



Application Note 02127

Tandem Mass Spectrometry for the Determination of Polybrominated Flame Retardants for RoHS Using the 240-MS Ion Trap Gas Chromatograph/Mass Spectrometer

John E. George, III and Tiffany Payne
Varian, Inc.

Introduction

Polybrominated diphenyl ethers (PBDE) are compounds structurally similar to polychlorinated biphenyls. There are 209 congeners that all have similar nomenclature. These compounds are chemically stable, persistent organic pollutants (POPs). Figure 1 shows the molecular structure of PBDE-100.

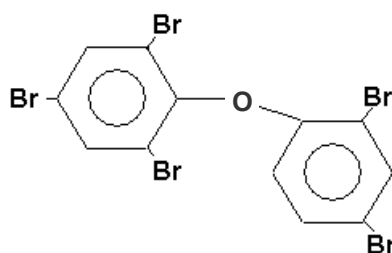


Figure 1. 2,2',4,4',6 - Pentabromodiphenylether (PBDE-100).

Polybrominated diphenyl ethers may be found in fire retardants, especially inside homes and vehicles. PentaBDE (brominated diphenyl ethers) is used largely in polyurethane foam for furniture cushions and mattresses. DecaBDE is used in carpet backing and fabric treatments. The global consumption reported for these compounds was 67 metric tons in 1999.¹

Beginning July 1, 2006, the Restriction of Hazardous Substances (RoHS) European Union (EU) directive started limiting the use of certain hazardous materials in products.² The restricted compounds include lead, mercury, cadmium, HexChrome, polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs). RoHS applies to eight categories of waste from electrical and electronic equipment.

The EU directive banned Penta and OctaPBDEs. DecaPBDE is currently exempt, but is included in this analysis because it is still a concern outside the EU.

Instrumentation

- Varian 240-MS Ion Trap GC/MS using internal ionization mode
- Varian CP-8400 AutoSampler

Sample Preparation

Representative samples were prepared by cryo-mill and grinding. For non-soluble polymers, Soxhlet extraction for 16 hours or microwave digestion was used.

GC/MS Conditions

Injection Volume: 1 µL
Injection Speed: 20 µL/sec
Injector Temp.: 100-300 °C at 200 °C/min
Hold 13 min
Pressure Pulse: 45 psi for 2.1 min
Split State: Initial split: 20:1,
Time 0.01 min, splitter closed
Time 2.00 min, splitter open 50:1
Carrier Gas: Helium at 1.2 mL/min, EFC,
constant flow mode
Column Temp.: 100 °C, 2.0 min hold,
25 °C/min to 320 °C, 5.0 min hold
Total run time 15.8 min
Column : FactorFour™ VF-5ht fused silica column,
15 m x 0.25 mm x 0.1 µm
(Varian Part Number CP9045)
Trap Temp.: 230 °C
Transfer Line Temp.: 280 °C
Manifold Temp.: 45 °C
Ionization Mode: Electron Impact
Target: 5000 counts
µScans Averaged: 3
Multiplier Offset : 0 V
Emission Current 40 µAmps
MS/MS Conditions: See Table 1

Table 1. MS/MS conditions for PBDE analysis.

BDE	Time (min)	Precursor Ion (m/z)	Isolation Window	Excitation Storage Level (m/z)	Excitation Amplitude (V)	Excitation Time (msec)	Frequency Number	Prod Ion Range (m/z)
28	6.67	406	5	178.9	1.50	20	11	200-416
47	7.49	486	5	214.1	1.90	20	11	300-496
99, 100	8.08, 8.27	566	11	249.3	2.00	20	11	350-576
153, 154	8.72, 8.98	644	11	283.7	2.00	20	11	400-654
183	9.62	724	11	318.9	2.60	20	11	400-734
205	10.65	802	13	353.3	2.30	20	11	500-812
206	11.45	880	13	387.7	2.30	20	11	600-890
209	12.68	960	14	422.9	2.70	20	11	700-970

Results and Discussion

Figure 2 shows a 50-ppb calibration standard in MS/MS mode. In this chromatogram, the target analytes have baseline separation and good peak shape. In addition, the separation is complete in less than 13 minutes. The peak labels correspond to the isomer numbers of the compounds listed in Table 2.

