GCxGC-(MS) methods

Pim Leonards
Outline

• Principles of GCxGC
• Selection of detectors
• PCB, PBDE analysis
• Other examples
Principles of GCxGC

- Selection of modulator
- 6 different modulators:
  - SWEEPER
  - LMCS
  - Quad N₂ (L) jet
  - Dual CO₂ jet
  - Loop CO₂
  - CFT

Selection of proper column combination
Selection 1\textsuperscript{st} and 2\textsuperscript{nd} dimension GC columns

- 1\textsuperscript{st} dimension
  - Apolar type phases:
    - DB-1, DB-5, CP-Sil 8 type of columns

2\textsuperscript{nd} dimension

<table>
<thead>
<tr>
<th>Commercial code\textsuperscript{a}</th>
<th>Stationary phase</th>
<th>Dimensions (m x mm x μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC-50</td>
<td>50% liquid crystalline-methylpolysiloxane</td>
<td>0.8 x 0.1, 0.1</td>
</tr>
<tr>
<td>007-65HT</td>
<td>65% phenyl-methylpolysiloxane</td>
<td>1.0 x 0.1, 0.1</td>
</tr>
<tr>
<td>VF-23ms</td>
<td>Proprietary (high cyano containing polymer; with absolute cyano content 70–90%)</td>
<td>1.5 x 0.1, 0.1</td>
</tr>
<tr>
<td>007-210</td>
<td>50% trifluoropropyl-methylpolysiloxane</td>
<td>2.0 x 0.1, 0.1</td>
</tr>
<tr>
<td>HT-8</td>
<td>8% phenyl-methylpolysiloxane (carborane)</td>
<td>1.0 x 0.1, 0.1</td>
</tr>
<tr>
<td>SupelcoWax-10</td>
<td>Polyethylene glycol</td>
<td>1.0 x 0.1, 0.1</td>
</tr>
</tbody>
</table>
How does it work?
Cryogenic modulator
How does GCxGC work?
How does GCxGC work?
How does GCxGC work?

Separation on the 2\textsuperscript{nd} dimension column
How does GCxGC work?
Principle and contour plots
Contour plot
Detectors for GCxGC systems

- Fast scanning detectors
  - Acquisition rate >20 Hz
- Low dead volume detectors

Commercial equipment
- GCxGC-FID
- GCxGC-ECD
- GCxGC-qMS
- GCxGC-ToF-MS
- GCxGC-AED not commercially available
GCxGC-μECD
GCxGC-μECD various contaminants

PCDD/Fs  
PCBs  
PBBs  
PBDEs  
PCDEs  
OCPs  
PCNs  
PCDTs


DB-1 × LC-50
GCxGC-μECD different column combination

PBDEs
PCBs
PCNs
PCDTs
PCDEs
PBBs
PCDD/Fs
OCPs

DB-1 × 007-65HT

Toxaphene

Korytar et al., 2005. J. Chromatogr. A, 1086, 29-44
GCxGC-μECD dust sample

DB-1×007-65HT

PBDEs

Polychlorinated alkanes

Background matrix separation from dioxins

GCxGC-ECD, DB-XLB x LC-50

1st dimension retention time [min]

2nd dimension retention time [s]

GCxGC-MS
GCxGC with qMS

- Requirements
  - Fast acquisition
  - Spectral quality: no skewing
Quadrupole MS

High acquisition rates
- short Rf setup time
- fast scanning

R_f setup time: 10.4 ms
Scan rate: 10000 amu/s
Scan width (amu):
- @ 50Hz: 96
- @ 33 Hz: 195
- @ 25 Hz: 296
No skewing
mass ratio plot (m/z 330/326)

[Graph showing a plot with data points representing mass ratio versus data point number for Shimadzu qMS]
Quality of spectra

Mass range scanned

<table>
<thead>
<tr>
<th>Mass range scanned (Da)</th>
<th>Minimum inter-scan delay (s)</th>
<th>Maximum scan speed: 6700 Da/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Scan time^a (s)</td>
</tr>
<tr>
<td>400</td>
<td>0.014</td>
<td>0.060</td>
</tr>
<tr>
<td>300</td>
<td>0.011</td>
<td>0.045</td>
</tr>
<tr>
<td>200</td>
<td>0.010</td>
<td>0.030</td>
</tr>
<tr>
<td>100</td>
<td>0.005</td>
<td>0.015</td>
</tr>
<tr>
<td>50</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

GCxGC-qMS

- Fast enough
- Selective enough
  - separation of coeluters
- Limited scanning range (300 Da)
- Not sensitive enough in EI
  - NCI required
Eel extract GCxGC-qMS PBDE analysis
GCxGC ToFMS

- Fast scan speed: 100-500 Hz
- No mass skewing
- Automated search
GCxGC-ToF-MS, Tern egg
Western Scheldt

Brominated compounds
Screening chemicals in household dust

GCxGC-ToFMS of an hexane extract of dust

Chlorinated and brominated compounds in house dust

- >10,000 peaks detected
- 145 compounds contain chlorine or bromine

Other compounds identified in household dust

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Number found by filter</th>
<th>Plausible on review</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine/bromine-containing</td>
<td>165</td>
<td>145 (93%)</td>
</tr>
<tr>
<td>Phthalates</td>
<td>52</td>
<td>33 (57%)</td>
</tr>
<tr>
<td>PAHs</td>
<td>145</td>
<td>94 (65%)</td>
</tr>
<tr>
<td>Nitro compounds</td>
<td>8</td>
<td>1 (13%)</td>
</tr>
</tbody>
</table>

Effect-directed analysis (EDA)

complex mixture of compounds

1st Fractionation

2nd Fractionation

Bioassay confirmation

Chemical identification
Combined sample treatment scheme chemical and bioassay analysis

Houtman et al. 2006
• Sediment sample from a harbour
• Bioassays
  • Dioxin like compounds (DR-CALUX)
  • Estrogenic compounds (ER-CALUX)
• Chemical identification
  • GC-MS
  • GCxGC-ToFMS

Houtman et al., 2006, Chemosphere 65, 2244–2252
Bioassay activity of the sediment

Houtman et al., 2006, Chemosphere 65, 2244–2252
Active fraction GCxGC-ToFMS

Houtman et al., 2006, Chemosphere 65, 2244–2252
Identified compounds and explained bioassay activity

• 76% of the estrogenic activity was explained by 17α-, 17β-estradiol and estrone
• 38% of dioxin-like activity explained by PAHs
Summary

• GCxGC is a powerful separation technique

• Separation of interfering compounds and matrix

• GCxGC is especially suitable for the separation of complex mixtures

• GCxGC combined with mass spectrometry can be used for the identification of “new” flame retardants