Potential of Gas Chromatography-Atmospheric Pressure Chemical Ionization-Tandem Mass Spectrometry for Screening of Hexabromocyclododecane

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Halogenated flame retardants [e.g. polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBP-A)] are widespread in the environment due to their use in a variety of electronics, clothes and furniture for enhancing fire safety.

BDE-28

TBBP-A
Due to their persistence, bioaccumulative and toxic properties, authorities have restricted the use of PBDEs. The European Union (EU) banned Penta-BDE and Octa-BDE mixtures in 2004 as well as Deca-BDE in electric and electronic products in 2009.

BDE-100

BDE-196

BDE-209
Due to the restrictions on PBDEs, the use of alternative BFRs was increased, like hexabromocyclododecane (HBCD) in polystyrene foams.

HBCD is classified by REACH as a substance of very high concern because of their toxicity, persistence and bioaccumulation. And currently it is assessed for inclusion in the Stockholm Convention.

Therefore, analytical methods are required to monitor their levels in food and environment.

16 stereoisomers are possible, but commercial mixtures are dominated by γ (90%) plus β and α (10%).
GC-APCI-MS/MS
Hexabromocyclododecanes

Technical Polysterene foam (160-170°C)

LC-ESI(neg)-MS/MS

HBCD
Hexabromocyclododecane (HBCD) is also a GC-amenable compound and GC-MS methods allow the determination of total HBCD concentrations obtaining similar results to LC-MS/MS methods.

However, GC-MS methods are not suitable if information about individual isomers is required.

Nevertheless, the availability of a sensitive and selective screening methods by GC-MS is still interesting as HBCD are found in the same fraction as PBDEs when applying conventional sample treatment for POPs analysis.

However, the selectivity offered by NCI under these circumstances is low as HBCD could yield overlap signals with some PBDE congeners.
**GC-APCI-MS/MS**

**Hexabromocyclododecane**

**Electron Ionization**

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

$\text{M}^{+}$

$\text{Br}$

$m/z$ 316.9537

$\text{C}_{12}\text{H}_{15}\text{Br}_{2}$

**GC-EI-HRMS**

**LOD $\approx$ 500 pg**
“APCI-like” soft ionization for GC eluate

- **Cone gas**: 150-200 L/hr
- **Corona current**: 0.8-2.2 μA
- **Transfer line**: 300 ºC
- **N₂**: 320 mL/min

Diagram showing the GC-APCI-MS/MS setup with labeled components:
- Ion Chamber
- Corona Discharge
- Column
- Transfer Line Inner
- Transfer Line Tip
- Source Enclosure Wall
- GC Wall
- GC Oven
- Make-up Gas
- GC eluate

**Modifiers** included in the setup.
GC-APCI-MS/MS
Hexabromocyclododecane
APGC
GC-APCI-MS/MS
Hexabromocyclododecane
APGC

Modifiers
(H₂O, MeOH)
GC-APCI-MS/MS
Hexabromocyclododecane
APGC

EI

APCI

[N-Br]^+:

[M-Br]^+:

M^+:

m/z 560.73 / 562.73
C_{12}H_{18}Br_5

N_2 charge transfer

MS/MS
**GC-APCI-MS/MS**

**Hexabromocyclododecane**

**APGC-MS/MS**

1: ScanWave DS of 563AP+ 4.26e7

**Hexabromocyclododecane**

**DIOXINS0576 1491 (38.975)**

1: ScanWave DS of 563AP+ 4.26e7

**DIOXINS0575 1497 (39.011)**

1: ScanWave DS of 560AP+

- 3x [HBr]
- 4x [HBr]
- 5x [HBr]

**GHBCDD_cal_10ppb**

1: ScanWave DS of 560AP+

**DIOXINS0678 Sm (Mn, 1x1)**

2: MRM of 3 Channels AP+ 562.6 > 239 (GHBCDD)

9.92e4 Area

2: MRM of 3 Channels AP+ 562.6 > 157 (GHBCDD)

2.90e5 Area

2: MRM of 3 Channels AP+ 562.6 > 129 (GHBCDD)

6.84e4 Area

**DIOXINS0678 Sm (Mn, 1x1)**

1: MRM of 3 Channels AP+ 560.4 > 237 (GHBCDD)

9.77e4 Area

1: MRM of 3 Channels AP+ 560.4 > 157 (GHBCDD)

