

## Comparison of Hexabromocyclododecane Determinations Using GC/MS and LC/MS/MS

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### Introduction

Hexabromocyclododecane (HBCD) is a major component within the brominated flame retardant compound class comprised of three diastereoisomers<sup>1</sup>. HBCD is used globally at an annual rate of 16,000 tons<sup>2</sup>. Recently, considerable attention has been focused on the analytical determination of HBCD in the environment. Currently, little information exists on the comparative instrumental determinations of HBCD between GC and LC techniques. Due to its labile nature, HBCD can either isomerically transform or breakdown in the GC liner. The application of LC/MS/MS and GC/MS to the analysis of HBCD is compared using both standard solutions and field samples consisting of Detroit River suspended sediments. Absolute responses are determined using increasing injector temperatures of 180 °C, 215 °C and 260 °C. While the GC/MS did not afford isomer-specific analyses, this technique offered simple and reliable measurements on the occurrence of total HBCD. Meanwhile, the LC/MS/MS provided baseline separation of all three isomers and a linear dynamic range comparable to the GC/MS.

### Materials and Methods

Analysis by GC/MS was conducted by using an Agilent 6890N gas chromatograph (HP-5MS 30m, 0.25 mm id., 0.25 µm) coupled to a 5973-inert MSD operated in negative ion chemical ionization mode. Bromine ions (m/z 79 and 81) were monitored using selected ion monitoring. LC/MS/MS determinations were made using an Agilent 1100 liquid chromatograph (Vydac C18, 10 cm x 2.1 cm id., 5 µm particle size) with a methanol:water (90:10) mobile phase at 0.1 mL/min. coupled to a MDS/Sciex QTRAP operated in electrospray ionization (ESI) mode. Quantitation was achieved by monitoring the m/z 641 [M-H] in multiple reaction monitoring mode (MRM). LC/MS/MS quantitation was based on deuterated HBCD internal standards whereas GC/MS determinations were calculated using external standards. Both gamma and technical mixtures of HBCD were purchased from Wellington Laboratories, Ontario.

Sediment samples were solvent extracted with acetone:hexane (50:50) using sonification and extracts were eluted through modified silica gel. Eluants were concentrated to a 1 ml final volume and solvent exchanged into acetonitrile and toluene for LC/MS/MS and GC/MS analysis, respectively.

### Results and Discussions

The calculated instrument detection limit was an order of magnitude lower when using the GC/MS-NCI versus the LC/MS/MS-ESI (Table 1). Although, variability and linear dynamic range (five orders of magnitude) exhibit a close similarity when using the ionization modes in our study. Improvements within the linearity range and ultimate sensitivity were observed when using the GC/MS and LC/MS/MS instruments in NCI and ESI modes, respectively, versus EI and APCI<sup>3</sup>.

A close relationship was observed between the Detroit River sediment HBCD concentrations calculated by the two analytical techniques (Table 2). Average percent mean difference for the sample set was 15.7 and sample concentration did not appear to affect this relationship.

An injector temperature of 215 °C produced the greatest HBCD response in both gamma and technical HBCD mixtures (Figure 1). Technical HBCD GC/MS response was, on average, 12% lower than g-HBCD.

The GC/MS offers a simple, sensitive and accurate determination of total HBCD. However, LC/MS/MS-ESI is recommended to determine isomer specific HBCD measurements within a wide concentration range (Figure 2).

Further investigate HBCD measurements between LC/MS/MS-ESI and GC/MS-NCI using multiple matrices, and to

conduct a more detailed comparative statistical analysis. A look into potential matrix effects when using LC/MS/MS-ESI will be investigated.

