

Fast, Sensitive and Reliable Analysis of Polybrominated Diphenyl Ethers by GC/MS

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Overview

Purpose

Develop a fast, sensitive and reliable instrument method for detecting polybrominated diphenyl ethers (PBDEs) in electrical and electronic products using fast GC/MS with simultaneous full scan/SIM technology.

Method

PBDE standards and extracted electric and electronic product samples were analyzed using a standard splitless injection of 1 μ L and Thermo Scientific DSQ™ single quadrupole mass spectrometer under simultaneous full scan/SIM in EI+ mode.

Results

The mixture of 21 PBDE congeners, including decabromodiphenyl ether, was analyzed under 11 minutes. Under simultaneous full scan/SIM acquisition mode, the calibration curves were generated with a correlation coefficient at least 0.999 from fg to ng levels. The detection limits for PBDEs were from fg to sub-pg on column depending on the congeners. The qualitative and quantitative analyses of unknown electric and electronic samples were obtained from the same chromatographic run by one injection. The robustness was also demonstrated over 100 samples sequence using the new Ion Bright™ Source.

Introduction

Polybrominated diphenyl ethers (PBDEs) as additive flame retardants in polymers are used in a wide range of materials such as electric and electronic equipment, textiles, paint, and furniture. Since these chemicals are not chemically bound, they may 'leak' from the polymer product, thus invading the environment through production, use, and recycling of products containing PBDEs. Published data show the widespread presence of PBDEs in the environment,¹ in the bodies of animals² (Thermo Scientific PolarisQ ion trap GC/MS was used for this study), and in humans.³ Due to environmental pollution and health concerns, the EU has issued two environmental directives in February 2003:

1. Directive on Waste Electrical and Electronic Equipment (WEEE Directive 2002/96/EC)
2. Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (ROHS Directive 2002/95/EC). PBDEs comprise one of six highly substances hazardous in the ROHS.

There are 209 PBDE congeners, and decabromodiphenyl ether (deca-BDE or BDE-209) is the major PBDE product in use. It also has a very high boiling point and molecular weight (m/z : 959 amu), thus placing difficult requirements on both the GC and MS systems. Finally, the electrical and electronic samples were analyzed based on this rapid method.

Method

Calibration solutions of PBDEs were obtained from Wellington Laboratories, Ontario, Canada, apart from Octa-BDE (BDE-203), which was from AccuStandard, USA. The electrical and electronic samples were cut and extracted with toluene/THF, and the clear extracted solutions were injected into the DSQ.

The DSQ used for this analysis was a 250 L/S turbo pump, and the TRACE GC Ultra™ was configured with a standard split/splitless injector with the analytical column of 10 m x 0.18 mm i.d. x 0.4 μ m Rtx-200. The instrument conditions are given in Figures 1-3.

Oven Method	
Initial Temperature (C):	120
Initial Time (min):	1.00
Number of Ramps:	1
Rate #1 (deg/min):	25.0
Final Temperature (C):	330
Hold Time (min):	2.00
Right SSL Method	
Base Temperature (C):	280
Mode:	Splitless
Splitless Time (min):	1.00
Right Carrier Method	
Mode:	Constant Flow
Flow rate (mL/min)	1.00
Interface Temperature (C):	310

Figure 1: Thermo Scientific TRACE GC Ultra instrument method

Key Words

- DSQ Series GC/MS
- Full Scan/SIM
- PBDE
- ROHS Directive 2002/95/EC
- WEEE Directive 2002/96/EC

Acquisition Time:					GC Run Time
Cal Gas:					Off
Reagent Gas:					Off
Acquire Profile:					No
Acq Threshold:					0
Source Temp:					270 C
Detector Gain:					3x105

SEG	SCAN EVENT 1 SIM			SCAN EVENT 2 FULL SCAN	RT WINDOW (min)
	Mass (m/z)	Width (amu)	Dwell (ms)	Mass Range (amu)	
1	248, 250	1	100	165-252	2.8-3.8
2	326, 328	1	100	165-332	3.8-4.9
3	406, 408	1	100	220-420	4.9-5.5
4	484, 486	1	100	300-500	5.5-6.48
5	564, 566	1	100	385-660	6.48-7.85
6	484, 486	1	100	460-660	6.9-7.85
7	561, 563	1	100	545-745	7.85-8.50
8	639, 641	1	100	620-820	8.5-9.5
9	797, 799	1	100	780-980	9.5-

Figure 2: DSQ instrument *Method A* under simultaneous Full Scan/SIM. Quantification of target component by SIM data; further confirmation and unknown identification by Full Scan data.