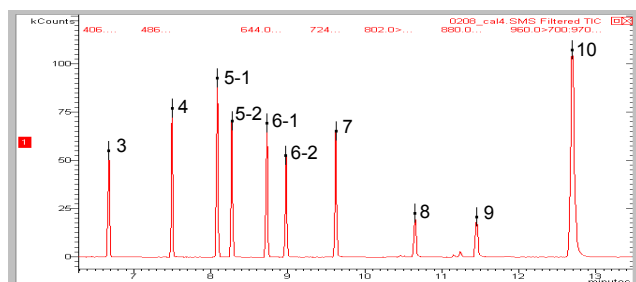


Figure 2. Chromatogram of a 50-ppb standard (with 500-ppb BDE 209) in MS/MS mode.

The BDE spectra are composed of M^+ and $[M-Br_2]^+$ clusters. In this analysis, the entire cluster was isolated as MS/MS precursors, and collision-assisted dissociation (CAD) was used to create the product cluster (without two Br atoms). This approach proved to be highly selective and very sensitive. Figure 3 shows example MS/MS spectra for this analysis.

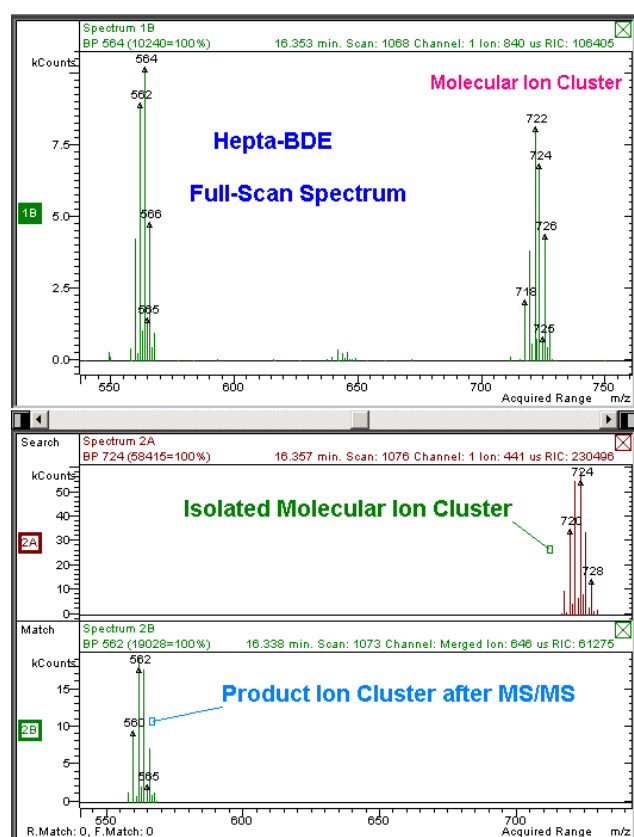


Figure 3. HeptaBDE full scan spectrum with molecular ion cluster (top), isolated molecular ion cluster (middle) and product ion cluster after MS/MS (bottom).

Table 2. Compound names and isomer numbers.

Isomer Number	Compound
3	BDE 28
4	BDE 47
5-1	BDE 99
5-2	BDE 100
6-1	BDE 153
6-2	BDE 154
7	BDE 183
8	BDE 205
9	BDE 206
10	BDE 209 (Deca)

This analytical method was very sensitive for low levels of the target compounds. Figure 4 shows a chromatogram of a 1-ppb injection of the tri- through octa-isomers.

