSIONENQUELLEN.
10. Boelrijk, N., and Hamill, W.H., J. Am. Chem. Soc., 84, 730. EFFECTS OF RELATIVE VELOCITY UPON GASEOUS ION-MOLECULE REACTIONS; CHARGE TRANSFER TO THE NEOPENTANE MOLECULE.
11. Boelrijk, A.I.M., and Babeliowsky, T.P.J.H., J. Am. Chem. Soc., 84, 3592. NEGATIVE TEMPERATURE COEFFICIENTS FOR ION-MOLECULE REACTIONS.
12. Boersch, H., and Schweda, S., Z. Physik, 167, 1. EINE INVERSE GEGENFELD-METHODE ZUR ENERGIESLALYSE VON ELECTRONEN UND IONEN-STRAHLEN.
13. Bransden, B.H., Proc. Phys. Soc. (London), 79, 190. THE LOW ENERGY SCATTERING OF POSITRONS BY HYDROGEN ATOMS.
14. Bulewicz, E.M., J. Chem. Phys., 36, 385. ELECTRON-MOLECULE AND ELECTRON-ATOM COLLISION CROSS SECTIONS FROM A CYCLOTRON RESONANCE STUDY OF FLAME GASES.
15. Bulewicz, E.M., and Padley, P.J., J. Chem. Phys., 36, 2231. ELECTRON-MOLECULE COLLISION CROSS SECTIONS IN THE BURNED GASES OF A VARIETY OF FUELS.
16. Brink, Gilbert O., Phys. Rev., 127, 1204. IONIZATION OF ALKALI ATOMS BY ELECTRON BOMBARDMENT.
17. Burge, R.E., and Smith, G.H., Proc. Phys. Soc. (London), 79, 673. A NEW CALCULATION OF ELECTRON SCATTERING CROSS SECTIONS AND A THEORETICAL DISCUSSION OF IMAGE CONTRAST IN THE ELECTRON MICROSCOPE.
18. Burke, P.G., and Smith, Kenneth, Revs. Modern Phys., 34, 458. THE LOW-ENERGY SCATTERING OF ELECTRONS AND POSITRONS BY HYDROGEN ATOMS.
19. Carleton, N.P., and Megill, L.R., Phys. Rev., 126, 2089. ELECTRON ENERGY DISTRIBUTION IN SLIGHTLY IONIZED AIR UNDER THE INFLUENCE OF ELECTRIC AND MAGNETIC FIELDS.
20. Chen, J.C.Y., and Magee, J.L., J. Chem. Phys., 36, 1407. EXCITATION OF MOLECULAR VIBRATION BY SLOW ELECTRON IMPACT.
21. Cloney, Robert D., Maçon, E.A., and Vanderslice, J.T., J. Chem. Phys., 36, 1103. BINDING ENERGY OF Ar_2^+ FROM ION SCATTERING DATA.
22. Cook, C.J., and Peterson, J.R., Phys. Rev. Letters, 9, 164. DIRECT AND DISSOCIATIVE IONIZATION CROSS SECTIONS FOR ELECTRONS IN N_2 .
23. Crable, Geo. F., and Kearns, G.L., J. Chem. Phys., 36, 558. CHARGE-EXCHANGE PHENOMENA IN A MASS SPECTROMETER.
24. Dahler, J.S., Franklin, J.L., Munson, M.S.B., and Field, F.H., J. Chem. Phys., 36, 3332. RARE-GAS MOLECULE-ION FORMATION BY MASS SPECTROMETRY. KINETICS OF Ar_2^+ , Ne_2^+ , and He_2^+ FORMATION BY SECOND- and THIRD-ORDER PROCESSES.
25. Damburg, R., and Peterkop, R., Proc. Phys. Soc. (London), 80, 563. EXCITATION OF HYDROGEN BY ELECTRON COLLISION ALLOWING FOR EXCHANGE AND 1s-2s-2p STRONG COUPLING.
26. Damburg, R., and Peterkop, R., Proc. Phys. Soc., (London), 80, 1073. APPLICATION OF THE MULTICHANNEL EFFECTIVE RANGE THEORY TO ELECTRON-HYDROGEN SCATTERING.
27. Damburg, R. Y., and Peterkop, R.K., Optics and Spectroscopy, 13, 338. STRONG BOND AND EXCHANGE TAKEN INTO ACCOUNT IN THE COLLISIONS OF ELECTRONS WITH HYDROGEN ATOMS.
28. Damburg, R.Y., and Peterkop, R.K., Zh. Eksp. Teor. Fiziki, 43, 1765. EXCITATION OF THE 2s and 2p LEVELS OF THE HYDROGEN ATOMS BY SLOW ELECTRONS.
29. Davies, D.K., Jones, F.L., and Morgan, C.G., Proc. Phys. Soc. (London), 80, 898. PRIMARY IONIZATION COEFFICIENT OF HELIUM.

30. Dawson, P.H., and Tickner, A.W., J. Chem. Phys., 37, 672. DETECTION OF H_5^+ IN THE HYDROGEN GLOW DISCHARGE.
31. De., M.L., Naturwissenschaften, 49, 228. ON THE DEPENDENCE OF ELECTRON SCATTERING CROSS-SECTION OF ATOMS ON THEIR ATOMIC NUMBER.
32. Dmitriev, I.S., Nikolaev, V.S., Fateeva, L.N., and Teplova, Y.A., Soviet Phys.-JETP, 15, 11. EXPERIMENTAL STUDY OF ELECTRON LOSS BY MULTIPLY CHARGED IONS IN GASES.
33. Dmitriev, I.S., Nikolaev, V.S., Fateeva, L.N., and Teplova, Y.A., Soviet Phys.-JETP, 16, 259. INVESTIGATION OF THE LOSS OF SEVERAL ELECTRONS BY FAST MULTIPLY CHARGED IONS.
34. Dunn, G. H., Geballe, R., Pretzer, D., Phys. Rev., 128, 2200. PRODUCTION OF LYMAN ALPHA RADIATION IN ION-ATOM COLLISIONS.
35. Field, F.H., Head, H.N., and Franklin, J.L., J. Am. Chem. Soc., 84, 1118. REACTIONS OF GASEOUS IONS. XI. IONIC REACTIONS IN BRYPTON-METHANE and ARGON-METHANE MIXTURES.
36. Fineman, M.A., and Petrocello, A. W., J. Chem. Phys., 36, 25. ELECTRON IMPACT STUDY OF CO USING A LOZIER APPARATUS.
37. Firsov, O.B., Soviet Phys. JETP, 15, 906. KINETICS OF EXOTHERMIC REACTIONS BETWEEN MOLECULES AND MOLECULAR IONS.
38. Fite, W.L., Rutherford, J.A., Snow, W.R., and vanLint, V.A.J., Discussions of Faraday Soc., 33, 264. ION-NEUTRAL COLLISIONS IN AFTERGLOWS.
39. Flaks, I.P., Ogurtsov, G.N., and Fedorenko, N.V., Soviet Phys. JETP, 14, 781. SLOW-IONS PRODUCED IN GASES UPON PASSAGE OF FAST ATOM AND ION BEAMS.
40. Flaks, I.P., Ogurtsov, G.N., and Fedorenko, N.V., Soviet Phys. JETP, 14, 1027. IONIZATION IN THE COLLISIONS OF Ne^{n+} WITH Xe ATOMS AND OF Xe^{n+} WITH Ne ATOMS ($n = 0, 2, 3, 4$).
41. Frost, L.S., and Phelps, A.V., Phys. Rev., 127, 1621. ROTATIONAL EXCITATION AND MOMENTUM TRANSFER CROSS SECTIONS FOR ELECTRONS IN H_2 and N_2 FROM TRANSPORT COEFFICIENTS.
42. Goodyear, C.C., and vonEngel, A., Proc. Phys. Soc. (London), 79, 732. DISSOCIATION AND IONIZATION OF HYDROGEN IN HIGH FREQUENCY DISCHARGES.
43. Gorshanova, A.F., and Damburg, R.Y., Optics and Spectroscopy, 12, 55. CONSIDERATION OF STRONG COUPLING IN COLLISIONS OF ELECTRONS WITH HYDROGEN ATOMS.
44. Griem, H.R., Baranger, M., Kolb, A.C., and Oertel, G., Phys. Rev., 125, 177. STARK BROADENING OF NEUTRAL HELIUM LINES IN A PLASMA.
45. Griem, H.R., and Shen, C.S., Phys. Rev., 125, 196. APPLICATION OF A DISPERSION RELATION TO THE ELECTRON IMPACT WIDTHS AND SHIFTS OF ISOLATED SPECTRAL LINES FROM NEUTRAL ATOMS.
46. Griem, H.R., Phys. Rev., 128, 515. STARK BROADENING OF ISOLATED SPECTRAL LINES FROM HEAVY ELEMENTS IN A PLASMA.
47. Haase, G., Kernenergie, 5, 419. STORENDE H-ANLAGERANG BEI DER MASSENSPEKTROMETRISCHEN ISOTOPENANALYSE.
48. Hanson, W.B., J. Geophys. Research, 67, 183. UPPER ATMOSPHERE HELIUM IONS.
49. Harrison, A.G., and Tait, J.M.S., Can. J. Chem., 40, 1986. CONCURRENT ION-MOLECULE REACTIONS LEADING TO THE SAME PRODUCT ION.
50. Henglein, A., Z. Naturforsch, 17a, 37. MASS SPECTROMETRIC OBSERVATIONS ON REACTIONS OF EXCITED IONS IN CARBON DISULFIDE AND SOME AROMATIC COMPOUNDS.
51. Henglein, A., Z. Naturforsch, 17a, 44. MASS SPECTROMETRIC OBSERVATION OF PERSISTANT ION-MOLECULE COMPLEXES OF ACRYLONITRILE AND OF BENZENE.

52. Henglein, A., and Miccini, G.A., Z. Naturforsch, 17a, 452. MASS SPECTROMETRIC OBSERVATIONS OF ELECTRON AND PROTON TRANSFER REACTIONS BETWEEN POSITIVE IONS AND NEUTRAL MOLECULES.
53. Herman, L., Felenbok, P., and Herman, R., J. Phys. Radium, 23, 979. PROCESSUS DE FORMATION D'IONS MOLECULAIRES D'AZOTE EN PRESENCE D'HELIUM.
54. Herzenberg, A., and Mandl, F., Proc. Roy. Soc. (London)A, 270, 48. VIBRATION EXCITATION OF MOLECULES BY RESONANCE SCATTERING OF ELECTRONS.
55. Heylen, A.E.D., Proc. Phys. Soc. (London), 80, 1109. THE INFLUENCE OF THE TOWNSEND-RAMSAUER EFFECT ON THE ELECTRON TRANSPORT COEFFICIENTS OF MOLECULAR GASES.
56. Hooper, J.W., Harmer, D.S., Martin, D.W., and McDaniel, E.W., Phys. Rev., 125, 2000. COMPARISON OF ELECTRON AND PROTON IONIZATION DATA WITH THE BORN APPROXIMATION PREDICTIONS.
57. Kaul, W., Taubert, R., Z. Naturforsch, 17a, 88. SEKUNDARREAKTIONEN IN EDELGAS-EDELGAS UND EDELGAS-STICKSTOFF-GEMISCHEN.
58. Kenty, C., Phys. Rev., 126, 1235. VOLUME RECOMBINATION, CONSTRICTION, and VOLT-AMPERE CHARACTERISTICS OF THE POSITIVE COLUMN.
59. Knewstubb, P.F., and Tickner, A.W., J. Chem Phys., 36, 684. MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. I. APPARATUS AND ITS APPLICATION TO THE POSITIVE COLUMN IN RARE GASES.
60. Knewstubb, P.F., and Tickner, A.W., J. Chem. Phys., 36, 684. MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. II. NEGATIVE GLOW IN RARE GASES.
61. Kupperman, A., and Raff, L.M., J. Chem. Phys., 37, 2497. DETERMINATION OF ELECTRONIC ENERGY LEVELS OF MOLECULES BY LOW-ENERGY ELECTRON IMPACT SPECTROSCOPY.
62. Kupriyanov, S.E., J. Phys. Chem. (USSR), 36, 107. DISSOCIATION OF EXCITED IONS.
63. Kupriyanov, S.E., Perov, A.A., Tunitskii, N.N., Zh. Eksp. Teor. Fiziki, 43, 763. DISSOCIATION CROSS SECTION OF THE D_2^+ ION WHEN IT COLLIDES WITH A DETEURIUM MOLECULE AND DISSOCIATES INTO D_2^{3+} AND D^+ .
64. Kupriyanov, S.E., Perov, A.A., Tunitskii, N.N., Zh. Eksp. Teor. Fiziki, 43, 1636. DISSOCIATION CROSS SECTION OF D_2^+ IONS IN THE ENERGY RANGE OF 3.5-100 keV when in COLLISION WITH D_2 MOLECULES.
65. Lee, A.R., and Hasted, J.B., Proc. Phys. Soc. (London), 79, 1049. IONIZATION OF ATOMS BY PROTONS.
66. Lichten, W., J. Chem. Phys., 37, 2152. SOME NEW METASTABLE STATES OF MOLECULES.
67. Marmet, P., and Morrison, J.D., J. Chem. Phys., 36, 1238. SECONDARY REACTIONS IN THE ION CHAMBER OF A MASS SPECTROMETER.
68. McFarland, R.H., and Soltysik, E.D., Phys. Rev., 127, 2090. POLARIZATION OF LIGHT RESULTING FROM THE EXCITATION OF HELIUM BY ELECTRONS.
69. McFarland, R.H., and Soltysik, E.A., Phys. Rev., 128, 1758. POLARIZATION OF THE $\lambda = 5876 \text{ \AA}$ AND $\lambda = 6679 \text{ \AA}$ LINES IN HELIUM EXCITED BY ELECTRONS.
70. McFarland, R.H., and Soltysik, E.A., Phys. Rev., 128, 2222. MAGNETIC-FIELD DEPENDENCE OF POLARIZED HELIUM LIGHT EXCITED BY ELECTRONS.
71. Morgan, G.H., and Everhart, E., Phys. Rev., 128, 667. MEASUREMENTS OF INELASTIC ENERGY LOSS IN LARGE-ANGLE Ar^+ on Ar COLLISIONS AT keV ENERGIES.
72. Muller, K.G., Z. Physik, 167, 1. DIE ELEKTRONENBEWEGUNG IM NEUTRALGAS BEI HOHEN ELEKTRISCHEN FELDERN.
73. Perel, J., Englander, P., and Bederson, B., Phys. Rev., 128, 1148. MEASUREMENTS OF TOTAL CROSS SECTIONS FOR THE SCATTERING OF LOW-ENERGY ELECTRONS BY LITHIUM, SODIUM, AND POTASSIUM.

74. Peterkop, R.K., Soviet Phys.-JETP, 14, 1377. INTERFERENCE EFFECTS IN THE IONIZATION OF HYDROGEN ATOMS BY ELECTRON IMPACT.
75. Peterkop, R.K., Optics and Spectroscopy, 13, 87. THE WAVE FUNCTION OF THE e-H COLLISION.
76. Pottie, R.F., Lorquet, A.J., and Hamill, W.H., J. Am. Chem. Soc., 84, 529. THE ENERGY DEPENDENCE FOR REACTION CROSS SECTIONS OF ION-MOLECULE REACTIONS OF CYCLOPROPANE IN THE MASS-SPECTROMETER.
77. Reuben, B.G., and Friedman, L., J. Chem. Phys., 37, 1636. ISOTOPIC HYDROGEN-ION-MOLECULE REACTIONS.
78. Romanov, V.E., Optics and Spectroscopy, 12, 54. CALCULATION OF THE CROSS SECTION FOR FREE-FREE TRANSITIONS OF AN ELECTRON IN THE FIELD OF A NEUTRAL HYDROGEN ATOM.
79. Roth, W., J. Chem. Phys., 37, 925. CHARGE TRANSFER CROSS SECTION FOR ELECTRONICALLY EXCITED N_2^+ WITH O ATOMS AT LOW ENERGY.
80. Rothe, E.W., Marino, L.L., Neyhaber, R.H., and Trujillo, S.M., Phys. Rev., 125, 582. ELECTRON IMPACT IONIZATION OF ATOMIC HYDROGEN AND OXYGEN.
81. Rudolph, P.S., Lind, S.C., and Melton, C.E., J. Chem. Phys., 36, 1031. IONIC COMPLEXES OF Xe AND C_2H_2 PRODUCED BY THE RADIOLYSIS OF THESE GASES.
82. Sazhinov, Y.G., and Kuprianov, S.E., Zh. Fiz. Khimii, 36, 1969. EXCITATION OF IONS FORMED IN THE IONIZATION OF MOLECULES BY ELECTRONS.
83. Schultz, G.J., and Dowell, J.T., Phys. Rev., 128, 174. EXCITATION OF VIBRATIONAL AND ELECTRONIC LEVELS IN O_2 BY ELECTRON IMPACT.
84. Seaton, M.J., Proc. Phys. Soc. (London), 79, 1105. THE IMPACT PARAMETER METHOD FOR ELECTRON EXCITATION OF OPTICALLY ALLOWED ATOMIC TRANSITIONS.
85. Seaton, M.J., Proc. Phys. Soc. (London), 80, 806. THE EFFECT OF COUPLING TO $n=3$ STATES ON BORN $1s-2s$ AND $1s-2p$ e-H COLLISION CROSS SECTIONS.
86. Schultz, G.J., Phys. Rev., 125, 229. VIBRATIONAL EXCITATION OF NITROGEN BY ELECTRON IMPACT.
87. Skinner, B.G., Proc. Phys. Soc. (London), 79, 717. EFFECT OF $2p_0-2p_{+1}$ COUPLING ON THE CROSS SECTION FOR EXCITATION OF THE $1s-2p$ TRANSITION OF ATOMIC HYDROGEN BY PROTON AND ALPHA PARTICLE IMPACT.
88. Smirnov, B.M., Soviet Phys.-JETP, 16, 81. INELASTIC COLLISIONS OF LIGHT ATOMS IN THE ADIABATIC APPROXIMATION.
89. Smith, A.C.H., Caplinger, E., Neynaber, R.H., Rothe, E.W., and Trujillo, S.M., Phys. Rev., 127, 1647. ELECTRON IMPACT IONIZATION OF ATOMIC NITROGEN.
90. Smith, K., McEachran, R.P., and Fraser, P.A., Phys. Rev., 125, 553. EFFECT OF VIRTUAL EXCITATION OF THE $2s$ STATE ON THE ELASTIC SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN.
91. Solov'ev, E.S., Il'in, R.N., Oparin, V.A., and Fedorenko, N.V., Soviet Phys.-JETP, 15, 459. IONIZATION OF GASES BY FAST HYDROGEN ATOMS AND BY PROTONS.
92. Talrose, V.L., Markin, M.I., Larin, I.K., Disc. Faraday Soc., 33, 257. THE REACTION $O^+ + N_2 \rightarrow NO^+ + N$.
93. Teplova, Y.A., Nikolaev, V.S., Dmitriev, I.S., and Fateeva, L.N., Soviet Phys.-JETP, 15, 31. SLOWING DOWN OF MULTICHARGED IONS IN SOLIDS AND GASES.
94. Theard, L.P., and Hamill, W.H., J. Am. Chem. Soc., 84, 1134. THE ENERGY DEPENDENCE OF CROSS SECTIONS OF SOME ION-MOLECULE REACTIONS.
95. vanEck, J., DeHeer, F.J., and Kistemaker, J., Physica, 28, 1184. EXCITATION PROCESSES IN HELIUM AND POLARIZATION OF THE RESULTING LIGHT INDUCED BY PROTON IMPACT (5-35) keV).

96. Veldre, V.Y., and Peterkop, R.K., Optics and Spectroscopy, 13, 257. CALCULATION OF THE DISTORTION OF THE INCIDENT s-WAVE IN THE IONIZATION OF THE HYDROGEN ATOM BY ELECTRONS.
97. Vorob'ev, A.A., Komar, A.P., and Korolev, V.A., Soviet Phys.-JETP, 16, 306. DECREASE OF FLUCTUATIONS OF THE IONIZATION PRODUCED BY ALPHA PARTICLES IN ARGON.
98. Wexler, S., and Jesse, N., J. Am. Chem. Soc., 84, 3425. CONSECUTIVE ION-MOLECULE REACTIONS IN METHANE.
99. Wilmenius, P., and Lindholm, E., Arkiv Fysik, 21, 97. DISSOCIATION OF METHANOL MOLECULE IONS FORMED IN CHARGE EXCHANGE COLLISIONS WITH POSITIVE IONS. ION-MOLECULE REACTIONS OF METHANOL WITH VERY SLOW POSITIVE IONS.

D. GASEOUS NEGATIVE IONS

1. Albrecht, G., Ecker, G., and Müller, K.G., Z. Naturforsch., 17a, 854. THEORIE DER KENTRAKTION DER POSITIVEN SAULE.
2. Albrecht, G., and Ecker, G., Z. Naturforsch., 17a, 848. THEORIE DER NICH-KONTRAHIERTEN POSITIVEN SAULE UNTER DEM EINFLUSS NEGATIVER IONEN.
3. Ansdell, D.A., and Page, F.M., Trans. Faraday Soc., 58, 1084. DETERMINATION OF ELECTRON AFFINITIES PART 4 - ELECTRON AFFINITIES OF THE SULPHYDRYL RADICAL AND THE SULPHUR ATOM.
4. Ardenne, M.V., Steinfeld, K., and Tummeler, R., Z. Physik. Chem., 221, 240. ERWEITERUNG DER EA - MASSENSPEKTROGRAPHISCHEN METHODE DURCH DEN MECHANISMUS DER ANLAGERUNG NEGATIVER IONEN AN MOLEKULE.
5. Baker, C.E., McGuire, J.M., and Muschlitz, J. Chem. Phys., 37, 2571. LOW ENERGY COLLISION CROSS SECTIONS OF H^- and OH^- IONS IN OXYGEN.
6. Batley, M., and Lyons, L.E., Nature, 196, 573. ELECTRON AFFINITIES OF ORGANIC MOLECULES.
7. Berry, R.S., Reimann, C.W., and Spokes, G.N., J. Chem. Phys., 37, 2278. ABSORPTION SPECTRA OF GASEOUS HALIDE IONS AND HALOGEN ELECTRON AFFINITIES: CHLORINE, BROMINE, AND IODINE.
8. Bhalla, M.S., and Craggs, J.D., Proc. Phys. Soc., (London), 80, 151. MEASUREMENT OF IONIZATION AND ATTACHMENT COEFFICIENTS IN SULPHUR HEXAFLUORIDE IN UNIFORM FIELDS.
9. Chanin, L.M., Phelps, A.V., and Biondi, M.A., Phys. Rev., 128, 219. MEASUREMENTS OF THE ATTACHMENT OF LOW-ENERGY ELECTRONS TO OXYGEN MOLECULES.
10. Chen, J.C.Y., and Magee, J.L., J. Chem. Phys., 36, 1407. EXCITATION OF MOLECULAR VIBRATION BY SLOW ELECTRON IMPACT.
11. Conway, D.C., J. Chem. Phys., 36, 2549. ATTACHMENT OF LOW-ENERGY ELECTRONS TO OXYGEN.
12. Cooper, J.W., and Martin, J.B., Phys. Rev., 126, 1482. ELECTRON PHOTODETACHMENT FROM IONS AND ELASTIC COLLISION CROSS SECTIONS FOR O, C, Cl, and F.
13. Curran, R.K., Phys. Rev., 125, 910. FORMATION OF NO_2^- by CHARGE TRANSFER AT VERY LOW ENERGIES.
14. Dalgarno, A., and Ewart, R.W., Proc. Phys. Soc., (London), 80, 616. SUM RULES FOR THE OSCILLATOR STRENGTHS OF H^- .
15. Edelson, D., Griffiths, J.E., and McAfee, K.B., J. Chem. Phys., 37, 917. AUTODETACHMENT OF ELECTRONS IN SULFUR HEXAFLUORIDE.
16. Edie, J.W., and Rohrllich, F., J. Chem Phys., 36, 623; erratum 37, 1151. NEGATIVE ATOMIC IONS II.
17. Ellison, F.O., J. Chem. Phys., 36, 3107. CALCULATION OF ATOMIC VALENCE STATE ENERGIES OF B, C, and N⁺ in BH_n^+ , CH_n^+ , and NH_n^+ , $n = 1$ to 4.