Acquisition Time:					GC Run Time
Cal Gas:					Off
Reagent Gas:					Off
Acquire Profile:					No
Acq Threshold:					0
Source Temp:					270 C
Detector Gain:					3x105

SEG	SCAN EVENT 1 SIM			SCAN EVENT 2 FULL SCAN	RT WINDOW (min)
	Mass (m/z)	Width (amu)	Dwell (ms)	Mass Range (amu)	
1	248, 250, 328, 330, 406, 408, 482, 484, 486, 562, 564, 566, 719, 721, 801, 803	1	10	150-900	2.5-10.2
2	799, 801	1	100	700-1000	10.2-

Figure 3: DSQ instrument *Method B* under simultaneous full scan/SIM. Quantification of target component and its isomers by SIM data; further confirmation and unknown identification by Full Scan data.

Results

A good separation of 21 congeners in a short run time (Figure 4) and full scan mass spectrum of deca-BDE (Figure 5) with correct molecular ion cluster was given using the DSQ GC/MS.

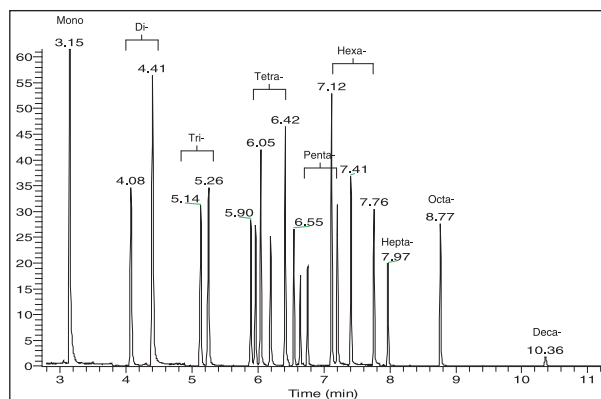


Figure 4: 200 pg/ μ L of 21 PBDE congeners were separated and analyzed by GC/MS in under 11 minutes.

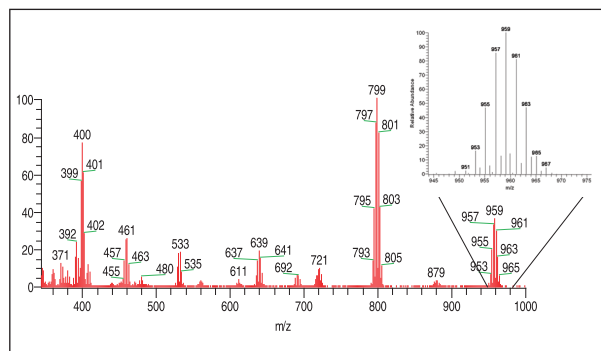


Figure 5: Full scan mass spectrum of deca-BDE with molecular ion cluster from m/z 951 to 967.

In general, when PBDEs were found in a sample, several PBDEs congeners were also found in that same sample. Using full scan data extracted from simultaneously full scan/SIM scan mode, identification of PBDEs congeners can be carried out without repeating the sample injection. Figure 6 shows that several octa-BDE isomers were found in the sample along with BDE-203. Because some of PBDE congeners are not available in the market and their RTs are not clear without their standards, the DSQ *Method B* (Figure 3) was recommended if the quantification of total PBDEs required. This avoids some isomers eluted outside the RT window in the MS *Method A* (Figure 2).

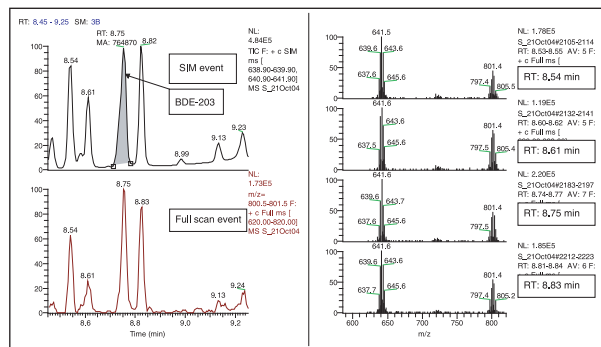


Figure 6: Identification of other octa-BDE congeners in the sample using full scan data extracted from simultaneously full scan/SIM scan mode.

