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A STUDY OF THE ANALYSIS OF POLYBROMINATED DIPHENYL ETHER FLAME RETARDANTS BY GC/MS/MS

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Introduction

Polybrominated diphenyl ether (BDE) flame retardants having been of increasing concern to environmental analysts in recent years, making front page news[1].Current analytical techniques for BDE analysis generally involve the use of HRGC-HRMS, a costly technique requiring highly trained operators. Methods have recently been published using single quadrupole GC/MS[2,3], or GC/MS/MS (iontrap)[4].

The purpose of this study was to investigate the suitability of a GC triple-quadrupole instrument for the analysis of BDEs, monitoring compound specific fragmentation patterns with the use of multiple reaction monitoring (MRM) acquisitions.

Materials and Methods

All analyses were performed using an Agilent 6890 GC oven directly interfaced to a Waters® Quattro micro™ GC mass spectrometer. The mass spectrometer was operated in EI+ mode for all analyses. Prior to analysis, the instrument was calibrated over the mass range 50 – 1200 Da using Tris(perfluoroheptyl)-1,3,5-triazine.

GC analysis was performed on 30 m DB1-HT, 250 µm i.d., 0.1 µm film; 15 m DB1-HT, 250 µm i.d., 0.1 µm film and 20 m DB5-ms 180 µm i.d., 0.18 µm film GC columns. All injections were made in splitless mode, using a 2 mm i.d. deactivated quartz injection liner with an injector temperature of 260 °C.

The GC temperature ramps employed for all injections are as follows:

20 m DB5-ms 140 °C/ 4 mins, 20 °C/min to 220°C,
30 °C/min to 315 °C, hold 19 mins.
He flow 0.6 ml/min, constant flow mode.

15 m DB1-HT 140 °C/ 1 min, 10 °C/min to 220 °C,
20 °C/min to 320 °C, hold 3 mins.
He flow 1 ml/min, constant flow mode.

30 m DB1-HT 140 °C/ 2 mins, 5 °C/min to 220 °C,
20 °C/min to 320 °C, hold 7 mins.
He flow 1 ml/min, constant flow mode.

Standards were acquired in full scan and precursor ion mode to investigate the most suitable transitions for MRM analysis. A five-point calibration curve, covering a total (congener specific) concentration range of 1-2000 pg on column was acquired in MRM mode, followed by solvent blank (nonane), sample extracts, solvent blank (nonane) and finally the BDE-CS3-E calibration standard as a QC check.

Results and Discussion

All PBDE congeners were identified by full scan GC/MS analysis, showing as major ions the $[M]^+$ or $[M\text{-}Br_2]^+$ isotopic cluster. Figure 1 shows the full scan mass spectra for the tetra brominated BDEs #47 and Figure 2 shows the full scan mass spectra for the deca brominated BDE#209.

From the ions observed by full scan MS, the most abundant ions were selected for product ion scanning, generally one ion from the $[M]^+$ cluster and one ion from the $[M\text{-}Br2]^+$ cluster, in order to achieve maximum sensitivity, but to also provide confirmatory ions. Figure 3 depicts the product scans for BDE#47, showing the spectrum for the $[M]^+$ precursor ion.

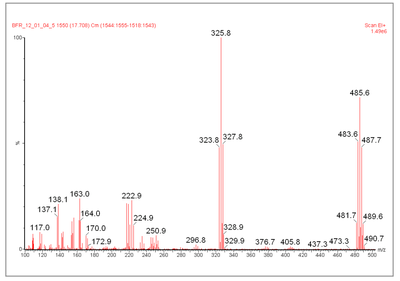

Figure 1. Full scan EI+ mass spectrum for BDE#47.

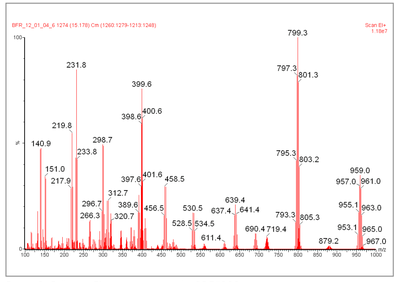

Figure 2. Full scan EI+ mass spectrum for BDE#209.

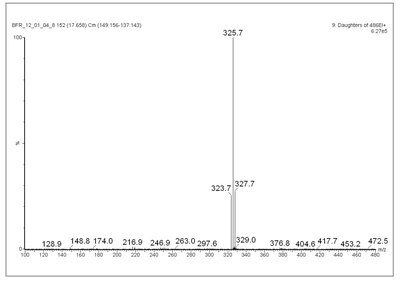

Figure 3. Product ion spectra for the precursor ion m/z 485.7 [M+].

