Photoionization Workshop Summary

“Photoionization (APPI/PI): Applications, Developments and Discussions”

65th ASMS Conference on Mass Spectrometry and Allied Topics, Indianapolis, IN
Monday, June 5th, 5:45 – 7:00 pm, Room 239

Organized by: Eleanor Riches and Ralf Zimmermann

We opened with a brief overview in the photoionization field and then we introduced our four discussion leaders:

- **Eric Reiner (Environmental Chemistry, APPI-MS, Environment Canada, Canada)**
  “ATMOSPHERIC PRESSURE PHOTO-ionization FOR GC-MS? Putting POPs in the Spotlight”

- **Priscila Lalli (Petroleomics, APPI-IMS-MS, Florida State University, USA)**
  “Structural Determination of Polycyclic Aromatic Hydrocarbons by Ion Mobility Mass Spectrometry”

- **Thomas Bierkandt (Combustion Chemistry, Synchrotron SPI-MS, Univ. Duisburg, Germany)**
  “Isomer-resolved Species Identification and Quantification by Synchrotron-based Photoionization Mass Spectrometry”

- **Andreas Walte (Thermal Process Analysis, REMPI/SPI-MS, Photonion GmbH, Germany, “Vacuum Photoionization Mass Spectrometry - An approach for online analysis of complex mixtures”)**

All speakers did an excellent job, explaining fundamentals and applications of APPI and PI. The workshop demonstrated a continued strong interest in this field as it attracted again a large audience (about 60-70 people), about the same as last year. We were very pleased with the allocation of Monday as the day of the APPI/PI workshop.

Again the start was slightly delayed due to attendees still collecting refreshments at 5:45. We suggest placing the refreshments in the back of the workshop rooms.

Each of the discussion leaders kept to their 10 min allotment of time, which allowed enough time for discussions.

**Selected Questions and Answers**

Q1: What is the source of humidity variation?
A1: Could be leakage in nitrogen generator

Q2: What is the difference between APCI and APPI regarding humidity effects?
A2: Adduct formation due to water is smaller with APPI

Q3: What are the advantages of APPI?
A3: Easier to analyse complex mixtures, e.g. house dust has thousands of compounds, therefore GCxGC APPI-MS helps a lot.

Q4: Have you used dopants in order to improve sensitivity, especially for compounds with low cross sections?
Photoionization (APPI/PI): Applications, Developments and Discussions

Monday, June 5\textsuperscript{th}, 5:45-7:00 pm
Room 239 (Indianapolis Convention Center)

Organized by Eleanor Riches and Ralf Zimmermann

Discussion Leaders (Presentation max. 10 min each)

- **Eric Reiner**  
  (Environmental Chemistry, APPI-MS, Environment Canada, Canada)

- **Priscila Lalli**  
  (Petroleomics, APPI-IMS-MS, Florida State University, USA)

- **Thomas Bierkandt**  
  (Combustion Chemistry, Synchrotron SPI-MS, Univ. Duisburg, Germany)

- **Andreas Walte**  
  (Thermal Process Analysis, REMPI/SPI-MS, Photonion GmbH, Germany)

- **Noam Tal**, Tel Aviv University, Israel

- **Yang Pan**, University of Science and Technology, Shanghai, China

- **Chip Cody**, JEOL

- **Xiang (Shawn) Li**, University of Maryland
APPI and PI Ionizes a wide range of compounds (polars to non-polars)

- Wide bandwidth ionizer

APPI features lower susceptibility to ion suppression than ESI or APCI, PI is ion suppression free

- Simpler clean-ups mean ease and better recoveries
- Use with faster chromatography and even flow injection analysis

Large linear dynamic range

- Great for quantitative analysis

Can APPI and PI be mainstream technologies or are they best suited for niche applications?
Photoionization (APPI): Important Niche Application for Explosives and Narcotics Trace Detection

Morpho Detection
IT4DX IMS

Implant Sciences
QS-B220 IMS

Bruker
DE-tector IMS

1st Detect

Why not APCI
Discharge sources in air create atmospheric NO₃⁻ ions that interfere with NO₃⁻ nitrate ions from nitrate explosives
Photoionization (APPI): Ion Source for LC-MS or direct infusion MS – Niche application?