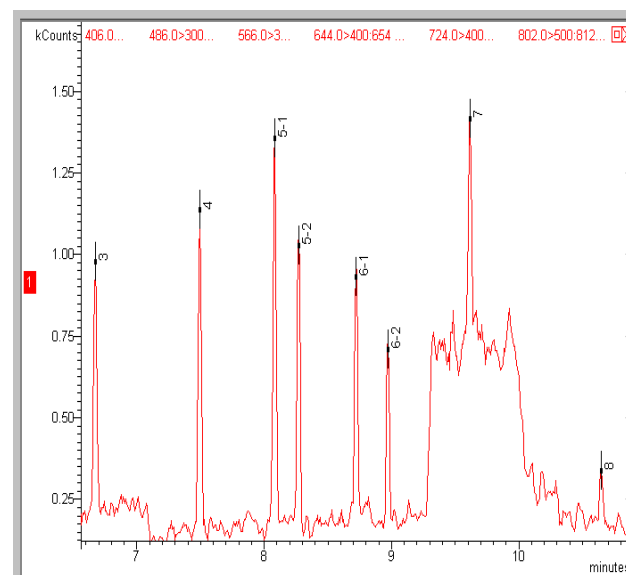


Figure 4. MS/MS chromatogram showing a 1-ppb injection of the tri-through octa-isomers.

For BDE 209, excellent sensitivity was demonstrated at 5 ppb (Figure 5). The signal-to-noise (S/N) ratio at this low level of analyte was 64 (peak-to-peak).

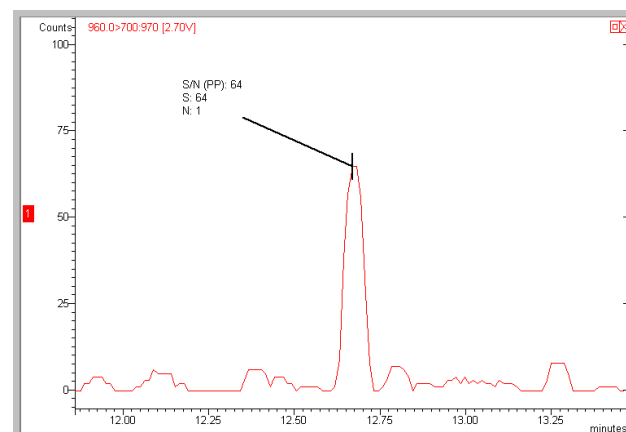


Figure 5. Chromatographic peak for BDE 209 at 5 ppb; S/N 64 (peak-to-peak).

The MS/MS spectrum shown in Figure 6 demonstrates how this MS/MS analysis provides the selectivity necessary to analyze BDE 209 at very low levels.

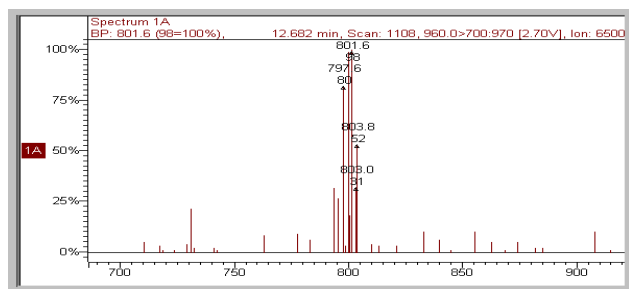


Figure 6. MS/MS product ion spectrum of the BDE 209 for a 5-ppb standard.