BDE	Precursor Ion	Product ion	Collision energy(eV)
mono bromo	248 [M] 250 [M]	141[-COBr] 141[-COBr]	15 15
di bromo	327.9 [M] 168.1 [M-Br2]	168.1 [-Br2] 139 [-COH]	20 20
tri bromo	407.8 [M] 248 [M-Br2]	248 [-Br2] 139 [-COBr]	15 30
tetra bromo	485.7 [M] 325.9 [M-Br2]	325.9 [-Br2] 138 [-COBr2]	20 45
penta bromo	565.6 [M] 403.8 [M-Br2]	405.8 [-Br2] 137 [-COBr3]	25 55
hexa bromo	643.5 [M] 483.7 [M-Br2]	483.7 [-Br2] 374.8 [-COBr]	20 30
hepta bromo	723.4 [M] 563.6 [M-Br2]	563.6 [-Br2] 454.7 [-COBr]	25 30
octa bromo	801.3 [M] 641.5 [M-Br2]	641.5 [-Br2] 534.6 [-COBr]	25 30
nona bromo	881.3 [M] 719.4 [M-Br2]	719.4 [-Br2] 612.5 [-COBr]	25 35
deca bromo	959.2 [M] 799.3 [M-Br2]	799.3 [-Br2] 639.5 [-Br2]	25 45

Table 1. Optimised Precursor and product ions for mono to deca brominated diphenyl ethers.

Table 1 shows the precursor ions, product ions, and optimal collision energies for each level of bromination from mono to deca bromo BDE.

Table 2 shows the precursor ions, product ions, and optimal collision energies for each level of bromination from mono to deca bromo BDE for the $^{13}C_{12}$ labelled internal standards. The transitions and collision energies from tables 1&2 were then used to create a 10 function MRM experiment, monitoring each level of bromination in single functions. To allow for possible retention time shifts of the first and last eluting congeners of some levels of bromination, the start and end time of functions 3,4,5,6,7 (tri-bromo to hepta-bromo) were overlapped (end time of previous function after start time of current function).

13C-BDE	Precursor Ion	Product ion	Collision energy(eV)
mono bromo	260 [M] 262 [M]	152.1[-COBr] 152.1[-COBr]	15 15
di bromo	339.9 [M] 339.9 [M]	151.1 [-COBr2] 180.1 [-Br2]	20 20
tri bromo	417.8 [M] 419.8 [M]	258 [-Br2] 260 [-Br2]	15 15
tetra bromo	497.8 [M] 337.9 [M-Br2]	337.9 [-Br2] 149.1 [-COBr2]	20 45
penta bromo	575.7 [M] 415.8 [M-Br2]	415.8 [-Br2] 148.1 [-COBr3]	25 55
hexa bromo	655.6 [M] 495.7 [M-Br2]	495.7 [-Br2] 335.8 [-Br2]	20 30
hepta bromo	733.5 [M] 573.6 [M-Br2]	573.6 [-Br2] 305.7 [-COBr3]	25 55
octa bromo	813.4 [M] 653.6 [M-Br2]	653.6 [-Br2] 545.7 [-COBr]	25 30
nona bromo	891.3 [M] 731.5 [M-Br2]	731.5 [-Br2] 623.4 [-COBr]	25 30
deca bromo	969.2 [M] 811.4 [M-Br2]	809.4 [-Br2] 651.5 [-Br2]	25 50

Table 2. Optimised Precursor and product ions for mono to deca brominated diphenyl ether $^{13}C_{12}$ labelled internal standards.

The limits of detection and quantification were calculated from the calibration curves acquired on each of the three GC columns. The DB5-ms column was found to give the optimum separation of close eluting congener pairs, specifically the tetra brominated BDEs #49 and #71. However, the LOD and LOQ for the hexa-deca brominated BDEs were much higher using this column. Table 3 presents the calculated LOD values for each of the three columns for the 27 target BDE's, with all values calculated from acquiring all target peaks in a single injection.

As can be seen, the 15m DB1-HT column produced the best overall sensitivity, while maintaining a 50 % valley between BDEs #49 and #71.

Name	20m DB5-ms LOD (pg)	15m DB1-HT LOD (pg)	30m DB1-HT LOD (pg)
BDE#3	0.054	0.052	0.126
BDE#7	0.054	0.053	0.099
BDE#15	0.132	0.144	0.261
BDE#17	0.069	0.08	0.137
BDE#28	0.072	0.085	0.142
BDE#49	0.152	0.154	0.189
BDE#71	0.163	0.13	0.183
BDE#47	0.144	0.133	0.177
BDE#66	0.184	0.172	0.235
BDE#77	0.696	0.587	0.771
BDE#100	0.364	0.255	0.189
BDE#119	0.41	0.248	0.198
BDE#99	0.348	0.252	0.2
BDE#85	0.919	0.582	0.459
BDE#126	3.093	1.984	1.607
BDE#154	0.686	0.349	0.316
BDE#153	0.912	0.376	0.436
BDE#138	1.352	0.534	0.494
BDE#156	2.115	0.727	0.64
BDE#184	1.141	0.394	0.439
BDE#183	1.271	0.425	0.495
BDE#191	2.129	0.563	0.706
BDE#197	1.902	0.801	1.43
BDE#196	3.275	0.974	1.885
BDE#207	5.607	1.259	4.928
BDE#206	18.243	2.082	9.711
BDE#209	53.539	1.594	11.088

Table 3. Comparison of LODs in pg injected for the three GC columns employed.