Name (IUPAC#)	r ²	DL* (pg/μL)	Name (IUPAC#)	r ²	DL* (pg/μL)
Mono-BDE (3)	0.9994	0.34	Hexa-BDE (154,153,138)	0.999-0.9991	0.35-0.64
Di-BDE (7,15)	0.999-0.9992	0.17-0.25	Hepta-BDE (183)	0.999	0.49
Tri-BDE (17,28)	0.999-0.9994	0.22-0.24	Octa-BDE (203)	0.999	0.65
Tetra-BDE (49,71,47,66,77)	0.999-0.9992	0.17-0.40	Deca-BDE (209)	0.9991	3.28
Penta-BDE (100,119,99,85,126)	0.999-0.9992	0.18-0.48			

Table 1: Compound list including the correlation coefficient and detection limit. Ten replicate blank samples spiked with 5 times the estimated detection limit were measured, and the detection limits (DL) were calculated based on the value of 3 times the standard deviation.

Because the cleanup was not applied during the sample preparation, the amount of co-extractable material from the samples was directly injected to the system and affected the instrument performance and reproducibility. The Ion Bright Source with high source temp of 270 °C was used in this method to avoid the contaminations from the samples matrices. Figure 7 shows the robustness of the system over 100 real sample analyses. The standards were used at the beginning and end of the sequence to check the system performance. The ion ratio of m/z 801/799 for deca-BDE in the samples was in the range of $\pm 15\%$ of expected ratio with average of 78.6%.

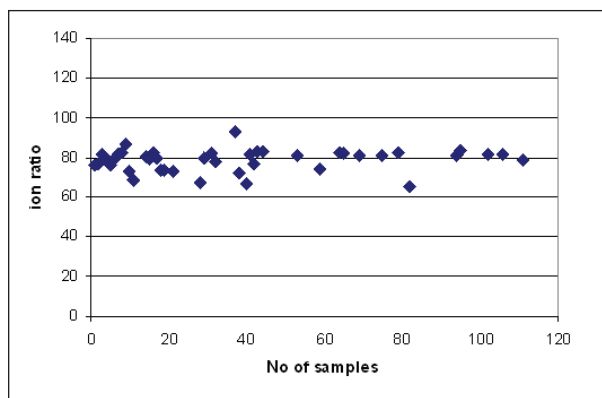


Figure 7: Stability of ion ratio for deca-BDE in the sequence including 14 injections of standards and 97 unknown samples. *Note:* deca-BDE was not found in some samples, and this plot shows that there is no effect on ion ratios throughout this set of samples. However, the matrices from those samples could still have an effect on instrument performance.

Conclusion

By combining a narrow bore GC column with fast scan rate of the DSQ quadrupole mass spectrometer, the mixture of 21 PBDE congeners including decabromodiphenyl ether were analyzed under 11 minutes. Without repeating the sample injection, the simultaneous acquisition of full scan and SIM data from the same chromatographic run was used for analyte confirmation in the electric and electronic samples, while retaining the sensitivity and selectivity of the target compound analysis by SIM. This also helps reduce the reporting of false positive results as the full scan data can be used to confirm identity using library search techniques (Figure 8). The typical detection limits for PBDEs were in the fg to sub-pg range on column, and linearity was demonstrated from fg up to ng levels (Figure 9 and Table 1). Using the Ion Bright Source with a high temperature allows running more samples with less downtime, saving on instrument maintenance costs and minimizing lost time.

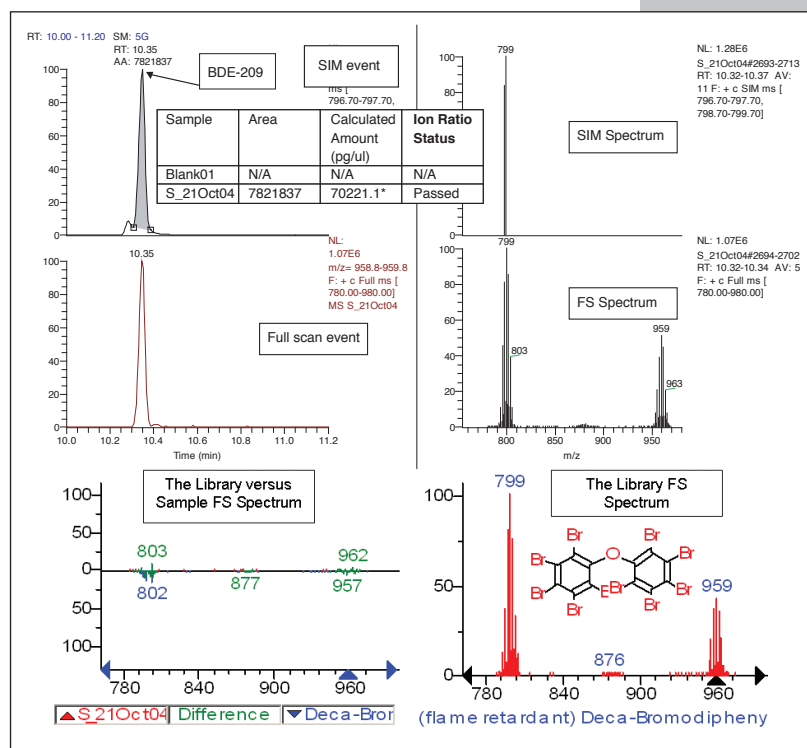


Figure 8: Under simultaneous full scan/SIM scan mode, SIM data was used for the quantification of target compound (BDE-209, deca-BDE); full scan data was used to confirm identity and reduce the reporting of false positive results for the real sample analysis.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

