Coupling Atmospheric Pressure Photoionization (APPI) with Differential Mobility Analysis (DMA) – Mass Spectrometry for the detection of non-polar environmental analytes within gaseous samples

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(European Society of Differential Mobility Analyzers)
Motivation and objectives

• **Motivation**
  Develop an ion source for the analysis of vapour samples containing non-polar analytes using DMA-MS technologies

• **Objectives**
  1. Prototype APPI-DMA-MS source design
  2. Characterize and identify key applications
  3. Refine source design: produce a commercially viable device
Key SEADM Technologies

- **Differential Mobility Analyzer (DMA)**
  - Integrates with MS to add an ion mobility dimension
  - Intended to reduce need for LC equipment
  - Minimizes sample throughput time
  - Provide high sensitivity, selectivity & reduce background levels

- **Secondary Electrospray Ionization (SESI)**
  - Based on a simple nanospray source configuration
  - Intended for the analysis of vapours
  - Demonstrated high sensitivity
**Differential Mobility Analyzer (DMA)**

- **The principle**

  - Continuous ion sampling / high duty cycle
  - Ion transmission up to 50%
  - Resolving power as high as 80
  - Complete mobility scans in less than 1 minute
Secondary Electrospray Ionization, SESI

Two modes:

1) Nanospray for liquid samples

2) SESI for vapour analysis
   - Gas-phase analyte ionization process
   - Electrospray charger ions

✓ Sub ppt LODs
✓ Reduced matrix impact
✓ Low flow configurations for increased sensitivity
Vapour Sampling Method

The Lab

Ionizer

DMA

MS

Thermal Desorber

Vapour Sampler

The Field
**SESI-DMA applications**

- Vapour analysis (explosive screening, breath, etc.)

- Mixture of explosives separated according to mobility.

- Detection limits in ppq range for vapour analysis.

- Cargo container screening / security applications.
Atmospheric Pressure Photoionization, APPI

Why APPI?

- ESI/SESII suitable for polars, not ideal for non-polars
- Applied typically to LC-MS methods; good for non-polar analysis
- Gas-phase chemical ionization method; adapts well to vapour analysis
- Dopant (D) generally used to enhance analyte (M) ionization efficiency

\[ D + h\nu \rightarrow D^{\bullet+} + e^- \]

Atmospheric Pressure Photoionization, APPI

- Analytes are efficiently ionized within the gas-phase through various pathways:
  
  Charge exchange, proton transfer, electron capture, charged adduction, etc.

- Works effectively in positive and negative ionization modes.

- Applicable to both polar and non-polar compounds.

  “Most universal source for LC-MS”

- Broad linear dynamic range.

- Minimal susceptibility to matrix effects.

- Comprehensive review of APPI-LC-MS fundamentals:

APPI-DMA Prototype Version 1.0

- Based upon 1st generation field-free APPI source configuration\(^3\)
- Shown to provide advanced sensitivity for LC-MS applications
- **2 configurations:**

   ![APPI-MS](image1)

   ![APPI-DMA-MS](image2)

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DIOXDETECTOR (Fast Atmospheric Dioxin Detection)

- Project objective: Method for quantification of dioxins and furans.
- Track PCDDs/PCDFs in air, soil and vegetable matter at surroundings of incineration facility.
- Samples collected and extracted
  - No direct vapour analysis
- APCI/ESI/SESI evaluated.
  - Insufficient sensitivity/ineffective
- **APPI developed to tackle problem.**
Method Development: fullscan

Negative mode:
- Analytes infused, toluene solvent
- Dioxins and furans - [M-Cl+O]⁻

Hexachlorodibenzodioxin and furan @ 2 ng/mL, in toluene @ 2 µL/min,
Suitability for Dioxin/Furan Screening

• SEADM: APPI-MS (no DMA);
  *AB Sciex 3200 series QTrap*

• Analysis of liquid standards

• LODs ranging from 0.15-1.40 pg;
  - most detected near 1 pg level

• Method suitable for trace analysis
  • NDAMN⁴ - (HR-GC-MS)

• Complying with regulations (US EPA Method 1613B1 and Regulation (EC) No. 1883/20062).

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The practical application: Dioxins & Furans – Site X

- Samples obtained from various locations
- Air (~700 m³), soil (~5 g) and biota/plant (~20 g) matter collected & extracted
- Samples delivered to SEADM for analysis
- Toxic equivalency (TEQ) estimated
- Project in early stages

Blue – January, Red – February, Green - March
• Method development: fullscan

Positive mode:
  • Analytes infused, toluene solvent
  • Polycyclicaromatic Hydrocarbons (PAHs) – M⁺

Ex. Benzo(ghi)perylene - 100 ng/mL in toluene @ 2 μL/min
Thermal desorption – APPI-MS

Benzo(a)pyrene, **BaP** – Desorbed at 250°C
MRM method; 12 consecutive samples
2 μL of 100 ng/mL – 200 pg

- Toluene added to auxiliary gas
Adding the DMA Mobility Element

Scan time < 1 min

8000 RPM

- Infusion of a standard PAH panel - 100 ppb in toluene @ 2 µL/min

14000 RPM

Impacting Mobility and Resolution

- DMA gas velocity or pump speed
- Gas selection (N₂, CO₂, Ar, etc.)
- Additives (Benzene, IPA, toluene, water, etc.)
• Separating isomers/congeners remains a technical challenge for the DMA
• Ex. BaP and BkF indistinguishable to MS; even in MRM mode

**Blue** – BaP + BkF  **Green** – BaP  **Red** – BkF

**Benzo(a)pyrene**

m/z - 252

**Benzo(k)fluoranthene**

m/z - 252

• Continued goal to improve DMA resolution
Deconvolution possible:

**Blue** – BaP + BkF  
**Red** – BaP  
**Green** – BkF

### Analyte Table

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<thead>
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<th>Analyte</th>
<th>Q1</th>
<th>Quantifier</th>
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<tr>
<td>Perylene</td>
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</tr>
</tbody>
</table>
PAH panel – Desorption APPI-DMA-MS

- Analytes deposited on a filter cartridge by micro pipette; desorbed at 250 °C
- Ion Mobility (Z) voltage optimized and fixed for each analyte
- Method suitable low level PAH detection (*Isomers often not separable*)
- Next step: collect real samples – demo full TD-APPI-DMA-MS workflow

1 μL standard panel - 100 ppb, 6 analytes (100 pg each)
Continued Focus

- Apply complete APPI-DMA-MS workflows:
  - Develop complete PAH vapour sampling method
- Expand range of applications:
  - PCBs, pesticides, explosives, biologicals
- Optimize APPI: evaluate alternative geometries & refine the design
- General goal to improve DMA resolving power and performance
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