3.05e5 Area

1: MRM of 3 Channels AP+ 560.4 > 129 (GHBCDD)

7.54e4 Area

**Q**

1.01

9.92e4 Area

6.49e4 Area

3.05e5 Area

**HBCD 10 pg/μL**

**GC column:** HP-5MS, Length 30m, id 0.25 mm, film thickness 0.25 μm.

**GC oven:** Init temp inicial 140°C; 10°C/min to 310°C (3 min)

**Constant flow:** 2 mL/min
GC-APCI-MS/MS
Hexabromocyclododecane
APGC-MS/MS

**IS:** $^{13}$C$_{12}$-HBCD

1-100 pg/μL

**Linearity**

$y = 0.0207x + 0.007$
$R^2 = 0.9999$

### GHBCDD_cal_10ppb

<table>
<thead>
<tr>
<th>Channel</th>
<th>Retention Time (min)</th>
<th>Area (μA)</th>
<th>Response (Area/IS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 560.4 &gt; 237 (GHBCDD)</td>
<td>17.00</td>
<td>6140</td>
<td>0.33</td>
</tr>
<tr>
<td>2: 560.4 &gt; 157 (GHBCDD)</td>
<td>17.00</td>
<td>18900</td>
<td>1.01</td>
</tr>
<tr>
<td>3: 560.4 &gt; 129 (GHBCDD)</td>
<td>17.00</td>
<td>4327</td>
<td>0.23</td>
</tr>
</tbody>
</table>

**HBCD 10 pg/μL**
GC-APCI-MS/MS
Hexabromocyclododecane
APGC-MS/MS

Linearity

\[ y = 0.0207x + 0.007 \]
\[ R^2 = 0.9999 \]

Sensitivity

1 pg on-column

LOD \approx 100 fg

1-100 pg/μL
IS: $^{13}$C$_{12}$-HBCD

HBCD 1 pg/μL
Application to samples

- Samples analyzed consisted in several **polyurethane foam (PUF) disks** used as passive sampling devices.
- Additional information about sampling sites, days of exposure, etc was already presented yesterday in communication #1265 (**New POPs in Ambient Air Samples using Passive Air Samplers**) in Advances in passive sampling for air and water session.
**GC-APCI-MS/MS**

**Hexabromocyclododecane**

**APGC-MS/MS**

**Application to samples**

HBCD 223 pg/µL in Mali PUF (extract #288)

- **Response (Area/IS)**: 4.62
- **HBCD 4.46 ng PUF⁻¹**

- **20 µL extract**

**resp (Area/IS)**

\[ y = 0.0207x + 0.007 \]

\[ R^2 = 0.9999 \]

- **Mali**

**Response (Area/IS)**

- **HBCD 223 pg/µL in Mali PUF (extract #288)**
- **HBCD 4.46 ng PUF⁻¹**

**GC-APCI-MS/MS**

**Hexabromocyclododecane**

**APGC-MS/MS**

**Application to samples**

- **MRL of 1 Channel AP+**
  - DIOXINS0702 Sm (Mn, 1x1)
  - 572.4 > 169 (GHBCDD)
  - 9.81e3
  - Area

- **MRL of 3 Channels AP+**
  - DIOXINS0702 Sm (Mn, 1x1)
  - 560.4 > 237 (GHBCDD)
  - 1.07e4
  - Area

- **MRL of 3 Channels AP+**
  - DIOXINS0702 Sm (Mn, 1x1)
  - 560.4 > 157 (GHBCDD)
  - 3.60e4
  - Area

- **MRL of 3 Channels AP+**
  - DIOXINS0702 Sm (Mn, 1x1)
  - 560.4 > 129 (GHBCDD)
  - 9.49e3
  - Area
**GC-APCI-MS/MS**

**Hexabromocyclododecane**

**Conclusions**

- **APGC** is a valuable ionization source for coupling **GC** to novel tandem mass spectrometers.

- **APGC** allows a “universal” **soft-ionization** for **GC**-amenable compounds.

- **APGC** allows selecting molecular ion/protonated molecule ($M^+$/MH$^+$) or **high mass** fragments as precursor ion rendering more **selective** and **sensitive** SRM transitions than **EI/NCI**.

- **GC-APGC-TQS** presents **good** analytical characteristics regarding **linearity**, **precision** and **limits of detection** for determination of **total** hexabromocyclododecane (**HBCD**) content in environmental samples (**PUF** disks).
Thank you for your attention

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