Determination of Polybrominated Diphenyl Ethers in Polymeric Materials Using the 6890 GC/5973N inert MSD with Electron Impact Ionization

Application

Environmental, Component Testing

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Abstract

Due to their ubiquitous appearance in the ecosphere, various polybrominated diphenyl ether formulations have been banned. A major application of PBDEs is to impart fire retardancy to plastics used in electronics and electrical applications. This application note details an approach to determining the PBDEs present in the technical formulations in polymers. The instrumental analysis uses GC/MS with selected-ion monitoring (SIM) to determine tri-BDEs through the decaBDE in 15 minutes. Full scan spectra are presented for the PBDEs with interpretation and to provide an explanation of the choices in SIM ions. To insure correct identification of the PBDE isomers and allow rapid and convenient implementation in the laboratory, Retention Time Locking is applied to an internal standard. A sample preparation scheme referenced in this document provides two flexible and simple approaches to processing polymeric materials for this instrumental technique. PentaBDE, OctaBDE and DecaBDE technical formulations are characterized under the method and results for a typical high-impact polystyrene sample are also presented.

Introduction

Polybrominated diphenyl ethers (PBDEs) are a major issue in discussions of persistent organic contaminants. The detection of PBDEs in essentially all compartments of the ecosystem, including human serum and breast milk, has resulted in a ban of the manufacture and use of certain PBDE formulations by the European Union (EU). Some companies have made it a policy not to allow these compounds in their components and have insisted their suppliers comply. Because the PBDEs are added at percent concentrations (as w/w), the usage of these formulations has been prodigious. Global consumption in 2001 was estimated at 7500, 3790, 56100 metric tons, for the PentaBDE, OctaBDE and DecaBDE technical formulations, respectively.

PBDE analysis even at these relatively high concentrations is challenging in several respects. The PBDEs are a complicated class of compounds and their utility in suppressing combustion also makes them relatively fragile and subject to degradation in GC analysis. This was demonstrated by using shorter GC columns to improve PBDE responses, the most significant improvement being for the deca-BDE (BDE 209) [1]. The loss in congener resolution is less important in this application because the technical mixtures most frequently applied in polymers predominantly consist of isomers extending from the tri-BDEs to the deca-BDE and far less than the 209 possible congeners. Distinguishing congeners on the basis of their electron impact (EI) mass spectrum may be possible since there appears to be some differences in their spectra, however the most reliable index remains retention time (RT). For this reason, compound

Retention Time Locking (RTL) is used to simplify identification and reproduction of the method in the user's laboratory.

Another complication is in sample preparation. There are several methods for extracting PBDEs from polymers each with advantages and disadvantages [2]. Of the many methods, the two approaches applied in processing samples for this application note are relatively inexpensive, simple, universal in application and in their acceptance, and allow for high sample throughput with minimal polymeric interferences. They are polymer dissolution and soxhlet extraction.

Experimental

Polymer samples were obtained from Agilent customers in the electrical and electronic component industries. Specific details of the polymer dissolution and soxhlet extraction methods are presented elsewhere [3]. In summary, the methods extract PBDEs from the sample via solvent, a dilution is made into toluene and PCB 209 is added to follow the dilution factor. Prior to injection, PCB 207 is added as an internal (injection) standard. Standards were made taking into account the potential percent concentration range of the PBDEs in polymeric samples and dilution factors used in the method.

PBDE standards were acquired from Cambridge Isotope Laboratories (Andover, MA) and AccuStandard (New Haven, CT). PCBs 209 and 207 were acquired from AccuStandard (New Haven, CT). Solutions were made in toluene of Burdick & Jackson solvent (VWR Scientific, San Francisco, CA).

