

## INNOVATIVE APPROACH FOR THE ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) BY QUADRUPOLE ION-TRAP MASS SPECTROMETRY

David Larrazábal, , María Ángeles Martínez, Begoña Fabrellas

*Fóssil Fuels Department, C.I.E.M.A.T., Avda. Complutense 22, 28040 Madrid, Spain.*

### **Introduction**

Fire has been a major cause of property damage and death throughout recorded history. During several past decades, modern technology has responded to this challenge by introducing heat-resistant chemicals to reduce risk of ignition and burning in a wide range of textile, plastic and building materials, as well as in electronic equipments used in commerce and households. Brominated flame retardants comprise approximately 25% of the volume of flame retardants used on a global scale, and are used in materials such as resins requiring highly flame-retardant response<sup>1</sup>. Some of them are additives mixed into polymers, not chemically bounded to the plastic or textile material, and therefore may separate or leach from the surface of such products into the environment. In particular, polybrominated diphenyl ethers (PBDEs) are believed to be slowly released over the product lifetime and incorporated into the food chain.

Considering the mounting evidence that PBDEs are air-transported in a similar way as chlorinated dioxins and furans, show lipophilic nature and have some structural similarities to PCBs and PCDD/Fs, polybrominated diphenyl ethers are emerging environmental contaminants whose persistence and/or potential for bioaccumulation cause large concern<sup>2</sup>.

In most analytical methods for brominated organic compounds, the purified extract is analysed by negative chemical ionisation mass spectrometry or high-resolution gas chromatography-mass spectrometry (HRGC-MS)<sup>3</sup>. Nevertheless, present paper reports analytical results based on an alternative technique using a gas chromatography-quadrupole ion trap mass spectrometry tandem system. Such option is presented as a low cost alternative for evaluating the presence of brominated persistent organic pollutants in different matrices.

### **Methods and materials**

All experiments were carried out using a calibration solution set BDE-CVS-A Brominated Diphenyl Ether HRMS (Wellington Laboratories, Ontario, Canada) comprising five individual solutions each containing 20 individual native brominated diphenyl ethers (Mono-BDE 3, Di-BDEs 7 and 15, Tri-BDEs 17 and 28, Tetra-BDEs 47, 49, 66, 71 and 77, Penta-BDEs 85, 99, 100, 119 and 126, Hexa-BDEs 148, 153 and 154, Hepta-BDE 183 and Deca-BDE 209) and 9 selected <sup>13</sup>C<sub>12</sub>-labelled PBDEs (Mono-[<sup>13</sup>C<sub>12</sub>]-BDE 3L, Di-[<sup>13</sup>C<sub>12</sub>]-BDE 15L, Tri-[<sup>13</sup>C<sub>12</sub>]-BDE 28L, Tetra-[<sup>13</sup>C<sub>12</sub>]-BDE 47L, Penta-[<sup>13</sup>C<sub>12</sub>]-BDE 99L, Hexa-[<sup>13</sup>C<sub>12</sub>]-BDEs 153L and 154L and Hepta-[<sup>13</sup>C<sub>12</sub>]-BDE 183L). All compounds were in nonane at concentrations of 1,0-400 ng/mL for native and 100 ng/mL for labelled congeners.

### **Instrumental**

A Varian Saturn 2000 GC/MS/MS device comprising of CP-3800 Gas Chromatograph coupled to a 2000 Ion-Trap Tandem Mass Spectrometer, 1079 Programmable Injector and CP-8200

Autosampler (Varian, Walnut Creek, CA, USA) was used as analytical toolkit. Software version 5.51 was employed. Splitless injection mode was adopted (Initially On, then Off for 0.01 min., and finally On again; Split Ratio: 60 ml/min), so that samples entered a high performance fused-silica capillary column Factor Four (30 m., 0.25 mm. of ID., 0.25  $\mu$ m film thickness) (Varian, Walnut Creek, CA, USA) with the following temperature programme: 90° C (hold 2 min.), then 90-145° C at 30° C/min., and finally 145-300° C (hold 1 min.) at 2° C/min., for a total time of analysis of 82 min. Injector was kept at a temperature of 325° C throughout the analysis. Samples were injected (upper and lower air gap) into the column using helium as carrying gas (constant flow rate of 1 ml/min.). During the analysis, temperatures of the transfer line and manifold were maintained at 280° and 250° C, respectively.

### **Results and discussion**

Optimisation of method parameters for the analysis of selected PBDEs was made according to the mode of operation of MS/MS theory: ionisation, ion isolation, fragmentation by collision-induced dissociation (CID) and ion detection<sup>4</sup>.