18. Ehrenson, S., J. Phys. Chem., 66, 706. A CLOSED FORM ANALYSIS OF THE LCAO-MO w-TECHNIQUE I OF POTENTIALS AND ELECTRON AFFINITIES.
19. Ehrenson, S., J. Phys. Chem., 66, 712. A CLOSED FORM ANALYSIS OF THE LCAO-MO w-TECHNIQUE II MECHANICS OF THE TECHNIQUE.
20. Fineman, M.A., and Petrocelli, A.W., J. Chem. Phys., 36, 25. ELECTRON IMPACT STUDY OF CO USING A LOZIER APPARATUS.
21. Frohner, F.H., Z. Physik, 170, 62. ERZENGUNG UND UNTERSUCHUNG NEGATIVER SPALTPRODUKT-IONEN.
22. Geltman, S., Astrophys. J., 136, 935. THE BOUND-FREE ABSORPTION COEFFICIENT OF THE HYDROGEN NEGATIVE ION.
23. Gerjuoy, E., and Krall, N.A., Phys. Rev., 127, 2105. DISPERSION RELATIONS FOR ELECTRON SCATTERING FROM ATOMIC HELIUM.
24. Green, M., J. Chem. Soc., 1962, 2819. TRIATOMIC MOLECULES AND IONS CONTAINING NINETEEN VALENCY ELECTRONS.
25. Gregory, N.L., Nature, 196, 162. DETECTION OF NANOGRAM QUANTITIES OF SULPHUR HEXAFLUORIDE BY ELECTRON CAPTURE METHODS.
26. Henning, H., Z. Physik, 169, 467. REKOMBINATIONEN - UND,, MINUS"- KONTINUM DER CHLORATOME.
27. Hubner, W., and Klett, C., Z. Naturforsch., 17a, 763. DER EINFLUSS VON SAUERSTOFF- UND WASSERDAMPFZUSATZEN AUF DIE IONENBEWEGLICHKEIT UND ELEKTRONEN-ANLAGERUNGSWAHRSCHEINLICHKEIT IN STICKSTOFF.
28. Hirst, D.M., and Linnett, J.W., J. Chem. Soc., 1962, 1035; erratum: Electronic structures and formulae: the allyl cation, radical, and anion, 3844. ELECTRONIC STRUCTURES AND FORMULAE: THE ALLYL CATION, RADICAL, AND ANION.
29. Hurst, G.S., O'Kelly, L.B., and Stockdale, J.A., Nature, 195, 66. QUASI-TRAPPING OF LOW-ENERGY ELECTRONS IN WATER VAPOR.
30. King, I.R., J. Chem. Phys., 37, 74. RECOMBINATION OF IONS IN FLAMES.
31. Khvostenko, V.I., J. Phys., Chem. (USSR), 36, 197. IONIZATION OF THIOPHEN AND SOME OF ITS DEVIATIVES BY ELECTRON IMPACT.
32. Knewstubb, P.F., and Sugden, T.M., Nature, 196, 1311. MASS-SPECTROMETRIC OBSERVATIONS OF NEGATIVE IONS IN FLAME GASES.
33. Landowne, R.A., and Lipsky, S.R., Anal. Chem., 34, 726. ELECTRON CAPTURE SPECTROMETRY, AN ADJUNCT TO GAS CHROMATOGRAPHY.
34. Levine, J., and Sanders, T.M., Phys. Rev. Letters, 8, 159. ANOMALOUS ELECTRON MOBILITY AND COMPLEX NEGATIVE ION FORMATION IN LOW-TEMPERATURE HELIUM VAPOR.
35. Lovelock, J.E., Nature, 195, 488. FREE ELECTRONS WITH THERMAL ENERGY: THEIR GENERATION FOR CHEMICAL USE.
36. Lovelock, J.E., Zlatkis, A., and Becker, R.S., Nature, 193, 540. AFFINITY OF POLYCYCLIC AROMATIC HYDROCARBONS FOR ELECTRONS WITH THERMAL ENERGIES: ITS POSSIBLE SIGNIFICANCE IN CARCINOGENESIS.
37. Pekeris, C.L., Phys. Rev., 126, 1470. 1^1S , 2^1S , and 2^3S STATES OF H^- and OF He.
38. Pilipenko, D.V., and Fogel, Y.M., Soviet Phys.-JETP, 15, 646. ELECTRON CAPTURE AND LOSS BY FAST HYDROGEN ATOMS PASSING THROUGH MOLECULAR GASES.
39. Scheel, N., and Griffing, V., J. Chem. Phys., 36, 1453. INTERACTION ENERGY OF AN ALKALI METAL WITH A RARE GAS.

40. Scherr, C.W., Silverman, J.N., and Matsen, F.A., Phys. Rev., 127, 830. PERTURBATION ENERGY COEFFICIENTS AND IONIZATION POTENTIALS OF THE GROUND STATE OF THREE-TO TEN-ELECTRON ISOELECTRONIC ATOMIC SERIES.
41. Schlumbohm, H., Z. Physik, 166, 192. ELEKTRONENLAWINEN IN ELEKTRONEGATIVEN GASEN. ZUR GLEICHZEITIGEN MESSUNG DES STOSSIONISIERUNG UND ANLAGERUNGSKOEFFIZIENTEN UND FÜR ELEKTRONEN UND DER GESCHWINDIGKEITEN POSITIVER UND NEGATIVER IONEN.
42. Schultz, G.J., Phys. Rev., 128, 178. CROSS SECTIONS AND ELECTRON AFFINITY FOR O⁻ IONS FROM O₂, CO, AND CO₂ BY ELECTRON IMPACT.
43. Scott, D.R., and Becker, R.S., J. Phys. Chem., 66, 2713. EXTENDED CALCULATIONS OF THE ELECTRON AFFINITIES OF POLYNUCLEAR AROMATIC HYDROCARBONS BY THE LCAO-MO w-TECHNIQUE.
44. Seman, M.L., and Branscomb, L.M., Phys. Rev., 125, 1602. STRUCTURE AND PHOTO-DETACHMENT SPECTRUM OF THE ATOMIC CARBON NEGATIVE ION.
45. Shultz, Phys. Rev., 125, 229. VIBRATIONAL EXCITATION OF NITROGEN BY ELECTRON IMPACT.
46. Synder, L.C., J. Phys. Chem., 66, 2299. A SIMPLE MOLECULAR ORBITAL STUDY OF AROMATIC MOLECULES AND IONS HAVING ORBITALLY DEGENERATE GROUND STATES.
47. Steiner, B., Seman, M.L., and Branscomb, L.M., J. Chem. Phys., 37, 1200. ELECTRON AFFINITY OF ATOMIC IODINE.
48. Wentworth, W.E., and Becker, R.S., J. Am. Chem. Soc., 84, 4263. POTENTIAL METHOD FOR THE DETERMINATION OF ELECTRON AFFINITIES OF MOLECULES: APPLICATION TO SOME AROMATIC HYDROCARBONS.
49. Whitten, R.G., and Poppoff, I.G., J. Geophys. Res., 67, 1183. ASSOCIATIVE DETACHMENT IN THE D REGION.
50. Zhirnov, V.A., Soviet Phys.-JETP, 15, 758. EFFECTIVE CROSS SECTION FOR PHOTOIONIZATION OF LITHIUM IONS.

IV. Ion-Molecule Reactions

Frank H. Field

1. Baker, C. E., J. M. McGuire, and E. E. Muschlitz, "LOW ENERGY COLLISION CROSS SECTIONS OF NEGATIVE HYDROGEN IONS AND HYDROXYL IONS IN OXYGEN," J. Chem. Phys. 37, 2571 (1962).
2. Boelrijk, N. A. I. N. and T. P. J. H. Babeliowsky, "NEGATIVE TEMPERATURE COEFFICIENTS FOR ION-MOLECULE REACTIONS," J. Am. Chem. Soc. 84, 3592 (1962).
3. Boelrijk, N. and W. H. Hamill, "EFFECTS OF RELATIVE VELOCITY UPON GASEOUS ION-MOLECULE REACTIONS. CHARGE TRANSFER TO THE NEOPENTANE MOLECULE," J. Am. Chem. Soc. 84, 730 (1962).
4. Cermak, V. and Z. Herman, "APPLICATION OF THE MASS SPECTROMETER IN THE STUDY OF DISSOCIATIVE CHARGE TRANSFER REACTIONS OF POLYATOMIC MOLECULES," COLLECTION CZECHOSLOV. Chem. Commun. 27, 406 (1962).
5. Comes, F. J., "MECHANISM OF FORMING DIATOMIC UNIPOSITIVE HELIUM IONS," Z. Naturforsch. 17A, 1031 (1962).
6. Comes, F. J. and W. Lessmann, "NEW EXCITATION STATE OF ARGON ABOVE THE IONIZATION BOUNDARY $2P_{3/2}$," Z. Naturforsch. 16A, 1396 (1961).
7. Comes, F. J. and W. Lessmann, "ION FORMATION IN NITROGEN," Z. Naturforsch. 17A, 704 (1962).
8. Clements, T. C. and E. W. Mueller, "OCCURRENCE OF A UNIPOSITIVE TRIATOMIC HYDROGEN ION IN THE FIELD IONIZATION OF HYDROGEN," J. Chem. Phys. 37, 2684 (1962).
9. Cloney, R. D., E. A. Mason, and J. T. Vanderslice, "BINDING ENERGY OF UNIPOSITIVE DIATOMIC ARGON ION FROM ION SCATTERING DATA," J. Chem. Phys. 36, 1103 (1962).
10. Crable, G. F. and G. L. Kearns, "CHARGE EXCHANGE PHENOMENA IN A MASS SPECTROMETER," J. Chem. Phys. 36, 558 (1962).
11. Dahler, J. S., J. L. Franklin, M. S. B. Munson, and F. H. Field, "RARE-GAS MOLECULE-ION FORMATION BY MASS SPECTROMETRY. KINETICS OF DIATOMIC ARGON (+) NEON (+), AND HELIUM (+) ION FORMATION BY SECOND AND THIRD ORDER PROCESSES," J. Chem. Phys. 36, 3332 (1962).
12. Dawson, P. H. and A. W. Tickner, "DETECTION OF PENTA-HYDROGEN (+) ION IN THE HYDROGEN GLOW DISCHARGE," J. Chem. Phys. 37, 672 (1962).
13. Field, F. H., H. N. Head, J. L. Franklin, "REACTIONS OF GASEOUS IONS. IONIC REACTIONS IN KRYPTON-METHANE AND ARGON-METHANE MIXTURES," J. Am. Chem. Soc. 84, 1118 (1962).
14. Firsov, O. B., "KINETICS OF EXOTHERMIC REACTIONS BETWEEN MOLECULES AND MOLECULAR IONS," Zh. Eksperim. i Teor. Fiz. 42, 1307 (1962).
15. Fite, W. L., A. C. H. Smith and R. F. Stebbings, "CHARGE TRANSFER IN COLLISION INVOLVING SYMMETRIC AND ASYMMETRIC RESONANCE," Proc. Roy. Soc. 268A, 527 (1962).
16. Friedman, L. and A. P. Irsa, "COLLISION INDUCED DISSOCIATION OF THE UNIPOSITIVE NITROUS OXIDE ION," J. Chem. Phys. 36, 1082 (1962).

17. Fuchs, R., "ION MOLECULE REACTIONS IN PARAFFINS, OLEFINS, AND ACETYLENES," Z. Naturforsch. 16A, 1026 (1961).
18. Galli, A., A. Giardini-Guidoni, and G. G. Volpi, "CHARGE EXCHANGE IN NOBLE GASES," Nuovo Cimento 26, 845 (1962).
19. Giese, C. F. and W. B. Maier, "ION MOLECULE REACTIONS STUDY WITH MASS ANALYSIS OF PRIMARY ION BEAM," J. Chem. Phys. 35, 1913 (1961).
20. Harrison, A. G. and J. M. S. Tait, "CONCURRENT ION-MOLECULE REACTION LEADING TO THE SAME PRODUCT ION," Can. J. Chem. 40, 1986 (1962).
21. Henglein, A., "MASS SPECTROMETRIC OBSERVATION OF PERSISTENT ION MOLECULE COMPLEXES OF ACRYLONITRILE AND OF BENZENE," Z. Naturforsch. 17A, 44 (1962).
22. Henglein, A. "MASS SPECTROMETRIC OBSERVATIONS ON REACTIONS OF EXCITED IONS IN CARBON DISULFIDE AND SOME AROMATIC COMPOUNDS," Z. Naturforsch. 17A, 37 (1962).
23. Henglein, A. and G. A. Muccini, "MASS SPECTROMETRIC OBSERVATION OF ELECTRON AND PROTON TRANSFER REACTIONS BETWEEN POSITIVE IONS AND NEUTRAL MOLECULES," Z. Naturforsch., 17A, 452 (1962).
24. Hoyland, W. R. and F. W. Lampe, "SINGLE-CENTER, SINGLE-DETERMINANT CALCULATION OF THE RELATIVE ENERGIES OF METHYL ION, METHYL RADICAL, METHANE, AND METHANATED PROTON ION. THE PROTON AFFINITY OF METHANE." J. Chem. Phys. 37, 1066 (1962).
25. Islam, M., J. B. Hasted, and H. B. Gilbody, and J. V. Ireland, "CHARGE TRANSFER REACTIONS OF DOUBLY CHARGED IONS," Proc. Phys. Soc. 79, 1118 (1962).
26. Jesse, W. P., and Platzman, R. L., "ISOTOPE EFFECT IN THE PROBABILITY OF IONIZING A MOLECULE BY ENERGY TRANSFER FROM A META-STABLE NOBLE GAS ATOM," Nature 195, 790 (1962).
27. Kaul, W. and R. Taubert, "SECONDARY REACTIONS IN INERT GAS-INERT GAS AND INERT GAS-NITROGEN MIXTURES," Z. Naturforsch. 17A, 88 (1962).
28. Knewstubb, P. F. and Tickner, A. W., "MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. I. APPARATUS AND ITS APPLICATION TO THE POSITIVE COLUMN IN RARE GASES," J. Chem. Phys. 26, 674 (1962).
29. Knewstubb, P. F. and A. W. Tickner, "MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. II. NEGATIVE GLOW IN RARE GASES," J. Chem. Phys. 36, 684 (1962).
30. Knewstubb, P. F. and A. W. Tickner, "MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. NITROGEN AND ITS MIXTURES WITH HYDROGEN AND OXYGEN." J. Chem. Phys. 37, 2941 (1962).
31. Kraus, K., W. Mueller-Duysing, and H. Nevert, "COLLISIONS OF SLOW NEGATIVE IONS WITH CHARGE TRANSFER," Z. Naturforsch. 16A, 1385 (1961).
32. Kuprianov, S. E., A. A. Perov, and N. N. Tunitsky, "CROSS SECTIONS FOR DISSOCIATION OF TRI-DEUTERO (+) IONS INTO DI-DEUTERO (+) AND DEUTERO (+) IONS IN COLLISIONS WITH DEUTERIUM MOLECULES." Zh. Tekh. Eksperim. Fiz. 43, 763 (1962).
33. Larin, I. K. and V. L. Talrose, "'LOADED' IONS AND THERMAL EQUILIBRIUM IONIZATION OF GASES," Kinetika i Kataliz 3, 305 (1962)

34. Lehrle, R. S., J. C. Robb, and D. W. Thomas, "MODIFIED TIME-OF-FLIGHT MASS SPECTROMETER FOR STUDYING ION-MOLECULE OR NEUTRAL PARTICLE-MOLECULE INTERACTIONS," J. Sci. Inst. 39, 458 (1962).
35. Marino, L. L., A. C. H. Smith, E. Caplinger, "CHARGE TRANSFER BETWEEN POSITIVE CESIUM IONS AND CESIUM ATOMS," Phys. Rev. 128, 2243 (1962).
36. Marmet, P. and J. D. Morrison, "SECONDARY REACTIONS IN THE ION CHAMBER OF A MASS SPECTROMETER," J. Chem. Phys. 36, 1238 (1962).
37. Martin, T. W., R. E. Rummell, and C. E. Melton, "HIGHER-PRESSURE MASS SPECTROMETRY," Science 138, 77 (1962).
38. McDaniel, E. W., D. W. Martin, and W. S. Barnes, "DRIFT TUBE-MASS SPECTROMETER FOR STUDIES OF LOW ENERGY ION MOLECULE REACTIONS." Rev. Sci. Inst. 33, 2 (1962).
39. Munson, M. S. B., F. H. Field, and J. L. Franklin, "HIGH PRESSURE MASS SPECTROMETRIC STUDY OF REACTIONS OF RARE GASES WITH NITROGEN AND CARBON MONOXIDE," J. Chem. Phys. 37, 1790 (1962).
40. Nikolaev, V. S., I. S. Dmitriev, L. N. Fateeva, and Y. A. Teplova, "CHANGE OF THE CHARGE OF VARIOUS IONS DURING THEIR INTERACTION WITH RESIDUAL GAS," Izv. Akad. Nauk SSSR Ser. Fiz. 26, 1430 (1962).
41. Pottie, R. F., A. J. Lorquet, and W. H. Hamill, "ENERGY DEPENDENCE FOR REACTION CROSS SECTIONS OF ION MOLECULE REACTIONS OF CYCLOPROPANE IN THE MASS SPECTROMETER," J. Am. Chem. Soc. 84, 529 (1962).
42. Rack, E. P. and A. A. Gordus, "REACTIONS OF HIGH ENERGY, EXCITED IODINE-128 IONS WITH GASEOUS MOLECULES," J. Chem. Phys. 36, 287 (1962).
43. Rapp, D. and W. E. Francis, "CHARGE EXCHANGE BETWEEN GASEOUS IONS AND ATOMS," J. Chem. Phys. 37, 2631 (1962).
44. Reagan, P. N., J. C. Browne, and F. A. Matsen, "NEW LOWER LIMIT FOR THE BINDING ENERGY OF THE HELIUM MOLECULE ION," J. Am. Chem. Soc. 84, 2650 (1962).
45. Ree, T. S., T. Ree, H. Eyring, and T. Fueno, "ACTIVATED COMPLEXES OF FAST BIMOLECULAR REACTIONS," J. Chem. Phys. 36, 281 (1962).
46. Reuben, B. G. and L. Friedman, "ISOTOPIC HYDROGEN-ION-MOLECULE REACTIONS," J. Chem. Phys. 37, 1636 (1962).
47. Roth, W., "CHARGE TRANSFER CROSS SECTION FOR ELECTRONICALLY EXCITED NITROGEN ION WITH OXYGEN ATOMS AT LOW ENERGY," J. Chem. Phys. 37, 925 (1962).
48. Rudolph, P. S., S. C. Lind, C. E. Melton, "IONIC COMPLEXES OF XENON AND ACETYLENE PRODUCED BY THE RADIOLYSIS OF THESE GASES," J. Chem. Phys. 36, 1031 (1962).
49. Sheldon, J. W., "CORRELATION OF RESONANCE CHARGE EXCHANGE CROSS SECTION DATA IN THE LOW ENERGY RANGE," Phys. Rev. Letters 8, 64 (1962).
50. Sholette, W. P. and E. E. Muschlitz, "IONIZING COLLISIONS OF META-STABLE HELIUM ATOMS IN GASES," J. Chem. Phys. 36, 3368 (1962).
51. Steyaert, J., Bouchat, J., J. M. Delfosse, "METHOD FOR MEASUREMENT OF THE EFFECTIVE CROSS SECTION FOR CHARGE EXCHANGE," Ann. Soc. Sci. Bruxelles 75, 188 (1961).

52. Talrose, V. L., "ION-MOLECULAR REACTIONS IN GASES," Pure Appl. Chem. 5, 455 (1962).
53. Theard, L. P. and W. H. Hamill, "ENERGY DEPENDENCE OF CROSS SECTIONS OF SOME ION MOLECULE REACTIONS," J. Am. Chem. Soc. 84, 1134 (1962).
54. Wexler, S. and N. Jesse, "CONSECUTIVE ION-MOLECULE REACTIONS IN METHANE," J. Am. Chem. Soc. 84, 3425 (1962).

V. Free Radicals and Chemical Kinetics

John T. Herron
National Bureau of Standards
Washington, D. C.

Mass spectrometric techniques continue to be used in measuring free radical ionization potentials. However the recent work of Elder et al (7) on the photoionization of alkyl free radicals casts grave doubt on the validity of previous interpretations of electron impact data. Only in the case of the methyl radical do they interpret the measured onset energy of 9.82 ± 0.04 e.v. as being the adiabatic ionization potential. For the other radicals the ionization potentials are given only as upper limits i.e. $C_2H_5 \leq 8.4$, $n-C_3H_7 \leq 8.1$, and $iso-C_3H_7 \leq 7.5$ e.v. These later values are about 0.5 e.v. lower than the corresponding electron impact values. A reconsideration of bond energies calculated from ionization and appearance potentials measured by electron impact thus seems in order, particularly in the case of larger molecules.

A large discrepancy has existed between the ionization potential of CH_2 radical as determined by optical spectroscopy (10.396 e.v.) and by electron impact (11.75 ± 0.1 e.v.). Berkowitz and Wexler (2) have attempted to resolve this issue by repeating the earlier electron impact experiments, in which the CH_2 radical was produced by the pyrolysis of CH_3N_2 . They found no evidence for the formation of the CH_2 radical.² Their negative result thus tends to cast some doubt on the earlier electron impact value.

A new value for $I(CH_2)$ is reported by Beck and Niehaus (1). By means of a double ionization procedure these workers have examined the neutral fragments resulting from electron impact. For $I(CH_2)$ they give 10.7 ± 0.5 e.v., in substantial agreement with the spectroscopic value. In addition they report $I(C_2H_5) = 8.16 \pm 0.1$, $I(C_2H_2) = 8.6 \pm 0.2$, $I(C_2H_5) = 8.7 \pm 0.1$, $I(CH_3) = 9.98 \pm 0.05$, and $I(H) = 13.6 \pm 0.2$ e.v.

Berkowitz (3) has determined the heat of formation of the CN radical from a study of the vapor in equilibrium with graphite and nitrogen between 2200°K and 2500°K. He calculated $\Delta H_f^\circ(CN) = 109$ kcal/mole and $D_0(CN) = 7.5 \pm 0.15$ e.v. Earlier electron impact measurements are reinterpreted. The appearance potential of CN^+ from CN is reported to be 14.2 ± 0.3 e.v.

Foner and Hudson (8) give experimental details on producing the HO_2 radical by reactions of H and O atoms, photolysis, and electrical discharge. The best method of producing HO_2 was a low power electrical discharge in H_2O_2 . In the course of this work they estimate upper limits for the following reactions: $H + H_2O_2$ $k \leq 1 \times 10^{-13}$; $O + H_2O_2$ $k \leq 4 \times 10^{-15}$; and $OH + H_2O_2$ $k \leq 4 \times 10^{-13}$ cm³ molecule⁻¹sec⁻¹. $I(HO_2)$ and $A(HO_2^+)$ H_2O_2 have been redetermined as 11.53 ± 0.02 and 15.36 ± 0.05 e.v. respectively. Using these values they calculate $D(H-O_2) = 47.1 \pm 2$, $D(H-OOH) = 89.6 \pm 2$ and $\Delta H_{298}^\circ(HO_2) = 5.0 \pm 2$ kcal/mole. The same authors (10) review mass spectrometric studies of inorganic free radicals with particular reference to their own extensive work.