Instrumental Configuration and Conditions

The 6890 GC and 5793N-inert MSD (mass selective detector) system configuration and conditions are given in Table 1. The GC is operated under constant flow conditions developed by applying RTL to lock the PCB 209 internal standard RT at 9.350 minutes. The 5973N inert MSD was equipped with the new Performance Electronics upgrade and allowed a single SIM group containing 24 ions to be used. The SIM ions are listed in Table 1 and were acquired with a dwell of 10-ms. This single SIM group method can be used to develop a preliminary method that can be further refined into multiple SIM groups by applying the AUTOSIM utility if the user wishes [4]. This is recommended for 5973-MSDs using standard electronics and targeting only congeners known to predominate in the particular technical mixture.

Table 1. GC and MSD Configuration and Parameters

Injection parameters

Injection mode	Pulsed splitless	
Injection volume	1 µL	
Injection port temperature	320 °C	
Pulse pressure and time	15.8 psi	1.80 min
Purge flow and time	50.0 mL/min	2.00 min
Gas saver flow and time	20.0 mL/min	3.00 min

DB-5ms Column and oven parameters

GC column	DB-5ms (15 m × 0.25 mm id, 0.1 µm film) (p/n: 122-5511)		
Flow and mode	1.8 mL/min	Constant flow	
RTL parameters	9.350 min	RTL compound PCB 209	
Detector and outlet pressure	MSD	Vacuum	
Oven temperature program	90 °C	1.00 min	
	20 °C/min	340 °C	2.00 min
Oven equilibrium time	1.0 min		
Total program time	15.5 min		
MSD transfer line temp	320 °C		

Mass spectrometer parameters

Tune parameters	Autotune
Electron multiplier voltage	Autotune + 400V
Solvent delay	6.5 min
Quadrupole temperature	150 °C
Inert source temperature	300 °C

Mass spectrometer SIM ions for single group

405.8	246.0	123.0
485.7	325.9	162.9
563.6	403.8	201.9
643.5	483.7	241.9
721.5	561.6	320.8
799.4	641.5	360.7
719.4	461.7	399.7
463.7	497.7	499.7

*Optional addition of *m/z* 280.8

Miscellaneous parts

Septa	5182-0739	BTO septa (400 °C)
Liner	5181-3315	Deactivated 4-mm id double taper
GC column ferrule	5181-3323	250 µm Vespel/Graphite
MSD interface ferrule	5062-3508	0.4-mm id preconditioned vespel/graphite

Results

Chromatography

After evaluating a series of columns the DB-5ms phase seems the best choice overall, which is consistent with the literature [1]. The literature shows that the shorter columns and thinner films are of benefit to improving the PBDE responses, especially deca-BDE (PBDE-209) [1] and this approach is applied here. The benefit appears in both response and also in shorter analysis times; elution of deca-BDE occurs in less than 15 minutes. The separation on the DB-5ms phase seems sufficient for characterizing PBDE additives in polymers since the desire is not so much the complete separation as it is the overall composition and contribution of the various isomers [5]. Nonetheless, the short analysis time makes RT reproducibility and accuracy more critical for correct assignments of the various PBDE isomers and this is greatly enhanced by applying RTL. A list of the Retention Time Locked elutions of the most prominent PBDEs is presented in Table 2. For reference, Figures 1, 2 and 3 present chromatograms of PentaBDE, OctaBDE, and DecaBDE technical mixtures with approximate elution windows of the various isomers.

Table 2. Prominent PBDE Congeners and their Locked RTs

Compound name	RTL RT (min)
PCB 207	8.69
PCB 209 (locking compound)	9.350
PBDE 17 (tri Br)	6.89
PBDE 28 (tri Br)	7.08
PBDE 71 (tetra Br)	7.97
PBDE 47 (tetra Br)	8.09
PBDE 66 (tetra Br)	8.25
PBDE 100 (penta Br)	8.82
PBDE 99 (penta Br)	9.06
PBDE 85 (penta Br)	9.43
PBDE 154 (hexa Br)	9.62
PBDE 153 (hexa Br)	9.93
PBDE 138 (hexa Br)	10.31
PBDE 183 (hepta Br)	10.73
? hepta PBDE	11.07
PBDE 190 (hepta Br)	11.23
PBDE 204 (octa)	11.62
PBDE 203 (octa)	11.78
? PBDE 196 (octa)	11.84
PBDE 205 (octa)	12.00
PBDE 208 (nona)	12.56
PBDE 207 (nona)	12.64
PBDE 209 (deca Br)	13.60