Matrix	GC-MSMS (ng/g)	HRGC-HRMS (ng/g)
Liquid stabilised biosolid	482	530
Liquid stabilised biosolid	311	350
dewatered biosolid	435	490
Fish tissue	8.81	8.8
Freeze dried fish tissue	139	150

Table 4. Determined concentrations of BDE #47 in a variety of environmental matrices.

Figure 4 shows the chromatograms for tetra-bromo BDE #47 in a freeze-dried fish tissue extract, at a level of 150ng/g dry weight. BDE #47 was detected in all of the samples at relatively high levels. The determined levels of the PBDEs were in good agreement with values obtained using high resolution GC-MS. Table 4 presents a comparison of the determined concentrations for BDE #47 in five sample extracts, quantified against the $^{13}C_{12}$ labelled BDE #47 internal standard.

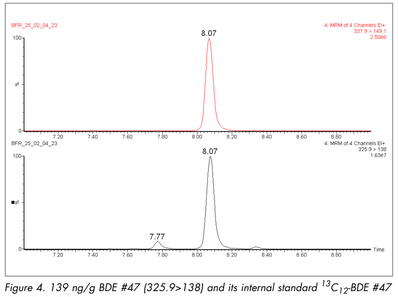

Figure 4. 139 ng/g BDE #47 (325.9>138) and its internal standard $^{13}C_{12}$-BDE #47 (337.9>149.1) in a fish tissue extract.

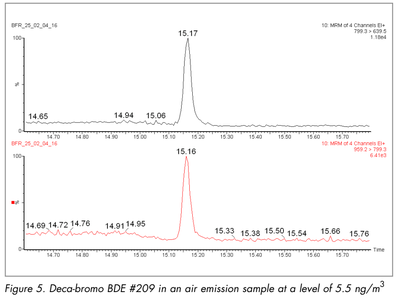

Figure 5. Deca-bromo BDE #209 in an air emission sample at a level of 5.5 ng/m^3

Figure 5 shows the chromatograms for the quantification ion (799.3>639.5 transition) and confirmation ion (959.2>799.3 transition) for deca-brom BDE #209 in an air emission sample, at a level of 5.5 ng/m^3.

At the end of each acquisition sequence, the midpoint calibration standard BDE-CS3-E was injected, with its response compared with the five point calibration curve at the beginning of the sequence. Table 5 presents the results for analysis using the 15 m DB1-HT column, for the calibration curve (mean RRF and RRF percentage relative standard deviation), and the QC standard injection (percentage concentration deviation).

As can be seen, the calibration %RSD values are all <15 %, and the response deviations are all <10 %, showing the excellent linearity and stability of response offered by a triple quadrupole mass spectrometer.

Name	RRF Mean	%RSD	Daily check % deviation
BDE#3	0.98	2.7	-1
BDE#7	3.2	1.9	3.9
BDE#15	1.18	3.2	1.3
BDE#17	1.32	4.6	6.3
BDE#28	1.25	3.9	2.9
BDE#49	0.96	1.3	-6.2
BDE#71	1.14	1.9	9.6
BDE#47	1.11	1.6	2.3
BDE#66	0.86	1.7	-1.8
BDE#77	0.25	4.1	-9.2
BDE#100	1.03	3.7	0.9
BDE#119	1.06	2.4	4.2
BDE#99	1.04	6.5	-3.6
BDE#85	0.45	2.9	-3.1
BDE#126	0.13	4	-6.5
BDE#154	1.01	4.1	4
BDE#153	0.83	1.6	-1.6
BDE#138	0.66	7.5	-6.4
BDE#156	0.48	10.3	-9.9
BDE#184	0.91	2.2	2.2
BDE#183	0.85	3.3	1.8
BDE#191	0.64	3	-6.1
BDE#197	0.96	4.7	-1.4
BDE#196	0.79	6.6	-9.3
BDE#207	0.76	3.6	-2.5
BDE#206	0.46	13.7	-4.2
BDE#209	1.22	1.9	1.5

Table 5. Calibration curve and calibration check standard results, using the 15 m DB1-HT GC column.

Conclusions

GC triple quadrupole MS provides a sensitive and easy to apply method for the analysis of brominated diphenyl ether flame retardants, offering a rapid analysis time while providing suitable confirmation of analyte presence. The fragmentation of PBDEs in the collision cell allows specific MRM transitions to be monitored for each level of bromination, giving a high degree of selectivity. The use of a 15 m DB1-HT GC column allowed good LOD/LOQ values to be obtained for all target peaks, at the expense of poorer separation of some congener pairs. The optimum method for the quantification of mono-deca brominated PBDEs would be the use of a 15 m DB1-HT column for hepta-deca brominated congeners, and a DB5-ms column for the determination of mono-hexa brominated PBDEs.

References

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