

## DETERMINATION OF HIGH MOLECULAR WEIGHT PBDE BY ISOTOPIC DILUTION IN ECNI-MS

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as additive flame-retardants in different types of appliances<sup>1</sup>. The increasing number of reports on the occurrence of PBDE in various environmental compartments such as air, sediment and biota raise concern about these compounds as global environmental contaminants<sup>2</sup>. In recent years the use of the technical decaBDE mixture, which contains up to about 98 % BDE-209, has increased, most likely due to pending regulations concerning the industrial use of PBDEs with a lower degree of bromination<sup>2</sup>. However, in an interlaboratory study by de Boer *et al.* it was concluded that the determination of BDE-209, decabromodiphenyl ether, is not under control for many of the laboratories<sup>3</sup>.

The separation and detection of PBDE is most commonly performed using gas chromatography (GC) with mass spectrometric detection (MS)<sup>4</sup>. High resolution MS (HRMS) operated in electron ionization (EI) mode offers a good sensitivity and the possibility to use <sup>13</sup>C-labeled standards for an accurate and precise determination of the BDE congeners utilizing isotopic dilution<sup>5</sup>. For low resolution MS (LRMS) the most sensitive operational mode is electron capture negative ion (ECNI) monitoring the [<sup>79</sup>Br] and [<sup>81</sup>Br] fragments. Generally this mode provides little structural information about the compounds compared to EI<sup>6</sup>. In this paper we propose <sup>13</sup>C-labeled BDE-209 as an internal surrogate standard and its application for quantification by isotopic dilution in LRMS ECNI.

### Materials and Methods

A PBDE standard mixture was prepared by dissolving individual BDE congeners in Supra Solve toluene. <sup>13</sup>C-labeled BDE 209 of 99 % purity was purchased from Cambridge Isotope Laboratories. The technical octa-mixture Bromkal 79-8 DE was used for study of the high molecular weight BDE congeners. Individual BDE congeners 196, 197, 206 and 207 (kind gift from Wellington Laboratories, USA) were used for identification of the high molecular weights BDE-congeners.

A GC/MS system designed for large volume injection and fast GC separation was used. A loop type injector enabled an injection volume of 200 µL by concurrent solvent evaporation<sup>7</sup>. The GC was an HP 5890 (Agilent Technologies), equipped with a column system consisting of a retention gap, a pre-column and an analytical column (DB-1 MS, 12 m, Ø = 0.25 mm, d<sub>f</sub> = 0.1 µm, J & W Scientific) connected in series. Total GC runtime was 13 min using a temperature program with an initial temperature of 97 °C held for 2.5 min, a linear temperature ramp of 45 °C/min to 190 °C and a second ramp of 25 °C/min to 325 °C that was held for 3 min. A Finnigan MAT TSQ 7000 mass spectrometer (ThermoFinnigan) was used for detection in ECNI mode. An electron energy of -175 eV was used for ionization of the methane buffer gas at a pressure of 1.2 kPa. Full scan mass spectra were obtained by scanning from m/z 75 to 970 with a scan time of 0.40 s. Air samples were collected in an electronics dismantling facility and prepared according to previously published work<sup>8</sup>.