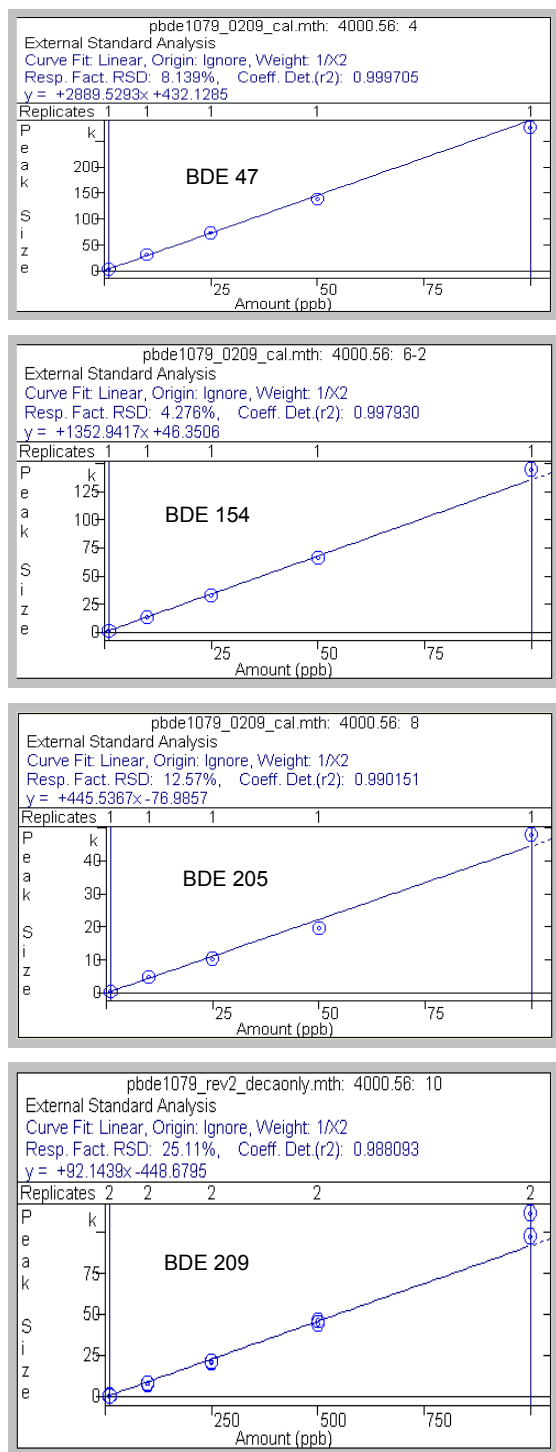


Figure 7. Calibration curves for BDE 47, 154, 205, and 209.

The International Electrotechnical Commission (IEC) method for this analysis designates that the calibration range is 50 to 500 ppb for all BDEs except Deca, which has a calibration range of 500 ppb to 5 ppm. In order to challenge the sensitivity of the analytical system for this analysis, calibration was performed from 1 to 100 ppb for all BDEs except Deca, which was calibrated from 10 ppb to 1 ppm. The calibration curves for BDE 47, BDE 154, BDE 205, and BDE 209 (Deca), are shown in Figure 7.

One of the great advantages of this analytical method is that complex plastic matrix digests can be diluted by a factor of 10 and still meet the required reporting limits of the IEC method. Even in a complex matrix, the sensitivity for the target analytes is consistent.

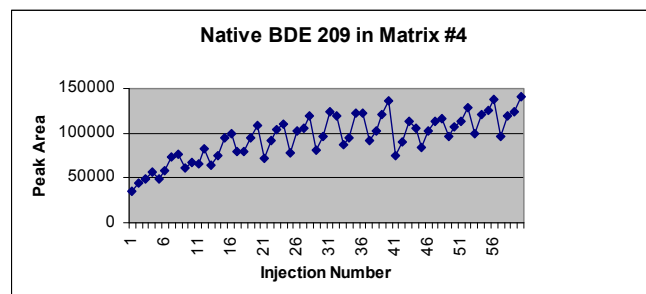


Figure 8. A chart showing peak area vs. injection number of matrix injections. Stability was observed after about 25 injections.

Initially, several injections of the matrix were needed to condition the liner since no internal standard was used. As seen in Figure 8, a stable signal in matrix was established after about 25 injections. This is commonly referred to as "matrix enhanced chromatographic response".

The chart shown in Figure 9 represents continuing calibration checks (CCCs) injected every 10 injections between RoHS acrylonitrile butadiene styrene (ABS) plastic extracts. Although some matrix enhanced chromatographic response is evident in Figure 8, the %RSD of the raw peak area for the CCCs remained less than 10% over 100 injections of the matrix.