Palmer and Lossing (24) report the following vertical ionization potentials HS , 10.50 ± 0.1 ; CH_3S , 8.06 ± 0.1 and phenyl-S, 8.63 ± 0.1 e.v. The radicals were produced by pyrolysis of the appropriate sulphides. Derived heats of formation are $\Delta H_f(HS) \leq 33.7$; $\Delta H_f(CH_3S) \leq 31.8$ kcal/mole. Taubert and Lossing (34) report vertical ionization potentials of four pentyl radicals as, neo-pentyl 8.33, 3-pentyl 7.86, 2-pentyl 7.73, and t-pentyl 7.12 e.v. The radicals were produced by the pyrolysis of appropriate hexyl nitrites. Agreement of the measured ionization potentials with those calculated by a semi-empirical group orbital method indicates that rearrangement of the radicals to more stable isomers does not occur.

The use of the mass spectrometer to study atomic reactions continues at an accelerated rate. Kebarle and Avrahami (15) produced H and D atoms by the sensitized decomposition of H_2S or D_2S and followed the rate of heterogeneous decay of the atoms. They calculate a recombination coefficient of $1.5 \pm 0.6 \times 10^{-3}$ (on Silica). Phillips and Schiff (26) have studied the reaction of H atom, produced in an electrodeless discharge, with NO_2 and O_3 . They give the following results: for $H + O_3 \rightarrow OH + O_2$ $k = (2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and for $H + NO_2 \rightarrow OH + NO$ $k = (4.8 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The NO_2 reaction is suggested as a suitable "titration" method for measuring H atom concentrations. They also present evidence for a reaction of vibrationally excited OH radicals with O_3 . Schiavello and Valpi (31) report on the reaction of H atoms (produced as in ref. (26)) with N_2H_4 , NH_3 and N_2O . They find for $N_2H_4 + H = H_2 + N_2H_3$, $k = 3.5 \times 10^{11} \exp \{-2000/RT\} \text{ mole}^{-1} \text{ cc sec}^{-1}$. Estimated rate data is given for the NH_3 and N_2O reactions.

Foner and Hudson (9) have made a detailed study of active nitrogen. Although its chemical properties indicate that active species other than ground state N atoms are present in active nitrogen, they were not detected in previous mass spectrometric work. The present workers detect, in addition to ground state N atoms, metastable $N(^2D)$ and $N(^2P)$ atoms. By adding helium to the nitrogen in the gas discharge the concentration of metastables was greatly enhanced. They also detected metastable N_2 molecules consisting of both vibrationally excited ground state N_2 and various vibrational states of the $A^3\Sigma_u^+$ state.

Phillips and Schiff (27) have studied the reactions of atomic nitrogen with a series of compounds. They report the following rate data: $N + O_3 \rightarrow NO + O_2$, $k \pm (5.7 \pm 1.4) \times 10^{-13}$; $N + NO \rightarrow N_2 + O$, $k = (2.2 \pm 0.6) \times 10^{-11}$; $O_3 + NO \rightarrow NO_2 + O_2$, $k = (2.1 \pm 0.5) \times 10^{-14}$; $O_3 + O \rightarrow 2O_2$, $k = (2.5 \pm 0.5) \times 10^{-14}$; and $O + NO_2 \rightarrow O_2 + NO$, $k = (2.5 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. They also conclude that the reaction $N + NO$ leads to the formation of vibrationally excited N_2 molecules having energies greater than 23.4 kcal/mole. This latter observation is reported in more detail elsewhere (20) (28). They find that the excited N_2 molecule reacts with ozone, and give for $O_3 + N_2^* \rightarrow N_2 + O_2 + O$, $k = (5.4 \pm 1.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Rates of collisional deactivation of N_2^* are also given.

In a series of papers on the design and use of collision free molecular beam sampling systems, Nutt and Biddlestone (21) (22) (23) report on the products of an electrodeless discharge in oxygen, and the reaction $O + NO_2$. In the former case their results are in considerable disagreement with those of other workers, i.e. the atomic species they detect is the metastable (1D) rather than the ground state species (3P). In addition, they do not detect metastable O_2 molecules. In the case of the reaction $O + NO_2$, interpreting the O atom as being in the metastable (1D) state, they conclude that the reaction has a collision efficiency of about 0.2.

Clyne and Thrush (5) have examined the reaction $^{18}O + NO_2$ and conclude on the basis of the purely statistical distribution of ^{18}O in the products, that the reaction proceeds through a transition state in which the three oxygen atoms are equivalent.

Heicklen and Johnston have used a time-of-flight instrument to study the photo-chemical oxidation of ethyl iodide (12) and methyl iodide (13). In this work the reaction mixture was continuously irradiated in a "stirred-flow" reactor separated from the ion source by a pin-hole leak. Although the results are rather complex, they were able to cast considerable light on the mechanisms of these reactions. It is significant that ozone was not detected in either case. Similar work on the photochlorination of trichloroethylene is reported by Huybrechts et al (14) which leads to data on the properties of the tetrachloroethyl radical. Again, the complexity of the system is noteworthy.

Hagemann (11) has studied the interaction of oxygen and sulphur in a high frequency discharge. SO and S₂O₂ were not detected. Molecular species identified at sampling times of about 1 sec. were SO₂, S₂O, S₂ and O₂.

Pham Dinh-Hoi (25) has studied the diffusion of hydrogen through palladium. No ionic species are observed coming directly from the surface. Molecular hydrogen is detected. Peaks are observed at m/e 1/2 and 3 only when the palladium is heated. This is probably a pressure effect.

Porter et al (29) have studied the reaction of BF₃ with BCl₃, B(OH)₃ and B₂O₃ (liquid). From measurements of the temperature dependence of the equilibrium constants they arrive at values for the heats of reaction, from which they compute ΔH_f BFCl₂ = -154.1 ± 1.0,; BF₂Cl = -211.9 ± 2.0, B(OH)₂F = -249.8, and B(OH)F₂ -260.2 ± 2.5 kcal/mole, at 298°K. In the case of the reaction BF₃(g) + B₂O₃(l) = (BOF)₃(g) they find $\Delta H^\circ = 3.46 \pm 0.30$ kcal/mole over the temperature interval 412 to 974°K. Porter and Smith (30) have studied the reactions of CF₃CCl₃ and CFCl₃ with graphite, from which they are able to estimate for the reaction F₂ + graphite → 2F (graphite), $\Delta H^\circ = -100.2 \pm 6$ kcal/mole F₂.

McKinley (19) has studied the reaction of a beam of chlorine gas with a nickel surface. He finds very little transfer of translational energy. An upper limit for the accommodation coefficient is reported to be 0.15.

Smith and Fite (32) have studied the reflection and dissociation of H₂ on tungsten using a mass spectrometer detector in conjunction with a modulated atomic beam. Above 2500°K it was found that the sticking probability of H₂ on tungsten approached a limiting value of 0.3. This work is reported in more detail elsewhere (33) along with results of experiments on the scattering of molecular hydrogen by polycrystalline nickel, and the reaction of molecular chlorine with nickel.

Lintz et al (18) have studied the oxidation of methane on a platinum filament. They find that the reaction commences at about 600°K which corresponds to the temperature at which the platinum surface is no longer completely covered with chemisorbed oxygen.

Cassuto (4) has examined the heterogeneous pyrolysis of dibutyl tertiary peroxide, dimethyl mercury, and diethyl mercury in the Knudsen pressure region. He reports activation energies, free radical mass spectra and sensitivities, and free radical recombination and reaction probabilities. This paper contains a detailed development of the necessary expressions for interpreting data in this pressure region.

Lehrle et al (17) describe a modified time-of-flight mass spectrometer for studying ion-molecule or neutral particle-molecule interactions.

Dawson and Tickner (6) have observed the H₅⁺ ion in the negative glow of the hydrogen glow discharge. They also observe an ion corresponding to H₅O⁺. Knewstubb and Tickner (16) have examined the ions in glow discharges in nitrogen and its mixtures with hydrogen and oxygen. The possible origins of the many ions observed are discussed.

V. Free Radicals and Chemical Kinetics

1. Beck, D. and Niehaus, A., J. Chem. Phys. 37, 2705 (1962), REACTIONS OF EXCITED BUTANE MOLECULES.
2. Berkowitz, J. and Wexler, S., J. Chem. Phys. 37, 1476 (1962), ON THE IONIZATION POTENTIAL OF THE CH_2 RADICAL.
3. Berkowitz, J., J. Chem. Phys. 36, 2533 (1962), HEAT OF FORMATION OF THE CN RADICAL.
4. Cassuto, A., Ann. de Chimie, 7, 249 (1962) (Thesis, Nancy 1962) ANALYSE DU FONCTIONNEMENT DES REACTEURS CYLINDRIQUES, EN REGIME MOLECULAIRE. APPLICATION A L'ETUDE PAR SPECTROMETRIE DE MASSE DES REACTIONS DES RADICAUX LIBRES METHYLE ET ETHYLE.
5. Clyne, M. A. A. and B. A. Thrush, Trans. Faraday Soc., 58, 511 (1962). ISOTOPIC INVESTIGATION OF THE REACTION OF OXYGEN ATOMS WITH NITROGEN DIOXIDE.
6. Dawson, P. H. and Tickner, A. W., J. Chem. Phys. 37, 672 (1962), DETECTION OF H_5^+ IN THE HYDROGEN GLOW DISCHARGE.
7. Elder, F. A., Giese, C., Steiner, B. and Inghram, M., J. Chem. Phys. 36, 3292 (1962), PHOTO-IONIZATION OF ALKYL FREE RADICALS.
8. Foner, S. N. and Hudson, R. L., J. Chem. Phys. 36, 2681 (1962), MASS SPECTROMETRY OF THE HO_2 FREE RADICAL.
9. Foner, S. N. and Hudson, R. L., J. Chem. Phys. 37, 1662 (1962), MASS SPECTROMETRIC STUDIES OF METASTABLE NITROGEN ATOMS AND MOLECULES IN ACTIVE NITROGEN.
10. Foner, S. N. and Hudson, R. L., "FREE RADICALS IN ORGANIC CHEMISTRY", p. 34, Advances in Chemistry Series, No. 36. American Chemical Society. Washington, D. C. (1962).
11. Hagemann, R., Compt. Rendu., 255, 899 (1962), ETUDE DE L'HEMIOXYDE DE SOUFRE S_2O PAR SPECTROMETRIE DE MASS.
12. Heicklen, J. and Johnston, H. S., J. Amer. Chem. Soc. 84, 4394 (1962) PHOTOCHEMICAL OXIDATIONS. I. ETHYL IODIDE.
13. Heicklen, J. and Johnston, H. S., J. Am. Chem. Soc. 84, 4030 (1962), PHOTOCHEMICAL OXIDATIONS. II. METHYL IODIDE.
14. Huybrechts, G., Meyers, L. and Verbeke, G., Trans. Faraday Soc. 58, 1128 (1962), STABILITY AND REACTIONS OF THE TETRA-CHLOROETHYL RADICAL.
15. Kebarle, P. and Avrahami, M., Can. J. Chem., 40, 2409 (1962), HYDROGEN ATOM RECOMBINATION IN THE FLOW SYSTEM ATTACHED TO A MASS SPECTROMETER AND USED FOR THE STUDY OF MERCURY-SENSITIZED REACTIONS.
16. Knewstubb, P. F. and Tickner, A. W., J. Chem. Phys. 37, 2941 (1962), MASS SPECTROMETRY OF IONS IN GLOW DISCHARGES. III. NITROGEN AND ITS MIXTURES WITH HYDROGEN AND OXYGEN.
17. Lehrle, R. S., Robb, J. C. and Thomas, D. W., J. Sci. Inst., 39, 458 (1962). A MODIFIED TIME-OF-FLIGHT MASS SPECTROMETER FOR STUDYING ION-MOLECULE OR NEUTRAL PARTICLE-MOLECULE INTERACTIONS.
18. Lintz, H. G., Pentenero, A. and LeGoff, P., J. Chim. Phys., 59, 933 (1962). ETUDE PAR SPECTROMETRIE DE MASSE DE LA COMBUSTION HETEROGENE DES VAPEURS ORGANIQUES SUR PLATINE
1. CAS DU METHANE AVEC EXCES D'OXYGENE.

19. McKinley, J. D., J. Phys. Chem. 66, 554 (1962), TRANSLATIONAL ENERGY ACCOMMODATION IN THE NICKEL-CHLORINE SURFACE REACTION.
20. Morgan, J. E., Phillips, L. F. and Schiff, H. I., Disc. Faraday Soc., No. 33, 118 (1962). STUDIES OF VIBRATIONALLY EXCITED NITROGEN USING MASS SPECTROMETRIC AND CALORIMETER-PROBE TECHNIQUES.
21. Nutt, C. W. and Biddlestone, A. J., Trans. Faraday Soc., 58, 1363 (1962), THEORY AND APPLICATION OF MOLECULAR-BEAM TECHNIQUES FOR THE DESIGN OF COLLISION-FREE SAMPLING SYSTEMS. Part 3 KNOCKING-ON COLLISIONS IN THE COLLIMATING CHAMBERS.
22. Nutt, C. W. and Biddlestone, A. J., Trans. Faraday Soc., 58, 1368 (1962), PART 4. APPEARANCE POTENTIAL AND SCATTERING CROSS-SECTION OF OXYGEN ATOMS FROM AN R.F. DISCHARGE (10 Mc/Sec).
23. Nutt, C. W. and Biddlestone, A. J., Trans. Faraday Soc., 58, 1376 (1962), PART 5. REACTION OF ATOMIC OXYGEN WITH NITROGEN DIOXIDE.
24. Palmer, T. F. and Lossing, F. P., J. Am. Chem. Soc., 84, 4661 (1962) FREE RADICALS BY MASS SPECTROMETRY. XXVIII. THE HS, CH₃S, AND PHENYL-S RADICALS: IONIZATION POTENTIALS AND HEATS OF FORMATION.
25. Pham Dinh-Hoi, Compt. Rendu., 255, 1724 (1962)., ETUDE AU SPECTROMETRE DE MASSE DE L'HYDROGENE DIFFUSE PAR LE PALLADIUM.
26. Phillips, L. F. and Schiff, H. I., J. Chem. Phys. 37, 1233 (1962), MASS SPECTROMETRIC STUDIES OF ATOMIC REACTIONS. III. REACTIONS OF HYDROGEN ATOMS WITH NITROGEN DIOXIDE AND WITH OZONE.
27. Phillips, L. F. and Schiff, H. I., J. Chem. Phys., 36, 1509 (1962), MASS SPECTROMETRIC STUDIES OF ATOM REACTIONS. I. REACTIONS IN THE ATOMIC NITROGEN-OZONE SYSTEM.
28. Phillips, L. F. and Schiff, H. I., J. Chem. Phys. 36, 3283 (1962), MASS SPECTROMETRIC STUDIES OF ATOM REACTIONS. II. VIBRATIONALLY EXCITED N₂ FORMED BY THE REACTION OF N ATOMS WITH NO.
29. Porter, R. F., Bidinosti, D. R., and Watterson, K. F., J. Chem. Phys., 36, 2104 (1962), MASS SPECTROMETRIC STUDY OF THE REACTIONS OF BF₃ (g) WITH BCl₃(g), B(OH)₃ (g), AND B₂O₃(l).
30. Porter, R. F. and Smith, D. H. J. Phys. Chem. 66, 1562 (1962), HEAT OF REACTION OF FLUORINE WITH GRAPHITE.
31. Schiavello, M. and Volpi, G. G., J. Chem. Phys. 37, 1510 (1962). REACTIONS OF HYDROGEN ATOMS WITH HYDRAZINE, AMMONIA, AND NITROUS OXIDE.
32. Smith, Joe N., Jr., and Fite, W. L., J. Chem. Phys. 37, 898 (1962), REFLECTION AND DISSOCIATION OF H₂ ON TUNGSTEN.
33. Smith, Joe N., Jr., and Fite, W. L., General Atomic Report GA-3136 (May 1962), RECENT INVESTIGATIONS OF GAS-SURFACE INTERACTIONS USING MODULATED-ATOMIC-BEAM TECHNIQUES.
34. Taubert, R. and Lossing, F. P., J. Am. Chem. Soc., 84, 1523 (1962), FREE RADICALS BY MASS SPECTROMETRY. XXVII. IONIZATION POTENTIALS OF FOUR PENTYL RADICALS.

VI. Quasi-Equilibrium Theory of Mass Spectra

A. L. Wahrhaftig

1. Beck, D. and Nishaus, A., REACTIONS OF EXCITED BUTANE MOLECULES. J. Chem. Phys. 37, 2705-8 (1962).
2. Benson, S. and Nangia, P. S., KINETIC ISOTOPE EFFECTS IN THE PYROLYSIS OF CYCLOPROPANE AND CYCLOBUTANE, J. Chem. Phys. 38, 18-25 (1963).
3. Bradley, J. W. and Rabinovitch, B. S., THE MECHANISM OF DISPROPORTIONATION OF ALKYL RADICALS, J. Chem. Phys. 36, 3498-9 (1962).
4. Bunker, D. L., MONTE CARLO CALCULATION OF TRIATOMIC DISSOCIATION RATES I. N_2O AND O_3 . J. Chem. Phys. 37, 394, (1962).
5. Chupka, W. A. and Kaminsky, M., ENERGY DISTRIBUTION AND FRAGMENTATION PROCESSES RESULTING FROM ELECTRON IMPACT ON PROPANE AND N-BUTANE. J. Chem. Phys. 35, 1991 (1961).
6. Coggeshall, N., STUDIES OF METASTABLE ION TRANSITIONS WITH A 180° MASS SPECTROMETER., J. Chem. Phys. 37, 2167 (1962).
7. Current, J. H. and Rabinovitch, B. S., DECOMPOSITION OF CHEMICALLY ACTIVATED ETHYL- d_3 RADICALS. PRIMARY INTRAMOLECULAR KINETIC ISOTOPE EFFECT IN A NONEQUILIBRIUM SYSTEM., J. Chem. Phys. 38, 783-95 (1963).
8. Denisor, E. T., MODEL OF CHAIN REACTIONS WITH DEGENERATE BRANCHING AND SEVERAL INTERMEDIATE PRODUCTS. Zh. Fiz. Khim. 36, 2352-61 (1962).
9. Hung, N. C. and Wilson, D. J., ANHARMONIC EFFECTS IN UNIMOLECULAR RATE THEORY. DYNAMICS OF A ROTATING ANHARMONIC TRIATOMIC MOLECULE. J. Chem. Phys. 38, 828-31 (1963).
10. Kanomata, I., MASS-SPECTROMETRIC STUDY ON IONIZATION AND DISSOCIATION OF DIETHYL ETHER ON ELECTRON IMPACT. Bull. Chem. Soc. Japan 34, 1596-9 (1961).
11. Kubin, R. F., Rabinovitch, B. S., Harrington, R. E., UNIMOLECULAR DECOMPOSITION OF CHEMICALLY ACTIVATED SEC-BUTYL AND SEC-BUTYL d_1 RADICALS. etc., J. Chem. Phys. 37, 937 (1962).
12. Kupriyanov, S. E., DISSOCIATION OF EXCITED IONS. Zh. Fiz. Khim. 36, 218 (1962).
13. Laidler, K. J., and Wojciechowski, B. W., ACTIVATED COMPLEXES IN UNIMOLECULAR REACTIONS. Chem. Soc. (London) Spec. Publ. No. 1b, 37 (1962).
14. McFadden, W. H. and Lounsbury, M., MASS SPECTRA OF THREE DEUTERATED BROMOBUTANES., Can. J. Chem. 40, 1965-75 (1962).
15. Momigny, J., RATE CONSTANTS FOR THE DECOMPOSITION OF METASTABLE POLYATOMIC IONS., Bull. Soc. Chim. Belges. 70, 291, (1961).
16. Monahan, J. E., and Stanton, H., MASS SPECTRA RESULTING FROM HIGH-ENERGY ELECTRON IMPACT ON SOME HYDROCARBON MOLECULES. J. Chem. Phys. 37, 2654 (1962).
17. Murgulescu, I. G., and Simon, Z., CALCULATIONS OF PRE-EXPONENTIAL COEFFICIENTS OF UNIMOLECULAR REACTIONS. Acad. Rep. Populare Romine, studii Cercetari. Chim. 10, 11 (1962).
18. Ibid., 10, 31 (1962).
19. Rabinovitch, B. S., INVERSE INTERMOLECULAR KINETIC ISOTOPE REACTIONS. Can. J. Chem. 39, 2609 (1961).

20. Rabinovitch, B. S., THE CLASSICAL APPROXIMATION IN UNIMOLECULAR REACTIONS AND MASS SPECTRA. J. Chem. Phys. 35, 2250 (1961).
21. Rabinovitch, B. S. and Current, J. H., OCCURRENCE OF LARGE NORMAL SECONDARY INTERMOLECULAR KINETIC ISOTOPE EFFECTS IN NON-EQUILIBRIUM SYSTEMS. Can. J. Chem. 40, 557 (1962).
22. Rice, O. K., EFFECTS OF QUANTIZATION AND OF ANHARMONICITY ON THE RATES OF DISSOCIATION AND ASSOCIATION OF COMPLEX MOLECULES. J. Phys. Chem. 65, 1588 (1961).
23. Schlag, E. W., UNIMOLECULAR RATES DUE TO MULTIPLE CRITICAL OSCILLATORS., J. Chem. Phys. 35, 2117 (1961).
24. Schlag, E. W. and Sandsmark, R. A., COMPUTATION OF STATISTICAL COMPLEX IONS AS APPLIED TO UNIMOLECULAR REACTIONS, J. Chem. Phys. 37, 168 (1962).
25. Shannon, J. S., STRUCTURES AND REACTIONS OF IONS FROM BENZYL ALCOHOL, o-, m-, AND p-HYDROXYBENZYL ALCOHOLS AND DERIVATIVES. Australian J. Chem. 15, 265 (1962).
26. Taubert, R., THE INITIAL ENERGY WITHIN THE FRAMEWORK OF THE STATISTICAL THEORY OF MASS SPECTRA, Z. Naturforsch 16a, 1394 (1961).
27. Vestal, M. and Rosenstock, H. M., OSCILLATOR MODELS IN UNIMOLECULAR REACTIONS. J. Chem. Phys. 35, 2008 (1961).
28. Vestal, M., Wahrhaftig, A. L. and Johnston, W. H., IMPROVED RATE EXPRESSION IN THE QUASIEQUILIBRIUM THEORY OF MASS SPECTRA. J. Chem. Phys. 37, 1276 (1962).
29. Wieder, G. and Marcus, R. A. DISSOCIATION AND ISOMERIZATION OF VIBRATIONALLY EXCITED SPECIES (II). UNIMOLECULAR REACTION RATE THEORY AND ITS APPLICATION. J. Chem. Phys. 37, 1835 (1962).
30. Wolfsberg, M., RATE CONSTANTS FOR THE UNIMOLECULAR DECOMPOSITION OF EXCITED MOLECULAR SPECIES NEAR THRESHOLD., J. Chem. Phys. 36, 1072 (1962).