Note - tentative identification of PBDE 196 was based on reference [1]

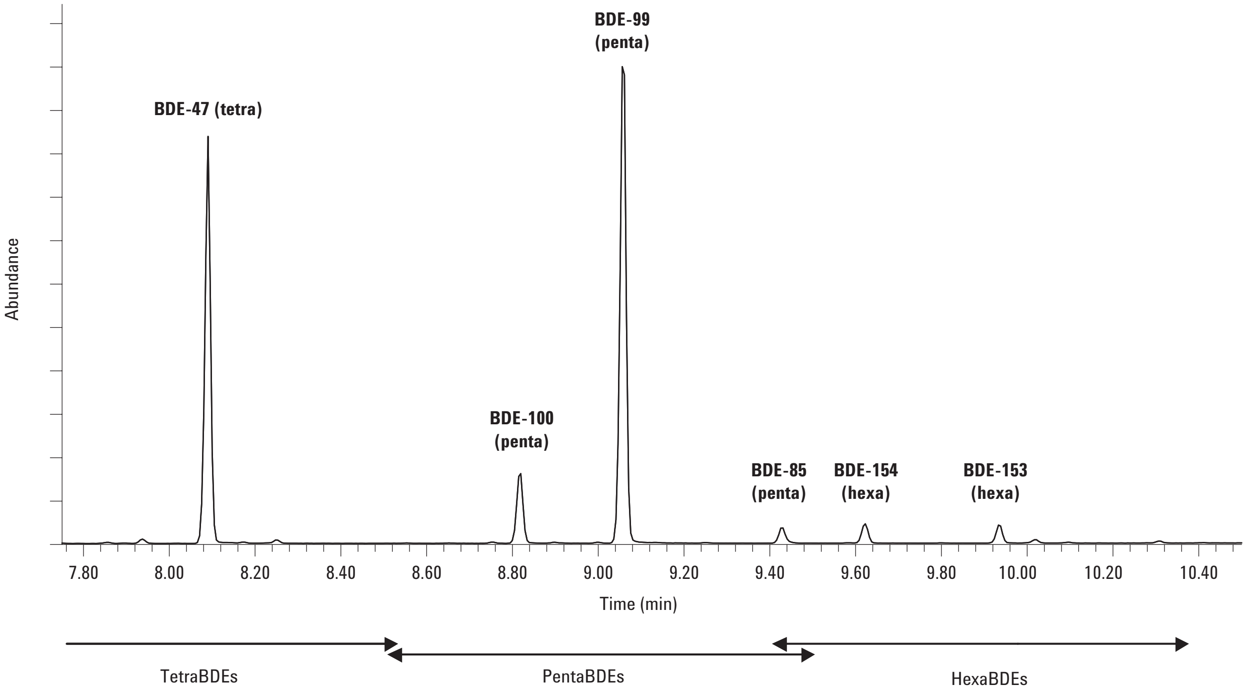

Figure 1 Reconstructed ion chromatogram (RIC) for the GC/MS EI-SIM acquisition of a PentaBDE technical mixture (Cambridge Isotope Laboratories).