### Results and Discussion

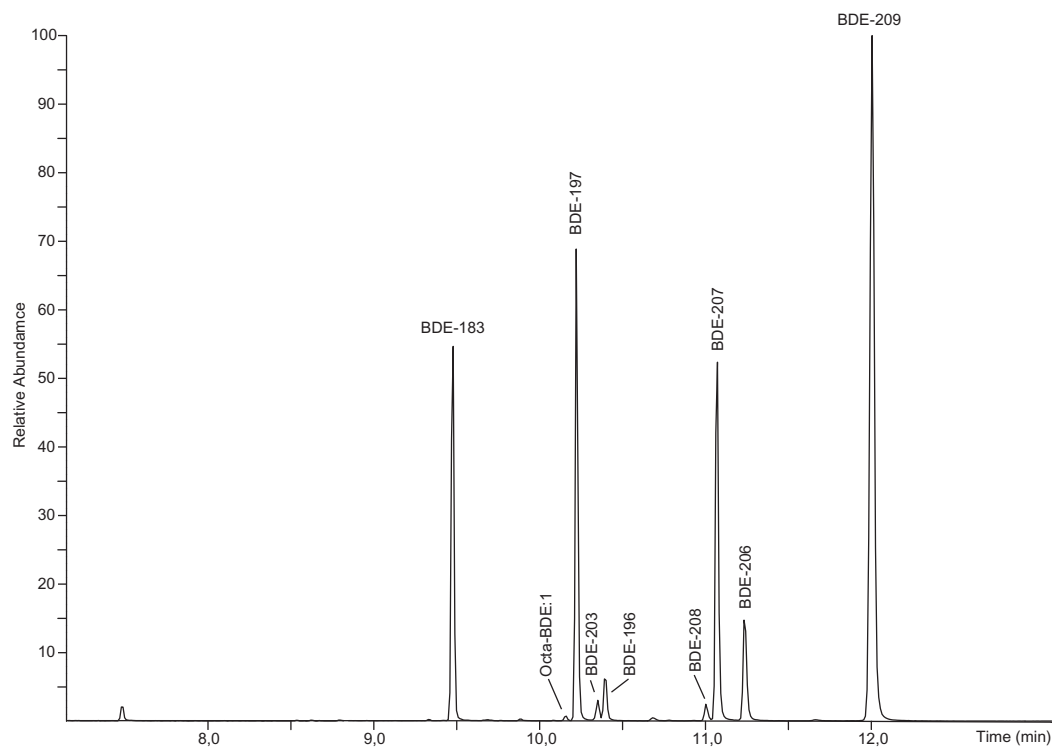
Figure 1 shows an ECNI fullscan of a technical octaBDE product (Bromkal 79-8DE) containing one hepta-BDE, 4 octa-BDE, the three nona-BDE and deca-BDE. A thorough investigation of the mass spectra of these compounds shows that the fragmentation depends on the structure. An important

observation is that the high molecular weight BDE congeners have a different fragmentation pattern compared to low molecular weight BDE-congeners. The mass spectrum of BDE-209 is shown in Figure 2. In contrast to the low molecular weight BDE-congeners where the [Br]<sup>-</sup> isotopes at m/z 79 and 81 are the dominating fragments, there are two large fragments at m/z 482 and 404 corresponding to the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> and [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> fragments respectively. These are formed by cleavage of the oxygen-carbon bond of the ether bridge and loss of a bromine. The [Br]<sup>-</sup> isotopes at m/z 79 and 81 respectively, is the second largest fragment. A trace of the molecular ion is also visible together with fragments corresponding to the loss on 1 to 5 bromines. The two first eluting nona-BDEs also exhibit this type of fragmentation. For BDE-208 the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> fragment is about 75 % and the [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> fragment about 35% of the [Br]<sup>-</sup> fragment. For BDE-207 the corresponding values are 80% and 55%, respectively. The last eluting, BDE-206, shows a different fragmentation pattern with the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> fragment being only about 10 % of the bromine ions and the [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> about 3%. The two first eluting octa-BDEs also show a high molecular weight fragment at m/z 404 corresponding to the [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> fragment, with about 70% and 74% of the [Br]<sup>-</sup> fragments for octa-BDE:1 and BDE-197 respectively. For BDE-203 the intensity is less than 1% for the [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> fragment compared to the [Br]<sup>-</sup> fragment and for BDE-196 it is about 3%. The only hepta-BDE (BDE-183) present in the mixture showed no fragment caused by cleavage of the ether bond. The second largest fragment, with an abundance of about 20% of the [Br]<sup>-</sup> fragment for BDE-183, is [M-2Br]<sup>-</sup>. The ECNI mass spectra of <sup>13</sup>C-labeled BDE-209 is similar to the native BDE-209 but at 6 Da higher m/z value for the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> (m/z 488) and [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup> (m/z 410) fragments respectively. Since there is an overlap in the isotopic pattern between the labelled and the native BDE-209 the selected ion monitoring (SIM) range has to be carefully selected to avoid erroneous quantification. The result from the quantification of PBDE in the air sample using a <sup>13</sup>C-labelled BDE-209 and SIM mode monitoring the [Br]<sup>-</sup>, [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> and [<sup>13</sup>C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> is presented in table 2. The different chromatograms in figure 3 show the response for different m/z monitored for selected BDE-congeners in the air sample. The signal to noise ratio for different fragments for the PBDE congeners in the Bromkal 79-8DE mixture together with the S/N values from the air sample is presented in table 1. From this table it is clear that the use of these mass fragments will significantly increase the sensitivity of the detection for some of these high molecular weight BDE-congeners. As an example the s/n ratio is increased about 19 times when monitoring the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> fragment compared to monitoring the [Br]<sup>-</sup> ion in the technical mixture and about 8 times higher in the air sample for BDE-209.