VII. Isotopic Abundance and Atomic Weight

E. J. Catanzaro

1. Allsopp, H. L., Roberts, H. R., Schreiner, C. D. L., and Hunter, D. R., *J. Geophys. Research*, 67, 5307 (1962), Rb-Sr AGE MEASUREMENTS ON VARIOUS SWAZILAND GRANITES.
2. Anders, E., *Science* 138, 431-433, (1962), TWO METEORITES OF UNUSUALLY SHORT COSMIC-RAY EXPOSURE AGE.
3. Aswathanarayana, U., *Nature*, 193, 470 (1962), AGE OF THE CUDDAPAH, INDIA.
4. Bailey, S. W., Hurley, P. M., Fairbairn, H. W., Pinson, W. H., Jr., *Geol. Soc. Amer. Bull.* 73, 1167 (1962), K-Ar DATING OF SEDIMENTARY ILLITE POLYTYPES.
5. Bassett, W. A., Kerr, P. F., Schaeffer, O. A., and Stoenner, R. W., *Geol. Soc. Amer. Bull.* 74, 221 (1962), POTASSIUM-ARGON AGES OF VOLCANIC ROCKS NEAR GRANTS, NEW MEXICO.
6. Bassett, W. A., Kerr, P. F., Schaeffer, O. A., and Stoenner, R. W., *Geol. Soc. Amer. Bull.* 74, 213 (1963), POTASSIUM-ARGON DATING OF THE LATE TERTIARY VOLCANIC ROCKS AND MINERALIZATION OF MARYSVALE, UTAH.
7. Bassett, W. A. and Giletti, B. J., *Geol. Soc. Amer. Bull.* 74, 209 (1963), PRECAMBRIAN AGES IN THE WIND RIVER MTS., WYOMING.
8. Bate, G. L., Huizenga, J. R., *Geochim. Cosmochim. Acta*, 27, 345 (1963), ABUNDANCES OF RUTHENIUM, OSMIUM, AND URANIUM IN SOME COSMIC AND TERRESTRIAL SOURCES.
9. Brown, J. S., *Econ. Geol.* 57, 673 (1962), ORE LEADS AND ISOTOPES.
10. Burger, A. J., Nicolaysen, L. O. and deVilliers, J. W. L., *Geochim. Cosmochim. Acta*, 26, 25-59 (1962), LEAD ISOTOPIC COMPOSITIONS OF GALENAS FROM THE WITWATERSRAND AND ORANGE FREE STATE, AND THEIR RELATION TO THE WITWATERSRAND AND DOMINION REEF URANINITES.
11. Burwash, R. A., Baadsgaard, H., and Peterman, Z. E., *J. Geophys. Research* 67, 1617 (1962), PRECAMBRIAN K-Ar DATES FROM THE WESTERN CANADA SEDIMENTARY BASIN.
12. Catanzaro, E. J., *J. Geophys. Research* 68, 2045 (1963), ZIRCON AGES IN SOUTHWESTERN MINNESOTA.
13. Cervenjak, Z., Ferrara, G., Tongiorgi, E., *Nature*, 197, 893 (1963). AGE DETERMINATION OF SOME YUGOSLAV GRANITES AND GRANODIORITES BY THE RUBIDIUM/STRONTIUM METHOD.
14. Charalambus, St. and Goebel, K., *Geochim. Cosmochim. Acta*, 26, 659 (1962), TRITIUM AND ARGON-39 IN THE BRUDERHEIM METEORITE.
15. Chow, T. J., Patterson, C. C., *Geochim. Cosmochim. Acta* 26, 263-308 (1962), THE OCCURRENCE AND SIGNIFICANCE OF LEAD ISOTOPES IN PELAGIC SEDIMENTS.
16. Clayton, R. N., *Science*, 140, 192 (1963), CARBON ISOTOPE ABUNDANCE IN METEORITIC CARBONATES.
17. Compston, W., and Pidgeon, R. T., *J. Geophys. Research* 67, 3493 (1962), RUBIDIUM-STRONTIUM DATING OF SHALES BY THE TOTAL-ROCK METHOD.
18. Confiantini, R., Togliatti, V., Tongiorgi, E., de Breuck, W., Picciotto, E., *Nature*, 197, 1096 (1963). GEOGRAPHICAL VARIATIONS OF OXYGEN-18/OXYGEN-16 RATIO IN SURFACE SNOW AND ICE FROM QUEEN MAUD LAND, ANTARCTICA.

19. Dalrymple, G. B., Geol. Soc. Amer. Bull. 74, 379 (1963), POTASSIUM-ARGON DATES OF SOME CENOZOIC VOLCANIC ROCKS OF THE SIERRA NEVADA.
20. Daughtry, A. C., Perry, D., Williams, M., Geochim. Cosmochim. Acta, 26, 857 (1962), MAGNESIUM ISOTOPIC DISTRIBUTION IN DOLOMITE.
21. Davis, G. L., Tilton, G. R., and Wetherill, G. W., J. Geophys. Research, 67, 1987 (1962), MINERAL AGES FROM THE APPALACHIAN PROVINCE IN NORTH CAROLINA AND TENNESSEE.
22. Davis, W. D., Mewherter, J. L., Geochim. Cosmochim. Acta, 26, 681, (1962), ABUNDANCE OF U-236 IN NATURE.
23. Deevey, E. S., Jr., Nakai, N., Stuiver, M., Science, 139, 407 (1963), FRACTIONATION OF SULFUR AND CARBON ISOTOPES IN A MEROMICTIC LAKE.
24. Dessau, G., Jensen, M. L., Nakai, N., Econ. Geol. 57, 410 (1962), GEOLOGY AND ISOTOPIC STUDIES OF SICILIAN SULFUR DEPOSITS.
25. Deuser, W. G. and Herzog, L. F., J. Geophys. Research, 67, 1997 (1962), RUBIDIUM-STRONTIUM AGE DETERMINATIONS OF MUSCOVITES AND BIOTITES FROM PEGMATITES OF THE BLUE RIDGE AND PIEDMONT.
26. Doe, B. R., J. Geophys. Research 67, 2895, (1962), RELATIONSHIPS OF LEAD ISOTOPES AMONG GRANITES, PEGMATITES, AND SULPHIDE ORES NEAR BALMAT, N.Y.
27. Eberhardt, P., Ferrara, G., Nature, 196, 665 (1962), CONFIRMATION OF THE ABSOLUTE AGE OF THE GRANODIORITE OUTCROP ON ELBA ISLAND WITH POTASSIUM-ARGON MEASUREMENTS.
28. Evernden, J. F., Richards, J. R., Nature, 192, 446 (1961) POTASSIUM-ARGON AGES AT BROKEN HILL, AUSTRALIA.
29. Fanale, F. P. and Kulp, J. L., Econ. Geol. 57, 735, (1962), THE HELIUM METHOD AND THE AGE OF THE CORNWALL, PA. MAGNETITE ORE.
30. Faul, H., Stern, T. W., Thomas, H. H., Elmore, P. L. D., Am. J. Sci., 261, 1 (1963). AGE OF INTRUSION AND METAMORPHISM IN THE NORTHERN APPALACHIANS.
31. Faure, G., Hurley, P. M. and Fairbairn, H. W., J. Geophys. Research, 68, 2323 (1963), AN ESTIMATE OF THE ISOTOPIC COMPOSITION OF STRONTIUM IN ROCKS OF THE PRECAMBRIAN SHIELD OF NORTH AMERICA.
32. Finley, H. O., Eberle, A. R., Rodden, C. J., Geochim. Cosmochim. Acta, 26, 911 (1962), ISOTOPIC BORON COMPOSITION OF CERTAIN BORON MINERALS.
33. Fisher, D. E., Science, 129, 752 (1963), "AGES" OF THE SIKHOTE ALIN IRON METEORITE.
34. Gast, P. W., Geochim. Cosmochim. Acta, 26, 927 (1962), THE ISOTOPIC COMPOSITION OF STRONTIUM AND THE AGE OF STONE METEORITES-I.
35. Gehlen, K. V., Nielsen, H., Ricke, W., Geochim. Cosmochim. Acta, 26, 1189 (1962), S-ISOTOPEN-VERHALTNISSE IN BARYT UND SULFIDEN AUS HYDROTHERMALEN GANGEN IM SCHWARZWALD UND JUNGERAN BARYTGANGEN IN SÜDDEUTSCHLAND UND IHRE GENETISCHE BEDEUTUNG.
36. Gentner, W., Lippolt, H. J., Schaeffer, O. A., Geochim. Cosmochim. Acta, 27, 191 (1963). ARGONBESTIMMUNGEN AN KALIUMMINERALIEN-XI DIE KALIUM-ARGON-ALTER DER GLASER DES NORDLINGER RIESES UND DER BOHMISCH-MAHRISCHEN TEKITE.

37. Godfrey, J. D., *Geochim. Cosmochim. Acta*, 26, 1215 (1962), THE DEUTERIUM CONTENT OF HYDROUS MINERALS FROM THE EAST-CENTRAL SIERRA NEVADA AND YOSEMITE NATIONAL PARK.
38. Goldberg, E. D., Koide, M., *Geochim. Cosmochim. Acta* 26, 417 (1962), GEOCHRONOLOGICAL STUDIES OF DEEP SEA SEDIMENTS BY THE IONIUM/THORIUM METHOD.
39. Green, W. D. and Damon, P. E., *Econ. Geol.* 58, 143 (1963). AGE OF CORNWALL, PENNSYLVANIA MAGNETITE ORE.
40. Hamilton, E., Harland, W. B., Miller, J. A., *Nature* 195, 1191 (1962), ISOTOPIC AGES FROM SOME SPITSBERGEN ROCKS.
41. Hill, C. R. and Crookall, J. O., *J. Geophys. Research*, 68, 2358 (1963), NATURAL OCCURRENCE OF U_{234} ENRICHED URANIUM.
42. Hulston, J. R. and McCabe, W. J., *Geochim. Cosmochim. Acta*, 26, 399-410 (1962), MASS SPECTROMETER MEASUREMENTS IN THE THERMAL AREAS OF NEW ZEALAND PART 2: CARBON ISOTOPE RATIOS.
43. Hurley, P. M., Brookins, D. G., Pinson, W. H., Hart, J. R., and Fairbairn, H. W., *Geol. Soc. Amer. Bull.* 72, 1807 (1961), K-Ar AGE STUDIES OF MISSISSIPPI AND OTHER RIVER SEDIMENTS.
44. Hurley, P. M., Heezen, B. C., Pinson, W. H., Fairbairn, H. W., *Geochim. Cosmochim. Acta*, 27, 393 (1963), K-Ar AGE VALUES IN PELAGIC SEDIMENTS OF THE NORTH ATLANTIC.
45. Hurley, P. M., Hunt, J. M., Pinson, W. H., Fairbairn, H. W., *Geochim. Cosmochim. Acta*, 27, 279 (1963), K-Ar AGE VALUES ON THE CLAY FRACTIONS IN DATED SHALES.
46. Hurley, P. M., Hughes, H., Pinson, W. H., Jr., and Fairbairn, H. W., *Geochim. Cosmochim. Acta* 26, 67 (1962), RADIOGENIC ARGON AND STRONTIUM DIFFUSION PARAMETERS IN BIOTITE AT LOW TEMPERATURES OBTAINED FROM ALPINE FAULT UPLIFT IN NEW ZEALAND.
47. Hurley, P. M., Hughes, H., Faure, G., Fairbairn, H. W., and Pinson, W. H., *J. Geophys. Research* 67, 5315 (1962), RADIOGENIC STRONTIUM-87 MODEL OF CONTINENT FORMATION.
48. Jager, E., *J. Geophys. Research* 67, 5293 (1962), Rb-Sr AGE DETERMINATIONS ON MICAS AND TOTAL ROCKS FROM THE ALPS.
49. Kaplan, I. R., Emery, K. O., Rittenberg, S. C., *Geochim. Cosmochim. Acta*, 27, 297 (1963), THE DISTRIBUTION AND ISOTOPIC ABUNDANCE OF SULPHUR IN RECENT MARINE SEDIMENTS OFF SOUTHERN CALIFORNIA.
50. Kirsten, T., Krankowsky, D., Zahringer, J., *Geochim. Cosmochim. Acta*, 27, 13 (1963), EDELGAS-UND KALIUM-BESTIMMUNGEN AN EINER GROSSEREN ZAHL VON STEINMETEORITEN.
51. Koczy, F. F., *Science* 134, 1978 (1961), RATIO OF THORIUM-230 TO THORIUM-232 IN DEEP-SEA SEDIMENTS.
52. Krummenacher, D., Merrihue, C. M., Pepin, R. O., Reynolds, J. H., *Geochim. Cosmochim. Acta* 26, 231 (1962), METEORITIC KRYPTON AND BARIUM VERSUS THE GENERAL ISOTOPIC ANOMALIES IN METEORITIC XENON.
53. Kulp, J. L., Kologrivov, R., Haller, J., Koch, L., *Nature*, 196, 160 (1962), FURTHER ISOTOPIC AGE MEASUREMENTS ON ROCKS FROM NORTHEASTERN GREENLAND.
54. Kulp, J. L., Kologrivov, R., Haller, J., Koch, L., *Nature*, 194, 953-955 (1962), POTASSIUM-ARGON AGES ON ROCKS FROM EASTERN GREENLAND.

55. Kuroda, P. K. and Manuel, O. K., J. Geophys. Research, 67, 4859 (1962), ON THE CHRONOLOGY OF THE FORMATION OF THE SOLAR SYSTEM. I. RADIOGENIC XENON 129 IN THE EARTH'S ATMOSPHERE.
56. Kuroda, P. K. and Crouch, W. W., Jr., J. Geophys. Research, 67, 4863 (1962), ON THE CHRONOLOGY OF THE FORMATION OF THE SOLAR SYSTEM. II. IODINE IN TERRESTRIAL ROCKS AND THE XENON 129/136 FORMATION INTERVAL OF THE EARTH.
57. Lippolt, H. J., Gentner, N., Geochim. Cosmochim. Acta, 26, 1247 (1962), ARGON BESTIMMUNGEN AN KALIUM-MINERALIEN-X. VERSUCHE DER KALIUM-ARGON-DATIERUNG VON FOSSILIEN.
58. Long, L. E., Geol. Soc. Amer. Bull., 73, 997, (1962), ISOTOPIC AGE STUDY, DUTCHESS CO., N. Y.
59. Long, L. E. and Kulp, J. L., Geol. Soc. Amer. Bull. 73, 969, (1962), ISOTOPIC AGE STUDY OF THE METAMORPHIC HISTORY OF THE MANHATTEN AND READING PRONGS.
60. Marshall, R. R., Geochim. Cosmochim. Acta, 26, 981 (1962), COSMIC RADIATION AND THE K^{40} -Ar 40 "AGES" OF IRON METEORITES.
61. Marshall, R. R., J. Geophys. Research 67, 2005 (1962), MASS SPECTROMETRIC STUDY OF THE LEAD IN CARBONACEOUS CHONDRITES.
62. Masuda, A., Nature, 197, 892 (1963), DISCREPANCY IN AGE-DETERMINATION INVOLVING RADIOGENIC ISOTOPES OF LEAD.
63. McDougall, I., J. Geophys. Research 68, 1535 (1963), POTASSIUM-ARGON AGE MEASUREMENTS ON DOLERITES FROM ANTARCTICA AND SOUTH AFRICA.
64. McDougall, I., Nature, 197, 344 (1963), POTASSIUM-ARGON AGES FROM WESTERN OAHU, HAWAII.
65. Merrihue, C. M., J. Geophys. Research 68, 325 (1963), EXCESS XENON 129 IN CHONDRULES FROM THE BRUDERHEIM METEORITE.
66. Merrihue, C. M., Pepin, R. O., and Reynolds, J. H., J. Geophys. Research 67, 2017 (1962), RARE GASES IN THE CHONDRITE PANTAR.
67. Murthy, V. R. and Schmitt, R. A., J. Geophys. Research 68, 911 (1963), ISOTOPE ABUNDANCES OF RARE-EARTH ELEMENTS IN METEORITES I. IMPLICATIONS OF SAMARIUM EUROPIUM, AND GADOLINIUM TO THE EARLY HISTORY OF THE SOLAR SYSTEM.
68. Murthy, V. R., J. Geophys. Research 67, 905 (1962), ISOTOPIC ANOMALIES OF MOLYBDENUM IN SOME IRON METEORITES.
69. Murthy, V. R., Geochim. Cosmochim. Acta 26, 481 (1962), THE ISOTOPIC COMPOSITION OF SILVER IN IRON METEORITES.
70. Murthy, V. R. and Patterson, C. C., J. Geophys. Research 67, 1161 (1962), PRIMARY ISOCHRON OF ZERO AGE FOR METEORITES AND THE EARTH.
71. Nicolaysen, L. O., Burger, A. J., and Liebenberg, W. R., Geochim. Cosmochim. Acta 26, 15 (1962), EVIDENCE FOR THE EXTREME AGE OF CERTAIN MINERALS FROM THE DOMINION REEF CONGLOMERATES AND THE UNDERLYING GRANITE IN THE WESTERN TRANSVAAL.
72. Pinson, W. H., Jr., Hurley, P. M., Mencher, E. and Fairbairn, H. W. Geol. Soc. Amer. Bull. 73, 907 (1962), K-Ar AND Rb-Sr AGES OF BIOTITES FROM COLUMBIA, SOUTH AMERICA.
73. Powell, J. L., Hurley, P. M., Fairbairn, H. W., Nature, 196, 1085 (1962), ISOTOPIC COMPOSITION OF STRONTIUM IN CARBONATITES.
74. Prezewlocki, K., Maydu, W., Thomas, H. H., Faul, H., Geochim. Cosmochim. Acta 26, 1069 (1962), AGE OF SOME GRANITIC ROCKS IN POLAND.

75. Rao, M. V. A., J. Geophys. Research 67, 1289 (1962), THE $\text{He}^3/(\text{He}^3 + \text{He}^4)$ RATIO IN PRIMARY COSMIC RADIATION.
76. Richards, J. R., J. Geophys. Research, 67, 869 (1962) ISOTOPIC COMPOSITION OF AUSTRALIAN LEADS. II. EXPERIMENTAL PROCEDURES AND INTERLABORATORY COMPARISONS.
77. Richards, J. R., Geochim. Cosmochim. Acta, 27, 217 (1963). ISOTOPIC COMPOSITION OF AUSTRALIAN LEADS. III. NORTHWESTERN QUEENSLAND AND THE NORTHERN TERRITORY-A RECONNAISSANCE.
78. Riley, G. H., Compston, W., Geochim. Cosmochim. Acta, 26, 1255 (1962), THEORETICAL AND TECHNICAL ASPECTS OF Rb-Sr GEOCHRONOLOGY.
79. Rosholt, J. N., Shields, W. R., Garner, E. L., Science, 39, 224 (1963), ISOTOPIC FRACTIONATION OF URANIUM IN SANDSTONE.
80. Rosholt, J. N., Emiliani, C., Geiss, J., Koczy, F. F. and Wangersky, P. J., J. Geophys. Research 67, 2907 (1962), $\text{Pa}^{231}/\text{Th}^{230}$ DATING AND $\text{O}^{18}/\text{O}^{16}$ TEMPERATURE ANALYSIS OF CORE A254-BR-C.
81. Russell, R. D., Slawson, W. F., Nature 194, 565 (1962), AGE OF THE CUDDAPAH, INDIA.
82. Shima, M., J. Geophys. Research 67, 4521 (1962), BORON IN METEORITES.
83. Shields, W. R., Murphy, T. J., Garner, E. L., Dibeler, V. H., J. Amer. Chem. Soc. 84, 1519, (1962), ABSOLUTE ISOTOPIC ABUNDANCE RATIO AND THE ATOMIC WEIGHT OF CHLORINE.
84. Shields, W. R., Garner, E. L., Hedge, C. E., and Goldrich, S. S., J. Geophys. Research 68, 2331 (1963), SURVEY OF $\text{Rb}^{85}/\text{Rb}^{87}$ RATIOS IN MINERALS.
85. Shutze, W., Geochim. Cosmochim. Acta 26, 617 (1962), UBER DIE DATIERUNG VON Pb-MINERALIEN.
86. Slawson, W. F. and Austin, C. F., Econ. Geol. 57, 21 (1962), A LEAD ISOTOPE STUDY DEFINES A GEOLOGICAL STRUCTURE.
87. Stauffer, H., J. Geophys. Research 67, 2023 (1962), ON THE PRODUCTION RATIOS OF RARE GAS ISOTOPES IN STONE METEORITES.
88. Stauffer, H., and Honda, M., J. Geophys. Research 67, 3503 (1962). COSMIC-RAY PRODUCED STABLE ISOTOPES IN IRON METEORITES.
89. Svec, H. J., Flesch, G. D., Capellon, J., Geochim. Cosmochim. Acta 26, 1361 (1962), THE ABSOLUTE ABUNDANCE OF THE CHROMIUM ISOTOPES IN SOME SECONDARY MINERALS.
90. Taylor, H. P., Jr., and Epstein, S., J. Geophys. Research 67, 4485, (1962), OXYGEN ISOTOPE STUDIES ON THE ORIGIN OF TEKTITES.
91. Taylor, H. P., Jr., and Epstein, J., Geol. Soc. Amer. Bull. 73, 461 (1962). RELATIONSHIP BETWEEN $\text{O}^{18}/\text{O}^{16}$ RATIOS IN COEXISTING MINERALS OF IGNEOUS AND METAMORPHIC ROCKS. PART 1. PRINCIPLES AND EXPERIMENTAL RESULTS.
92. Taylor, H. P., Jr., and Epstein, S., Geol. Soc. Amer. Bull. 73, 675 (1962), RELATIONSHIP BETWEEN $\text{O}^{18}/\text{O}^{16}$ RATIOS IN COEXISTING MINERALS OF IGNEOUS AND METAMORPHIC ROCKS. PART 2. APPLICATION TO PETROLOGIC PROBLEMS.
93. Thode, H. G., Monster, J. and Dunford, H. B., Geochim. Cosmochim. Acta 25, 159 (1961), SULPHUR ISOTOPE GEOCHEMISTRY.
94. Thode, H. G., Dunford, H. B. and Shima, M., Econ. Geol. 57, 565 (1962). SULFUR ISOTOPE ABUNDANCES IN ROCKS OF THE SUDBURY DISTRICT AND THEIR GEOLOGICAL SIGNIFICANCE.

95. Thurber, D. L., J. Geophys. Research 67, 4518 (1962), ANOMALOUS U^{234}/U^{238} IN NATURE.
96. Tilton, G. R., Hart, S. R., Science, 140, 357 (1962). GEOCHRONOLOGY.
97. Tilton, G. R., Wetherill, G. W. and Davis, G. L., J. Geophys. Research 67, 4011 (1962), MINERAL AGES FROM THE WICHITA AND ARBUCKLE MTNS., OKLAHOMA, AND THE ST. FRANCIS MTNS., MISSOURI.
98. Umemoto, S., J. Geophys. Research 67, 375 (1962), ISOTOPIC COMPOSITION OF BARIUM AND CERIUM IN STONE METEORITES.
99. Vinogradov, A. P., Tugarinov, A. I., Geochim. Cosmochim. Acta 26, 1283-1300 (1962), PROBLEMS OF GEOCHRONOLOGY OF THE PRECAMBRIAN IN EASTERN ASIA.
100. Weber, J. N., Keith, M. L., Science 138, 900, (1962), CARBON ISOTOPE COMPOSITION AND THE ORIGIN OF CALCAREOUS COAL BALLS.
101. Wasserburg, G. J., Wetherill, G. W., Silver, L. T. and Flawn, P. T., J. Geophys. Research 67, 4021 (1962), A STUDY OF THE AGES OF THE PRECAMBRIAN OF TEXAS.

