Application Note: 30098

DFS - Analysis of Brominated Flame Retardants with High Resolution GC/MS

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Key Words

- Flame Retardants (PBDE)
- HRGC / HRMS
- Multiple Ion Detection (MID)
- Persistant Organic Pollutants (POPs)
- RoHS / WEEE

Introduction

Polybrominated diphenyl ethers (PBDEs) are among the most important and widely used flame retardants in a variety of different industrial products. They are found worldwide in matrices, moving them into the focus of recent legislation banning certain PBDE congeners[1]. EU directive 2003/11/EC prohibits the use of Penta-BDE and Octa-BDE for the member states of the European community[2].

As a result analysis of PBDEs have received increased interest due to their known toxicity. Similar to dioxins/furans and PCB's (polychlorinated biphenyls) polybrominated diphenyl ethers exist in a higher number of congeners (209) (Figure 1).

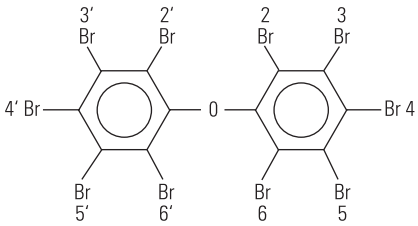

Figure 1: PBDE chemical structure, here Deca-BDE.

The most efficient analysis technique by far for these three application areas is high resolution GC/MS using isotope dilution technique for quantitation with highest precision and significance.

Experimental Conditions

All measurements were carried out on the Thermo Scientific DFS high resolution GC/MS coupled to a Thermo Scientific TRACE GC Ultra™ gas chromatograph equipped with a split/splitless injector (Figure 2).

Samples were injected using the Thermo Scientific TriPlus™ autosampler. The injection volume was 1 µL of each sample measured. A Thermo Scientific TRACE TR-5MS GC column with the following dimensions was used for gas chromatographic separation of the injected compound:
15 m, 0.25 mm ID, 0.1 µm film thickness.
The temperature program applied is given in Table 1.

GC PARAMETERS	
Injector temperature	280 °C
Splitless time	1.5 min
Purge flow	50 mL/min
Column type	Thermo Scientific TRACE TR-5MS 15 m x 0.25 mm (0.1 µm)
Carrier gas flow rate	1 mL/min
Oven temperature program	120 °C (2 min)
	15 °C/min - 230 °C
	5 °C/min - 270 °C
	10 °C/min - 330 °C (5 min)
Transfer line temperature	280 °C

Table 1: GC parameters.

Figure 2: Thermo Scientific DFS - High Resolution GC/MS with two TRACE GC Ultra™ and TriPlus™ Autosampler.

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The mass spectrometric resolution applied was 1,000 (10 % valley definition) for spectrum acquisition and 10,000 for quantitation and confirmation, see Table 2.

MS TUNING PARAMETERS	
Ionization mode	EI positive
Electron energy	40 eV
Source temperature	270 °C
Resolution	10,000 (10 % valley)

Table 2: MS tuning parameters.

Preliminary GC/MS scan experiments were carried out to get specific mass spectra of the different brominated congeners to identify the most intensive mass peaks. These experiments were carried out at a resolution of 1,000, scan range 75 to 1,000 amu magnet scan with scan speeds of 0.5 s/dec.

For the target compound analysis method, the mass spectrometer was operated in multiple ion detection mode (MID). At resolution 10,000, the MID lock mass technique is used to assure exact and fast jumping to the target masses by varying the acceleration voltage.

PFK is used as internal mass reference. PFK provides each MID window with a specific lock and calibration mass (see Table 3).

In every single MID measurement cycle, the instrument automatically carries out an electric mass calibration taking these two reference masses as calibration points. This unique principle of high resolution MID with two reference masses in each MID window secures the highest mass precision, stability and ruggedness necessary for routine target compound analysis on a high resolution mass spectrometer. For all native PBDE congeners as well as for all 13C labeled internal PBDE standards, one quantitation mass and one ratio mass were implemented in the MID setup (see Table 3).

