

S S



G. Asher Newsome

and the ASMS History Committee

These landmark papers represent significant developments in mass spectrometry ionization. They are not the *only* important publications of their respective eras – no research occurs in a vacuum (pun intended), and a methodology is rarely so perfect as first disclosed that it goes long unmodified – but they are foundational.

the mass spectrographs hitherto used. On page 78 of "Mass **SPARK SOURCE**

ransformation experiments.

NEW METHODS IN MASS SPECTROSCOPY

ARTHUR JEFFREY DEMPSTER

The recent study of nuclear transformations and the

evaluation of the energy changes in terms of mass changes

has subjected our atomic weight determinations to an un-

expected criticism. If we are to keep agreement with these

nuclear observations it seems necessary to assume masses

for several of the lighter elements larger by a factor of I in

3000 than those hitherto accepted. Although this discrep-

the masses of oxygen and helium only, still it is desirable to

increase the accuracy of atomic mass determinations, as they

serve as a test of the nuclear changes deduced from atomic

RESOLVING POWER IN MASS SPECTROSCOPY

The main limitation to increased accuracy in mass deter-

ninations is in the comparatively small resolving power of

ancy is probably due to a slight error in the comparison of

Dempster, AJ. (1935) New methods in mass spectroscopy.

> Ion Source for Mass Spectrography R. F. K. HERZOG AND F. P. VIEHBÖCK

I. Physics Institute, University of Vienna, Vienna, Austria

or negative ions only can leave the cathode because positive ions

are strongly linked to the cathode by the electric field. Those few

neutral molecules only, which are ionized by accident on the axis

of the discharge tube, especially near the anode, may leave the

tube in form of canal-rays, if they are not scattered by gas

molecules. Though the number of these particles may be very

small and therefore the intensity low, this process has been

successfully tried in many investigations in mass spectrograph

(1) There are two electric fields: First the electric field in the

canal-ray tube (A), (see Fig. 1) which is completely separated

from the electric field immediately in front of the trial-substance

(C). The first one produces the beam (B) of canal-rays, which

causes the sputtering. The second one has the right direction to

remove and accelerate the positive ions of the trial-substance

SECONDARY IONIZATION

Herzog, RFK; Viehböck, FP.

"lon source for mass spectrography." *Phys*

Rev. 76, p855.

FIELD IONIZATION

Gomer, R; Inghram, MG. (1955)

"Applications of field ionization to mass

spectrometry." J Am Chem Soc, 77(2),

Determination of Unsaturated Hydrocarbons

by Low Voltage Mass Spectrometry

ion of the mass spectrum has, if it could be

LOW VOLTAGE IONIZATION

Field, FH; Hastings, SH. (1956)

"Determination of unsaturated

hydrocarbons by low voltage mass

spectrometry." Anal Chem, 28(8), p1248.

F. H. FIELD and S. H. HASTINGS

for analysis in a mass spectrograph. It is produced by the

(2) The sputtering takes place in a high vacuum, because the

We have improved this method very materially:

cylinders (D) and (E), which are at different voltages.

Γ is known that the cathode material of a canal-ray tube

sputters during the discharge. In this case neutral molecules

Proc Am Phil Soc, 75, p755

Honig, RE. (1963)

ER-INDUCED EMISSION OF ELECTRONS AND POSITIVE IONS FRO

METALS AND SEMICONDUCTORS

Princeton, New Jersey

A recent mass spectrographic study of the laser-induced emission of charged particles from solids reported 2 that thermal positive ions were observed for metals, but not for semiconductors. The present

refults in terms of surface temperature.

itors. A small fraction of the incident laser beam is obllowing parameters were investigated: (1) the deflected by a glass platelet P onto a photodiode

no pulses; (2) a comparison of electron and ion pulses; (2) a comparison of electron and ion arrents and total numbers emitted by metals and emiconductors; and (3) estimates of surface temperature of that are between 0.1 and 1 μ sec wide and are

tures and energy losses for different materials. coincident with the laser spikes as well as with Topermit the simultaneous oscillographic detection each other. Thus it is clear that a fast thermal

of electrons and ions, the simple diode structure rather than a photoelectric, process must be rewith associated circuitry shown in Fig. 1 was used. The laser beam emitted by a 1/4 × 3-in. cooled This agrees with the results obtained for electrons

external lens L through window W onto one of two made similar observations for electrons, but mis-