VIII. Miscellaneous

H. M. Rosenstock and M. Krauss

Books

1. Bates, D. R., Ed., "ATOMIC AND MOLECULAR PROCESSES", Academic Press, New York (1962).
2. Biemann, K., "MASS SPECTROMETRY, ORGANIC CHEMICAL APPLICATIONS" McGraw Hill, New York (1962).
3. Elliott, R. M., Ed., "ADVANCES IN MASS SPECTROMETRY, Vol. II" Pergamon Press, New York (1963).
4. McLafferty, F. W., Ed., "MASS SPECTROMETRY OF ORGANIC IONS", Academic Press, New York (1963).
5. Reed, R. I., "ION PRODUCTION BY ELECTRON IMPACT", Academic Press, New York (1962).
6. Streitwieser, A., "MOLECULAR ORBITAL THEORY FOR ORGANIC CHEMISTS", John Wiley and Sons, New York (1961).
7. Wu, T. Y. and Omura, T., "QUANTUM THEORY OF SCATTERING", Prentice-Hall, Englewood Cliffs (1962).

Articles

1. Beckey, H. D., "FIELD IONIZATION MASS SPECTRA OF ORGANIC MOLECULES, I. n-PARAFFINS FROM C₁ TO C₉", Z. Naturforsch 17a, 1103 (1962).
2. Dunn, G. H., "ANISOTROPIES IN ANGULAR DISTRIBUTIONS OF MOLECULAR DISSOCIATION PRODUCTS", Phys. Rev. Letters 8, 62 (1962).
3. Jackson, E. A., "NON-LINEAR COUPLED OSCILLATORS, I and II", J. Math. Phys. 4, 551, 686 (1963).
4. Olmstead, J. A., "FORMATION OF ENERGETIC FRAGMENT IONS BY BOMBARDMENT OF ORGANIC MOLECULES WITH SLOW ELECTRONS", UCRL-10687 (1963).
5. Omura, I., "MASS SPECTRA AT LOW IONIZING VOLTAGE AND BOND DISSOCIATION ENERGIES OF MOLECULAR IONS FROM HYDROCARBONS" Bull Chem. Soc. Japan 34, 1228 (1961).
6. Omura, I., "STUDY ON UNIMOLECULAR DECOMPOSITION OF EXCITED OLEFIN IONS", Bull. Chem. Soc. Japan 35, 1845 (1962).
7. Rapp, D., Green, M. I. and Englander-Golden, P., "IONIZATION OF ATOMS AND DIATOMIC MOLECULES BY ELECTRON IMPACT", Lockheed Missiles and Space Company, Sunnyvale, California. Technical Report, no number (1963).
8. Tsuchiya, T., "HIGH KINETIC ENERGY FRAGMENT IONS FROM ALIPHATIC HYDROCARBONS UNDER ELECTRON IMPACT, I. MEASUREMENT AND HIGH-KINETIC ENERGY METHYL IONS FROM 1,3-BUTADIENE", Bull Chem. Soc., Japan 35, 1221 (1962).
9. Tsuchiya, T., "HIGH KINETIC ENERGY FRAGMENT IONS FROM ALIPHATIC HYDROCARBONS, II. PROPANE", J. Chem. Phys. 36, 568 (1962).
10. Whitten, G. Z. and Rabinovitch, B. S., ACCURATE AND FACILE APPROXIMATION FOR VIBRATIONAL ENERGY LEVEL SUMS, J. Chem. Phys. 38, 2466 (1963).

BIBLIOGRAPHY OF HIGH MOLECULAR WEIGHT MASS SPECTROMETRY

PREPARED BY SUBCOMMITTEE III

MAY 1963

1. Aczel, T.; Bartz, K. W.; Lumpkin, H. E.; and Stehling, F. C., "Characterization of Aromatics in Light Catalytic Cycle Stock by Spectrometric Techniques - Compound Types of the General Formula C_nH_{2n-12} and C_nH_{2n-14} ," Anal. Chem. 34, 1821 (1962).
2. Aczel, T., and Lumpkin, H. E., "Correlations of Mass Spectra with Structure in Aromatic Oxygenated Compounds, Benzoate-Type Esters," Anal. Chem. 34, 33 (1962).
3. American Petroleum Institute Project 44, Catalog of Mass Spectral Data, Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas.
4. Antonaccio, L. D.; Pereira, N. A.; Gilbert, B.; Vorbrueggen, H.; Budzikiewicz, H.; Wilson, J. M.; Durham, Lois J.; Djerassi, Carl, "Alkaloid Studies. XXXIII. Mass Spectrometry in Structural and Stereochemical Problems. VI. Polyneuridine, A New Alkaloid from Aspidosperma Polyneuron, and Some Observations on Mass Spectra of Indole Alkaloids," J. Am. Chem. Soc. 84, 2161 (1962).
5. Arya, V. P., Ryhage, R., "Mass Spectrometry of Natural Products. Molecular Formula of Nimbin," J. Sci. Ind. Res. (India) 21A, 283 (1962).
6. Bartz, K. W.; Aczel, Thomas; Lumpkin, H. E.; and Stehling, F. C., "Characterization of Aromatics from Light Catalytic Cycle Stocks by Spectrometric Techniques - Compound Types of the General Formula C_nH_{2n-16} and C_nH_{2n-18} ," Anal. Chem. 34, 1814 (1962).
7. Baun, W. L., and Fischer, D. W., "Mass Spectra of Amino Acids Using a Radio-Frequency Spark Source," Anal. Chem. 34, 294 (1962).
8. Biemann, Klaus, Mass Spectrometry, McGraw-Hill Book Company, Inc., New York 36, New York, 1962.
9. Biemann, K., "The Application of Mass Spectrometry in Organic Chemistry: Determination of the Structure of Natural Products," Angew. Chem. 1, 98 (1962).
10. Biemann, K., "Determination of the Structure of Natural Products by Mass Spectrometry," Ind. Chim. Belge. 27, 1319 (1962).
11. Biemann, K., "Application of Mass Spectrometry in Organic Chemistry, Especially for Structure Determination of Natural Products," Angew. Chem. 74, 102 (1962).
12. Biemann, K.; Burlingame, A. L.; and Stauffacher, D., "Application of Mass Spectrometry to Structure Problems. VII. Condylocarpine," Tetrahedron Letters 1962, 527.
13. Biemann, K., and McCloskey, J. A., "Application of Mass Spectrometry to Structure Problems. VI. Nucleosides," J. Am. Chem. Soc. 84, 2005 (1962).
14. Biemann, K., and McCloskey, J. A., "Mass Spectra of Organic Molecules. II. Amino Acids," J. Am. Chem. Soc. 84, 3192 (1962).
15. Biemann, K., and Spiteller, G., "Application of Mass

- Spectrometry to Structure Problems. VIII. Quebrachamine," *J. Am. Chem. Soc.* 84, 4578 (1962).
16. Budzikiewicz, H., and Djerassi, Carl, "Mass Spectrometry in Structural and Stereochemical Problems. I. Steroid Ketones," *J. Am. Chem. Soc.* 84, 1430 (1962).
 17. Budzikiewicz, H.; Wilson, J. M.; and Djerassi, C., "Mass Spectroscopy and Its Application to Structural and Stereochemical Problems--Steroid Sapogenins," *Monatsh. Chem.* 93, 1033 (1962).
 18. Clancy, D. J., and Spilners, I. J., "Analysis of Ferrocenes by Mass Spectrometry," *Anal. Chem.* 34, 1839 (1962).
 19. Dinh-Nguyen, Nguyen, Ragnar Ryhage, Stina Stallberg-Stenhagen, and Einar Stenhagen, "Mass Spectrometric Studies. VIII. A Study of the Fragmentation of Normal Long-Chain Methyl Esters and Hydrocarbons Under Electron Impact with the Aid of Deuterium-Substituted Compounds," *Arkiv for Kemi Band 18 nr 21*, pp. 393 (1961).
 20. Djerassi, C.; Antonaccio, L. D.; Budzikiewicz, H.; Wilson, J. M.; and Gilbert, B., "Mass Spectrometry in Structure and Stereochemical Problems--Structure of the Aspidosperma Alkaloid Aspidosperma," *Tetrahedron Letters* 1962, 1001.
 21. Djerassi, C.; Brewer, H. W.; Budzikiewicz, H.; Orazi, O. O.; and Corral, R. A., *Experientia* 18, 113 (1962).
 22. Djerassi, C.; Budzikiewicz, H.; Wilson, J. M., "Mass Spectrometry in Structural and Stereochemical Problems. Unsaturated Pentacyclic Triterpenoids," *Tetrahedron Letters* 1962, 263.
 23. Djerassi, C.; Budzikiewicz, H.; Wilson, J. M.; Gosset, J.; Le Men, J.; Janot, M. M., "Mass Spectrometry in Structural and Stereochemical Problems. Vincadifformine. Alkaloids of Vinca-Difformis," *Tetrahedron Letters* 1962, 235.
 24. Djerassi, C.; Flores, S. E.; Budzikiewicz, H.; Wilson, J. M.; Durham, L. J.; LeMen, J.; Janot, M. M.; Plat, M.; Gorman, M.; Neuss, N., *Proc. Natl. Acad. Sci. U.S.*, 48, 113 (1962).
 25. Djerassi, C.; George, T.; Finch, N.; Lodish, H. F.; Budzikiewicz, H.; and Gilbert, B., "Mass Spectrometry in Structural and Stereochemical Problems. V. Refractine and Aspidofractine," *J. Am. Chem. Soc.* 84, 1499 (1962).
 26. Djerassi, Carl; Wilson, J. M.; Budzikiewicz, H.; Chamberlin, J. W., "Mass Spectrometry in Structural and Stereochemical Problems. XIV. Steroids with One or Two Aromatic Rings," *J. Am. Chem. Soc.* 84, 4544 (1962).
 27. Dubov, S. S.; Khokhlova, A. M.; and Radionova, N. P., "Mass Spectra of Some Poly and Per Fluoridated Azo and Azoxy Compounds," *Zh. Vses. Khim. Abshchestva in D. L. Mendeleeva* 7, 692 (1962).
 28. Elliott, R. M., Editor, *Advances in Mass Spectrometry*, Volume 11, Pergamon Press, London, 1962.
 29. Fitzgerald, M. E.; Cirillo, V. A.; and Galbraith, F. J., "Mass Spectrometric Method for Analysis of Petroleum Distillates in the Furnace Oil-Kerosene Boiling Range," *Anal. Chem.* 34, 1276 (1962).
 30. Gilbert, B.; Ferreira, M.; Owellen, R. J.; Swanholm, C. E.; Budzikiewicz, H.; Durham, L. J.; Djerassi, C., "Mass Spectrometry in Structural and Stereochemical Problems. Pyrifoline and Refractidine," *Tetrahedron Letters* 1962, 59.

31. Godbole, E. W., and Kebarle, P., "Ionization and Dissociation of Deuterated Ethyl and Isopropyl Acetates and Ethyl Formate under Electron Impact," *Trans. Faraday Soc.* 58, 1897 (1962).
32. Gohlke, R. S., and McLafferty, F. W., "Mass Spectrometric Analysis--Aliphatic Amines," *Anal. Chem.* 34, 1281 (1962).
33. Grikit, I. A., "Effect of the Sample Structure and Its Mass on the Results of Spectral Analysis," *Zavodak Lab.* 28, 1327 (1962).
34. Hall, L. H., and Koski, W. S., "On the Nature of Some Higher Boron Hydrides Produced in Radiation-Induced Reactions in Penta- and Decaborane," *J. Am. Chem. Soc.* 84, 4205 (1962).
35. Hartung, G. K., and Jewell, D. M., "Carbazoles, Phenazines, and Dibenzofuran in Petroleum Products; Methods of Isolation, Separation, and Determination," *Anal. Chim. Acta* 26, 514 (1962).
36. Henglein, Arnim, "Mass Spectrometric Observations on Reactions of Excited Ions in CS₂ and Some Aromatic Compounds," *Z. Naturforsch* 17A, 37 (1962).
37. Hirata, Y., and Yamamura, S., "Application of Mass Spectrometry to Organic Chemistry--Review," *Yuki, Gosei, Kagaku, Kyokai. Shi.* 20 (1962).
38. Hobrock, Brice G., and Kiser, Robert W., "Electron Impact Spectroscopy of Propylene Sulfide," *J. Phys. Chem.* 66, 1551 (1962).
39. Horton, J. C.; Thomas, J. R.; Warren, V. L., "Mass-Spectrometric Determination of Molybdenum-Uranium Ratios in Mixtures of the Hexafluorides," *U. S. Atomic Energy Comm. K-1433*, 9 pages (1962).
40. Klaas, P. J., and McSweeney, W. P., "Gasoline Type Analysis by Mass Spectrometer Using Computer Assembled Matrices," *Anal. Chem.* 34, 30 (1962).
41. Kocmetkov, N. K.; Vulfson, N. S.; Chizhov, O. S.; and Zolotarey, B. M., "Mass Spectrometry Investigation of Hydrocarbons, Methyl Esters of Monosaccharides," *Dokl. Akad. Nauk. U.S.S.R.* 147, 1369 (1962).
42. Latham, D. R.; Ferrin, C. R.; and Ball, J. S., "Identification of Fluorenones in Wilmington Petroleum by Gas-Liquid Chromatography and Spectrometry," *Anal. Chem.* 34, 311 (1962).
43. Laune, J. "Mass Spectrometry in the Field of Cyclanes and Their Derivatives," *Ind. Chim. Belge.* 27, 245 (1962).
44. Lawrey, D. M. G., and Paulson, Joseph F., "Further Elucidation of Hydrocarbon Types in Olefinic Gasoline by Mass Spectrometry," *Anal. Chem.* 34, 538 (1962).
45. MacDonald, C. G., and Shannon, J. S., "Mass Spectrometry--Random Hydrogen Rearrangement in Aromatic Molecular Ions," *Australian J. Chem.* 15, 771 (1962).
46. Manufacturing Chemists Association Research Project, Catalog of Mass Spectral Data, Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas.
47. McLafferty, F. W., "Mass Spectrometric Analysis--Aliphatic Halogenated Compounds," *Anal. Chem.* 34, 2 (1962).
48. McLafferty, F. W., "Mass Spectrometric Analysis--Aromatic Halogenated Compounds," *Anal. Chem.* 34, 16 (1962).

49. McLafferty, F. W., "Mass Spectrometric Analysis--Aliphatic Nitriles," *Anal. Chem.* 34, 26 (1962).
50. Meyerson, S., Vander Haar, "Multiply Charged Organic Ions in Mass Spectra," *J. Chem. Physics* 37, 2458 (1962).
51. Monseur, X.; Goutarel, R.; Le Men, J.; Wilson, J. M.; Budzikiewicz, H.; Djerassi, C., "Structure of Mosambine (Diplorrhynchine). Alkaloids of *Diplorrhynchus Condyllocarpon Mossambicensis* (Apocynaceae). Application of the Mass Spectrograph to the Problem of the Structure and Stereochemistry," *Bull. Soc. Chim. France* 1962, 1088.
52. Natalis, P., "Recording by Mass Spectrometry of the Cis and Trans Isomeric Forms in Dialkylcyclohexanes," *Bull. Classe Sci. Acad. Roy. Belg.* 48, 554 (1962).
53. Peterson, L. E., "Analysis of Steroids by Mass Spectrometry," *Chem. and Ind.*, page 264 (1962).
54. Peterson, Lowell, "Mass Spectra of Some Highly Substituted Pregnanes and Pregnenes," *Anal. Chem.* 34, 1781 (1962).
55. Plat, M.; Dokhac'Manh, D.; Le Men, J.; Janot, M. M.; Budzikiewicz, H.; Wilson, J. M.; Durham, L. J.; Djerassi, C., "Structure of Vincamine and of 11-Methoxy Vincamine. Alkaloids of *Periwinkle*. Application of the Mass Spectrograph to the Problems of Determining the Structure and the Stereochemistry," *Bull. Soc. Chim. France* 1962, 1082.
56. Plat, M.; Le Men, J.; Janot, Maurice M.; Wilson, J. M.; Budzikiewicz, H.; Durham, L. J.; Nakagawa, Y.; Djerassi, C., "Mass Spectrometry in Structural and Stereochemical Problems. Tabersonine (Alkaloids of *Amsonia-Tabernaemontana*)," *Tetrahedron Letters* 1962, 271.
57. Polyakova, A. A., and Khmel'nitskii, R. A., "Mass-Spectrometric Method for Determination of Five and Six-Membered Naphthene Hydrocarbons in Gasolines," *Zhurnal Prikladnoi Khimii* 34, 1569 (1961).
58. Polyakova, A. A.; Khmel'nitskii, R. A.; and Medveden, F. A., "Mass Spectrometric Analysis of Products with a High Content of Unsaturated Hydrocarbons," *Khim. Tekhnol. Toplin. Masel* 7, 59 (1962).
59. Polyakova, A. A. Khmel'nitskii, R. A., "Mass Spectrometric Determination of Paraffin Hydrocarbons of Normal and Branched Structure," *Khim. i Tekhnol. Topliv i Masel* 7, 70 (1962).
60. Polyakova, A. A., and Petrov, A. A., "Mass Spectra and the Structure of Organic Compounds. VI. Mass Spectra of Alkenyl Vinylacetylenes," *J. Gen. Chem. U.S.S.R.* 31, 3278 (1961).
61. Polyakova, A. A., and Petrov, A. A., "Mass Spectra and the Structure of Organic Compounds. Mass Spectra of 1-tert-alkyl-1,3-butadienes," *Zh. Obshch. Khim.* 32, 1415B (1962).
62. Popjak, G.; Cornforth, J. W.; Cornforth, R. H.; Ryhage, R.; and Goodman, D. S., *J. Biol. Chem.* 237, 56 (1962).
63. Reed, R. I., and Wilson, J. M., "Electron Impact and Molecular Dissociation of Methyl Substituted Diphenyl Ethers," *Chem. Ind.* 1962, 1428.
64. Reese, Robert M., "Review of Fundamental Developments in Analysis--Mass Spectrometry," *Anal. Chem.* 32, 243R (1962).
65. Sanadze, G. G., "Mass Spectrometric Identification of an Isoprene-Type Compound in the Volatile Exudates of Plant Leaves," *Soobshcheniya Akad. Nauk. Gruzin. U.S.S.R.* 27, 747 (1962).

66. Schnedes, H. K.; Burlingame, A. L.; and Biemann, K., "Application of Mass Spectrometry to Structure Problems," *Tetrahedron Letters* 1962, 993.
67. Shannon, J. S., "Studies in Mass Spectrometry. I. Structures and Reactions of Ions from Benzyl Alcohol, Ortho-, Meta-, and Parahydroxybenzyl Alcohols, and Their O-deuterated Derivatives," *Australian J. Chem.* 15, 265 (1962).
68. Sharkey, A. G., Jr.; Shultz, J. L.; and Friedel, R. A., "Application of Low-Ionizing Voltage Mass Spectrometry to Oils Derived from Coal," *Fuel* 41, 359 (1962).
69. Sharkey, A. G., Jr.; Shultz, J. L.; and Friedel, R. A., "Mass Spectrometric Determination of the Ratio of Branched to Normal Hydrocarbons up to C₁₈ in Fischer-Tropsch Product," *Anal. Chem.* 34, 826 (1962).
70. Spiteller, G., "Ortho Effect in the Mass Spectra of Aromatic Compounds," *Monatsh. Chem.* 92, 1147 (1962).
71. Spiteller, G.; Brunne, C.; Heyns, K.; and Gruetzracher, H. F., "Mass Spectrometric Investigation of the Structure of Thermally Labeled and Difficultly Volatile Organic Compounds," *Z. Naturforsch* 178, 856 (1962).
72. Spiteller, G.; Chatterjee, A.; Battacharya, A.; and Deb, A., "Application of Mass Spectrometry to the Classification of the Structure of Alkaloids," *Monatsh. Chem.* 93, 1220 (1962).
73. Spiteller, G., and Spiteller, M., "Application of Mass Spectrometry to the Explanation of the Structure of Alkaloids. The Basic Ingredient of the Bark of *Aspidosperma Oblongum*," *Monatsh. Chem.* 93, 795 (1962).
74. Struck, A. H. Research Division, American Cyanamid Company, 1937 West Main Street, Stamford, Connecticut.
75. Tunitsky, N. N.; Kuprizanov, S. E.; Perov, A. A., "Mass Spectrum of Molecules and Radiation Chemistry," *Izv. Akad. Nauk, U.S.S.R., Otd. Khim. Nauk.* 11, 1945 (1962).
76. Wanless, G. A. "Analysis of Copolymers by Pyrolysis and Mass Spectrometry," *J. Polymer Sci.* 62, 263 (1962).

BIBLIOGRAPHY of published and unpublished material pertaining to
new instruments and techniques in mass spectrometry for 1962.

Prepared by Subcommittee V
ASTM Committee E-14

1. Ackermann, R. J., Rauh, E. G., and Thorn, R. J., "Effect of Oxygen on the Vapor Pressure of Uranium," *Journal of Chemical Physics* **37**, pp 2693-8 (1962).
2. Ackerman, Marcel, Droward, Jean, and others, "Vaporization of Compounds and Alloys at High Temperature. Part V. Mass Spectrometric Study of Gaseous Molecules Above the Ag Sn, Au Sn, and Cu Sn Alloys," Report for March 1960 - March 1961 on Refractory Inorganic Non-Metallic Materials, Contract AF 61 (052) 225, Proj. 7350.
3. Ackerman, Marcel, Stafford, Fred E., and Verhaegen, Georges, "Vaporization of Compounds and Alloys at High Temperature. Part VI. Studies of the Vapors of the Systems Au-Cr and Au-Pd by Mass Spectrometry," Report for March 1960 - March 1961 on Refractory Inorganic Non-Metallic Materials, Contract AF 61 (052) 225, Project 7350.
4. Aczel, Thomas, Bartz, K. W., Lumpkin, H. E., Stehling, E. F. C., "Characterization of Aromatics in Light Catalytic Cycle Stock by Spectrometric Techniques Compound Types of the General Formula C_nH_{2n-12} and C_nH_{2n-14} ," *Anal. Chem.* p. 1821, Vol. 34, No. 13, December, 1962.
5. Aczel, Thomas and Lumpkin, H. E., "Correlation of Mass Spectra with Structure in Aromatic Oxygenated Compounds. Benzoate type esters," *Anal. Chem.*, p. 33, Vol. 34, No. 1, January, 1962.
6. Agafonov, I. L., Devyatykh, G. G., Frolov, I. A., and Larin, N. V., "Mass Spectrum of Germane," *Zh. Fiz. Khim.* 36, 1367-8 (1962).
7. Ahearn, A. J., "Vacuum Spark Mass Spectroscopy of Solids," Unpublished Work.
8. Ahearn, A. J., and Thurmond, C. D., "Mass Spectrographic Detection of Molecular Species in Group III-V Compounds," *Journal of Physical Chemistry*, Vol. 66, p. 575-576.
9. Alekseevskii, N. E., Dubrovin, A. V., and Karstens, G. E., "The Use of Mass Spectrometers with Nonuniform Magnetic Fields in Gas Analysis," *Zh. Fiz. Khim.* 34, 1275-9 (1960).
10. Allison, Samuel K., and Kamegai, M., "Lithium Ion Sources," *Rev. Sci. Instr.* 32, 1090-2 (1961).
11. Almquist, E., Broude, C., Clark, M. A., Duehner, J. A., and Litherland, A. E., *Can. J. Physics* 40, 954-63, (1962).
12. Anderson, R., Cooke, G. M., Kenyon, L. C., Jr., and Mathiason, R. L., "The Tensimeter, A New Vacuum Gage," *Rev. Sci. Instr.* 32, 780-3 (1961).
13. Antonaccio, L. D., Pereira, Nuno A., Dilbert, B., Vorbrueggen, H., Budzikiewicz, H., Wilson, J. M., Durham, Lois J., and Djerassi, Carl, "Alkaloid Studies. XXXIII. Mass Spectrometry in Structural and Stereochemical Problems. VI. Polyneuridine, A New Alkaloid from *Aspidosperma Polyneuron* and Some Observations on Mass Spectra of Indole Alkaloids," *Journal of the American Chemical Society*, 84, 2161-2169, (1962).
14. Apgar, E., "Rapid Evaluation of Carbon Monoxide and Nitrogen Contributions to Mass Spectra," *Vacuum* 11, 288-9 (1961).
15. Ardenne, M. V., Lorenz, E., and Westmeyer, H., "A Gettering Ionization Vacuum Pump with Titanium Vaporization and High Starting Pressure," *Exptl. Tech. Physik* 10, No. 1, 1931 (1962).
16. Arikawa, T., Higaki, H., Kaneko, S., Iwata, G., and Miyamoto, G., "A Study of Perfect Focusing Mass Spectrometer," *J. Phys. Soc. Japan*, 17, 711-712, (1962).
17. Attree, A. W., Cabell, M. J., Cushing, R. L., and Pieroni, J. J., *Can. J. Physics* 40, 194-201, (1962).