- Most MS vendors offer a commercially available APPI ionization source – wide availability to all MS users
- Operates at atmospheric pressure so is fully compatible with liquid (or gas) flow introduction at high flow rates
- Has been utilized in diverse fields of analysis:
  - Petroleomics
  - Pharmaceutical
  - Food
  - Environmental
  - Some limited work related to biological samples
Most MS vendors offer a commercially available APPI ionization source – wide availability to all MS users.
Photoionization (PI): Applications for specific niche purposes

- Many PI-MS applications for on-line detection (Laser- or Lamp-PI) or as detector for gas chromatography or thermal analysis
- Vacuum ionization: No susceptibility to ion suppression but lower sensitivity than EI (PI cross sections, VUV-photon generation)
- High selectivity (no/little fragmentation)
- Mainly niche, but systems are becoming commercially available
Photoionization (PI): Applications for specific niche purposes

Example: On-line Polycyclic aromatic Hydrocarbon detection on Single Aerosol Particles (Zimmermann et al., TOD pm 4.10)
PUTTING POPS IN THE SPOTLIGHT

Robert A. Di Lorenzo*, Vladislav Lobodin†, Sladjana Besevic‡, Karl J. Jobst‡, Eric J. Reiner‡,

* - Department of Physiology and Experimental Medicine, Hospital for Sick Children, Toronto, Ontario, Canada
† - National High Field Magnetic Laboratory, Florida State University, Tallahassee, Florida, USA
‡ - Laboratory Services Branch, Ontario Ministry of the Environment and Climate Change, Toronto, Ontario, Canada
Atmospheric pressure ionization naturally compatible with GC
- No flow-related suppression
- APCI is a “soft” ionization technique
  - Predominantly molecular ions
Waters Xevo G2-XS

(1) Atmospheric pressure ionization of GC analytes
(2) Transfer of all ions with quadrupole (RF-only)
(3) TOF mass analysis of all ions
(4) Potential for simultaneous MS and MS/MS
MIXED-MODE IONIZATION

Charge Transfer:
\[ \text{N}_2^+ + \text{M} \rightarrow \text{M}^+ + \text{N}_2 \]

Proton Transfer:
\[ \text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2 \]
\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} \]
\[ \text{H}_3\text{O}^+ + \text{M} \rightarrow \text{H}_2\text{O} + \text{MH}^+ \]

- Degree of protonation is variable day-to-day
- Particularly problematic during the summer
- Can lead to quantification issues
MODIFIED APGC SOURCE

- APCI ionizes a wide range of compounds
  - Chemical noise
  - Siloxane contamination
  - Mixed mode ionization
- Custom built APPI source for APGC
  - Reaction chamber removed
  - Replaced with ESI-type cone inlet
  - Hole drilled in top of APGC housing
  - Waters APPI lamp added
    - Kr, Xe, Ar

VLADISLAV LOBODIN, PhD
Research Faculty
National High Magnetic Field Lab
Florida State University
GC-MS on an LC-MS instrument

High carrier gas flows are possible!
MODIFIED APGC SOURCE

- APCI ionizes a wide range of compounds
  - Chemical noise
  - Siloxane contamination
  - Mixed mode ionization
- Custom built APPI source for APGC
  - Reaction chamber removed
  - Replaced with ESI-type cone inlet
  - Hole drilled in top of APGC housing
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    - Kr, Xe, Ar

VLADISLAV LOBODIN, PhD
Research Faculty
National High Magnetic Field Lab
Florida State University
APPI eliminates siloxane contamination from column bleed

- Less chemical noise in individual mass channels due to enhanced selectivity
- No interference from dehalogenation products during ionization
Prototype atmospheric pressure photoionization (APPI) source

Mixed mode ionization is reduced in GC-APPI

- APPI sensitivity comparable to APCI
- Single-mode ionization only
  - No protonation observed in APPI

Photo-oxidation results in structure-diagnostic peaks

(a)

(b)

Retention Time (min)