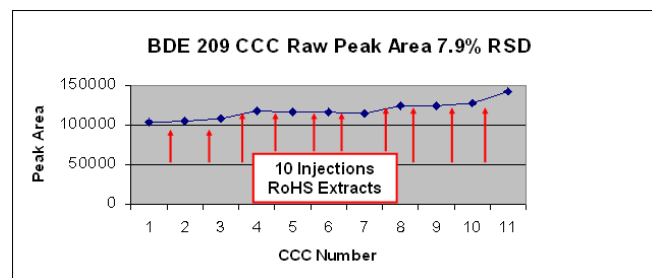


Figure 9. Continuing calibration checks injected between every 10 injections of RoHS extracts. The extracts were not diluted.

Figure 10 shows a BDE 209 detection by MS/MS in plastic extract. The MS/MS product ion cluster provides clear, unambiguous identification for BDE 209.

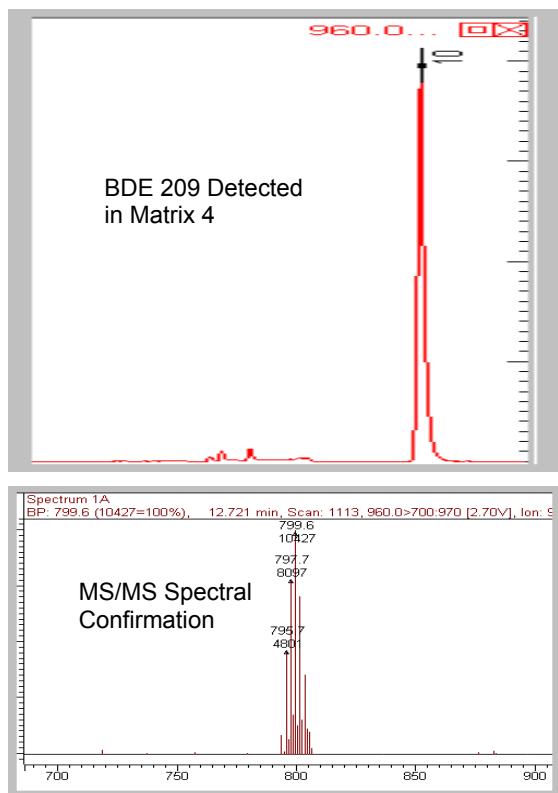


Figure 10. Chromatogram showing BDE 209 in an ABS plastic extract (top) and MS/MS product ion cluster (bottom).

Conclusion

Varian provides a robust RoHS solution for analyzing PBDEs in complex matrices within 16 minutes. It includes the highly sensitive 240-MS GC/MS with the inert FactorFour™ VF-5ht column and a rapid analytical method. The Varian 240-MS system has unsurpassed sensitivity that allows for increased flexibility in the sample preparation and absolute confidence in the results. In addition, the programmable temperature capability of the injector used in this low cost internal ionization system reduced thermal degradation of the heavier PBDEs, adding to analytical sensitivity and robustness.

References

1. Zhu, L.Y. and Hites, R.A.; Determination of Polybrominated Ethers in Environmental Standard Reference Materials, *Anal. Chem.*, **75**, 6696–6700, 2003.
2. OJ L 37, 13.2.2003, p. 24. Directive as amended by Directive 2003/118/EC (OJ L 345, 31.12.2003, p. 106).

FactorFour, Varian and the Varian logo are trademarks or registered trademarks of Varian, Inc. in the U.S. and other countries.
© 2009 Varian, Inc.

These data represent typical results.
For further information, contact your local Varian Sales Office.

Varian, Inc.
www.varianinc.com
North America: 800.926.3000, 925.939.2400
Europe The Netherlands: 31.118.67.1000
Asia Pacific Australia: 613.9560.7133
Latin America Brazil: 55.11.3238.0400