18. Bajeu, G., Comsa, G., and Gelberg, A., "A Mass Spectrometer of the Omegatron Type," Acad. Rep. Populare Romine, Studii Cercetari Fiz. 12, 427-34 (1961).
19. Baker, F. A., "Mechanism of Electrical Gas Clean-Up in a Hot-Cathode Ionization Gage," Vide 17, No. 99, 256-66 (1962).
20. Barber, M., Craig, R. D., Elliott, R. M., and Green, B. N., "Investigation of Performance of a New Double Focusing Mass Spectrometer for Chemical Analysis," Unpublished Work.
21. Barber, M., Farren, J., and Linnett, J. W., "Mass Spectrometric Sampling through a Pinhole Leak in the Adiabatic Flow Region," Chem. Ind. 1962, No. 14, 656-7.
22. Barrington, A. E., "Sensitivity of Ion Pump Leak Detector," Rev. of Scientific Inst. Vol. 33, No. 10, October, 1962.
23. Bartz, K. W., Aczel, Thomas, Lumpkin, H. E., and Stehling, F. C., "Characterization of Aromatics from Light Catalytic Cycle Stocks by Spectrometric Techniques. Compound Types of the General Formula C_nH_{2n-16} and C_nH_{2n-18} ," Anal. Chem. p. 1814, Vol. 34, No. 13, December, 1962.
24. Baun, W. L., and Fischer, D. W., "Mass Spectra of Amino Acids Using a Radio Frequency Spark Source," Anal. Chem. P. 294, Vol. 34, No. 2, February, 1962.
25. Baun, William L., and Fischer, David W., "Analysis of Refractory Metals Using A New Solid Source Double Focusing Mass Spectrometer," Report for May - Dec. 1960 on Experimental Techniques for Materials Research, Proj. 7364.
26. Bazinet, M. L., and Mervitt, Charles, Jr., "Techniques for the Mass Spectrometric Analysis of Volatile Compounds Isolated from Natural Sources," Anal. Chem. p. 1143, Vol. 34, No. 9, August, 1962.
27. Beck, D., and Niehaus, A., "Reactions of Excited Butane Molecules," Journal of Chemical Physics 37, pp. 2705-8, (1962).
28. Beckey, H. D., and Wagner, G., "Analytical Applications of a Mass Spectrometer Equipped with Field Emission Ion Source," Unpublished Work.
29. Bentley, P. G., Bishop, J., and Leece, J., "Mass Spectrometer for Investigating Low Concentrations of Free Radicals in Gases," U.K. At. Energy Authority TRG Rept. 66 (CA), 9 pp. (1961).
30. Berecz, Istvan, and Schadek, Janos, "An Electromagnetically Controlled High-Vacuum Valve," At. Kozlemen. 2, 249-50 (1960).
31. Berkowitz, J., "Heat of Formation of the CN Radical," Journal of Chemical Physics 36, pp. 2533-9, (1962).
32. Berkowitz, J. and Marquart, J. R., "Mass Spectrometric Study of the Magnesium Halides," Journal of Chemical Physics 37, pp 1853-65, (1962).
33. Berkowitz, J., Marquart, J. R., and Chupka, W. A., "Composition of Sulfur Vapor," Unpublished Work.
34. Berkowitz, J., Tasman, H. A., and Chupka, W. A., "Double-Oven Experiments with Lithium Halide Vapors," Journal of Chemical Physics 36, pp 2170-9, (1962).
35. Berkowitz, J. and Wexler, S., "On the Ionization Potential of the CH_2 Radical," Journal of Chemical Physics 37, pp 1476-7, (1962).
36. Berry, Clifford E., "Remarks on High Resolution Mass Spectroscopy," Unpublished Work.
37. Beske, Horst E., "A Bakeable (Ultra) High Vacuum Valve of Small Height," Vackuum-Tech. 10, 212-13 (1961).
38. Betts, J. F. and O'Halloran, G. J., "Miniaturized Bendix Time-Of-Flight Mass Spectrometers," Unpublished Work.
39. Bichin, L. P., and Alekseev, I. V., "A Simplified Device for Mass Spectrometric Microdetermination of Stable Isotopes," Voprosy Med. Khim. 7, 437-41.

40. Biemann, K., "The Use of High-Resolution Mass Spectrography in the Determination of the Structure of Organic Molecules," Unpublished Work.
41. Biemann, K. and Spiteller, G., "Application of Mass Spectrometry to Structure Problems. VIII. Quebrachamine," *Journal of the American Chemical Society*, 84, 4578-4586, (1962).
42. Black, D. R., McFadden, W. H., and Corse, Jr., "Studies in the Mass Spectra of Short Chain Esters," Unpublished Work.
43. Blackmore, D. R. and Hinshelwood, C., "Inhibition and Acceleration of Paraffin Decomposition by Nitric Oxide," *Proc. Royal Soc. (London)*, 268, 21 (1962).
44. Blanc, Claude, Blanc, Daniel, Degeilh, Andre, and Malessot, Claude, "Measurement of Molecular Flow Traversing the Leak of a Mass Spectrometer," *J. Phys. Radium* 23, Suppl. 37A-39A (1962).
45. Blue, G. D., Ehlert, T. C., Green, J. W., and Margrave, J. L., "Mass Spectrometric Studies of Inorganic Fluorides," Unpublished Work.
46. Boelrijk, N., and Hamill, W. H., "Effects of Relative Velocity Upon Gaseous Ion-Molecule Reactions; Charge Transfer to the Neopentane Molecule," *Journal of the American Chemical Society*, 84, 730-734, (1962).
47. Borowitz, J. L., "The Relative Volatilities of the System $H_2O^{17}-H_2O^{16}$," *Journal of Physical Chemistry*, Vol. 66, No. 8, Aug. 1962. p. 1412-14.
48. Botter, R., "Determination En Valeur Absolue de La Teneur Isotopique de l'Hydrogene Par Spectrometrie de Masse," Unpublished Work.
49. Bradley, R. C. and Ruedl, E., "Ions Sputtered from Copper," *Journal of Applied Physics*, 33, 6, 880-888 (1962).
50. Bradley, Richard C., "Investigation of Solid Surfaces by Field Emission Microscopy and Mass Spectrometry," Final Report February 1, 1960 - January 31, 1962, Contract AF 49 (638) 748.
51. Brown, R., Craig, R. D., James, J. A., and Wilson, C. M., "Analysis of Trace Impurities by Spark Source Mass Spectrometry," *Eng. J.*, 407-13 (1961).
52. Brown, R. and Wolstenholme, W. A., "Analysis of Insulating Powders," Unpublished Work.
53. Brubaker, W. M., "The Ion Pump," *Instr. Meas., Chem. Ala., Elec. Quant., Nucleonics Process Control, Proc. Intern. Conf., Stockholm* 1, 297-304 (1960) (Pub. 1961).
54. Brubaker, W. M., "The Quadrupole Mass Filter," *Instr. Meas., Chem. Anal., Elec. Quant., Nucleonics Process Control, Proc. Intern. Conf., Stockholm* 1, 305-15 (1960) (Pub. 1961).
55. Brubaker, Wilson M. and Taul, Johannes, "Operating Parameters for a Quadrupole Mass Spectrometer," Unpublished Work.
56. Brunnee, C., Delgmann, L., and Kronenberger, K., "Construction Details and Performance of a New Commercial Quadrupole Filter," Unpublished Work.
57. Brunnee, C., Jenckel, L., and Kronenberger, K., "Continuous Mass Spectrometric Analysis of Fractions Separated by Gas Chromatography," *Z. Anal. Chem.* 189, 50-66 (1962).
58. Budzikiewicz, Hubert and Djerassi, Carl, "Mass Spectrometry in Structural and Stereochemical Problems. I. Steroid Ketones," *Journal of the American Chemical Society*, 84, 1430-1439, (1962).
59. Bunich, A. O., Voinov, A. P., and Tomasheva, M. P., "Sampling of Gases for Analysis," *Nauch. Zapiski Odessk. Politekh. Inst.* 18, 87-92 (1959).
60. Buchler, Alfred, "Some New Experiments in High-Temperature Mass-Spectrometry," Unpublished Work.

61. Calame, Gerald P., and White, Frederick A., "A Proposed Analysis of the Charge State of Recoil Atoms Produced by High Energy Electron Impact," Unpublished Work.
62. Cameron, J. A., King, H. J., Eastwood, H. R., and Summers-Gill, R. G., *Can. J. Physics* 40, 931-42 (1962).
63. Carette, J. D., and Kerwin, L., "Mass Spectrometric Study of Red Phosphorus," *Can. J. Phys.* 39, 1300 (1961).
64. Carlson, C. E., and Magnuson, G. D., "High Efficiency Low-Pressure Ion Source," *Review of Scientific Instr.* Vol. 33, No. 9, September, 1962.
65. Carlson, T. A., and White, R. M., "Decomposition of $(\text{CH}_3\text{Xe}^{131})^+$ Following the Nuclear Decay of $\text{CH}_3\text{I}^{131}$," *Journal of Chemical Physics* 36, pp. 2883-7, (1962).
66. Carmichael, J. H. and Waters, P. M., "Re-Emission of Ionically Pumped Helium by Helium Ion Bombardment," *Journal of Applied Physics*, 33, 4, 1470-1475 (1962)
67. Cassuto, A., "Variations of Mass Spectra with Temperature between -95° and 200°C. ," *Comptes Rendus*, 252, 1311-13 (1961).
68. Chantreau, J., "Calculation of the Trajectories of Ions in an Ion Source of the Nier Type in the Presence of an Auxiliary Magnetic Field," *Comptes Rendus*, 695-7 (1961).
69. Charles, D., "Electronics in Analysis. An Example: The Mass Spectrometer," *Chimie Analytique* 44, (No. 2), 49-60 (1962).
70. Chih-Shun Lu & Carr, "Electrostatic Quadrupole Lens Pair for Mass Spectrometers," *Rev. of Scient. Instr.* Vol. 33, No. 8, August, 1962.
71. Chupakhin, M. S., and Gradshtain, E., "Directed Ion Formation in a Three-Band Source of Ions of a Mass Spectrometer," *Dokl. Akad. Nauk SSSR* 142, 337-9(1962).
72. Chupakhin, M. S., and Miller, Yu. M., "Mass Spectrometric Analysis of Impurities in Pure Materials," *Zavodskaya Lab.* 27, 1009-12 (1961).
73. Chupka, W. A., "Kinetic Energy on Fragments of Unimolecular Decomposition," Unpublished Work.
74. Ciric, M. M. and Pupezin, J. D., "Separation of Lithium Isotopes on the Amberlite IR-120 Cation Exchanger," *Bulletin of the Boris Kidrich Institute of Nuclear Sciences, Belgrade.* 13 - #2, 29 - 45 (1962).
75. Cirillo, V. A., Skahan, D. J., Hollis, Betty, and Morgan, H., "Rapid Mass Spectrometric - Gas Chromatographic Analysis of Non-Olefinic Naphthas," *Anal. Chem.* p. 1353, Vol. 34, No. 10, September, 1962.
76. Clancy, Donald J., and Spilners, Ilgvars J., "Analysis of Ferrocenes by Mass Spectrometry," *Anal. Chem.* p. 1839, Vol. 34, No. 13, December, 1962.
77. Cobine, J. D., and Burger, E. E., "Ionization Gage for Transient Gas Pressures," *Rev. Sci. Instr.* 32, 717-20 (1961).
78. Coggeshall, N. D., "Initial Kinetic Energy Discrimination Effects in Crossed-Field Ion Sources," *Journal of Chemical Physics* 36, pp. 1640-7, (1962).
79. Coggeshall, N. D., "Studies of Metastable Ion Transitions with a 180° Mass Spectrometer," *Journal of Chemical Physics* 37, pp. 2167-75, (1962).
80. Colin, R., and Drowart, J., "Thermodynamic Study of Tin Sulfide and Lead Sulfide Using a Mass Spectrometer," *Journal of Chemical Physics* 37, pp. 1120-25, (1962).
81. Comes, F. J., and Lessmann, W., "Ion Formation in Nitrogen," *Z. Naturforsch.* 17a, 704-5 (1962).
82. Cook, H. D., "The Determination of Fluorine in ZrO_2 Corrosion Films by Spark Source Mass Spectrography," Unpublished Work.

83. Cornu, Ayme, "Analytical Applications of Low Voltage Mass Spectrometry," Publ. Group. *Avan. Methodes Spectrog.* 1961, 369-84.
84. Crable, G. F., and Kearns, G. L., "Charge-Exchange Phenomena in A Mass Spectrometer," *Journal of Chemical Physics* 36, pp. 558-9, (1962).
85. Crable, G. F., and Kearns, G. L., "Effect of Substituent Groups on the Ionization Potentials of Benzenes," *Journal of Physical Chemistry*, Vol. 66, p. 436-439.
86. Crawford, E., Roberts, M. W., and Kemball, C., "Hydrogenation of Ethylene on Sintered Nickel Films," *Transaction of the Faraday Society* 58, 1761-7 (1962).
87. Cseko, Gyula, "Mass Spectrometric Method for Determining the Solubility of Gases," *Magyar Kem. Folyoirat* 67, 306-9 (1961).
88. Dahler, J. S., Franklin, J. L., Munson, M. S. A., and Field, F. H., "Rare-Gas Molecule-Ion Formation by Mass Spectrometry. Kinetics of Ar_2^+ , Ne_2^+ , and He_2^+ Formation by Second and Third Order Processes," *Journal of Chemical Physics* 36, pp 3332-44, (1962).
89. Daly, N. R., "A New Type of Positive Ion Detector for the Simultaneous Measurement of Two Ion Beams," Unpublished Work.
90. Dawson, P. H., and Tickner, A. W., "Detection of H_5^+ in the Hydrogen Glow Discharge," *Journal of Chemical Physics* 37, pp 672-73, (1962).
91. Debus, G. H., "The Determination of Mass Discrimination in a Mass Spectrometer," *Nucl. Instr. Methods* 16, 63-8 (1962).
92. DeJardin, G., Mesnard, G., Usan, R., and Caboud, B., "Study of the Evolution of Emissive Materials from Cathodes of Alkaline Earth Oxides," *Comptes Rendus*, 255, 1712-14 (1962).
93. De Vaux, L., Gabriel, R., and Others, "Surface Recombination of Molecular Fragments," Report for July 1, 1958-August 31, 1960 on Surface and Interface Phenomena Matter, Contract AF 33 (616) 5976, Proj. 7022.
94. Dibeler, V. H., and Rosenstock, H. M., "Metastable Transitions in Small Molecules," Unpublished Work.
95. Diesen, R. W., "Mass Spectral Studies of the Kinetics Behind Shock Waves. The Thermal Decomposition of Hydrazine," Unpublished Work.
96. Dietz, L. A., "Electrostatic Field Correction Using Tapered Rose Shims," *Rev. Sci. Instr.* 32, 859-60 (1961).
97. Dietz, L. J. et al., "Internal Standard Technique for Precise Isotopic Abundance Measurements in Thermal Ionization Mass Spectrometry Corr.," *Anal. Chem. P.* 709, Vol. 34, No. 6, May, 1962.
98. Dinh-Hoi, P., "Mass Spectrometric Study of the Diffusion of Hydrogen through Palladium," *Comptes Rendus*, 255, 1724-6 (1962).
99. Djerassi, Carl, Brewer, H. W., Budzikiewicz, H., Orazi, Orfeo O., and Corral, Renee A., "The Structures of the Aspidosperma Alkaloids Spegazzinine and Spegazzinidine," *Journal of the American Chemical Society*, 84, 3480-3485, (1962).
100. Djerassi, Carl, Wilson, J. M., Budzikiewicz, H. and Chamberlin, J. W., "Mass Spectrometry in Structural and Stereochemical Problems. XIV. Steroids with One or Two Aromatic Rings," *Journal of the American Chemical Society*, 84, 4544-4552, (1962).
101. Doering, W. Von E., Willcott, M. R., III, and Jones, N., Jr., "The Structure of Two Minor Products of the Pyrolysis of Thujone," *Journal of the American Chemical Society*, 84, 1224-1228, (1962).
102. Drowart, J., Colin, R., and Verhaegen, G., "Thermochemical Studies at High Temperatures," Unpublished Work.

103. Duenmiller, S., "Use of the Omegatron for the Analysis of Partial Pressures in a High Vacuum," *Vakuum-Tech.* 10, 131-8 (1961).
104. Duke, J. F., "Application of Solid Source Mass Spectrometry to Determine the Purity of Materials for Semiconductor Purposes," *Ultrapurif. Semicond. Mater.*, Proc. Conf., Boston, Mass. 1961, 294-315 (Pub. 1962).
105. Dunn, Gordon H., "Anisotropy in Angular Distribution of Molecular Dissociation Products," Unpublished Work.
106. Durand, George, "Method Permitting the Direct Measurement by Mass Spectrometer of the Isotopic Relations of Lead Contained in Traces of Pitch-Blende Without Previous Chemical Treatment," *Comptes Rendus*, 254, 1032-4 (1962).
107. Earnshaw, D. G., Cook, G. L., and Dinneen, G. U., "A Study of Selected Ions in The Mass Spectra of Benzenethiol and Deuterated Benzenethiol," Unpublished Work.
108. Eash, M. A., Gohlke, R. S., "Mass Spectrometric Analysis - A Small Computer Program for the Analysis of Mass Spectra," *Anal. Chem.* p. 713 Vol. 34, No. 6, May, 1962.
109. Ebert, A. A., Jr., "Use of a Getter-Ion-Type Pump with a Mass Spectrometer," *Appl. Spectry.* 15, 152, 154-5 (1961).
110. Edelson, D., Griffiths, J. E., and McAfee, K. B., Jr., "Autodetachment of Electrons in Sulfur Hexafluoride," *Journal of Chemical Physics* 37, pp 917-18 (1962).
111. Egan, Clark J., Langlois, G. E., and White, R. J., "Selective Hydrocracking of C₉- to C₁₂- Alkylcyclohexanes on Acidic Catalysts. Evidence for the Paring Reaction," *Journal of the American Chemical Society*, 84, 1204-1212, (1962).
112. Ehrhardt, H. and Erbse, U., "Scattering of Low-Energy Electrons at Molecules," Unpublished Work.
113. Elder, F. A., Giese, C., Steiner, B., and Inghram, M., "Photo-ionization of Alkyl Free Radicals," *Journal of Chemical Physics* 36, pp 3292-6, (1962).
114. Elsaesser, F., and Kienel, G., "A High-Efficiency, Metal, Cold Trap for Ultrahigh-Vacuum Systems," *Vakuum-Tech.* 9, 119-21 (1960).
115. Errede, L. A., and DeMaria, F., "The Chemistry of Xylylenes. XV. The Kinetics of Fast Flow Pyrolysis of p-Xylene," *Journal of Physical Chemistry*, Vol. 66, No. 12, Dec. 1962, pp 2664-72.
116. Eschbach, H. L., and Peperle, W., "Demountable Ultrahigh-Vacuum Valve of Large Cross Section," *Vakuum-Tech.* 10, 210-12 (1961).
117. Ezoe, H., and Hayashi, T., "Alternating-Current Amplification of Ion Currents in The Mass Spectrometer," *Rika Gaku Kenkyusho Hokoku* 37, 135-7 (1961).
118. Ezoe, H., and Hayashi, T., "Direct-Current High-Voltage Stabilizer," *Kika Gaku Kenkyusho Hokoku* 37, 138-41 (1961).
119. Ezoe, H., Hayashi, T., and Nagai, K., "Industrial Mass Spectrometer," *Scientific Papers of the Institute of Physical and Chemical Research (Japan)*, 56, 138-144, (1962); *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 10, 13-20, (1962).
120. Ezoe, H., and Nakagawa, S., "A Method to Measure or Control Magnet Field Intensity by Means of a Cathode-Ray Tube (II)," *Scientific Papers of the Institute of Physical and Chemical Research (Japan)*, 56, 133-137, (1962); *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 9, 157-161, (1961).
121. Farrar, H., Fickel, H. R., and Tomlinson, R. H., *Can. J. Physics*, 40, 1017-26 (1962).
122. Field, F.H., and Munson, M. S. B., "A Method for the Determination of Mass Spectrometer Ionization Chamber Pressures," Unpublished Work.

123. Field, F. H., Head, Harlan N., and Franklin, J. L., "Reactions of Gaseous Ions. XI. Ionic Reactions in Krypton-Methane and Argon-Methane Mixtures," *Journal of the American Chemical Society*, 84, 1118-1122, (1962).
124. Fineman, M. A., and Petrocelli, A. W., "Electron Impact Study of CO Using a Lozier Apparatus," *Journal of Chemical Physics* 36, pp 25-32, (1962).
125. Finley, H. O., Clickner, M. R., Leuang, E. E., Jr., "Evaluation of The Accuracy of Surface Ionization Mass Spectrometric Data," Unpublished Work.
126. Finley, H. O., Eberle, A. R., and Rodden, C. J., "Mass Spectrometric Analysis of B^{10} in Boron Materials," Unpublished Work.
127. Fiquet-Fayard, F., "Remarks on the Multiple Ionization of Argon by Electron Impact from 0 to 500 Volts," *J. Chimie Phys.* 59, 439-41 (1962).
128. Fisher, I. P., and Lossing, F. P., "Ionization Potential of Benzynes," Unpublished Work.
129. Fisher, I. P., and Lossing, F. P., "Relation Between Ionization Potential and Electronegativity in Isoelectronic Free Radicals," Unpublished Work.
130. Fite, Wade L., "Charge Exchange Reactions," Unpublished Work.
131. Fitzgerald, M. E., Cirillo, V. A., and Galbraith, F. J., "Mass Spectrometric Method for Analysis of Petroleum Distillates in the Furnace Oil - Kerosine Boiling Range," *Anal. Chem.* p. 1276, Vol. 4, No. 10, September, 1962.
132. Flaks, I. P., Ogurtsov, G. N., and Fedorenko, N. V., "Slow-Ions Produced in Gases Upon Passage of Fast Atom Ion Beams," *Soviet Physics JETP*. Apr. 62, Vol. 14, #4, pp 781-788.
133. Flournoy, J. M., "Thermal Decomposition of Gaseous Dimethylnitramine," *Journal of Chemical Physics* 36, pp 1106-7, (1962).
134. Flournoy, J. M., "Thermal Decomposition of Gaseous 2,2-Dinitropropane," *Journal of Chemical Physics* 36, pp 1107-8, (1962).
135. Foner, S. N., and Hudson, R. L., "Ionization and Dissociation of Hydrogen Peroxide by Electron Impact," *Journal of Chemical Physics* 36, pp 2676-80, (1962).
136. Foner, S. N., and Hudson, R. L., "Mass Spectrometry of the HO_2 Free Radical," *Journal of Chemical Physics* 36, pp 2681-8, (1962).
137. Foner, S. N., and Hudson, R. L., "Mass Spectrometric Studies of Metastable Nitrogen Atoms and Molecules in Active Nitrogen," *Journal of Chemical Physics* 37, pp 1662-7, (1962).
138. Friedman, L., "Some Recent Experimental Mass Spectrometer Studies in the Chemistry Department of Brookhaven National Laboratory," Unpublished Work.
139. Friedman, Henry L., "The Products of Flash Pyrolysis of Phenol-Formaldehyde by Time-of-Flight Mass Spectroscopy," Unpublished Work.
140. Frost, D. C., Mak, D., and McDowell, C. A., "The Photoionization of Nitrogen Dioxide," *Can. J. Chem.* 40, 1064-67 (1962).
141. Fucugauchi, L. A., Tamura, S., and Komori, T., "Europium Determination in Some Rare Earth Elements by Isotope Dilution Method," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 9, 161-163, (1961).
142. Galbraith, F. J., and Cirillo, V. A., "Analysis of Paraffin Wax in the C_{16} - C_{36} Range by Mass Spectrometry," Unpublished Work.
143. Gallegos, Emilio J., and Kiser, Robert W., "Electron Impact Spectroscopy of the Four- and Five- Membered, Saturated Heterocyclic Compounds Containing Nitrogen, Oxygen and Sulfur," *Journal of Physical Chemistry*, Vol. 66, p 136-145.
144. Glick, R. E., and Llewellyn, J. A., "Ionization Cross Sections," Unpublished Work.

