Atmospheric Pressure Photo Ionisation in Environmental Chemistry

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The Netherlands
Outline

- Principles APPI
- Experimental observations
- Environmental chemistry: Applications
  - Positive ionisation
  - Negative ionisation
APPI principle

- Published in 2000 by Bruins and co-workers
- First application of photo ionisation in combination with LC-MS
- Ionisation energy lamp < LC eluent
Krypton Lamp
V.U.V. (Vacuum Ultra Violet)

- Most common lamp used for photo ionisation
- Two emission wavelengths
  \[ E = \hbar \cdot \nu \]
- Two ionisation energies
- 10.03eV and 10.64eV (4:1)
Ionisation energy

Components with IE < lamp

Don’t use solvent modifiers:

- Ammonium has a high proton affinity
- Acids may lead to signal suppression due to competition with positively and negatively charged particles

Use “Dopant” liquid (5-10% of solvent flow) with an I.E. < lamp

<table>
<thead>
<tr>
<th>Component</th>
<th>Ionisation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>15.58</td>
</tr>
<tr>
<td>Water</td>
<td>12.62</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>12.20</td>
</tr>
<tr>
<td>Oxygen</td>
<td>12.07</td>
</tr>
<tr>
<td>Krypton lamp</td>
<td>10.03/10.64</td>
</tr>
<tr>
<td>Methanol dimer</td>
<td>8.74</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.70</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.24</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.83</td>
</tr>
</tbody>
</table>
Mechanisms I

Direct APPI

\[ M + h\nu \rightarrow M^* \]

If ionisation energy \( E = h\nu \) < Ionisation energy:

\[ M^* \rightarrow M^+ + e^- \]

"solvent" APPI (S):

\[ M + S + h\nu \rightarrow [M + H]^+ + [S - H]^- \]

‘Electron capture’, charge transfer:

\[ M + e^- \rightarrow M^- \]

\[ M + S + e^- \rightarrow [M + S]^- \]

\[ O + e^- \rightarrow O^- ; M + O^- \rightarrow [M + O]^- \]
Mechanisms II

Dopant APPI

\[
D + h\nu \rightarrow D^+ + e^- 
\]

(1) charge transfer
\[
D^+ + M \rightarrow D + M^+ \quad (E_{AD} > E_{AM})
\]

(2) Proton transfer
\[
D^+ + M \rightarrow [D - H]^+ + [M + H]^+ \quad (P_{AM} > P_{A[D-H]^+})
\]
Practical experiences
Reversed phase system

Auxiliary gas

HPLC/FFF effluent

Dopant in flow 20-100 µl/min

APPI dopants

Injections of anthracene standard solution, FIA in QTOF

No dopant

\[ [M+H]^+ \]
\[ [M]^+ (~10\%) \]

10% toluene

\[ [M+H]^+ \]
\[ [M]^+ (~50\%) \]

10% toluene + 0.05% anisole

\[ [M+H]^+ \]
\[ [M]^+ (~550\%) \]
# Applications APPI

<table>
<thead>
<tr>
<th>Category</th>
<th>Detection</th>
<th>Modified from Vughs and Kolkman, BTO 2013.236 (s), KWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>Cai et al. 2005/Wang et al. 2012</td>
<td>MS/MS</td>
</tr>
<tr>
<td>Hormones</td>
<td>Yamamoto et al. 2006/Wang et al. 2012</td>
<td>MS/MS</td>
</tr>
<tr>
<td>Toxines</td>
<td>Capriotti et al. 2012</td>
<td>MS/MS</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Itoh et al. 2009/Yamamoto et al. 2012</td>
<td>MS/MS</td>
</tr>
<tr>
<td>PAHs</td>
<td>Hollosi 2012</td>
<td>MS/MS</td>
</tr>
<tr>
<td>Azarenes</td>
<td>Brulik et al. 2013</td>
<td>MS/MS</td>
</tr>
<tr>
<td>Fullerenes</td>
<td>Li et al. 2012/Nunez et al. 2013; Emke et al. 2015</td>
<td>Ion trap/Orbitrap and FTICR</td>
</tr>
<tr>
<td>Screening</td>
<td>Chiaia-Hernandez</td>
<td>Orbitrap</td>
</tr>
</tbody>
</table>
LC Retention experiments (courtesy: Jort Hammer, UvA)

Applications

Neg mode: [M-H]⁻

Pos mode: [M]⁺

1. Uracil (t₀)
2. Anthracene
3. Pyrene
4. Chrysene
5. Benzo[k]fluoranthene
6. Benzo[ghi]perylene
Penta BDE MS

Applications

$[\text{M-Br+O}]^-$

$[\text{M-HBr+O}_2^-]$
### Sorption to micro/nano plastics

(courtesy Eugenie Troia, UvA)

#### Pos mode:
\[ [M]^+ \]

#### Neg mode:
\[ [M-Br+O]^- \]

<table>
<thead>
<tr>
<th>1</th>
<th>Phenanthrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Anthracene</td>
</tr>
<tr>
<td>3</td>
<td>Pyrene</td>
</tr>
<tr>
<td>4</td>
<td>Tetra BDE</td>
</tr>
<tr>
<td>5</td>
<td>Penta BDE</td>
</tr>
<tr>
<td>6</td>
<td>Octa BDE</td>
</tr>
</tbody>
</table>
Azaarenes (Brulik et al. J.Chrom.A, 2013)

Naphthalene  →  Anthracene  →  Phenanthrene

Quinoline  →  Acridine  →  Phenanthridine

8-OH Quinoline  →  Acridone  →  Phenanthridinone

Applications

LC-MS/MS, positive mode
Results Azaarenes  (Brulik et al. J.Chrom.A 2013)

Real sediment sample chromatogram

Mean concentrations in ng/g dw (n=9) in the sediments from Dutch rivers (Rhine at NWW and W-Scheldt)

Average concentrations (ng/g dw) of sum of OH-PANHs, PANHs and PAHs. (Rotterdam April n=5, Rotterdam November n=2, Hansweert n=3)
Fullerenes
Fullerene analysis with HPLC-HESI-Orbitrap, negative mode

- Buckyprep column (normal phase)
- Eluent: toluene/acetonitrile
- Electron donor methanol post column infusion
- Interface HESI
- Tube lens 200 V

Calibration
HPLC-HESI-Orbitrap: different calibration curves for every adduct
Fullerenes
Fullerene analysis with HPLC-APPI-Orbitrap, negative mode

- Buckyprep column (normal phase)
- Eluent: toluene
- Interface APPI (no dopant necessary)
- Tube lens 200 V
- Linear 0.025 µg/l – 128 µg/l

HPLC (toluene) - APPI-Orbitrap

APPI of Fullerenes, identification

Influence of presence of methanol in toluene on the isotopic pattern

Infusion: 25% methanol : 75% toluene

Infusion: 100% toluene

Theoretical

C60: C60 p/igs, s/p:10) Chrg -1 R: 3000 Res. Pwr. @FWHM

Conclusions

- APPI is a promising technique for identification and quantification of apolar emerging compounds.
- Apolar compounds including Fullerenes can be very well analysed in negative mode by APPI/MS:
  - Low LODs, wide linear response ranges, little adduct formation.
  - Potential for widening non target screening scope.
- In positive mode many components can be ionised, but:
  - Background problems from atmospheric contamination.
- APPI in positive mode combined with Orbitrap: applications far from simple. May be solved by using APPI unit in N₂-pressurised/flushed box.
- Target screening: use APPI-QqQ.
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