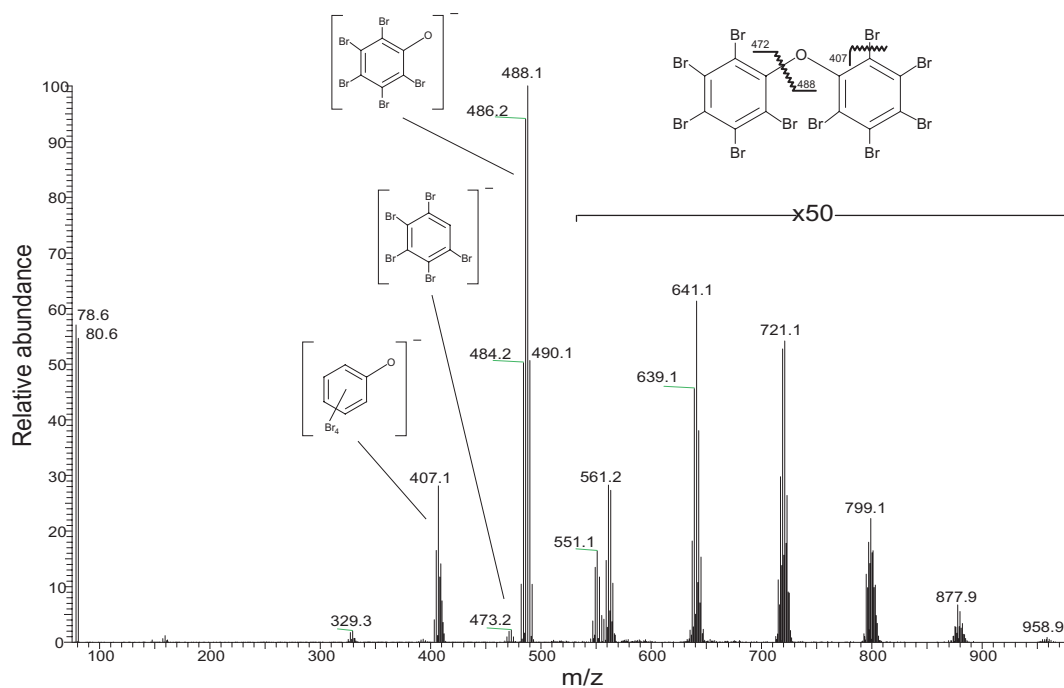
The fragmentation of the high molecular weight BDE-congeners significantly differs from that of the low molecular weight congeners. For BDE-congeners which yields high mass fragments such as the [C<sub>6</sub>Br<sub>5</sub>O]<sup>-</sup> and [C<sub>6</sub>Br<sub>4</sub>O]<sup>-</sup>, it is possible to use <sup>13</sup>C-labeled standards and thus overcoming one of the major drawbacks with the commonly used ECNI method. More structural information and a greater specificity is also provided for these compounds when monitoring the high m/z range fragments compared to the traditional mode of ECNI monitoring of the bromine ions. Further, at higher m/z ranges the chemical noise level is lower, providing better S/N values.

Congener \ Fragment	S/N in an air sample			S/N in Bromkal 79-8DE		
	Br <sup>-</sup>	C <sub>6</sub> Br <sub>4</sub> O <sup>-</sup>	C <sub>6</sub> Br <sub>5</sub> O <sup>-</sup>	Br <sup>-</sup>	C <sub>6</sub> Br <sub>4</sub> O <sup>-</sup>	C <sub>6</sub> Br <sub>5</sub> O <sup>-</sup>
Octa-BDE:1	<i>n.d</i>	46	<i>n.d</i>	22	202	<i>n.d</i>
BDE-197	166	1465	<i>n.d</i>	1455	33001	59
BDE-203	111	<i>n.d</i>	10	204	28	18
BDE-196	85	44	<i>n.d</i>	417	296	10
BDE-208	<i>n.d</i>	18	24	69	311	401
BDE-207	74	317	461	1297	9624	8453
BDE-206	19	7	16	910	355	747
BDE-209	130	246	1047	1434	8815	27552