LASER IONIZATION

By F. H. Field, J. L. Franklin, and M. S. B. Munson

CHEMICAL IONIZATION

Field, FH; Franklin; JL; Munson

MSB. (1963)

"Reactions of gaseous ions. XII. High-

pressure mass spectrometric study of

methane." J Am Chem Soc, 85(22),

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 45, NUMBER 7 1 OCTOBER 196

Mass-Spectrometric Studies of Corona Discharges in Air at Atmospheric Pressures

Letter presents new work which gives a more com- of the large current pulses, the adjustable volta

time correlation of individual laser, electron, and D (Philco Type L4501).

CONTENT ANALYSIS

A. metal, Ta dependence
A. semiconductor, Ge C. laser-induced

'Laser-induced emission of electrons and positive ions from metals and semiconductors." App Phys Lett, 3(1), p8.

reported in this paper.

For methane the reactions

to about 2 J, the charged particle spikes form a continuous pulse that is several hundred micro-

Organic Mass Spectrometry, 1972, Vol. 6, pp. 1171 to 1181. Heyden & Son Limited. Printed in Northern Irelan

NEGATIVE CHEMICAL IONIZATION MASS SPECTRA

OF POLYCYCLIC CHLORINATED INSECTICIDES

Field desorption mass spectrometry: A technique for the study of thermally unstable

mely weak or no parent ion peaks in the electron impact mass spectra. Fi is

generally regarded as a "soft" method of ionization. This characteristic feature of

FI is, however, only of limited - or no - value if the molecules are so unstabl that the major part is decomposed thermally during the sample evaporation price

oven which is put in a position near the ionization zone. The micro oven is introdu

ture of the bonds between different molecules is, in many cases, of the same orde of magnitude as the energy for thermal splitting of smaller molecules from large

in the electron impact (EI) mass spectrum of p-glucose, but very intense in the F

mass spectrum, elimination of water is still an intense process in the case of field

onization. That this is a thermal process will be shown later. Methods of sampl

FIELD DESORPTION

Beckey, HD. (1969)

technique for the study of thermally

Mass Spectrom Ion Phys, 2(6), p500.

"Field desorption mass spectrometry: A

unstable substances of low volatility." Int J

ed through a vacuum lock by means of a sliding rod.

to the ionization process.

Field ionization mass spectrometry (FIMS) has been established for a number of years as a technique for the study of molecules which exhibit only extre

Normally a small quantity of the solid organic sample is placed in a micro

The sample is then evaporated by heat transfer. The energy required for run

Fig. 1 shows that although the parent ion intensities are negligibly small

epartment of Chemistry, Florida State University Tallahassee, Florida 32306, USA

(Received 19 November 1971; accepted (revised) 29 March 1971)

ethane, isobutane or methylene chloride as the enhancement gas are presented for a series of chlo inated polycyclic insecticides. All of the compounds examined except 1-hydroxychlordene yielde spectra are the prominent peaks at masses greater than that of the molecule ion formed via ion

NEGATIVE CI

Dougherty, RC; Dalton, J; Biros, FJ. (1972)

"Negative chemical ionization mass spectra of polycyclic chlorinated insecticides." Org Mass Spectrom, 6(11) Pulsed Positive Negative Ion Chemical Ionization Mass Donald F. Hunt,* George C. Stafford, Jr., Frank W. Crow, and John W. Russel

ionization (CI) mass spectra is described. The capability of this technique, and negative ion CI mass spectrometry in general, to provide a hundred- to a thousand-fold increase in sample

 $AB + e \rightarrow AB^-$ resonance capture (1) $AB + e^- \rightarrow A \cdot + B^-$ dissociative resonance capture (2) $AB+e \rightarrow A^++B^-+e \qquad \text{ion-pair production} \qquad (3) \qquad \begin{array}{ll} \text{scribed in this paper.} \\ \text{Until recently the most useful method of producing negation} \end{array}$

ELECTRON CAPTURE NICI

Hunt, DF; Stafford, GC; Crow,

FW; Russell, JW. (1976) "Pulsed positive negative ion chemica ionization mass spectrometry." Anal Chem, 48(14), p2098.