145. Godbole, E. W., and Kebarle, P., "Ionization and Dissociation of Deuterated Ethyl and Isopropyl Acetates and Ethyl Formate Under Electron Impacts," Transactions of the Faraday Society 58, 1897-1904 (1962).
146. Gohlke, R. S., "Time-of-Flight Mass Spectrometry: Application of Capillary Column Gas Chromatography," Anal. Chem. p 1332, Vol. 34, No. 10, September, 1962.
147. Gohlke, R. S., and McLafferty, F. W., "Mass Spectrometric Analysis - Aliphatic Amines," Anal. Chem. p 1281, Vol. 34, No. 10, September, 1962.
148. Goodrich, G. W., and Wiley, W. C., "Resistance Strip Magnetic Electron Multiplier," Rev. Sci. Instr. 32, 846-9 (1961).
149. Gordon, Alvin S., and Smith, S. Ruven, "A Study of the Protolysis of Cyclohexane and Acetone. I. Some Reactions of the Cyclohexyl Radical," Journal of Physical Chemistry, Vol. 66, p. 521-524.
150. Gotoh, M., "Ultra High Vacuum Mass Spectrometer," Shinku (Journal of the Vacuum Society of Japan), 5, 62-68, (1962).
151. Gowenlock, B. G., Haynes, R. M., and Majer, J. R., "Electron Impact Measurement of Some Organomercury Compounds," Transactions of the Faraday Society 58, 1905-7 (1962).
152. Gray, Thomas J., Hulbert, Samuel F., and Benson, David, "Correlation Between Various Physical and Chemical Properties of Oxide Surfaces and Their Constitution," Rept. for Dec. 58 - Nov. 60, on Surface and Interface Phenomena of Matter, Contract AF 33 (616) 6188, Proj. 7022.
153. Greene, Frank T., and Gilles, Paul W., "Mass Spectrometric Studies of New High Molecular Weight Boron Sulfides," Unpublished Work.
154. Grishaeu, I. S., and Shenderovich, A. M., "Errors Due to the Dead Time of Counters Operating in Conjunction with Pulsed Sources," J. Exptl. Theoret. Phys. (U.S.S.R.) 41, 410-416, (August, 1961), JETP 14, 2, (February, 1962).
155. Groweg, D. H., and Billian, C. J., "Microinlet System for Mass Spectrometer Analysis of Small Gaseous Inclusions in Glass," Instr. Soc. Am. Conf. Preprint 132-59, 6 pp. (1959).
156. Grubbs, W. J., Snider, G. H., Scott, F. I., and Bloom, J., "A New Continuous Quantitative Gas Analysis Method," Unpublished Work.
157. Habfast, K. E., "Construction Details of and First Results Obtained with a New Commercial Mattauch-Type Mass Spectrograph," Unpublished Work.
158. Haefer, R. A., "The Ion Baffle in Conjunction with an Air-Cooled Oil Diffusion Pump," Vakuum-Tech. 11, 41-4 (1962).
159. Hagemann, R., "Determination of the Heat of Formation of S₂O by the Mass Spectrometer," Comptes Rendus, 255, 1102-3 (1962).
160. Hagemann, R., "Mass Spectrometric Study of the Suboxide of Sulfur," Comptes Rendus, 255, 899-900 (1962).
161. Hall, L. H., and Koski, W. S., "On The Nature of Some Higher Boron Hydrides Produced in Radiation-Induced Reactions in Penta- and Decaborane," Journal of the American Chemical Society, 84, 4205-4207 (1962).
162. Hamill, W. H., "Atom and Ion Exchange Reactions," Unpublished Work.
163. Hannay, N. B., "Mass-Spectrographic Analysis of Solids," Science 134, 1220-5 (1961).
164. Harless, H. R., "Mass Spectrometry of Oximes," Unpublished Work.
165. Harrison, A. G., and Shannon, T. W., "An Electron Impact Study of Chloromethyl and Dichloromethyl Derivatives," Can. J. Chem. 40, 1730-37 (1962).
166. Harrison, A. G., and Tait, J. M. S., "Concurrent Ion-Molecule Reactions Leading to the Same Produce Ion," Can. J. Chem. 40, 1986-96 (1962).

167. Hashmi, S. Z. R., "Ion Vacuum Gage," J. Sci. Ind. Res. (India) 21B, 138-9 (1962).
168. Hasted, J. B., and Chong, A. Y. J., "Electron Capture Processes for Multiply Charged Ions," Proc. Phys. Soc., 80, 441 (1962).
169. Hayashi, T., "On the Space Charge Effect in a Velocity Modulation Type Mass Spectroscope," Scientific Papers of the Institute of Physical and Chemical Research (Japan), 56, 206-208, (1962).
170. Henglein, A., and Muccini, G. A., "Mass-Spectrometric Studies of Negative Ions with Neutral Molecules," Chem. Effects Nucl. Transform., Proc. Symp., Prague 1960, 87-98 (Pub. 1961).
171. Henglein, A., and Muccini, G. A., "Mass Spectrometric Observations of Electron and Proton Transfer Reactions Between Positive Ions and Neutral Molecules. Part II," Unpublished Work.
172. Henneberg, Dieter, "Combination of Gas Chromatography and Mass Spectrometry for the Analysis of Organic Mixtures," Z. Anal. Chem. 183, 12-23 (1961).
173. Herzog, R. F., "Instrumentation for the Determination of the Composition of the Upper Atmosphere," Technical Progress Rept. 15 March - 15 June, 1961, Contract NAS 6-270.
174. Herzog, Richard F., and Poschenrieder, Walter P., "Inverted Magnetron Type Mass Spectrometer," Unpublished Work.
175. Hickam, William M., and Sweeney, George G., "Spark Source Mass Spectroscopy for Microanalysis of Solids," Unpublished Work.
176. Hildenbrand, D. L., and Theard, L. P., "Thermodynamic Properties of Rocket Combustion Products," Quarterly Technical Report #3, May 1, 1962, p. 19, Contract AF 04 (611) (7442).
177. Hintenberger, H., "Instrumentation and Techniques of High Resolution Mass Spectrometry," Unpublished Work.
178. Hirota, K., Fueki, K., and Otouma, H., "On the Dissociation of Ethanol Molecular Ions Formed by Charge-Exchange-Collisions with Positive Ions," Shitsuryo Bunseki (Mass Spectroscopy-Japan), 9, 180-181, (1961).
179. Hirota, K., Fueki, K., and Otouma, H., "Theoretical Investigation on Ionization Dissociation of Ethanol," Nippon Kagaku Zasshi (J. Chem. Soc. Japan), 83, 30-31 (1962).
180. Hirt, Thomas J., and Wightman, James P., "Mass Spectrum of Carbon Suboxide," Journal of Physical Chemistry, Vol. 66, July (1962), p. 1756.
181. Hobrock, Brice G., and Kiser, Robert W., "Electron Impact Spectroscopy of Propylene Sulfide," Journal of Physical Chemistry, Vol. 66, No. 8, Aug. 1962, p. 1551.
182. Hobrock, Brice G., and Kiser, Robert W., "Electron Impact Spectroscopy of Sulfur Compounds. I. 2-Thiabutane, 2-Thiapentane, and 2,3-Dithiabutane," Journal of Physical Chemistry, Vol. 66, p. 1648-52 (1962) July.
183. Hobrock, B. C., and Kiser, Robert W., "Electron Impact Spectroscopy of Tetramethylgermanium, Trimethylsilane and Dimethylmercury," Journal of Physical Chemistry, Vol. 66, p. 155-158.
184. Hodgson, F., Neil, and Desjardins, Michel, "Elemental Associations Observed in the Radio Frequency Spark Source," Unpublished Work.
185. Hutchison, Dwight A., Pobo, Louis G., and Brookshier, William K., "An Ion Source Using a Parallel-Plate Electron-Energy Selector," Unpublished Work.
186. Inokuti, M., "Ionization of the Methane Molecule by Electron Impact," Journal of Chemical Physics 37, pp 2387-93, (1962).
187. Islam, M., Hasted, J. B., Gilbody, H. B., and Ireland, J. V., "Charge Transfer Reactions of Doubly Charged Ions," Proc. Phys. Soc., 79, 1118 (1962).

188. Istomin, V. G., "Nitrogen Ions in the Upper Atmosphere and Nocturnal Ionization of the E Region," translated from Doklady Akademii Nauk, SSSR, Vol. 137, No. 5, April 1961, pp 1102-1105.
189. Jahn, P., and Zaehring, J., "Mass Spectrometer Investigations in Ultrahigh Vacuum," *Vakuum-Tech.* 10, 138-41 (1961).
190. James, L. H., and Carter, G., "Bombardment Induced Re-Emission of Ionically Pumped Inert Gas from a Glass Surface," *British Journal of Applied Physics*, 13, #1, 2-8 (1962).
191. Jense, Andreas V., Goshgarian, Berge B., and Dane, Norman E., "Solid Combustion Products Analysis by Spark Source Mass Spectrometry," Unpublished Work.
192. Jordan, P., and Tgetgel-Schelling, C., "A Micro Exchange Method for the Determination of Deuterium in Water by Mass Spectrometry," *Helv. Chim. Acta* 45, 703-11 (1962).
193. Jortner, Joshua, and Stein, Gabriel, "Deuterium Isotope Effects in the Photochemical Evolution of Hydrogen from Aqueous Ferrous Solution," Vol. 66, No. 11, Nov. 1962, p. 2200-04.
194. Judson, C. M., Blanchard, C. G., and Comaford, D. J., "Performance of a High Resolution Mass Spectrometer," Unpublished Work
195. Judson, C. M., Howard, R. F., and McKinney, C. R., "Performance of an Analytical Mass Spectrometer," Unpublished Work.
196. Judson, C. M., and Hull, C. W., "Precision, Accuracy, and Sensitivity in Spark Mass Spectrometry," Unpublished Work.
197. Junk, G. A., and Svec, H. J., "The Mass Spectra of Dipeptides," Unpublished Work.
198. Jupel, Richard E., Nolan, Melvin, Keena, Robert G., Kite, Mark, and Scheel, Lester D., "Identification of Pyrolysis Products of Polytetrafluoroethylene," Unpublished Work.
199. Kaufman, Joyce J., Koski, W. S., Kuhns, L. J., and Law, R. W., "Appearance and Ionization Potentials of Selected Fragments from Decaborane, $B_{10}H_{14}^+$," *Journal of the American Chemical Society*, 84, 4198-4205, (1962).
200. Kebarle, P., and Avrahami, M., "Hydrogen Atom Recombination in the Flow System Attached to a Mass Spectrometer and Used for the Study of Mercury-Sensitized Reactions," *Can. J. Chem.* 40, 2409-11 (1962).
201. Kebarle, P. and Godbole, E. W., "Ionization and Fragmentation of Some Molecules by High Energy Electrons," *Journal of Chemical Physics* 36, pp 302-5, (1962).
202. Kel'man, V. M., and Gall, L. N., "Mass Spectrometers with Two-Dimensional Magnetic Prisms," *Zhur. Tekh. Fiz.* 31, 1083-91 (1961).
203. Kendall, B. R. F., "Automatic Data Processing for a Sensitive Time-of-Flight Mass Spectrometer," *J. Sci. Instrum.* 39, 267 (1962).
204. Kendall, B. R. F., "Increasing the Resolving Power of Mass Spectrometers and Other Analytical Instruments," *Rev. Sci. Instr.* 32, 758-60 (1961).
205. Kendall, B. R. F., "Resolving-Power Multiplier for Mass Spectrometers," *The Review of Scientific Instruments*, Vol. 33, No. 1, January, 1962.
206. Kendrick, E., "A Mass Scale Based on $CH_2 = 14.0000$ for High Resolution Mass Spectrometry of Organic Compounds," Unpublished Work.
207. Kerr, J. T., "Some Preliminary Data on the Detection of Ions Sputtered from Glass Surfaces," Unpublished Work.
208. Kiser, R. W., "Studies of the Shapes of Ionization-Efficiency Curves of Multiply Charged Monoatomic Ions. I. Instrumentation and Relative Electronic-Transition Probabilities for Krypton and Xenon Ions," *Journal of Chemical Physics*, 36, pp 2964-8, (1962).

209. Klass, P. J., and McSweeney, W. P., "Gasoline Type Analysis by Mass Spectrometer Using Computer Assembled Matrices," *Anal. Chem.* p. 30, Vol. 34, No. 1, January 1962.
210. Klaver, R. F., and Teeter, R. M., "A New Digitizer for Mass Spectra," Unpublished Work.
211. Klumb, H., and Ihm, H., "High Frequency Mass Spectrometer in High Vacuum," *Vakuum-Tech.* 10, No. 8, 231-5 (1961).
212. Knewstubb, P. F., and Tickner, A. W., "Mass Spectrometry of Ions in Glow Discharges. I. Apparatus and Its Application to the Positive Column in Rare Gases," *Journal of Chemical Physics*, 36, pp 674-83, (1962).
213. Knewstubb, P. F., and Tickner, A. W., "Mass Spectrometry of Ions in Glow Discharges. II. Negative Glow in Rare Gases," *Journal of Chemical Physics*, 36, pp 684-93, (1962).
214. Knewstubb, P. F., and Tickner, A. W., "Mass Spectrometry of Ions in Glow Discharges. III. Nitrogen and Its Mixtures with Hydrogen and Oxygen," *Journal of Chemical Physics*, 37, pp 2941-9, (1962).
215. Kobayakawa, M., Hayashi, S., and Titani, T., "Formation of Nitric Oxide at the Preparation of Nitrogen Gas for Mass Spectrometric Analysis," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 10, 34-36, (1962).
216. Latham, D. R., Ferrin, C. R., and Ball, J. S., "Identification of Fluorenones in Wilmington Petroleum by Gas-Liquid Chromatography and Spectrometry," *Anal. Chem.* p. 311, Vol. 34, No. 3, March, 1962.
217. Larey, David M. G., and Paulson, Joseph F., "Further Elucidation of Hydrocarbon Types in Olefinic Gasoline by Mass Spectrometry," *Anal. Chem.*, p. 538, Vol. 34, No. 4, April, 1962.
218. Lees, D. A., "Mass Spectrometry," *Research XIV*, 1-8 (1961).
219. Lee, R. W., "The Diffusion of Hydrogen in Natural and Synthetic Fused Quartz," Unpublished Work.
220. Lehrle, R. S., Robb, J. C., and Thomas, D. W., "A Modified Time-of-Flight Mass Spectrometer for Studying Ion-Molecule or Neutral Particle-Molecule Interactions," *J. Sci. Instrum.*, 39, 458 (1962).
221. Leigh, Charles H., "Research and Advanced Development Div., AVCO Corp., Wilmington, Mass. Exploratory Research on the Vaporization of Solids," Final Report, May 1, 1962, 64 p., Contract Nonr - 305100.
222. Leipziger, F. D., "Isotopic Analyses with a Spark Source Mass Spectrograph," Unpublished Work.
223. Lichtman, David, "Mass Spectrometer System for Beam-Surface Interaction Studies," Unpublished Work.
224. Liebl, Helmut J., and Herzog, Richard F. K., "Ion Source for Solid Materials," Unpublished Work.
225. Lilly, A. C., Jr., and Weismann, T. J., "Ion Beam Profiles in Three Dimensional Fields," Unpublished Work.
226. Lincoln, Kenneth A., "A Simple Display System for Recording Rapid Changes in Mass Spectra," Unpublished Work.
227. Lintz, H. G., Pentenero, A., and LeGoff, P., "The Mass Spectrometric Study of the Heterogeneous Combustion of Organic Vapors on Platinum. I. The Reaction of Methane with Excess Oxygen," *J. Chimie Phys.* 59, 933-40 (1962).
228. Loeffler, Mary H., Goodman, Ruth, "Automatic Assembly of Matrices for Mass Spectrometric Calculations," *Anal. Chem.*, p. 713, Vol. 34, No. 6, May, 1962.
229. Love, H. M., and White, J. J., "Mass Spectrometric Study of Sodium and Rubidium Diffusion in Tungsten," Unpublished Work.

230. Lumpkin, H. E., and Aczel, Thomas, "Low Voltage Sensitivities of Aromatic Hydrocarbons," Unpublished Work.
231. Maeda, K., and Kawashima, T., "Power Supply for Ion Source of Mass Spectrometer in Electrotechnical Laboratory," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 10, 21-28 (1962).
232. Magari, S., and Hotta, "Storage Tube Mass Spectrometer Recorder," *Rev. of Scient. Inst.* Vol. 33, No. 2, February, 1962.
233. Maisden, D. G. H., "Panoramic Mass Spectrometer," *Rev. of Scient. Inst.* Vol. 33 No. 3, March, 1962.
234. Majer, J. R., and Patrick, C. R., "Electron Impact of Some Halogenated Aromatic Compounds," *Transactions of the Faraday Society*, 58, 17 (1962).
235. Margoninski, Y., Wolsky, S. P., and Zdanuk, E. J., "Omegatron Tube Employing a Lanthanum Boride Filament," *Vacuum* 11, 287-8 (1961).
236. Marmet, P., "Neutralization of Fringing Magnetic Fields in the Ion Source of a Mass Spectrometer," *Rev. of Scient. Inst.* Vol. 33, No. 2, February, 1962.
237. Marmet, P. and Morrison, J. D., "Secondary Reactions in the Ion Chamber of a Mass Spectrometer," *Journal of Chemical Physics* 36, pp 1238-44, (1962).
238. Martin, T. W., and Barnes, W. S., "Mass Spectrometric Study of Ion-Molecule Reactions Occurring at Thermal Energies Under Gas Kinetic Conditions," Final Interim Report, 31 March 1962, 11 pp. Contract AF 18 (600) 1524.
239. Martin, T. W., and Rummell, R. E., "New Studies on the Diffusion of Hydrogen Through Hot Palladium," Unpublished Work.
240. Martin, T. W., Rummel, R. E., and Melton, L. E., "High-Pressure Mass Spectrometry," *Science*, 138, 77-83, Oct. 12, 1962.
241. Masuda, Y., "The Abnormal Peaks in Mass Spectra," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 9, 171-179 (1961).
242. McAdams, D. R., Lane, L., and Lemley, J. G., "Ion-Counting for Rapid Measurements with Time-of-Flight Mass Spectrometers," Unpublished Work
243. McCrea, J. M., "Photographic Indexing Technique for Evaluating Emulsion Uniformity of Spectrographic Plates," Unpublished Work.
244. McDaniel, E. W., "Drift Tube - Mass Spect. for Studies of Low-Energy Ion-Molecule Reactions," *Rev. Sci. Instr.*, Vol. 33, No. 1, January, 1962.
245. McDaniel, E. W., and Martin, D. W., "Drift Tube Mass Spectrometer for Studies of Thermal-Energy Ion-Molecule Reactions," U. S. Dept. Com., Office Tech. Serv., PB Report, 148,965, 29 pp. (1960).
246. McFadden, W. H., and Lounsbury, M., "The Mass Spectra of Three Deuterated Bromobutanes," *Can. J. Chem.* 40, 1965-75 (1962).
247. McGowan, J. William, "Long Lived Excited Ions in Collision Mass Spectrometry," Unpublished Work.
248. McGowan, W., and Kerwin, L., "Comparative Mass Spectra Using Carbon and Tungsten Filaments," *J. Chimie Phys.*, 59, 927-8 (1962).
249. McKinney, C. R., and Maynes, D., "Mass Discrimination in Electron Multiplier Ion Detectors," Unpublished Work.
250. McLafferty, F. W., "Mass Spectrometric Analysis - Aliphatic Halogenated Compounds," *Anal. Chem.* P-2 Vol. 34, No. 1, January, 1962.
251. McLafferty, F. W., "Mass Spectrometric Analysis - Aliphatic Nitriles," *Anal. Chem.* P-26, Vol. 34, No. 1, January, 1962.
252. McLafferty, F. W., "Mass Spectrometric Analysis - Aromatic Halogenated Compounds," *Anal. Chem.* P-16, Vol. 34, No. 1, January, 1962.

253. Mead, W. L., and Wilde, A. J., "Mass Spectrum of Vanadyl Etioporphyrin," Chem. and Ind. (London) 1961, 1315.
254. Melton, C. E., "Ionization and Excitation Processes in, Argon, Krypton, and the C₂ Hydrocarbons Produced by Various Means," Journal of Chemical Physics 37, pp 562-66, (1962).
255. Meyer, Richard T., "An Improved Oscilligraphic Camera Technique for Time-Resolved Mass Spectrometer Data Recording," Unpublished Work.
256. Meyerson, Seymour, "Mass Spectra of Diaryl Sulfones," Unpublished Work.
257. Meyerson, Seymour, "Organic Ions in the Gas Phase. Phenylated Cyclopropane Ion in the Decomposition of 3-Phenylpentane," Unpublished Work.
258. Meyerson, S., and VanderHaar, R. W., "Multiply Charged Organic Ions in Mass Spectra," Journal of Chemical Physics 37, pp 2458-61, (1962).
259. Michael, E. J., and Marshall, D. J., "Tandem Magnetic Analyzer Mass Spectrometer Systems," Unpublished Work.
260. Michijima, M., Okano, J., Fujinaga, A., Ogata, K., "Residual Gases in Metal Vacuum System," Skinku (Journal of the Vacuum Society of Japan), 5, 22-27, (1962).
261. Michejda, C. J., Tarbell, D. S., and Saunders, W. H., Jr., "An O¹⁸ Tracer Study of the Composition of Benzoic sec-Butylcarbonic Anhydride: the Absence of Alky-Oxygen Cleavage," Journal of the American Chemical Society, 84, 4113-4115, (1962).
262. Milne, Thomas A., "Mass Spectrometer Study of Metal Containing Flames," Quarterly Technical Summary Report #1; 1 Oct. - 31 Dec. 1961, Contract Nonr - 359900.
263. Milne, Thomas A., "Mass Spectrometer Study of Metal-Containing Flames," Quarterly Technical Summary Report #3, 1 April - 30 June 1962, Contract Nonr - 359900.
264. Milne, J. D., Pryor, A. W., and Whitem, R. N., "Filament Current Controller for M.S. 5 Mass Spectrometer," J. Sci. Instrum. 39, 237 (1962).
265. Milton, J. C. D., and Frase, J. S., Can. J. Physics, 40, 1626-63 (1962).
266. Monahan, J. E., and Stanton, H. E., "Mass Spectra Resulting from High-Energy Electron Impact on Some Hydrocarbon Molecules," Journal of Chemical Physics 37, pp. 2654-61, (1962).
267. Moreau, J., "Vacuum Gages that Use Radioactive Materials," Vide 17, No. 99, 222-6 (1962).
268. Moreland, P. E., Jr., and Bainbridge, K. T., "A Direct Determination of the 3H-3He Mass Difference," Unpublished Work.
269. Morito, N., Omura, I., and Noda, T., "Multiplendisersion Mass Spectrometer (I)-Apparatus and Improvement in Resolving Power," Shitsuryo Bunseki (Mass Spectroscopy-Japan), 10, 6-12, (1962).
270. Mosharrafa, M., and Oskram, H. J., "Design and Construction of a Mass Spectrometer for the Study of Basic Processes in Plasma Physics," Report for July 1960 - July 1961 on Project Definder, Contract Nonr - 71037.
271. Mullaney, D., "Breakable High Conductance Vacuum Valve," Review of Scientific Inst. Vol. 33, No. 9, p. 1003, September, 1962.
272. Muller, Erwin W., "Field Emission Studies of Metal Surfaces," December 1961, 104 p., Contract AF 49 (638) 504; Continuation of Contract AF 18 (600) 672.
273. Munson, M. S. B., Field, F. H., and Franklin, J. L., "High-Pressure Mass Spectrometric Study of Reactions of Rare Gases with N₂ and CO," Journal of Chemical Physics 37, pp. 1790-9, (1962).

