Fast GC-TOFMS for High-throughput Screening of Environmental Contaminants

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Outline

• Challenges in monitoring water quality

• GC-TOF MS for water analysis
  – Potential limitations?

• Three potential solutions:
  – Deconvolution
  – Separation capacity of GCxGC
  – Soft electron ionisation
Monitoring water quality

- Focus is generally on “priority” substances, but what about those of emerging concern?

- Always need lower detection limits

- New monitoring methods and analytical techniques are now necessary
Issues with current methodology

- 1D GC-MS is not able to resolve all components
- Grab sampling is limited
BenchTOF technology

Proprietary design

- Differentially pumped source and analyser chambers
- Direct extraction optimises sensitivity
- Multi-stage reflectron optimises resolution

-2000 V

3000 V
Benefits of GC-BenchTOF MS

Fast trace-level analysis

95 pollutants in less than 10 minutes

2 – 200 pg on column

- Phenol: \( R^2 = 0.9985 \)
- Permethrin: \( R^2 = 0.9997 \)
- Indeno[1.2.3-cd]pyrene: \( R^2 = 0.9995 \)
Problem #1: Is there enough separation capacity?
Potential solution?

Deconvolution
Real-time analysis

Results available on-the-fly
Confident identification of co-eluting peaks

Deconvolution of four pollutants
Another potential solution?

GCxGC TOF-MS
Analytical system

GC×GC-TOF MS

Column set:
1st dimension: SGE BPX5, 30 m × 0.25 mm × 0.25 µm;
2nd dimension: SGE BPX50, 2 m × 0.1 mm × 0.1 µm;

Modulator:
Zoex ZX1 loop modulator
1 m as for second dimension
Modulation period = 5 s
Screening by passive sampling and GCxGC-TOF MS

- Overcomes the limitations of grab sampling
- Designed to concentrate hydrophobic chemicals (with log Kow > 4)
Passive sampling of river water

Over a 4-week period

Semi-permeable membrane device (SPMD)

PCBs
PAHs
Pesticides
Identification of emerging contaminants

Polycyclic musks

- Not restricted to priority pollutants – those of emerging concern are also monitored.

2D extracted-ion chromatogram (EIC) for m/z 215, 229, 243 and 258.
### Increased confidence in identification

<table>
<thead>
<tr>
<th>Compound</th>
<th>Class</th>
<th>NIST library match</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>GCxGC (no deconvolution)</td>
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<tr>
<td>Acenaphthylene</td>
<td>PAH</td>
<td>932</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>PAH</td>
<td>944</td>
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<tr>
<td>1,1'-Biphenyl, 2,2',3,4-tetrachloro-</td>
<td>PCB</td>
<td>870</td>
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<tr>
<td>2,3,3',5,5',6-Hexachloro-1,1'-biphenyl</td>
<td>PCB</td>
<td>844</td>
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<td>DDT</td>
<td>Pesticide</td>
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<tr>
<td>Atrazine</td>
<td>Pesticide</td>
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<tr>
<td>Chlorpyrifos</td>
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<tr>
<td>Endrin</td>
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<td>842</td>
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<tr>
<td>Galaxolide</td>
<td>Polycyclic Musk</td>
<td>879</td>
</tr>
</tbody>
</table>
Problem #2: Weak molecular ions &/or similar spectra

Challenges in soft ionisation

• Source-switching
• Optimise additional parameters
• Sensitivity loss
• Poor isomer speciation
Soft electron ionisation

With no inherent loss in sensitivity

Select-eV

70 eV

16 eV

12 eV
Selectivity enhancement at low eV

Reduced ionisation of common background/carrier gases

- Ionisation potential of common gases in GC–MS
  - CO₂: 13.8 eV
  - N₂: 15.6 eV
  - H₂: 15.4 eV
  - He: 24.6 eV
**Hexachlorocyclopentadiene**

- **NIST MF = 845**
- **BenchTOF**
  - S/N = 2420 (m/z 272)
  - Greater than 15x increase in signal-to-noise for m/z 272
Etridiazole

NIST MF = 819

- Simplified spectrum at 11 eV
- Greater than 25x increase in signal-to-noise for m/z 246
Polycyclic Musks

Galaxolide (HHCB)

Match factor = 879
Metalaxyl

70 eV

14 eV
Summary

• GC-TOF MS enables fast & simple, ultra trace-level detection of targets and unknowns in environmental samples.

• GCxGC-TOF MS gives enhanced separation and confident identification when screening complex matrices.

• Select-eV provides:
  – Simplified spectra for higher peak capacity
  – Improved sensitivity and selectivity
  – Complementary spectra for confident identification capacity
Thank you for listening!

Any Questions?

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