Intensity (Counts x 10^5)

m/z
PHOTO-OXIDATION OF BDEs

- Few ions other than charge-transfer and proton transfer products observed in APCI.
- APCI in-source fragments primarily consist of debromination of protonated ions.
- APPI produces photo-oxidation products and fragments.
- Photo-oxidation is enhanced with increasing O₂ concentration.
- Ultrahigh purity N₂ from cylinder vs N₂ generator as make-up gas.
- Can potentially be used for structural diagnostics at the expense of molecular ion intensity.
ISOMER SPECIFIC OXIDATION

Br₅-BDEs

Br₆-BDEs

EPA Method 1614A (PBDE Analysis)
Critical separation is of BDE 49 & 71
<40% valley requirement
APPI quantification of BDE congeners shows excellent agreement with NIST standard reference materials

- SRM 2585 – Household Dust
- SRM 1944 – New York/New Jersey waterway sediment

Analysis performed using rapid GC method

- RTX-1614 column (15 m x 0.25 mm x 0.1 µm)
- Ramped from 90°C to 330°C
- Temperature program reflects max. instrument ramp rate
- 10 min total analysis time
- BDE-209 elutes in ~8 min
- 3 mL/min He flow
 METHOD PERFORMANCE

- Method is in excellent agreement with CRM certified values for a number of different compounds groups
- Low relative standard deviation
SUMMARY

- APPI is a new ionization source for the analysis of POPs by GC-MS.
- APPI eliminates mixed-mode ionization issues experienced with APCI.
- APPI can reduce chemical noise due to sample matrix and column bleed.
- APPI has equivalent sensitivity to APCI, specifically for the analysis of BDEs and other selected halogenated POPs.
- APPI can potentially differentiate between structural isomers with characteristic photo-ionization products.
- APPI is quantitative.
- Flows need to be optimized between column and MS entrance.
Structural Determination of Polycyclic Aromatic Hydrocarbons by Ion Mobility Mass Spectrometry

Priscila M. Lalli, Ph.D.
Petroleomics
Relate Chemistry to Production and Refinery Behavior

Hydrocarbons
Aromatics
PAH
Polar species

- Hydrocarbons
- Aromatics
- PAH
- Polar species
Electrospray Ionization (ESI)

Atmospheric Pressure Photoionization (APPI)

Basic

Acidic
Methods

Experimental Collision Cross Section (CCS)

- 14 PAH model compounds
- APPI(+) Ion Mobility -TOF MS (Synapt G2-Si, Waters Corp.)
- Helium (3.4 mbar)

Theoretical Collision Cross Section

- Hypothetical Structures
- Structure optimization: Gaussian 04 (DFT B3LYP/6-311G(d,p))
- CCS calculation: Mobcal (Projection Approximation, Exact Hard Spheres Scattering Model (EHS) and Trajectory Method (TM)).

Fourier Transform Ion Cyclotron Resonance MS

- APPI(+) FT-ICR MS @ 9.4 T (Rp ~ 800,000 at m/z 400; ~ 100-400 ppb mass error)
% Relative Abundance

Heteroatomic Classes

IBP-343 °C to 600-650 °C

APPI(+) FT-ICR MS
Canadian Bitumen
VGO cuts
Experimental Collision Cross Sections

Model Compounds / Isomeric Sets

**DBE = 12**
- Pyrene - 83.95 Å²
- Fluoranthene – 84.99 Å²
- Benzo[ghi]perylene – 99.09 Å²
- Indeno[1,2,3-cd]pyrene – 100.71 Å²

**DBE = 13**
- Triphenylene – 90.42 Å²
- Chrysene – 91.15 Å²
- Benzo[a]anthracene – 91.51 Å²
- Benzo[b]anthracene – 91.77 Å²

**DBE = 15**
- Benzo[e]pyrene
  - 94.66 Å²
- Perylene
  - 95.12 Å²
- Benzo[a]pyrene
  - 95.23 Å²
- Benzo[b]fluoranthene
  - 96.14 Å²
- Benzo[k]fluoranthene
  - 96.64 Å²