#### *Ionisation*

Since parent ions experience impacts with electrons of 70 eV within the ion-trap cavity, ionisation of molecular ions is produced. Electron impact analysis in scan mode allows both selecting most abundant parent ions for each congener as well as showing their characteristic patterns of fragmentation. Excepting for mono-BDE in which two characteristic losses were noticed, [M-Br] and [M-CO], and di-BDE wherein [M-Br<sub>2</sub>] and [M-COBr] seemed to be the most intense signals (similar losses of M-COCl have been widely reported for polychlorinated compounds such as dioxins and furans<sup>5</sup>), fragmentation pattern was dominated in all cases by loss of two bromine atoms, [M-Br<sub>2</sub>]. Despite this is more likely to occur as degree of bromination increases, no subsequent losses of three, four, five,.. bromine atoms were significantly observed. In addition, such characteristic loss did not occur for 3,3',4,4'-Tetra-BDE 77 and 3,3',4,4',5-Penta-BDE 126, being a possible explanation to such behaviour the presence of two pairs of bromine atoms in *ortho*-position (3,3',4,4'-), which would confer more planarity and stability to the molecule. It is also important to state that no signal was observed for deca-brominated congener during time of analysis, what may suggest its decomposition at high temperatures as has been largely pointed by some authors in literature<sup>6</sup>.

#### *Ion Isolation*

Application of different radiofrequency voltages to the ion-trap electrodes allows both selective ejection of non-desired ions and confinement of parent clusters of interest to be subsequently subjected to fragmentation. Since operational parameters of the device limits isolation of ions to those with mass to charge ratios below 650 m/z units, trapping of parent ions for [<sup>13</sup>C<sub>12</sub>]-hexa- (656 m/z) and hepta-brominated congeners (native and labelled, 724 and 736 m/z respectively) was not afforded. Therefore, isolation of the product ion [M-Br<sub>2</sub>] was selected for those groups of homologues. Table 1 shows optimised values (q = 0.4) for Excitation Storage Level (ESL), parameter responsible for confinement of ions within the ion-trap cavity.

#### *Fragmentation*

Fragmentation occurs by collision-induced dissociation (CID) between trapped ions and helium molecules and depends on type of collision (resonant/non resonant mode) as well as on energy of such collisions (excitation amplitude). Non-resonant excitation mode was adopted because, in contrast to resonant, this is more useful with cluster ions wherein fragmentation takes place by

rupture of single bonds (such as C-Br for PBDEs), with no significant re-arrangements within the molecule after breaking. Energy of collision was optimised employing the Automated Software Development (AMD) toolkit, which allows firstly a rough and then a fine adjustment of the excitation amplitude. Excitation amplitude increases with number of ions stored in the trap and consequently with ESL value. In non-resonant mode only values of excitation amplitude below 100 v are permitted by software, what explains differences between optimised ESL value and the corresponding obtained when using the “q calculator” automated ESL calculation toolkit. Optimised values of excitation amplitude for each congener are shown in Table 1.

**Table 1:** MS/MS parameters for the analysis of mono- to heptabrominated diphenyl ethers.

Compound	Ret. Time (min.)	Parent ion (m/z)	Product Ion (m/z)	ESL (m/z)	EA (v)
4-MonoBDE (3)	15.429	260	179/181	114	98
4-Mono[ <sup>13</sup> C <sub>12</sub> ]-BDE (3L)	15.457	248	167/169	110	96
2,4-DiBDE (7)	24.280	328	166/168/170	105	68
4,4'-Di[ <sup>13</sup> C <sub>12</sub> ]-BDE (15L)	27.307	340	178/180/182	105	92
4,4'-DiBDE (15)	27.343	328	166/168/170	105	96
2,2',4'-TriBDE (17)	35.570	406	244/246/248	125	85
2,4,4'-Tri[ <sup>13</sup> C <sub>12</sub> ]-BDE (28L)	37.210	418	256/258/260	125	90
2,4,4'-TriBDE (28)	37.254	406	244/246/248	125	90
2,3',4',6'-TetraBDE (71)	45.542	486	324/326/328	115	74
2,2',4,5'-TetraBDE (49)	45.884	486	324/326/328	115	74
2,2',4,4'-Tetra[ <sup>13</sup> C <sub>12</sub> ]-BDE (47L)	47.008	498	336/338/340	125	86
2,2',4,4'-TetraBDE (47)	47.047	486	324/326/328	115	80
2,3',4,4'-TetraBDE (66)	48.626	486	324/326/328	115	74
3,3',4,4'-TetraBDE (77)	50.974	486	324/326/328	115	(a)
2,2',4,4',6'-PentaBDE (100)	54.145	564	402/404/406	125	88
2,3',4,4',6'-PentaBDE (119)	55.126	564	402/404/406	125	79
2,2',4,4',5'-Penta[ <sup>13</sup> C <sub>12</sub> ]-BDE (99L)	56.460	576	414/416/418	125	83
2,2',4,4',5'-PentaBDE (99)	56.497	564	402/404/406	125	83
2,2',3,4,4'-PentaBDE (85)	60.210	564	402/404/406	125	82
3,3',4,4',5'-PentaBDE (126)	61.189	564	402/404/406	125	(a)
2,2',4,4',5,6'-Hexa[ <sup>13</sup> C <sub>12</sub> ]-BDE (154L)	62.016	656	494/496/498	100	(b)
2,2',4,4',5,6'-HexaBDE (154)	62.068	644	482/484/486	100	(b)
2,2',4,4',5,5'-Hexa[ <sup>13</sup> C <sub>12</sub> ]BDE (153L)	65.100	656	494/496/498	100	(b)
2,2',4,4',5,5'-HexaBDE (153)	65.127	644	482/484/486	100	(b)
2,2',3,4,4',6'-Hexa[ <sup>13</sup> C <sub>12</sub> ]BDE (139L)	65.976	656	494/496/498	100	(b)
2,2',3,4,4',5'-HexaBDE (138)	68.858	644	482/484/486	100	(b)
2,2',3,4,4',5',6'-Hepta[ <sup>13</sup> C <sub>12</sub> ]-BDE (183L)	73.008	736	574/576/578	100	(b)
2,2',3,4,4',5',6'-HeptaBDE (183)	73.035	724	562/564/566	125	(b)