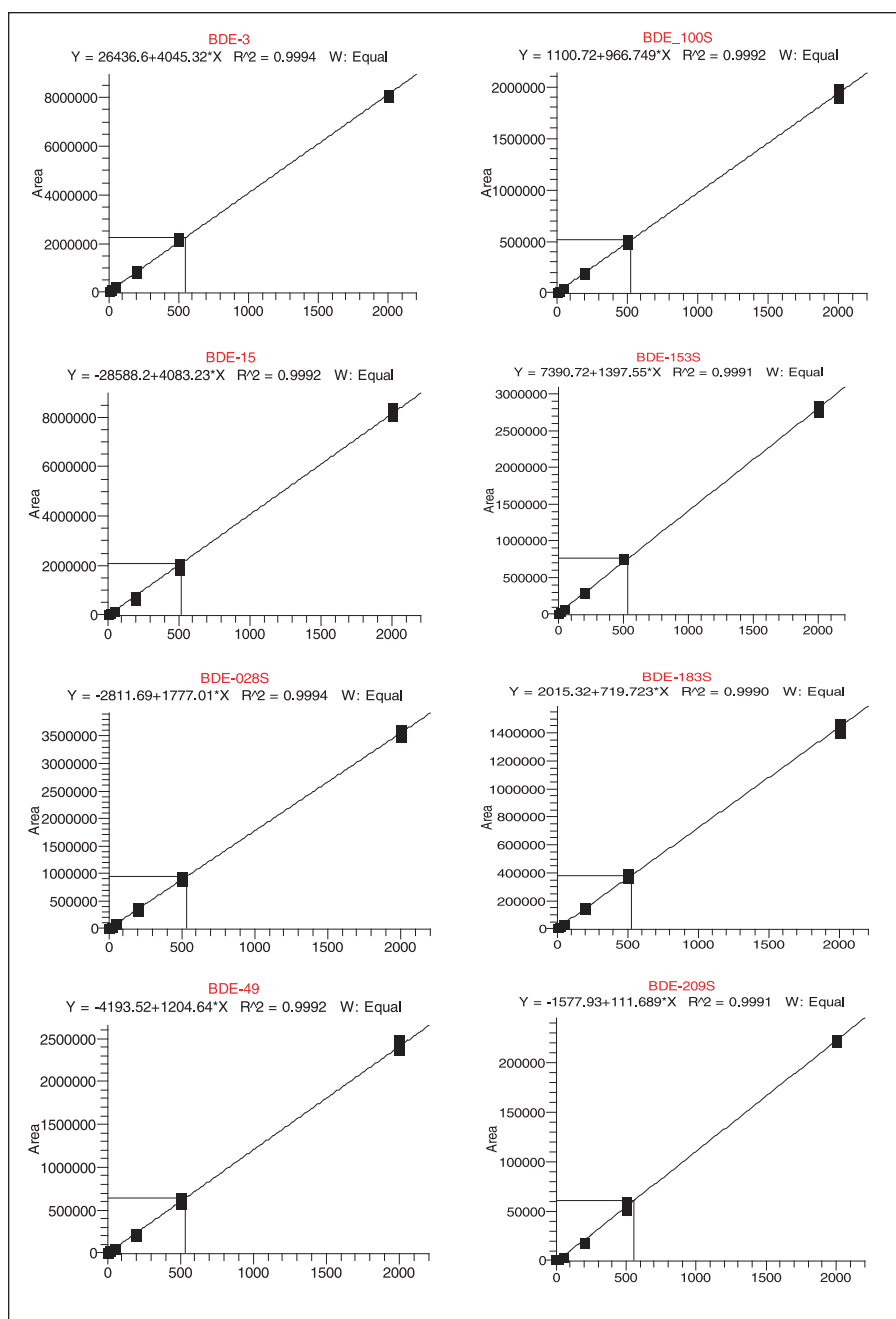


Figure 9: Calibration curves of PBDEs showed the linearity from 0.5 pg/μL to 2,000 pg/μL except Deca-BDE from 5 pg/μL to 2,000 pg/μL.

References

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