**Standard Deviation:** 0.01 – 0.10%

**Collision Cross Section**
## Experimental Collision Cross Sections for Sample

<table>
<thead>
<tr>
<th>m/z</th>
<th>Molecular Formula</th>
<th>DBE</th>
<th>Experimental CCS(_{\text{He}}) (Å²)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>202.2560</td>
<td>C(<em>{16})H(</em>{10})</td>
<td>12</td>
<td>84.78</td>
<td>0.03</td>
</tr>
<tr>
<td>254.1096</td>
<td>C(<em>{20})H(</em>{14})</td>
<td>14</td>
<td>96.13</td>
<td>0.06</td>
</tr>
<tr>
<td>252.0939</td>
<td>C(<em>{20})H(</em>{12})</td>
<td>15</td>
<td>94.95</td>
<td>0.04</td>
</tr>
<tr>
<td>276.0939</td>
<td>C(<em>{22})H(</em>{12})</td>
<td>17</td>
<td>100.13</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Fluoranthene (84.99 Å²)

Not 9-Phenylanthracene (98.89 Å²)

Benzo[e]pyrene or Perylene

Inconclusive

## Experimental and Theoretical Collision Cross Sections

### Isomeric set C\(_{20}\)H\(_{12}\), DBE = 15

<table>
<thead>
<tr>
<th>Name</th>
<th>PA (Å²)</th>
<th>EHS (Å²)</th>
<th>TM (Å²)</th>
<th>Experimental CCS(_{\text{He}}) (Å²)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[e]pyrene</td>
<td>93.75</td>
<td>96.79</td>
<td>91.49</td>
<td>94.66</td>
<td>0.04</td>
</tr>
<tr>
<td>Perylene</td>
<td>93.89</td>
<td>96.66</td>
<td>93.24</td>
<td>95.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>94.89</td>
<td>97.91</td>
<td>92.55</td>
<td>95.23</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>96.77</td>
<td>100.28</td>
<td>94.12</td>
<td>96.14</td>
<td>0.03</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>97.7</td>
<td>101.54</td>
<td>95.26</td>
<td>96.64</td>
<td>0.04</td>
</tr>
</tbody>
</table>

PA method: best agreement with experimental CCS with % deviations of 1.0 to 3.0 %,
Theoretical Collision Cross Sections

Hypothetical Structures (C_{20}H_{14}, DBE = 14)

- 4,5-dihydrobenzo[pqr]tetraphene: 95.51 Å²
- Trypticene: 98.32 Å²
- 1,1-PR-binaphthyl: 98.77 Å²
- 9-Phenylanthracene: 99.75 Å²
- 1-Phenylanthracene: 100.08 Å²
- 2,2-binaphthyl: 103.18 Å²

Sample: 96.13 Å²
Conclusion

Ion mobility mass spectrometry was able to give insight into the structure of PAHs in a VGO cut from Canadian bitumen by comparison of experimental $CCS_{(He)}$ of ions in the sample with those of model compounds and/or by comparison with theoretical $CCS_{(He)}$ calculated for hypothetical structures.

PAHs with more peri-condensed aromatic rings were found to be more compact than those linearly fused.

PAHs with a more rounded shape are more compact than those with elongated structures.

PAHs with an island structure are more compact than their isomers with archipelago structure.
Photoionization Workshop

Isomer-resolved Species Identification and Quantification by Synchrotron-based Photoionization Mass Spectrometry

Thomas Bierkandt and Tina Kasper

65th ASMS Conference on Mass Spectrometry and Allied Topics
June 4 – 8, 2017, Indianapolis, Indiana
Combustion processes and world energy consumption

- Currently more than 80% of world energy use supplied by fossil fuels
- Fossil fuels also in 2040 most important primary energy carrier

- Combustion is a major source of air borne pollutants such as NOx, VOCs, PAHs and soot
- Pollutants are fuel-dependent

Development of alternative combustion strategies and use of biofuels

Understanding combustion processes is of crucial interest
Combustion is a complicated mix of chemistry and gas dynamics

Laminar premixed low-pressure flames

Chemical composition:
- Which species are present?
  - Key reaction species and highly reactive radicals
- How large are their concentrations?

Reaction kinetics:
- Which species react with each other?
- How fast are those reactions?