Californium-252 Plasma Desorption

Nuclear particles are used to probe biomolecules.

to identify and characterize complex bio-molecules. Among these is the mass spec-trometer, which can serve for analytical measurements and can give structural in-formation as well from fragmentation pat-terns. Mass spectroscopy has had limited prefit in the spectroscopy has had limited by the spectrum of the spec

PLASMA DESORPTION

Macfarlane, RD; Torgerson, DF.

(1976)

"Californium-252 plasma desorption mass

spectroscopy." Science, 191(4230), p920.

A new ion source for mass spectrometry. J Chem Soc, Chem Commun, 7, p324.

(Department of Chemistry, U.M.I.S.T., P.O. Box 88, Sachville Street, Manchester M60 1QD

Fast Atom Bombardment of Solids (F.A.B.): A New Ion Source for

Mass Spectrometry

By Michael Barber, Robert S. Bordoli, R. Donald Sedgwick * and Andrew N. Tylei

FAST ATOM BOMBARDMEN

Surman, DJ; Vickerman, JC.

"Fast atom bombardment quadrupole

mass spectrometry."

D; Tyler, A. (1981)

"Fast atom bombardment of solids (FAB)

Barber, M; Bordoli, R; Sedgwick

ФИЗИЧЕСКАЯ ХИМИЯ М.Л. АЛЕКСАНДРОВ, Л.Н. ГАЛЛЬ, Н.В. КРАСНОВ

МЕТОЛ МАСС-СПЕКТРОМЕТРИЧЕСКОГО АНАЛИЗА БИООРГАНИЧЕСКИХ ВЕЩЕСТВ

(Представлено академиком Е.П. Велиховым 28 IX 1983

ОКСТРАКЦИЯ ИОНОВ ИЗ РАСТВОРОВ ПРИ АТМОСФЕРНОМ ЛАВЛЕНИИ

AP ION SPRAY

Alexandrov, ML; Gall, LN; Krasnov, NV; Nikolaev, VI; Pavlenko, VA; Shkurov, VA

"Extraction of ions from solutions under atmospheric pressure as a method for mass spectrometric analysis of

bioorganic compounds." Dokladi USSR

Acad Sci, 274(6), p379.

have made improvements on all stages of mass spectrometer (ion source, mass separation. detector. electronics)

has been developed in order to analyze non-volatile, thermally

DETECTION OF HIGH MASS MOLECULES BY LASER DESORPTION TIME-OF-FLIGHT MASS SPECTROMETRY

The construction of the laser desorption time-of-flight mass analyzer is shown in Fig.1. Figure 2 shows the block diagram of TOF spectrum measurement system.

N: laser (Wavelength: 337nm, Pulse width: about 15nsec

MALDI

Tanaka, K; Ido, Y; Akita, S; Yoshida, Y; Yoshida, T. (1987) "Detection of High Mass Molecules by Laser Desorption time-of-Flight Mass Spectrometry." 2nd Japan-China Joint S*ymposium on MS*, Takarazuka, Japan.

Laser Desorption Ionization of Proteins with Molecular Masse Exceeding 10 000 Daltons

compounds in the mass range above 10 000 daitons seeme to be exclusively the domain of plasma desorption ma spectrometry (PDMS) (1-4). In 1987 Tanaka et. al. (5) re , but sample amounts in the 10-μg range were necessa

EXPERIMENTAL SECTION

RESULTS AND DISCUSSION

MALDI

Karas, M; Hillenkamp, F. (1988) "Laser desorption ionization of proteins with molecular masses exceeding 10,000 Daltons." Anal Chem, 60(20), p2299.