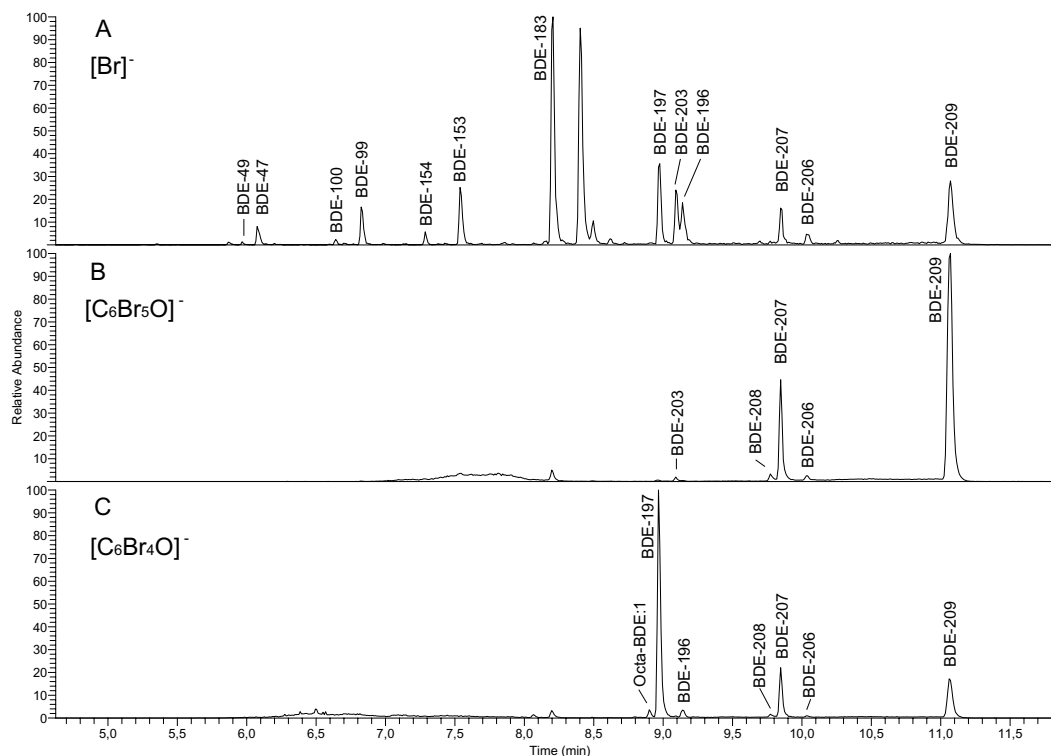
**Table 1:** The signal to noise (S/N) ratio for different fragments



**Figure 1:** Chromatogram of the technical mixture Bromkal 78-9 DE obtained by fullscan ECNI.



**Figure 2:** ECNI mass spectra of BDE-209



**Figure 3:** Ion trace chromatograms of an air sample from an electronics dismantling facility.

BDE congener	2	3	7	13	17	49	47	100	99	154	153	183	190	203	209
ng/m <sup>3</sup>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.12	1.03	0.15	0.98	0.32	1.29	4.64	<i>n.d.</i>	0.59	14.8

**Table 2:** Levels of the PBDEs found in an air sample from an electronics dismantling facility.

### Acknowledgements

Dr Brock G. Chittim and Dr Gilles Arsenault (Wellington Laboratories INC, USA) for kind gift of individual high molecular weight BDE congeners.

### References

1. WHO/IPCS, Environmental Health Criteria 162, Brominated Diphenyl Ethers. 1994.
2. de Wit C.A. (2002) Chemosphere 46, 583.
3. de Boer, J. and W. Cofino, P. (2002) Chemosphere 46, 625.
4. Thomsen C., Haug L.S., Lundanes E., G. Becher G., and Lindström G. (2000) Organohalogen Compd. 47, 194.
5. Alaei M., Sergeant D.B., Ikonomou M.G. and Luross J.M. (2001) Chemosphere 44, 1489.
6. Eljarrat, E., S. Lacorte, and D. Barcelo, (2002) J. Mass Spectrom. 37, 76.
7. Grob, K., On-Line Coupled LC-GC. Chromatographic methods, 1991, Heidelberg: Hutig.
8. Tollbäck, P., Björklund J., and Östman C., (2003) J. Chrom. A, 991, 241.