Combustion kinetics of monoterpenes: Poster on Wednesday (WP 122)

Isobutane
Challenges in flame sampling

Methods for observing key reaction species (radicals) are required.

Details of the chemistry are very important.

Wanted:
Identification of different isomers and rapid tunability from 5-16 eV (VUV).
Ionization methods in flame-sampling molecular-beam mass spectrometry

<table>
<thead>
<tr>
<th></th>
<th>Electron ionization (EI)</th>
<th>Single-photon ionization (SPI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity</td>
<td>No</td>
<td>High</td>
</tr>
<tr>
<td>Energy resolution</td>
<td>Low (&lt; 20)</td>
<td>High (10000 for VUV lasers)</td>
</tr>
<tr>
<td>(E/ΔE)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fragmentation</td>
<td>Can be a problem</td>
<td>“soft ionization”</td>
</tr>
<tr>
<td>Tunability</td>
<td>Fast</td>
<td>Limited and time-consuming</td>
</tr>
<tr>
<td>Beam</td>
<td>Very high flux (continuous)</td>
<td>High flux (pulsed, low repetition rate)</td>
</tr>
</tbody>
</table>

Is there a light source which combines the best of both worlds?

Synchrotron radiation
Synchrotron-based flame chemistry experiments

- **ALS**
  - Premixed flame
  - Counter-flow diffusion flame
  - Jet-stirred reactor

- **NSRL**
  - Premixed flame
  - Counter-flow diffusion flame
  - Jet-stirred reactor

- **Soleil/SLS**
  - Premixed flame
  - Pyrolysis flow reactor
  - Pyrolysis reactor

- **BESSY**
  - Premixed flame

<table>
<thead>
<tr>
<th></th>
<th>ALS</th>
<th>NSRL</th>
<th>SLS</th>
<th>Soleil</th>
<th>BESSY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon flux [1/s]</td>
<td>$10^{14}$</td>
<td>$10^{12}$</td>
<td>$10^{11}$</td>
<td>$10^{11}$</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>E/ΔE</td>
<td>300</td>
<td>2000</td>
<td>4000</td>
<td>200000</td>
<td>85000</td>
</tr>
<tr>
<td>Energy range [eV]</td>
<td>7-30</td>
<td>7-20</td>
<td>5-30</td>
<td>5-40</td>
<td>6-40</td>
</tr>
<tr>
<td>m/Δm</td>
<td>3500</td>
<td>3000</td>
<td>300</td>
<td>300</td>
<td>&lt;10000</td>
</tr>
<tr>
<td>Technique</td>
<td>PIMS</td>
<td>PIMS</td>
<td>PEPICO</td>
<td>PEPICO</td>
<td>PIMS</td>
</tr>
</tbody>
</table>
Species identification and quantification

Variation of burner position

Constant photon energy

Variation of photon energy

Constant burner position
Species identification and quantification

- Variation of burner position
- Photon energy constant

- Variation of photon energy
- Burner position constant

Photoionization Workshop
Isomer resolution – the big advantage of synchrotron radiation for ionization

Example: C$_9$H$_8$ isomers

- Photoionization efficiency (PIE) curve
  - Good signal-to-noise
  - Detection limit: $x_1 \sim 10^{-7}$
  - First onset can be assigned to indene
  - Larger isomers have typically similar PIE curves
  - Only one isomer identified

- Number of isomers increases with m/z
- Isomers react differently

How can PEPICO improve isomer resolution?
iPEPICO: imaging photoelectron photoion coincidence spectroscopy

**Electron detector** (delay line anode)

**Ions**

**Electron triggers the ions’ TOF**

**Velocity map image**

**Velocity map image**

**Threshold electrons**

**hot electrons**

**Measured in coincidence**

**Time-of-flight spectrum**

**Signal**

**TOF / μs**

**Burner**

**Flame**

**AB**

**AB^+ + e^-**

**E_{i}(AB) + hv**

**E_{i}(AB^+) + E_{kin}(e^-) + IE**

**Low extraction field 120 V/cm**

**Molecular beam**

**Sampling nozzle**

**Skimmer**

**I(on detector (MCP)**

**Photoionization Workshop**
ms-TPES help to identify isomers

Example: C\textsubscript{8}H\textsubscript{9} isomers

- Photoionization efficiency (PIE) curve
  - First onset can be assigned to indene
  - Only one isomer identified