Standards were supplied by Wellington Laboratories and appropriately diluted in order to obtain lower concentrated solutions. For the scan experiments, standard solutions containing only native congeners are needed at concentrations in the ng/µL range. The standards used in this application did not contain Octa- and Nona-BDEs.

MID WINDOW NO.	REFERENCE MASSES (PFK)		TARGET MASSES	MID CYCLE TIME
	L = LOCK MASS	C = CALI MASS		
1 - Tri-BDE	392.9753 (L)	430.9723 (C)	(403.8041), 405.8021, 407.800, 417.8424, 419.8403	0.55 s
2 - Tetra-BDE	480.9688 (L)	492.9691 (C)	(483.7126), 485.7106, 487.7085, 495.7529, 497.7508	0.55 s
3 - Penta-BDE	554.9644 (L)	592.9627 (C)	(561.6231), 563.6211, 565.6190, 575.6613, 577.6593	0.60 s
4 - Hexa-BDE	480.9688 (L)	504.9691 (C)	(559.6082), 561.6062, 563.6042, 493.7372, 495.7352	0.60 s
5 - Hepta-BDE	554.9644 (L)	592.9627 (C)	(559.6082), 561.6062, 563.6042, 573.6457, 575.6436	0.70 s
6 - Deca-BDE	754.9531 (L)	766.9531 (C)	797.3349, 799.3329, (801.3308), 809.3752, 811.3731	0.90 s

Table 3: MID setup, MID lock mode (masses in brackets: optional second ratio mass for native PBDE).

Results

Scanning Experiments

The full scan results proved that for all bromination degrees, the molecular ion and the fragment ion showing the loss of 2Br atoms are the most abundant ions (Figure 3).

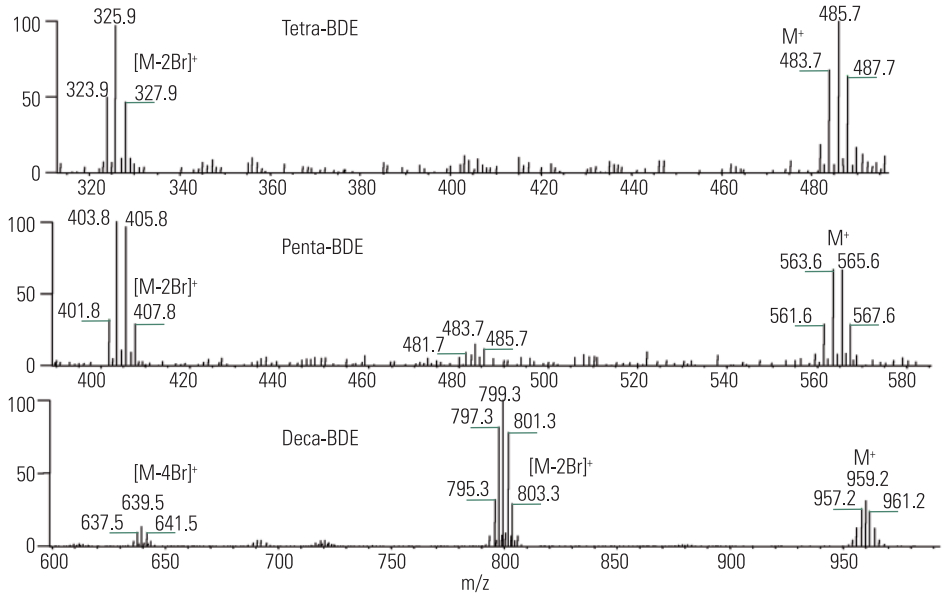

Figure 3: Full scan mass spectra allowing comparison of M^+ and $[M-2Br]^+$ isotope peak intensities.