Atmospheric Sampling Glow Discharge Ionization Source for

Scott A. McLuckey,* Gary L. Glish, Keiji G. Asano, and Barry C. Grant

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 3783.

the Determination of Trace Organic Compounds in Ambient Air

1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1962 1964 1966 1968 1970 1972 1974 1976 1978 1980 1982 1984 1986 1988 // 1990 2000

New Picogram Detection System Based on a Mass

Spectrometer with an External Ionization Source at

E. C. Horning, M. G. Horning, D. I. Carroll, I. Dzidic, and R. N. Stillwei

solvents. Positive ions are formed by a complex series of



LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

JOURNAL OF SCIENCE

[FIFTH SERIES.]

OCTOBER 1897.

XL. Cathode Rays. By J. J. THOMSON, M.A., F.R.S.

Cavendish Professor of Experimental Physics, Cumbridge*

L in the hope of gaining some information as to the

nature of the Cathode Rays. The most diverse opinions are

held as to these rays; according to the almost unanimous opinion of German physicists they are due to some process

GAS DISCHARGE

Thomson, JJ. (1897)

"Cathode rays." Phil Mag, 44(5), p293.

TPHE experiments † discussed in this paper were undertaken

THE PROPERTIES OF SLOW CANAL RAYS.

THE following paper contains an account of experiments with positive rays under more varied pressure conditions and of slower speed than those generally used. In the usual canal ray tubes the potential is limited very largely by the vacuum; for instance, if the pressure is about 0.005 mm. of mercury, the potential with ordinary tubes is of the order of 20,000 volts. In this investigation the subject was first approached from the side of the light emission and later the analysis by electric and magnetic deflection was made.

Light Emission. The first to examine the light excited by slow positive rays was Stark e arranged a secondary cross field in the negative glow in a ust

SLOW CANAL RAYS

Dempster, AJ. (1916) "The properties of slow canal rays." Phys

Rev, 8, p651.

A NEW METHOD OF POSITIVE RAY ANALYSIS.

THE analysis of positive rays is based on the determination of the ratio of the charge to the mass of various constituents. The corresponding measurement for the negative corpuscle has however been carried to a much greater degree of accuracy by means of methods involving the magnetic deflection of the rays through large angles, and the refocusing of rays which make slightly varying angles with each other. Apart from the accuracy of the measurement, there is also in these methods a great resolution between slightly different speeds; thus Rutherford and Robinson¹ have separated distinct groups of β rays from RaC which differ by 2 per cent. in energy; also the photographs given by Classen² for electrons show such sharpness that if electrons had masses differing by as little as I in 100, the various groups would be separated. With positive rays the slit method used by Richard son3 is suitable for weak sources and allows a fairly exact measurement of a mean molecular weight, but the curves given in the above paper show that the power of separating different elements is very small The method used by J. J. Thomson is capable of comparatively great

resolving power, elements being sharply separated which differ in molecular resolving power, elements being sharply separated which differ in molecular resolving power.

ular weight by I in 16,4 but this is obtained only with a great loss in

WEHNELT CATHODE

Dempster, AJ. (1918) "A new method of positive ray analysis." Phys Rev, 11, p316.

PHYSICS: F. L. MOHLER A PHOTO-IONIZATION EXPERIMENT WITH HYDROGEN By F. L. Mohler* BUREAU OF STANDARDS, DEPARTMENT OF COMMERCE

New England States. If all the water power sence of casium). But the tendency of the

of the United States were to be similarly decessium to be held by such a surface has there

all plants having three or four times the casium film remains on the surface at an eve

capacity of the estimated minimum potential higher filament temperature. The film the

dition should be fully considered in estimating the first being of electro-negative, the second of

till be available in any State at the present
In this way the eæsium film remains intac

A TUNGSTEN filament was mounted in a On lowering the temperature the cosium fila

consisting of three parts insulated from one to its former value. At temperatures it

nother. In this way, on the guard ring prin- low those at which evaporation is

ple, the electron emission from the central preciable, the saturation current from a casi

portion of the filament could be measured, so covered surface is expressed within the pro-

pletely covering the filament even at filament a value of 1.38 volts for the Richardson wor