- ms-TPES
  - Fingerprint of each species
  - Three isomers instead of one
  - Measuring threshold photoelectrons increases the selectivity
  - Not for all species because higher averaging times
ms-TPES help to identify isomers

Example: C₈H₉ isomers

- Photoionization efficiency (PIE) curve
  - First onset can be assigned to indene
  - Only one isomer identified

- ms-TPES
  - Fingerprint of each species
  - Three isomers instead of one
  - Measuring threshold photoelectrons increases the selectivity
  - Not for all species because higher averaging times

Thank you for your attention
Vacuum Photoionization Mass Spectrometry
An approach for online analysis of complex mixtures

Author: Sven Ehlert, Andreas Walte

ASMS Photoionization Workshop June 2017
Basic idea of Vacuum Photo Ionization Mass Spectrometry

PIMS - Soft photo ionization in \textit{vacuum} (no fragmentation as in EI-MS and no matrix effects as in CI-MS)

direct MS analysis
(including effective matrix suppression e.g. N\textsubscript{2}, O\textsubscript{2}...)

**Introduction:**

Photo ionization

Mass spectra of Diesel

```
**diesel El-MS**
* alkane fragments
* cyclic alkane fragments
* phenylated alkane fragments

**diesel SPI-MS (cross section corrected)**
* alkanes, naphthalenes
* cyclic alkanes, biphenyls
* bicyclic alkanes, fluorenes
* benzenes
* indanes/tetralins
```
Introduction:
Photo ionization - SPI

Vacuum UV Single Photon Ionization (SPI)

• incoherent VUV radiation (excimer lamp, e.g. 9.8 eV [126nm]), glow discharge lamps, e.g. filled with Kr, 10.0 & 10.6eV [123.9 & 116.9nm], or deuterium lamps, e.g. 10.8….3.1eV [115…400nm])
• ionization with laser photons (118 nm ,10.5 eV)
• soft ionization of most organic compounds
• ppb on-line concentration range
SPI-Lamp Setup

SPI-MS setup with EBEL VUV – Light Source
Introduction: Photo ionization - REMPI

Resonance-Enhanced Multiphoton Ionization (REMPI)

- ionization by UV laser pulses (210-270 nm, \(\sim 10^7\) W/cm²)
- highly efficient soft two-photon ionization of aromatics
- ppb/ppt on-line concentration range
Introduction:
Photo ionization - SPI and REMPI

Mass spectra of Diesel

fragment-free/less overview
especially selective for aromatic compounds
heavy fragmentation
Laser Setup

**SPI-Setup**

- **Heated transfer line**
- **Capillary**
- **Inlet system & Ionisation chamber**
- **Reflectron TOF-MS**

- **Analyte**
- **Laser System**
  - **SHG/THG**
  - **Nd-YAG Laser**

- **118 nm**
- **355 nm**

- **Instrumentation control, Data acquisition & Display**

**REMPI-Setup**

- **Heated transfer line**
- **Capillary**
- **Inlet system & Ionisation chamber**
- **Reflectron TOF-MS**

- **Analyte**
- **Laser System**
  - **OPO with SHG**
  - **SHG/THG**
  - **Nd-YAG Laser**

- **220 - 354 nm**
- **355 nm 1064 nm**

- **Instrumentation control, Data acquisition & Display**
Products & Applications

LM2X-PHOTO-TOF-MS
SMOKE ANALYZER

PHOTO-TOF-MS
CUSTOMIZED GAS ANALYZER

TG-PIMS
THERMOGRAVIMETRY- PHOTOIONIZATION MS

Lamp VUV SPI Source

Lamp VUV SPI Source

Lamp or Laser VUV SPI
fixed or tuneable Laser REMPI
Application: Tobacco & Marihuana

THC flower joint

- Nicotine (162 m/z)
- THC (314 m/z)

Graph showing mass versus signal intensity with peaks at 162 and 314 m/z.