[M]+· # BR	M		M+2		M+4		M+6		M+8		M+10		M+12		[M-2BR]
1	247.984	100	249.982	98											100
2	325.894	51	327.892	100	329.890	49									100
3	403.805	34	327.892	100	407.801	97									100
4			483.713	68	485.711	100	487.709	65							100
5			561.624	51	563.622	100	565.620	97							85
6					641.532	76	643.530	100	645.528	73					60
7					719.443	61	721.441	100	723.439	97					55
8							799.351	81	801.349	100	803.347	78			50
9							877.262	68	879.260	100	881.258	97			40
10									957.171	85	959.168	100	961.166	81	25

[M-2BR]+ # BR0	M		M+2		M+4		M+6		M+8		M+10		M+12	[M-2BR]
1														0
2														0
3														0
4	323.879	51	325.877	100	327.875	49								95
5	401.789	34	403.787	100	405.785	97								100
6			481.698	68	483.696	100	485.694	65						100
7			559.608	51	561.606	100	563.604	97						100
8					639.517	76	641.515	100	643.513	73				100
9					717.427	61	719.425	100	721.423	97				100
10							797.336	81	799.333	100	801.331	78		100

Table 4: Exact PBDE masses and relative PBDE mass intensities of $M^{+\cdot}$ versus $[M-2Br]^+$.

The change of the most intense ion from $M^{+\cdot}$ to $[M-2Br]^+$ is typically observed between Penta-BDE and Hexa-BDE. The loss of 2Br is slightly temperature dependent (GC and ion source temperatures).

Therefore, with different instrument conditions, the transition of the most abundant ion from $M^{+\cdot}$ to $[M-2Br]^+$ might be shifted to Tetra/Penta- or Hexa/Hepta-BDE.

In general, the relative intensity $[M-2Br]^+ / M^{+\cdot}$ increases with the degree of bromination. For Deca-BDE, the intensity gain when using the $[M-2Br]^+$ mass peak for MID detection is at least a factor of 4 compared to $M^{+\cdot}$.

MID Detection

Mass spectrometer tuning parameters similar to those typically used for dioxin/PCB analysis also provided optimum sensitivity for PBDE analysis. Experiments using higher or lower electron energies did not lead to any recognizable advantage.

The use of PFK as internal mass reference is mandatory, because lock and cali masses in the high mass range are needed (e.g. for Deca-BDE). Autotuning for the highest sensitivity was carried out on PFK mass 480.9688.

All congeners in the employed PBDE standard could be separated on the 15 m TRACE TR-5MS column (Figure 4). Similar to dioxins, the PBDE congeners are separated on unpolar columns by group in the order of their bromination degree. The use of a short 15 m column with a thin film is recommended to analyze the thermolabile Deca-BDE more efficiently.