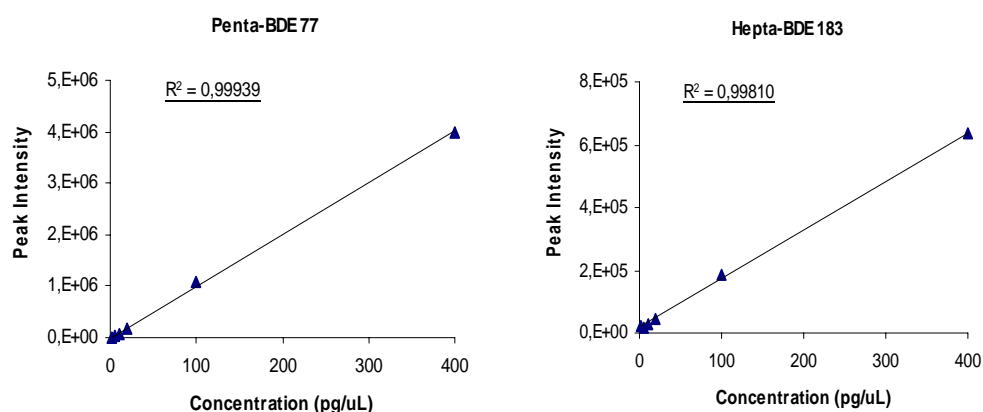
(a) Fragmentation is not noticed. (b) Only first fragmentation was observed (loss of two bromine atoms). No subsequent loss of bromine occurred.

#### Detection

After formation of ions by collision-induced dissociation, a ramp of radiofrequency along with the axial modulation field are used for sequential screening of such ions in the electromultiplier, thereby generating their characteristic mass spectra. In the MS/MS mode of analysis, a target TIC value (total ion count) of 2.000 was selected in order to minimise charge-space effects. Masses monitored in each case corresponded to  $[M-Br]^+$  for mono-BDEs and  $[M-Br_2]^+$  for di- to hepta-

BDEs (see Table 1). Confirmation criteria for identification and quantification of PBDEs included simultaneous presence of all  $m/z$  monitored within  $\pm 1$  second, with signal-to-noise ratio  $> 3$ .

Once method parameters were optimised, calibration lines in the range of 1-400  $\mu\text{g}/\mu\text{L}$  were obtained for each of the 20 native polibrominated diphenyl ethers, excepting for deca-BDE 209. Good linearity was observed in all cases, with correlation coefficient values ranging from 0.99810 for Hepta-BDE 183 to 0.99981 for Di-BDE 7. Two examples of calibration lines for Tetra-BDE 77 and Hepta-BDE 183 are illustrated in Figure 1.



**Figure 1:** Calibration lines for Penta-BDE 77 and Hepta-BDE 183.

### Conclusions

A novel analytical methodology for qualitative and quantitative determination of polibrominated diphenyl ethers has been developed. Although performance of High Resolution Gas Chromatography-Quadrupole Ion-Trap Mass Spectrometry seems to be appropriated for this kind of analysis, further work should be done in terms of limits of detection, repeatability and accuracy of the method. However, next stages of research will be focused both on the analysis of real samples and assessment of possible matrix effects.

### References

1. Wenning, R.J.; (2002) *Chemosphere* 46, 779.
2. WHO 1997. Flame retardants: A general Introduction. IPCS, Environmental Health Criteria 192. WHO, Geneva.
3. Alaei, M.; Sergeant, D.B.; Ikononou M.G. and Luross, J.M.; (2001) *Chemosphere* 44: 1489-1495.
4. Plomley, J.B.; Lausevic, M. and March, R.E.; (2000) *Mass Spectrometry Reviews*, 19: 305-365.
5. Chess, E.K. and Gross, M.L.; (1987). *Analytical Chemistry*, 52: 2057-2061.
6. Eljarrat, E.; Lacorte, S. and Barceló, D.; (2002) *J. Of Mass Spectrometry*, 37: 76-84.