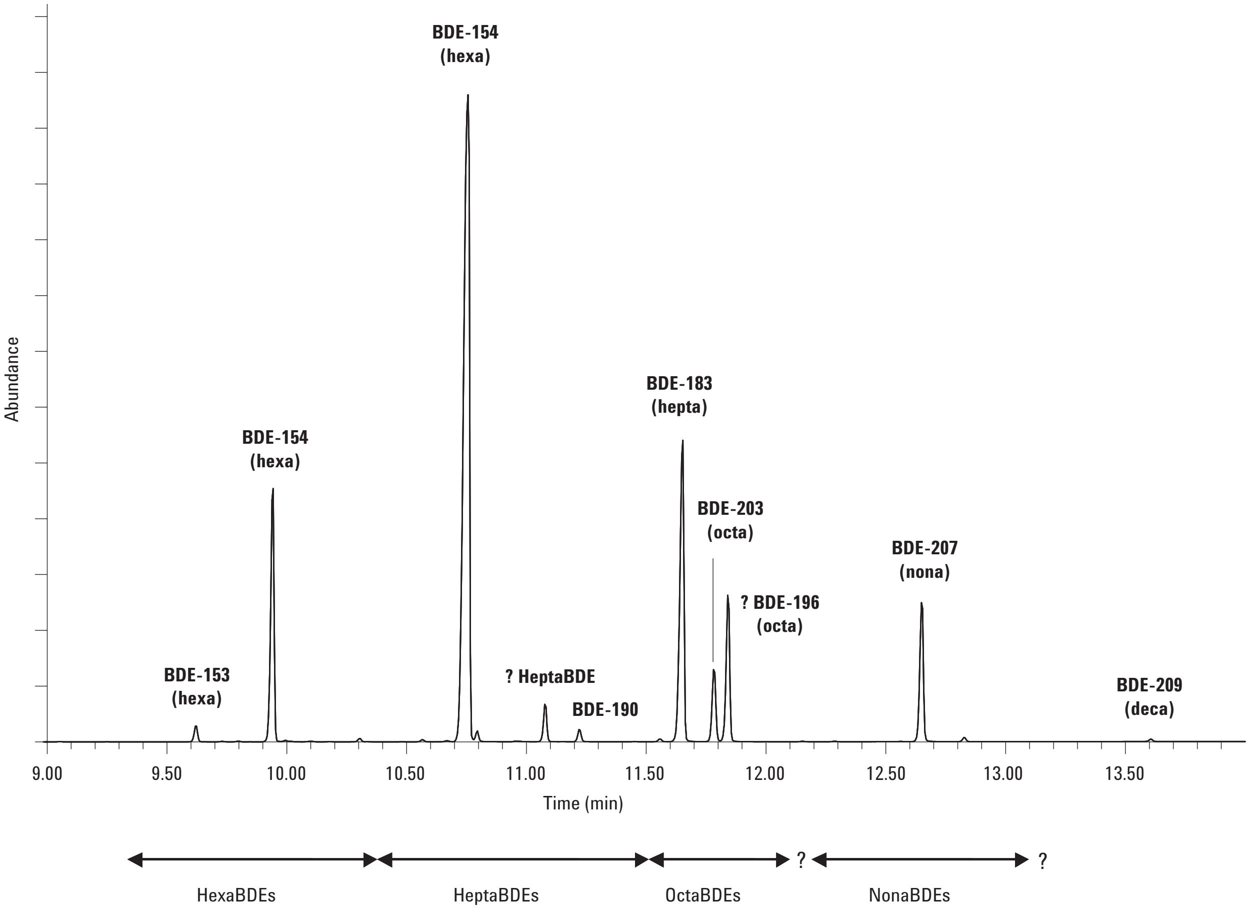

Figure 2 RIC for the GC/MS EI-SIM acquisition of a OctaBDE technical mixture (Cambridge Isotope Laboratories)