274. Munson, M. S. B., Franklin, J. L., and Field, F. H., "A Mass Spectrometric Study of Homonuclear and Heteronuclear Rare Gas Molecule Ions," Unpublished Work
275. Muschlitz, E. E., Jr., "Ion Source for Low-Energy Negative Ions," Rev. of Scient. Inst. Vol. 33, No. 4, April, 1962.
276. Narten, Alfred, "Separation Factors in the NO-NOBr System," Journal of Physical Chemistry, Vol. 66, No. 6, June 1962, page 1180.
277. Newton, Amos S., and Sciamanna, A. F., "A Metastable State of the Doubly Charged Carbon Dioxide Ion," Unpublished Work.
278. Nier, A. O., Eckelman, W. R., and Lupton, R. A., "A Mass Spectrometer for Isotope Ratio Analyses," Anal. Chem. p. 1358, Vol. 34, No. 11, October, 1962.
279. Noda, T., "Analysis of Ion Trajectory in Mass Spectrometer with Circular Magnetic Field," Oyo Butsuri (Journal of Applied Physics, Japan), 31, 11-22, (1962).
280. Nutt, C. W., and Biddlestone, A. J., "Theory and Application of Molecular-Beam Techniques for the Design of Collision-Free Sampling Systems," Transactions of the Faraday Society 58, 1363 (1962).
281. Nutt, C. W., and Biddlestone, A. J., "Appearance Potential and Scattering Cross-Section of Oxygen Atoms from an R. F. Discharge (10 Mc/sec)," Transactions of the Faraday Society 58, 1368 (1962).
282. Nutt, C. W., and Biddlestone, A. J., "Reaction of Atomic Oxygen with Nitrogen Dioxide," Transactions of the Faraday Society 58, 1376 (1962).
283. O'Halloran, G. J., "A Breathable Atmosphere Composition Analyzer for Aerospace Applications," Paper presented at the 14th National Aerospace Electronics Conference, Dayton, Ohio, (14-16 May 1962).
284. O'Halloran, G. J. and Fluegge, R. A., "Plasma Analysis with the Bendix Time-of-Flight Mass Spectrometer," Unpublished Work.
285. O'Halloran, G. J., and Wyess, W. R., "The Model 17-Series Bendix Time-of-Flight Mass Spectrometer," Unpublished Work.
286. Okamoto, J., Nakajima, Y., Tsuyama, H., Omura, I., Morito, N., Onuki, H., and Kakuta, M., "Isotopic Analysis with a Mass Spectrometer. I. Natural Abundances of Magnesium Isotopes," Bunseki Kagaku 8, 171-5 (1959).
287. Omura, I., and Morito, N., "Mass Spectrometric Measurements of Negative Ions," Shitsuryo Bunseki (Mass Spectroscopy-Japan), 10, 29-33, (1962).
288. Oshima, S., and Nishishita, T., "Type Analysis of Paraffinic Hydrocarbons by Mass Spectrometry," Shitsuryo Bunseki (Mass Spectroscopy-Japan), 9, 164-170, 1961.
289. Oskam, H. J., "Research in Gaseous Electronics," Final Interim Report, 15 Sept. 1958 - 1 Sept. 1961, Contract AF 49 (638) 378, Proj. 9653.
290. Owens, E. B., "The Effect of Ion Mass and Ion Energy on the Sensitivity of Ilford Q₂ Plates as Ion Detectors in Mass Spectrometry," Applied Spectroscopy 16, pp. 148-50, 1962.
291. Owens, E. B., and Sherman, A. M., "Mass Spectrographic Lines of the Elements," Tech. Report No. 265, Contract AF 19 (604) 7400.
292. Palmer, T. F., and Lossing, F. P., "Free Radicals by Mass Spectrometry. XXVIII. The HS, CH₃S, and Phenyl-S Radicals: Ionization Potentials and Heats of Formation," Journal of the American Chemical Society, 84, 4661-4664, 1962.
293. Pascalsau, M., and Muller, A., "Adaptation of the Leak Detector PTI-4A to Mass Spectrometric Analyses," Acad. Rep. Populare Romine, Inst. Fiz. Atomica si Inst. Fiz., Studii Cercetari Fiz. 12, 157-64 (1961).
294. Patterson, H., and Wilson, H. W., "New Mass Spectrometer Solid Source Arrangement for the Simultaneous Analysis of Two Samples," J.Sci. Instrum. 39, 84.

295. Perie, M., and Chemla, M., "Determination of Traces of Boron by Isotopic Dilution Using the Mass Spectrometer," *Comptes Rendus*, 254, 1429-31 (1962).
296. Perie, M. and Chemla, M., "Mass Spectrometric Determination of Traces of Lithium by Isotope Dilution," *Comptes Rendus*, 252 (1961).
297. Perkins, George D. and Pollock, David H., "Study for Improvement of Materials Central Mass Spectrometer," Final Report 1 March 1961 - 28 February 1962 on Materials Analysis and Evaluation Techniques, Contract AF 33 (616) 7932, Proj. 7360.
298. Peterson, Lowell, "Mass Spec. All Glass Heated Inlet," *Anal. Chem.*, p. 1850, Vol. 34, No. 13, December, 1962.
299. Peterson, Lowell, "Mass Spectra of Some Highly Substituted Pregnanes and Pregnenes," *Anal. Chem.*, p. 1781, Vol. 34, No. 13, December, 1962.
300. Pitaevskii, L. P., "Electron Recombination in a Monatomic Gas," *J. Exptl. Theoret. Phys. (U.S.S.R.)* 42, 1326-1329, May, 1962, *JETP* 15, 5, 919-921, November, 1962.
301. Phillips, L. F., and Schiff, H. I., "Mass Spectrometric Studies of Atom Reactions. I. Reactions in the Atomic Nitrogen-Ozone System," *Journal of Chemical Physics* 36, pp. 1509-17, (1962).
302. Phillips, L. F., and Schiff, H. I., "Mass Spectrometric Studies of Atom Reactions. II. Vibrationally Excited N_2 Formed by the Reaction of N Atoms with NO ," *Journal of Chemical Physics* 36, pp. 3283-6, (1962).
303. Phillips, L. F., and Schiff, H. I., "Mass Spectrometric Studies of Atomic Reactions. III. Reactions of Hydrogen Atoms with Nitrogen Dioxide and with Ozone," *Journal of Chemical Physics* 37, pp. 1233-8, (1962).
304. Porter, R. F., Bidinosti, D. R., and Watterson, K. F., "Mass Spectrometric Study of the Reaction of BF_3 with BCl_3 , $B(OH)_3$, and B_2O_3 ," *Journal of Chemical Physics* 36, pp. 2104-8, 1962.
305. Pottie, Roswell F., Lorquet, Andree J., and Hamill, William H., "The Energy Dependence for Reactions Cross Sections of Ion-Molecule Reactions of Cyclopropane in the Mass Spectrometer," *Journal of the American Chemical Society*, 84, 529-530, 1962.
306. Pupezin, J., Ciric, M., and Lazarevic, "The Isotope Analysis of Lithium on a Mass Spectrometer," *Bulletin of the Boris Kidrich Institute of Nuclear Sciences Belgrade*, 13 - #2, 77-83 (1962).
307. Rabinovitch, B. S., "Some Aspects of Unimolecular Reactions," Unpublished Work.
308. Rapp, Donald, "A Review of the Theory of Charge Exchange Between Gaseous Ions and Molecules," Unpublished Work.
309. Rebbert, R. E., and Ausloos, P., "The Photolysis and Radiolysis of $CH_3N_2CH_3$ and $CH_3N_2CH_3-CD_3N_2CD_3$ Mixtures," *Journal of Physical Chemistry*, Vol. 66, No. 11, November, 1962, p. 2253-58.
310. Redhead, P. A., Kornelsen, E. V., and Hobson, J. P., *Can. J. Physics* 40, 1814-36, 1962.
311. Reich, G., "Sensitivity and Resolving Power of the Omegatron," *Vakuum Tech.* 10, No. 8, 242-6 (1961).
312. Reuben, B. G., and Friedman, L., "Isotopic Hydrogen-Ion-Molecule Reactions," *Journal of Chemical Physics* 37, pp. 1636-42, 1962.
313. Robinson, Charles F., Bell, Norton W., and Others, "A Mass Spectrometer System for Materials Research. Phase III," Report for 1 Jan. 1960 - 28 Feb. 1961, on Materials Analysis and Evaluation Techniques, Contract AF 33 (616) 5571, Proj. 7360).

314. Robinson, U. F., Perkins, G. D., and Bell, N. W., "Mass Spectrometer System for Materials Research," Instr. Meas., Chem. Anal., Elec. Quant., Nucleonics Process Control, Proc. Intern. Conf., Stockholm 1, 260-70 (1960).
315. Roboz, John, "Analytical Studies with Spark Source Mass Spectrograph," Unpublished Work.
316. Roboz, John, "Determination of Gas Content of Metals with Spark Source Mass Spectrograph," Unpublished Work.
317. Rohwedder, W. K., Selke, E., and Bitner, E. D., "Source and Multiplier Modifications of a Time-of-Flight Mass Spectrometer to Increase Sensitivity," Unpublished Work.
318. Rosenstock, H. M., and Dibeler, V. H., and Harllee, F. N., "Initial Preparation and Metastable Transitions," Unpublished Work.
319. Rudolph, P. S., Lind, S. C., and Melton, C. E., "Ionic Complexes of Xe and C_2H_2 Produced by Radiolysis of These Gases," Journal of Chemical Physics 36, pp. 1031-5, 1962.
320. Rubb, Richard L., "Research in Trace Emission Spectroscopy," Final Report 1 Feb. 1961 - 1 Feb. 1962, Contract AF 19 (604) 8013, Proj. 4608.
321. Sandler, Y. L., and Hickam, W. M., "A Method for Studying the Chemisorption and Exchange of Gases on Surfaces," Unpublished Work.
322. Sauer, M. C., Jr., and Dorfman, L. M., "The Radiolysis of Ethylene; Details of the Reformation of Decomposition Products," Journal of Physical Chemistry, Vol. 66, p. 322-325.
323. Schaefer, E. J., Nichols, M. H., "Mass Spectrometer for Upper Air Measurements," Am. Rocket Soc. J. 31, 1773-6 (1961).
324. Schiavello, M. and Volpi, G. G., "Reactions of Hydrogen Atoms with Hydrazine, Ammonia, and Nitrous Oxide," Journal of Chemical Physics 37, pp. 1510-13, 1962.
325. Schissel, P. O., "Production of Oxygen and Carbon Monoxide from Carbon Dioxide in an Ionization Gauge," Journal of Applied Physics, 33, 8, 2659-2660 (1962).
326. Schissel, P. O., and Trulson, O. C., "Mass Spectrometric Study of the Vaporization of the Titanium-Boron System," Journal of Physical Chemistry, Vol. 66, No. 8, August, 1962, p. 1492-96.
327. Selke, E., Scholfield, C. R., Evans, C. D., and Dutton, H. J., "Mass Spectrometry and Lipid Research," J. Am. Oil Chemists' Soc. 38, 614-15 (1961).
328. Schug, John C., "Metastable Ion Intensities," Unpublished Work.
329. Shapiro, I., Good, C. David, and Williams, Robert E., "The Carborane Series: $B_nC_2H_{n+2}$. I. $B_3C_2H_5^1$," Journal of the American Chemical Society, 84, 3837-3840, 1962.
330. Sharkey, A. G., Shultz, J. L., and Friedel, R. A., "Comparison of Mass Spectrometric and Gas Chromatographic Analyses of High-Boiling Oils from Coal," Unpublished Work.
331. Sharkey, A. G., Shultz, J. L., and Friedel, R. A., "Mass Spectrometric Determination of the Ratio of Branched to Normal Hydrocarbons up to C_{18} in Fischer-Tropsch Prod.," Anal. Chem., p. 826, Vol. 34, No. 7, June, 1962.
332. Sharp, T. E., Rosenstock, H. M., and Zwanzig, R., "Ionization of Polyatomic Molecules," Unpublished Work.
333. Shields, W. R., Garner, E. L., and Dibeler, V. H., "Absolute Isotopic Abundances of Terrestrial Silver," Journal of Research, National Bureau of Standards, 66A, #1, 1-3, (1962).
334. Shields, William R., Murphy, Thomas J., Garner, Ernest L., and Dibeler, Vernon R., "Absolute Isotopic Abundance Ratio and the Atomic Weight of Chlorine," Journal of the American Chemical Society, 84, 1519-1522, (1962).

335. Shooter, D., and Farnsworth, H. E., "A Search for Hydrogen-Deuterium Exchange on Clean Germanium Surfaces," *Journal of Physical Chemistry*, Vol. 66, p. 222-224.
336. Sjogren, Hakan, and Lindholm, Einar, "Higher Ionization Potentials in Alcohols and Water Measured by Electron Impact," Unpublished Work.
337. Slattery, J. C., and Kemp, "Plasma Potential Probe Using Electron Time-of-Flight," *Rev. of Scient. Inst.* Vol. 33, No. 4, April, 1962.
338. Smith, A. J., Marshall, D. J., Cambey, L. A., and Michael, E. J., "A Mass Spectrometer for the Study of Sputtering," Unpublished Work.
339. Snyder, L. R., Howard, H. E., and Ferguson, W. C., "Determination of Hydrocarbon Types in Kerosene Range Distillates by Mass Spectrometry," Unpublished Work.
340. Solov'ev, E. S., Il'in, R. N., Oparin, A., and Fedorenko, N. V., "Ionization of Gases by Fast Hydrogen Atoms and by Protons," *Leningrad Physics-Technical Institute, Academy of Sciences, USSR, J. Exptl. Theoret. Phys. (U.S.S.R.)* 42, 659-668, March, 1962, *JETP* 15, 3, 459-464, September, 1962.
341. Spitzer, E. J., and Sites, J. R., "Isotopic Mass Spectrometry of the Elements," Unpublished Work.
342. Spokes, G. N., and Evans, B. E., "A Study of the Ions Present in Active Nitrogen Using a Quadrupole Mass Spectrometer," Unpublished Work.
343. Steele, W. C., Nichols, L. D., and Stone, F. G. H., "An Electron Impact Investigation of Some Organoboron Difluorides," *Journal of the American Chemical Society*, 84, 1154-1158, (1962).
344. Steele, W. C., and Stone, F. G. A., "An Electron Impact Study of 1,1,1-Trifluoroethane, 1,1,1-Trifluoropropane and 3,3,3-Trifluoropropene," *Journal of the American Chemical Society*, 84, 3450-3454, (1962).
345. Steinberg, H. A., "High Vacuum Technology and Equipment," *Chem. Engr.*, 69, #17, 117, (1962).
346. Stokes, S. and Fox, R. B., "Photolysis of Poly- α -Methylstyrene," *Journal of Polymer Science* 56, 507-517, (1962).
347. Stevens, M. R., "Ionization Potential Study of High Molecular Weight Compounds," Unpublished Work.
348. Studier, Martin H., "Continuous Ion Source for the Bendix Time-of-Flight Mass Spectrometer," Unpublished Work.
349. Studier, Martin H., and Sloth, Eric N., "Mass Spectrometric Studies of Rare Gas Compounds," Unpublished Work.
350. Socha, Arthur J., and Willardson, Robert K., "Analytical Techniques," Unpublished Work.
351. Sugawara, S., "Distribution of Magnetic Flux in a Magnet," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 9, 152-157, (1961).
352. Sugiura, Toshio, "The Secondary Emission Electron Multiplier Tube Used on a Mass Spectrometer and Its Amplification of Ion Currents," *Bull. Chem. Soc. Japan* 35, 1257-62 (1962).
353. Taubert, R., "The Initial Energy Within the Framework of the Statistical Theory of Mass Spectra," *Z. Naturforsch.* 16a, 1394-5 (1961).
354. Taubert, R., and Lossing, F. P., "Free Radicals by Mass Spectrometry. XXVII. Ionization Potentials of Four Pentyl Radicals," *Journal of the American Chemical Society*, 84, 1523-1526, (1962).
355. Testerman, M. K., Raible, R. W., Grimes, G. B., Williams, J. R., and Gilliland, B. E., "A Study of Different Designs of Cold Electron Sources Capable of Mass Spectrometric Application," Unpublished Work.

356. Theard, Lowell P., and Hamill, William H., "The Energy Dependence of Cross Sections of Some Ion-Molecule Reactions," *Journal of the American Chemical Society*, 84, 1134-1139, (1962).
357. Theard, L. P., and Hildenbrand, D. L., "Reaction of Beryllium Oxide with Water Vapor," Unpublished Work.
358. Thomason, Edward M., "Development of a Solid State Digitizer for Mass Spectrometers," Unpublished Work.
359. Thorness, R. B., and Nier, Alfred O., "All-Metal Valve for Ultrahigh-Vacuum Use," *Rev. Sci. Instr.* 32, 807-10 (1961).
360. Tominega, G., and Tuzi, Y., "Design Chart for Trochoidal Vacuum Analyzer," *Shinku (Journal of the Vacuum Society of Japan)*, 5, 492-502, (1962).
361. Troitskii, V. S., "The Mean Free Path of Molecules in a Molecular Beam," *J. Exptl. Theoret. Phys. (U.S.S.R.)* 41, 389-390, (August, 1961), *JETP* 14, 2, 281, (February, 1962).
362. Tsuchiya, T., "High-Energy Fragment Ions from Aliphatic Hydrocarbons under Electron Impact. II. Propane," *Journal of Chemical Physics* 36, pp 568-9, (1962).
363. Tsuda, M., "On the Double Oven Method of Mass Spectrometer for Relative Partial Pressure Measurements," *Shitsuryo Bunseki (Mass Spectroscopy-Japan)*, 10, 37-41, (1962).
364. Turnbull, J. C., Rudy, W. G., and Collins, R. H., "Electron Tube Materials, Gases and Getters," Final Report for 1 Feb. 1961 - 31 Jan. 1962, on A Research Study of Gases and Getters for Electron Tubes, with the Objective of Obtaining Greatly Improved Electrical Reliability, Performance, and Life, Contract DA 36-039-SC-87390.
365. Van Wijnngaarden, V., and Duchworth, H. E., *Can. J. of Physics* 40, 1749-64 (1962)
366. Varadi, Peter F., and Etree, Kitty, "Operation of the Quantitative and Qualitative Ionization Detector and Its Application for Gas Chromatographic Studies," *Anal. Chem.* p. 1417, Vol. 34, No. 11, October, 1962.
367. Verhaegen, Georges, Stafford, Fred E., and Ackerman, Marcel, "Vaporization of Compounds and Alloys at High Temperature - Part III. Mass Spectrometric Studies of the Molecules BC₂ in the Vapor Above the System Boron - Carbon," Report for March, 1960 - March, 1961, on Refractory Inorganic Non-Metallic Materials, Contract AF 61 (052) 225, Proj. 7350.
368. Vestal, M. L., Drause, M., Wharfattig, A. L., and Johnston, W. H., "The Coincidence Mass Spectrometer," Unpublished Work.
369. von Koch, H., and Lindholm, E., "Dissociation Reactions of Hydrocarbons Formed in Collisions with Positive Ions," Unpublished Work.
370. Wade, Yasuo, and Kiser, Robert W., "Electron Impact Spectroscopy of Some Substituted Oxiranes," *Journal of Physical Chemistry*, Vol. 66, p. 1652-57 (1962) July.
371. Wagner, C. D., "Radiation-Polymerization of Ethylene: Evidence for Ion-Molecule Condensation," *Journal of Physical Chemistry*, Vol. 66, No. 6, June 28, 1962, p. 1158.
372. Wallace, Robert A., and Roboz, John, "Use of Spark Source Mass Spectrograph as a Milliprobe Analyzer," Unpublished Work.
373. Warnecke, R. J., and Warnecke, Monique, "Analysis with an Omegatron-Type Mass Spectrometer of Gases in OFEC Copper for Electronic Tubes," *Vide* 17, No. 98, 150-9 (1962).
374. Weston, Ralph E., Jr., and Seltzer, Stanley, "The Secondary Deuterium Isotope Effect in the Pyrolysis of Dimethylmercury," *Journal of Physical Chemistry*, Vol. 66, No. 11, p. 2192-99, November, 1962.

375. Wexler, S., "Change States of Molecular Fragments from CCl_3Br Following Nuclear Decay of $\text{Br}^{80\text{m}}$ and Br^{82} ," *Journal of Chemical Physics* 36, pp. 1992-8, (1962).
376. Wexler, S., and Jesse, N., "Consecutive Ion-Molecule Reactions in Methane," *Journal of the American Chemical Society*, 84, 3425-3432, (1962).
377. Wolfsberg, M., "Rate Constants for the Unimolecular Decomposition of Excited Molecular Species Near Threshold," *Journal of Chemical Physics* 36, pp. 1072-7, (1962).
378. Yamamoto, S., "Electrical Power Sources of the Mass Spectrometer," *Shinku (Journal of the Vacuum Society of Japan)*, 5, 450-454, (1962).
379. Yates, W. A., Griffiths, L. B., and Hill, R. J., "An Ultrahigh-Vacuum Valve," *Vakuum-Tech.* 11, 122-3 (1962).
380. Zeganesco, M., "Mass Spectrum Deduced from an Equation of Propagation Containing Partial Derivatives of Infinite Order," *Comptes Rendus*, 252, 3198-200 (1961).
381. Zmbov, K. F., "Effect of Freon 12 on the Thermal Ionization of Uranium on Tungsten," *Bulletin of the Boris Kidrich Institute of Nuclear Sciences, Belgrade*, 13 - #2, 17-28 (1962).
382. Geophysics Corp. of America, Bedford, Mass., "Instrumentation for the Determination of the Composition of the Upper Atmosphere," *Technical Progress Report* October 22, 1960 - March 15, 1961, Contract NAS 5-270.
383. NBS Hydrocarbon Std. Materials Transferred to American Petroleum Institute, N.B.S. Vol. 46, October, 1962.
384. "New Unified Scale Adopted for Atomic Wts.," *National Bureau of Standards*, Vol. 46, February, 1962.