THERMAL IONIZATION

Langmuir, I; Kingdon, KH. (1923)

"Thermionic effects caused by alkali

vapors in vacuum tubes." Science, 57

effects due to the cooling by the leads were able error of temperature measurement, b

euum tube in the axis of a cylindrical anode reforms and the electron emission returns

up to temperatures of about 900° K., and a

emits saturation currents of about 0.3 amper

temperatures the casium film evaporates off in

part and the electron emission falls rapid

 $i = 60.2 \ T^2e^{-b_0/T} \ amps. \ per \ cm.^2$

his temperature (below a visible red hea

the amount of potential water power that may electro-positive atoms (ions

liminated. With metallic casium in the tube Dushman's equation

SPECIAL ARTICLES

VAPORS IN VACUUM TUBES

25° C. the cæsium vapor forms an adsorbed

THERMIONIC EFFECTS CAUSED BY ALKA

A sensitive method of detecting photo-electric ionization of a gas has been described by Dr. Foote and the author. The gas is contained in a two-electrode, thermionic tube with conditions so adjusted that the electron current is limited by space charge. Production of positive ions by incident radiation will neutralize the space charge and produce a very much magnified change in the thermionic current. A paper now in press² describes measurements of the photo-ionization of some monatomic gases by discharge in the same gas. A double thermionic tube was used in which one unit produced a discharge at controlled current and voltage while the other unit detected photo-ionization excited by the radiation from the discharge. Electrical shielding prevented diffusion of ions and electrons from one thermionic unit to the other. The experiments showed that little if any photo-ionization is produced with discharge voltages equal to or less than the first ionization potential but that there was a large effect at potentials sufficient to give double ionization or soft X-ray excitation Thus the effect furnishes a sensitive method of detecting any critical potentials which give rise to radiation of higher frequency than the

PHOTOIONIZATION

Mohler, FL. (1926) "Photo-ionization experiment with hydrogen." Proc Natl Acad Sci, 12, 494.

A NEW METHOD OF POSITIVE RAY ANALYSIS AND ITS APPLICATION TO THE MEASUREMENT OF IONI-ZATION POTENTIALS IN MERCURY VAPOR

By Walker Bleakney PHYSICS LABORATORY, UNIVERSITY OF MINNESOTA (Received June 8, 1929). A new method of positive ray analysis is described which lends itself particularly well to the study of the nature of the ions formed by single electron impact in gases, the efficiency of their production, and the measurement of their ionization potential The novel feature of the method is the use of the uniform magnetic field of a large

ions. The ions are then pulled across the magnetic field and subjected to an e/mSome preliminary results are given for mercury vapor in which the ionization potentials of Hg²⁺, Hg³⁺, and Hg⁴⁺ are found at 30, 71, and 143 volts respectively. HE object of this paper is to describe a new method of positive ra

analysis1 which may be quite generally applied to the study of (1) the nature of the ions formed by single electron impact in gases, (2) the efficiencies of the production of these ions, and (3) the accurate measurement of their ionization potentials. Some preliminary results are given on the values of the first, second, third, and fourth ionization potentials in mercury vapor.

ELECTRON IONIZATION Bleakney, W. (1929)

"A new method of positive-ray analysis and its application to the measurement of ionization potentials in mercury vapor." Phys Rev, 34, p157.

(1) Analysis of gas mixtures. Table I shows that parent peaks predominate in almost all cases investigated. For example, no peaks over 0.1%, except the parent ion, were observed with acetone. By contrast electron impact ionization of this gas produces 19 peaks of comparable intensity. The extreme simplicity of the spectra often permits the use of isotopic peaks for the direct determination of chemical formulas.

(2) Determination of transient intermediates in photochemical, thermal or radiation processes. For example, we are currently looking for the control of the cont

N. G. Ingbram and R. Comer, J. Chem. Phys., 22, 1279 (1954).
It has recently come to our notice that similar conclusions reg mechanism were rached by: N. Kirchens, Naturais, 6, 136
g, on the basis of Müller's results' and field induced changes in
mission patterns.