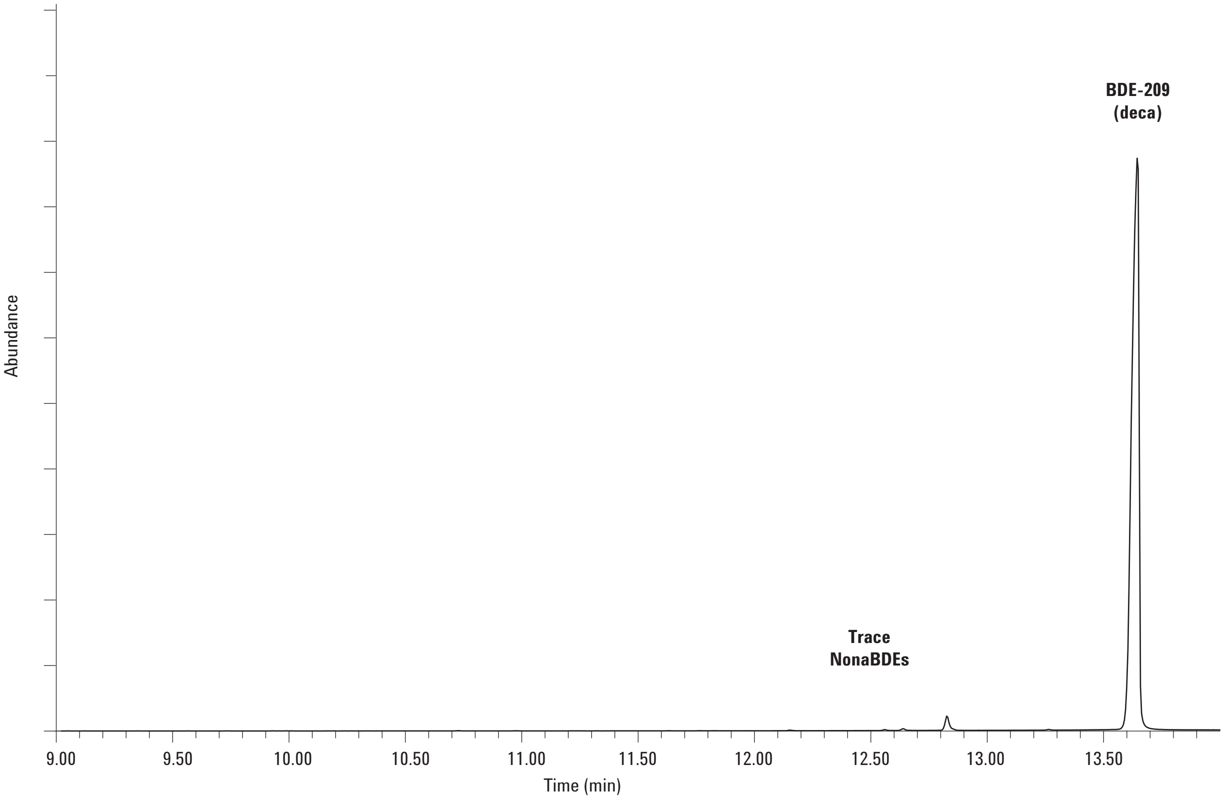

Figure 3 RIC for the GC/MS EI-SIM acquisition of a DecaBDE technical mixture (Cambridge Isotope Laboratories).

PBDE Spectral Interpretation

The EI ionization mass spectra of the PBDE congeners are rich in details and partially described in the literature [7]. Among the isomers the spectra are expected to be approximately identical in pattern and fragmentation pathway. Figure 4 presents a full scan spectrum of a hexabrominated-DE, PBDE-138, obtained at a source temperature of 300 °C. The spectrum shows the isotope cluster due to the molecular ion (643 *m/z*) and an intense cluster (484 *m/z*) consistent with the loss of Br_2. The mass assignment of the *m/z* 484 cluster is consistent with the result of $[M\text{-}Br_2]^+$, that is, $[C_{12}H_4OBr_4]^+$, and shows the tetrabrominated pattern (18 : 69 : 100 : 65 : 16). The next highest abundance isotope cluster appears around 242 *m/z*. Figure 4 shows this cluster and the cluster at *m/z* 484, $[M\text{-}Br_2]^+$. The isotope cluster patterns are similar, which suggests the same degree of bromination, but the fragment mass assignments are half those of the 484 cluster and mass spacing is not 2 but 1 *m/z* unit. While it is possible this is due to overlapping fragments, the close correspondence in patterns lead the authors to propose that this isotope cluster is due to double-charged fragments; that is, $[M\text{-}Br_2]^{+2}$. Recently, this assignment was confirmed by high-resolution MS and the results will be published elsewhere [8]. This $[M\text{-}Br_2]^{+2}$ fragment is common among the PBDEs congeners and grows in relative abundance as the degree of bromination increases: approximately in 10% tetraBDEs; 15% in pentaBDEs; 20%–25% in hexaBDEs and heptaBDEs; 45% in octaBDEs; 60% in nonaBDEs; and > 80% in decaBDE. Figures 5, 6, 7, 8 and 9 show spectra for several PBDEs. We have also observed the same phenomena for the polybrominated biphenyls (PBBs). We also find the ratios vary within an isomeric series more than in PCBs.