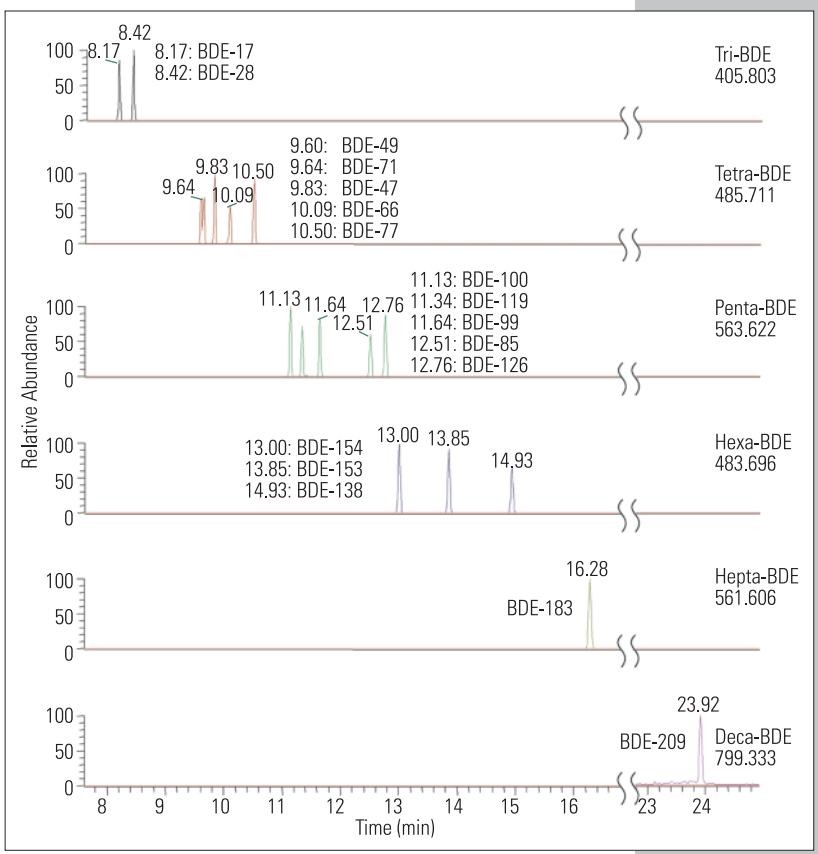

Figure 4: GC/MS mass chromatogram of a 6 window run with typical PBDE separation by bromination degree.

As shown in Figure 4, limits of quantitation (LOQs) similar to those for dioxin and PCB analysis can be achieved with the DFS for the analysis of the far higher boiling PBDEs (Figure 5). Also the quantitation linearity proved to fulfill highest standards (Figure 6).

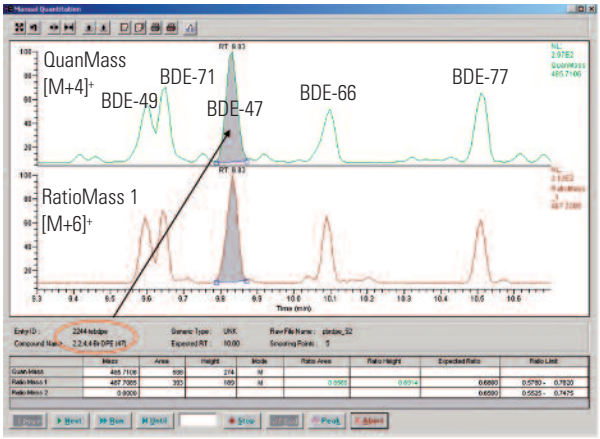

Figure 5: 25 fg Tetra-BDE; Quantitation in TargetQuan showing one quantitation and one ratio mass (PBDE-47).

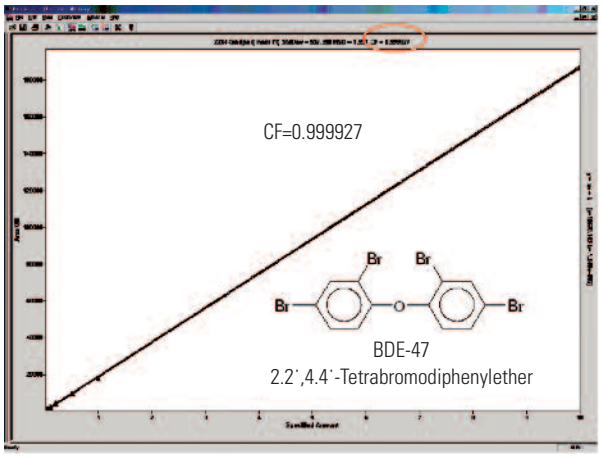

Figure 6: Linearity for PBDE-47 (25, 50, 100, 200, 500, 1000, 10000 fg/µL).

Conclusions

Using the DFS high resolution GC/MS, polybrominated diphenyl ethers (PBDE) can be analyzed with highest selectivity providing LOQs in the low femtogram range. The same analytical significance required in the analysis of dioxins and PCBs proved to be feasible for PBDEs as well. For further information please visit our website www.thermo.com/dfs.

References

[1] California Legislature Bill No. 302, Chaptered August 11, 2003

[2] European Parliament and Council Directive 2002/95/EC on the Restriction of Hazardeous Substances (RoHS). European Parliament and Council Directive 2002/96/EC on Waist Electrical and Electronic Equipment (WEEE).

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