RECEIVED DECEMBER 3, 1954

INTRODUCTION

region of the system. Thus the mass spectrometer would detect species which are not representative of the system under study. To avoid these possible complisions of the system under study. To avoid these possible complisions of the system under study. one atmosphere have been of interest not only as an aid to the understanding of the mechanism of formation of various products of the discharge but also in relating the data to ion-molecule reactions which may be occurring in both upper and lower regions of the atmosphere. The recent report on some of the ions of low mass number at various altitudes in the upper atmosphere and the suggestion of the possibility of the formation of ion clusters such as (H₂O)_AH+ further demonstrate the need for laboratory simulation of the prevailing conditions in order to examine the detailed prevailing conditions in order to examine the detailed mechanism of the formation of these ions. The possibility that charge-exchange processes and/or direct ionization of water molecules followed by ion-molecule

EXPERIMENTAL

CORONA DISCHARGE

Shahin, MM. (1966) "Mass-spectrometric studies of corona discharges in air at atmospheric pressures." J Chem Phys, 45, p2600.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 5 1 SEPTEMBER 1968

Molecular Beams of Macroions

MALCOLM DOLE, L. L. MACK, AND R. L. HINES*

R. C. Mobley,† L. D. Ferguson, and M. B. Alice Bendix Research Laboratories, Southfield, Michigan

(Received 19 April 1968)

By means of electrospraying a dilute polymer solution into an evaporation chamber, negative macroions can be produced and a molecular beam formed by sampling the gaseous mixture of macroions, solvent, and nitrogen molecules with a nozzle-skimmer system of the Kantrowitz-Gray type. The macroion current can be detected by a Faraday cage after the light ions have been repelled from the beam by negative voltages on a repeller grid. Theoretical repeller voltages which best agree with the observed are those calculated by assuming a macroion velocity within 2% of the estimated supersonic beam velocity of 743 m sec⁻¹. Polystyrene macroions of 51 000 weight-average amu tend to form dimers and trimers in the beam while larger polystyrene macroions of 411 000 weight-average amu appear mostly to be multiply charged single species. The results demonstrate that definite mass/charge states can be formed by the electrospray technique, that a considerable monochromatization of macroion velocities in the beam takes bake, and that the

ELECTROSPRAY

Phys, 49(5), p2240.

INTRODUCTION

solvents. Positive ions are formed by a complex series of ion molecule reactions. The ionization reaction for the sample may involve either proton transfer or charge transfer. Negative ions are formed by either resonance or dissociative capture of thermal electrons, or by ion-molecule interactions. In a favorable case (very little adsorp-**ATMOSPHERIC PRESSURE**

IONIZATION (63Ni FOIL) Horning, EC; Horning, MG; Carroll, DI; Dzidic, I; Stillwell, RN. (1973)

"New picogram detection system based on a mass spectrometer with an external ionization source at atmospheric pressure." Anal Chem, 45(6), p936.

a discharge, was later employed in a liquid chrome eaph-mass spectrometer-computer (LC-MS-COM) a tical system (3, 4). The primary purpose of the work

It has never been possible to obtain intact gas-phase macromolecules by evaporation inasmuch as the vapor pressure of a high polymer such as polyethylene of 14 000 amu can be calculated to have a room temperature of the 10-48 atm. On heating a macromolecules on a mica-backed film of evaporated carbon by spraying a dilute solution of a high polymer onto the carbon and by allowing the solvent to evaporate. The

Dole, M; Mack, LL; Hines, RL; Mobley, RC; Ferguson, LD; Alice, MB. (1968) "Molecular beams of macroions." J Chem

the gas phase in a mixture of solvent and nitrogen

Atmospheric Pressure Ionization Mass Spectrometry: Corona Discharge Ion Source for Use in Liquid Chromatograph–Mass Spectrometer-Computer Analytical System

Institute for Lipid Research, Baylor College of Medicine, Houston, Texas 77025

A corona source for a liquid chromatograph—mass spectrometer—computer analytical system is described. The performance was compared with that of the ^{6-Ni}t source previously employed with direct injection of samples. Both ion sources gave the same positive ions with solvents and test compounds. The corona source had a larger dynamic response range. A separation of several polynuclear hydrocarbons was demonstrated; API detection was compared with UV detection. With isooctane as the solvent, the hydrocarbons formed MH⁺ ions through solvent-mediated ion molecule reactions. Selective ion detection was used to monitor the sultion of each hydrocarbon.