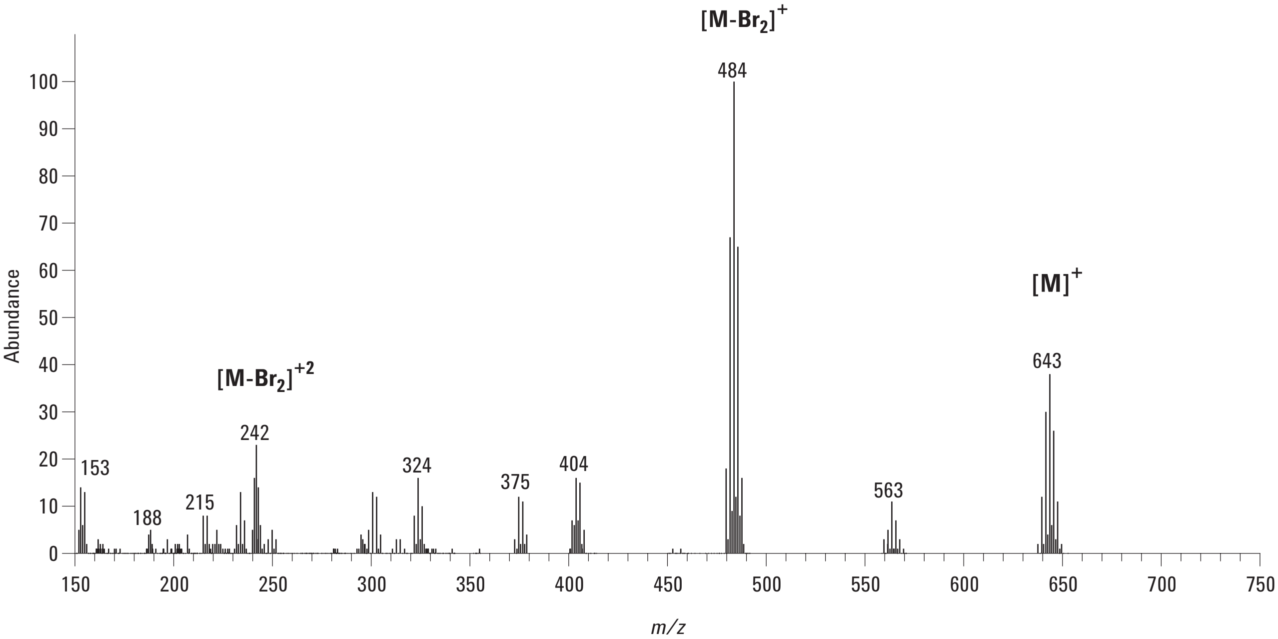

Figure 4 Normalized EI mass spectrum of a hexabrominated-DE, PBDE-138, obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.