Chemical structures of THC and Nicotine are shown.
Applications
Thermogravimetry–PIMS device
Applications
Thermogravimetry–PIMS device
Applications

Analysis of oil (R820 crude oil): Thermogravimetry–PIMS device

Asphaltene decomposition

(Semi)volatile
Applications
Analysis of Asphaltene (C5/C7)

TA-REMPI-MS Asphaltene C5

TA-REMPI-MS Asphaltene C7
Applications

Experimental setup for roasting test at University of Rostock

Detail view I: Sampling

Detail view II: Sampling
Applications

Experimental setup for roasting test at University of Rostock

<table>
<thead>
<tr>
<th></th>
<th>Slow</th>
<th>Normal</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init temp.</td>
<td>200°C</td>
<td>200°C</td>
<td>200°C</td>
</tr>
<tr>
<td>Heating step</td>
<td>3,5</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Appr. time</td>
<td>20 min</td>
<td>11 min</td>
<td>6 min</td>
</tr>
<tr>
<td>Start weight</td>
<td>100 g</td>
<td>100 g</td>
<td>100 g</td>
</tr>
<tr>
<td>End weight</td>
<td>66-73 g</td>
<td>71-75 g</td>
<td>70-78 g</td>
</tr>
</tbody>
</table>
Applications

SPI mass spectrum of Robusta coffee roast gas (lin. & log scale)
Applications

SPI mass spectrum of Arabica coffee roast gas (lin. & log scale)

More complex lipid composition (typical for Arabica)
Applications

REMPI mass spectrum of *Arabica* coffee roast gas (lin. & log scale)

aromatic coffee-oil components (typical for Arabica)
Applications

REMPI mass spectrum of Robusta coffee roast gas (lin. & log scale)
Further Application

• Analysis of environmental gases and aerosol particle
  Hyphenation of a EC / OC thermal–optical carbon analyzer to photo-ionization time-of-flight mass spectrometry: an off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter; Atmos. Meas. Tech., 8, 3337-3353, 2015

• Engine emission (ship diesel, car engine...)
  Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation Original Research Article; Atmospheric Environment, Volume 94, September 2014, Pages 467-478
  Real-time analysis of aromatics in combustion engine exhaust by resonance-enhanced multiphoton ionisation time-of-flight mass spectrometry (REMPI-TOF-MS); Analytical and Bioanalytical Chemistry July 2012, Volume 404, Issue 1, pp 273–276

• Pyrolysis Experiments (e.g. wood combustion...)
  Online Analysis of Biomass Pyrolysis Tar by Photoionization Mass Spectrometry; Energy & Fuels 2016 30 (3), 1555-1563
Thank you for your attention!

More Info: www.photonion.de
A4a: Not yet, but is a good idea.

A4b: Waters: the AP source has an extra holder in the source which can be used for dopants.

A4c: Dopant can be used to tune selectivity

Q5: Is Waters going to commercialize GC-APPI systems?

A5: It is still under investigation, but not in the near future.

Q6: Can APPI also be used to measure organic sulfur compounds (e.g. PAH with sulfur)?

A6a: Yes, it is very good for ionizing organic sulfur compounds. In general less polar compounds can be better ionized by APPI than by ESI.

A6b: Isobaric compounds can be separated by IMS

Q7: Is it possible to do quantitative work with synchrotron-PI or other vacuum PI?

A7a: Yes, the relative ionization efficiency has to be determined. Databases of photoionization cross sections are available.

A7b: An easy approach to obtain photoionization cross sections is to use a gas chromatography to separate many compounds with known concentrations and use PI-MS to detect.

Q8: Different PI sources were shown, is there a standard best source?

A8: There are less expensive sources (glow discharge) and more expensive ones (Laser SPI, REMPI). What source to choose depends on the application, e.g. what is the required detection limit in the application.

We made reference to asking questions using the app, but the first contributor from the audience commented that it is quicker to speak than type, so we decided not to use the app. Anyway for that size of audience it seemed not to make sense. We heard positive feedback from many attendees. We intend to distribute a pdf version of this report to the interest group members upon agreement of the speakers. The planning process for next year’s workshop is already in progress.

The briefing material is attached.

Eleanor and Ralf