APCI-LCMS

spectrometry: Corona discharge ion system." Anal Chem, 47(14), p2369.

D. I. Carroll, I. Dzidic, R. N. Stillwell, K. D. Haegele, and E. C. Horning

Carroll, DI; Dzidic, I; Stillwell, RN;

Haegele, KD; Horning, EC. (1975)'Atmospheric pressure ionization mass

source for use in a liquid chromatographmass spectrometer-computer analytical Inductively Coupled Argon Plasma as an Ion Source for Mass Spectrometric Determination of Trace Elements

Robert S. Houk, Velmer A. Fassel, Gerald D. Flesch, and Harry J. Sved Department of Chemistry, University of Surrey, Guildford, Surrey, England GU2 5X

Southeast Environmental Research Laboratory—USEPA, Athens, Georgia 3060

lasma (ICP) to generate a relatively high number density of ositive ions derived from elemental constituents. A small

INDUCTIVELY-COUPLED **PLASMA**

Houk, RS; Fassel, VA; Flesch, GC; Svec, HJ; Gray, AL; Taylor, CE. (1980)

Inductively coupled Argon plasma as an ion source for mass spectrometric determination of trace elements." Anal Chem, 52, p2283.

acetone, 25 °C, 0.25 h), gave the free enone 5c² as a colorless

A New Soft Ionization Technique for Mass
Spectrometry of Complex Molecules

(12) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. J. Am. Chem. Soc. 1975, 07, 110

Sorowitz, I. J.; Caspar, E. W.; Crouch, R. K.; Yee, K. C. J. Org. Chem. 1972, 37, 3873.
 Rubottom, G. M.; Mott, R. C.; Krueger, D. S. Synth. Commun. 1977, 237

Kuwajima, I.; Nakamura, E. J. Am. Chem. Soc. 1975, 97, 3257. Or, NMR (CDCl₃) § 6.3–5.8 and 5.2–4.8 (ABX multiplets, CH==CH₂), at

TO M.S. (<10°5 TORR)

(17) NMR (CD C), 2 7, 15 (t. 1, J = 9 Hz, CH=), 9 (18) (18) Methyl doublet 4, 10 13, 48, 90, 90; Compare the C-2 methyl-doublet onances in 2,3-dimethyleyclohexanone, 8₀, 90, 93, 8_{mn}, 90?. Peffer, P. E.; man, S. F. J. Orç Chem. 1972, 72, 2435.
(19) Cutler, A.; Ehntholi, D.; Giering, W. P.; Lennon, P.; Raghu, S. Rasha, A.; Rosselbum, M.; Tanercek, 1.; Welh, D. J. Am. Chem. Soc. 1976, 1938, A.; Rosselbum, M.; Tanercek, 1.; Welh, D. J. Am. Chem. Soc. 1976.

932 J. Am. Chem. Soc., Vol. 102, No. 18, 1980

(11) Giering, W. P.; Rosenblum, M.; Tancrede, J. J. Am. Chem. Soc. 1972, 94, 7170.

In a number of areas of organic and modernic of the mass, high sensitivity mass spectror applicable to thermally lability independent of the modernic of t

v n.o. (s, x, Cp), 5.70 (m, 3, OCH₂, OCH), 2.45 (m, 2, CH₂CO), 1.70 (m, 8, CH₂), 1.22 (t, 3, J = 7 Hz, CH₂), 1.15 (s, 3, CH₂).

(23) NMR (CCCl₂) 6.60 (q, 1, J₄, J₄) = 2.8 Hz, CH=0, 5.1 (t, 2, J₄) = 1 Hz, CH₂=0, 2.4 (m, 2, CH₂CO), 1.21 (m, 6, CH₂), 1.18 (s, 3, CH₂).