Table 1.

| <b>HBCD IDL Determinations (pg injected)</b> |           |             |              |             |
|--|-----------|-------------|--------------|-------------|
|  | <b>n</b>  | <b>Mean</b> | <b>% RSD</b> | <b>IDL</b>  |
| <b>GC/MS</b>                                 | <b>10</b> | <b>0.98</b> | <b>9.6</b>   | <b>0.17</b> |
| <b>LC/MS/MS</b>                              | <b>10</b> | <b>12.1</b> | <b>8.5</b>   | <b>5.3</b>  |

Table 2.

| <b>Data Comparison of Detroit River Sediment Samples (ng/g)</b> |              |              |             |             |             |             |             |             |             |
|---|--------------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| <b>Sample No.</b>   | <b>1</b>     | <b>2</b>     | <b>3</b>    | <b>4</b>    | <b>5</b>    | <b>6</b>    | <b>7</b>    | <b>8</b>    | <b>9</b>    |
| <b>GC/MS</b>  | <b>0.340</b> | <b>0.262</b> | <b>1.09</b> | <b>1.23</b> | <b>1.45</b> | <b>1.80</b> | <b>2.75</b> | <b>3.25</b> | <b>5.30</b> |
| <b>LC/MS/MS</b>   | <b>0.347</b> | <b>0.163</b> | <b>1.93</b> | <b>1.25</b> | <b>0.77</b> | <b>1.21</b> | <b>2.28</b> | <b>2.63</b> | <b>3.65</b> |
| <b>% Mean Difference</b>  | <b>0.99</b>  | <b>23.3</b>  | <b>27.8</b> | <b>1.06</b> | <b>30.3</b> | <b>19.5</b> | <b>9.34</b> | <b>10.6</b> | <b>18.4</b> |

Figure 1.

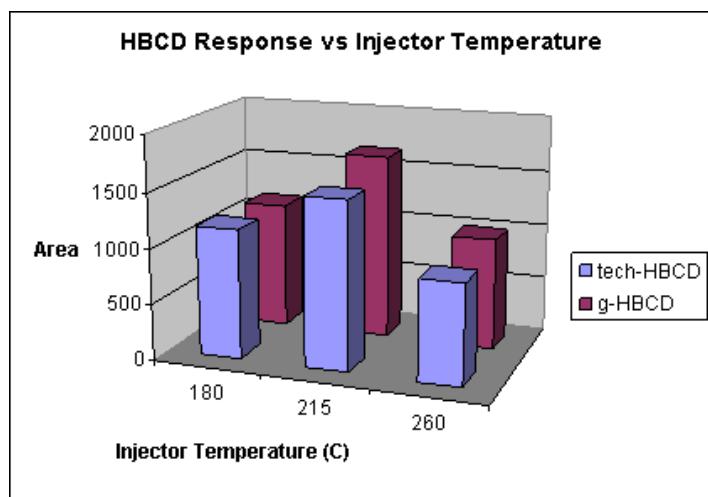
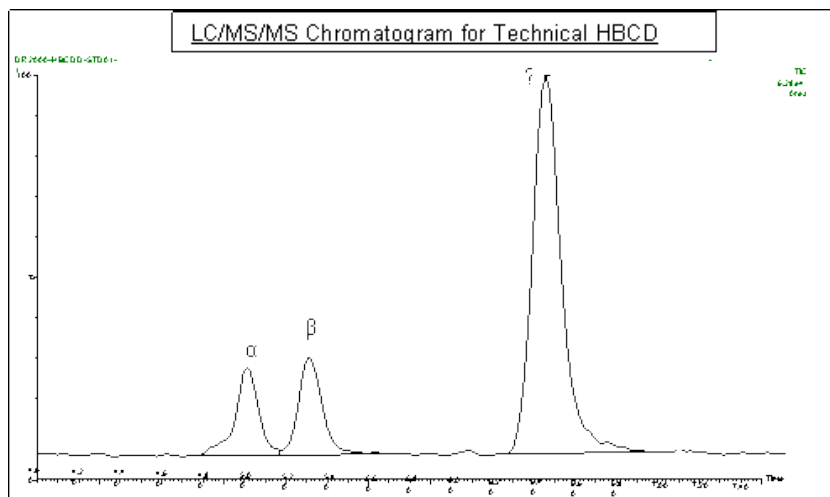


Figure 2.



## References

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