A study of the analysis of polybrominated diphenyl ether flame retardants by GC-MSMS

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Introduction

Polybrominated diphenyl ether (BDE) flame retardants having been of increasing concern to environmental analysts in recent years and has made 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-MSMS (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 peformed 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.
GC analysis was performed on 30m DB1-HT, 250µm i.d., 0.1µm film; 15m DB1-HT, 250µm i.d., 0.1µm film and 20m DB5-ms 180µm i.d., 0.18µm film GC columns. All injections were made in splitless mode, using a 2mm i.d. deactivated quartz injection liner with an injector temperature of 260°C.
The GC temperature ramps employed for all injections are as follows:-
20m DB5-ms 140°C/4mins, 20°C/min to 220°C, 30°C/min to 315°C, hold 19mins. He flow 0.6ml/min, constant flow mode.
15m DB1-HT 140°C/1min, 10°C/min to 220°C, 20°C/min to 320°C, hold 3mins. He flow 1ml/min, constant flow mode.
30m DB1-HT 140°C/2mins, 5°C/min to 220°C, 20°C/min to 320°C, hold 7mins. He flow 1ml/min, constant flow mode.
Prior to analysis, the instrument was calibrated over the mass range 50 – 1200 Da using Tris(perfluoroheptyl)-1,3,5-triazine.

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 1-2000pg 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.
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 $[M\text{-}Br_2]^+$ cluster, in order to achieve maximum sensitivity, but to also provide confirmatory ions. Figure 1 depicts the product scan for BDE#47, showing the spectra for the $[M]^+$ precursor ion.

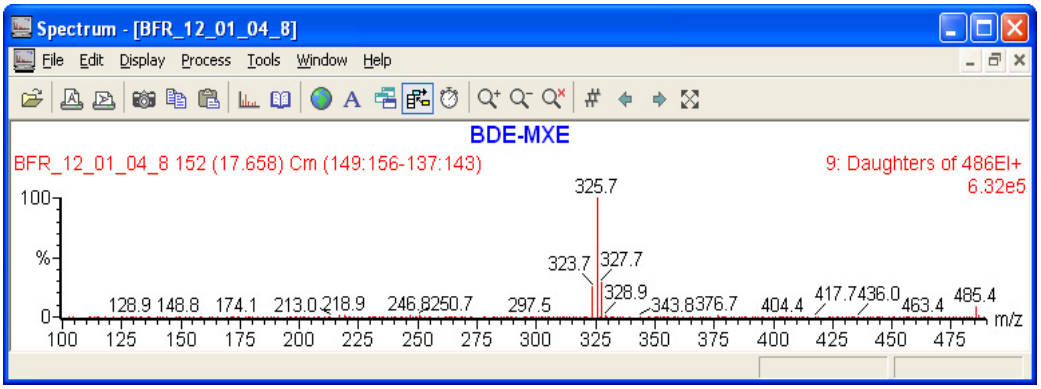

Figure 1. Product ion spectra for the precursor ion m/z 485.7 (M+)

Table 1 shows the precursor ions, product ions, and optimal collision energies for each level of bromination from mono to deca bromo BDE. $^{13}C_{12}$ labelled internal standards were optimised in the same way to provide internal standard transitions.
The transitions and collision energies 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).

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. The 15m DB1-HT column produced the best overall sensitivity, whilst maintaining a 50% valley between BDEs#49 and #71.
The determined levels of the PBDEs were in good agreement with values obtained using high resolution GC-MS. Table 2 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 2 presents the chromatogram for BDE#47, and the 13C12-BDE#47 internal standard at a level of 139 ng/g in a fish tissue extract.

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

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

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

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 3 presents the results for analysis using the 15m DB1-HT column, for the calibration curve (mean RRF and RRF percentage relative standard deviation), and the QC standard injection (percentage concentration deviation).

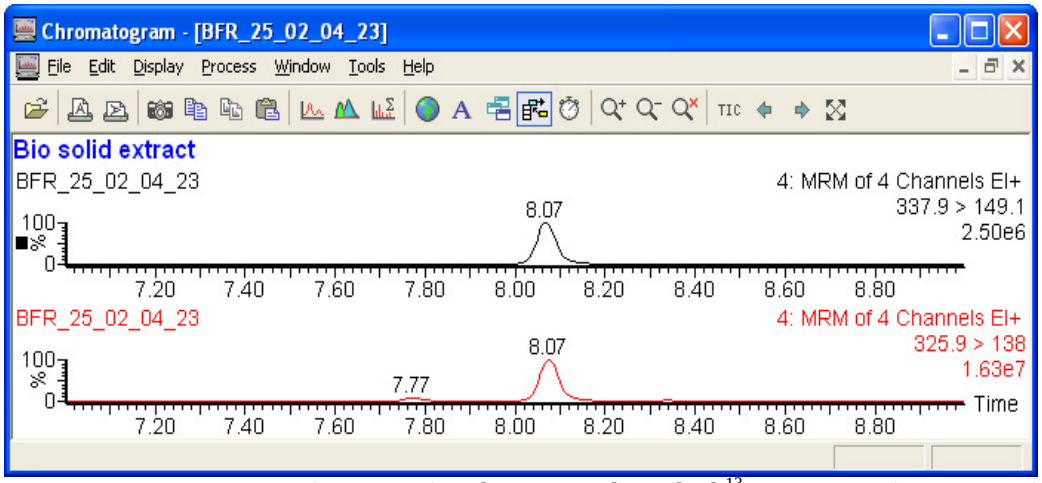

Figure 2. 139ng/g BDE#47 (325.9>138) and it's internal standard $^{13}C_{12}$-BDE#47 (337.9>149.1) in a fish tissue extract.

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

Table 3. Calibration curve and calibration check standard results, using the 15m 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 whilst 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 15m 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 15mDB1-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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