(5) M. A. Posthumus, P. G. Kistemakef, H. L. C. Meuzeliaar, and M. C. Ten Noever de Brauw, Anal. Chem. 50, 985 (1978).

(6) A. Benningboven and W. K. Sichtermann, Anal. Chem. 50, 1180 (1978).

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THERMOSPRAY

Blakley, CR; Carmody, JJ; Vestal

ML. (1980)

"A new soft ionization technique for mass

spectrometry of complex molecules." *J Am*

Chem Soc, 102(18), p5931.

A. L. Burlingame, C. H. L. Shackleton, I. Howe, and O. S. Chizho & Chem., 80, 368 (1978).
 H. R. Schulten, Adv. Mass Spectrom., 7A, 83 (1978).
 M. S. B. Munson, Anal. Chem., 49, 772A (1977).
 R. D. Madcarlane and D. F. Torgerson, Science (Washington, D.C. N. D. Madcarlane and D. F. Torgerson, Science (Washington, D.C.

Electrospray Ion Source. Another Variation on the Free-Jet Theme Masamichi Yamashita† and John B. Fenn* Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520 (Received: April 19, 1983)

ELECTROSPRAY

Yamashita, M; Fenn, JB. (1984)

"Electrospray ion source. Another variation

on the free-jet theme." J Phys Chem,

88(20), p4451.

Ревельский Н. А., Яшин Ю. С., Вознесенский В. Н., Курочкин В. К., Костяновский Р. Г.

МАСС-СПЕКТРОМЕТРИЯ С ФОТОИОНИЗАЦИЕЙ

ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ Н.АЛКАНОВ, СПИРТОВ.

КЕТОНОВ, СЛОЖНЫХ ЭФИРОВ И АМИНОВ

ноны — $H^+(H_2O)_n$, а также $O_2^+(H_2O)_k$, $NO^+(H_2O)_m$, NH_4 и др., получают-

ся в результате реакции кластерообразования, которая является основ-

AP PHOTOIONIZATION

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The detection of trace quantities of organic compounds in mbient air is a commonly encountered problem often re-

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Atmospheric Pressure Photoionization: An Ionization Method for Liquid

нических соединений широко применяется ионизация электронным уда-ром (ЭУ) и химическая понизация (ХИ). В 1973 г. предложен способ масс-спектрометрического анализа с ХИ при атмосферном давлении (ИАД) [1, 2]. Первичные ионы-реагенты гене руются из газа-носителя в коронном разряде или под действием злучения. Состав ионов-реагентов в условиях ИАД зависит от приме

ethod, large quantities of an ionizable dopant are added gases have higher values. Selective ionization of the analyte of te vapor generated from the LC eluant, allowing for a tabundance of dopant photoions to be produced. the doubt also relied upon the LC also relied upo Because the ion source is at atmospheric pressure, and the collision rate is high, the dopant photoions react to completion with solvent and analyte molecules present time the ion source. Using APPI, at an LC flow rate of 200 pL/

Thus, the early PILC methods, particularly those that incorporate

APPI-LCMS Robb, DB; Covey, TR; Bruins, AP.

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chromatography-mass spectrometry." Anal Chem, 72(15), p3653.

Chromatography-Mass Spectrometry Damon B. Robb,†.‡ Thomas R. Covey,§,II and Andries P. Bruins*,† University Center for Pharmacy, University of Groningen, Antonius Deusinglaan 1, 9713 AV Groningen, The Netherlands, and MDS SCIEX, 71 Four Valley Drive, Concord, Ontario, Canada, L4K 4V8 Atmospheric pressure photoionization (APPI) has been successfully demonstrated to provide high sensitivity to successfully demonstrated to provide high sensitivity to the LC-MS analysis. A vacuum-ultraviolet lamp designed for photoionization detection in gas chromatography is used sa source of 10-eV photoion. The mixture of samples and solvent eluting from an HPLC is fully evaporated prior to introduction into the photoionization region. In the new have 1Ps in the range of 7-10 eV, while the common GC carrier method. Izes quantifies of an ionizable donant are added