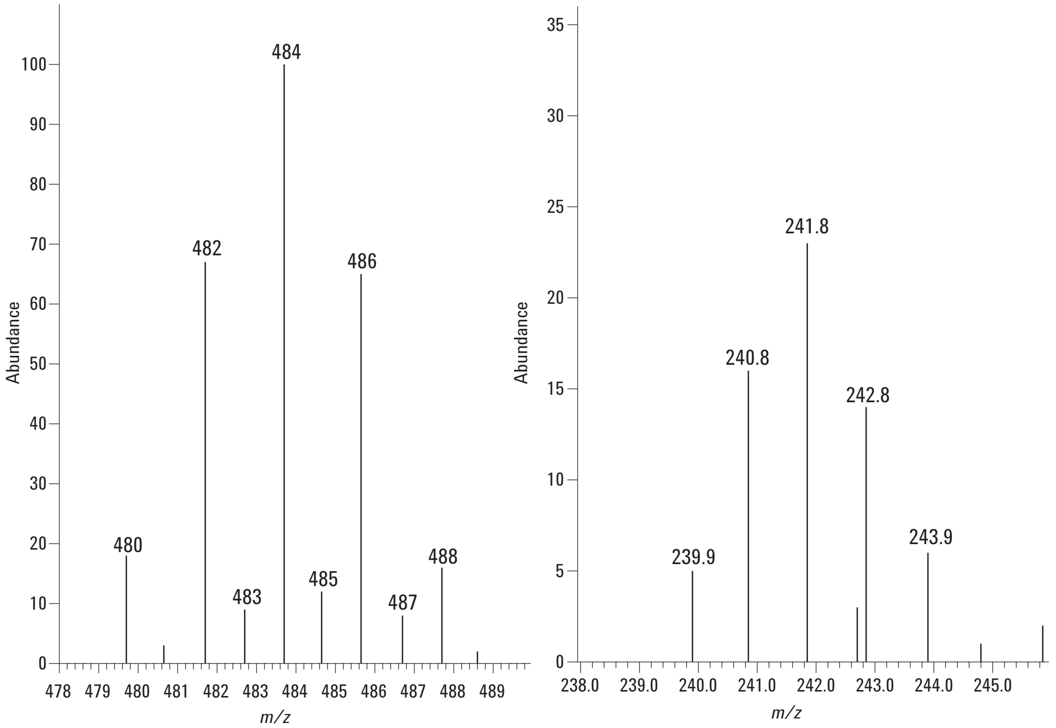

Figure 5 Sections of the normalized EI mass spectrum of the hexabrominated-DE, PBDE-138, for the [M-Br$_2$]$^+$ and proposed [M-Br$_2$]$^{+2}$ clusters.

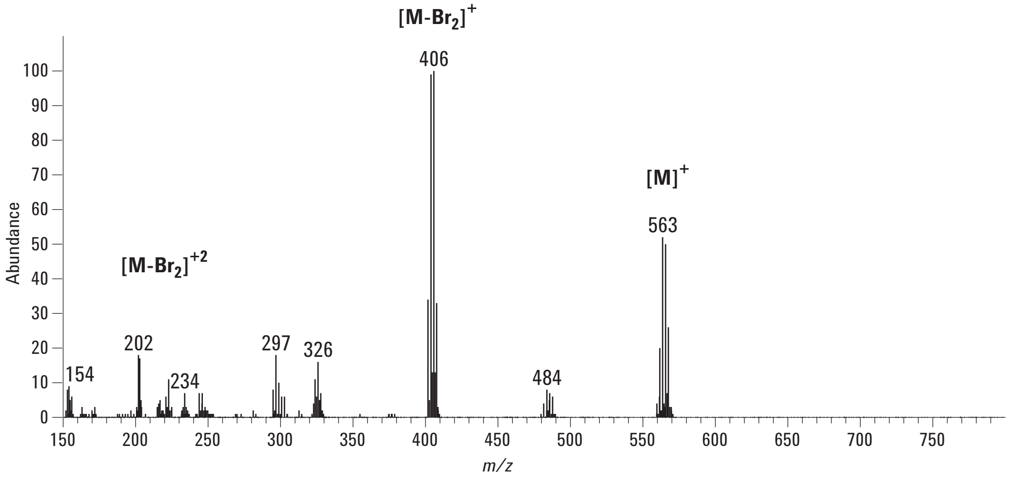

Figure 6 Normalized EI mass spectrum of a pentabrominated-DE obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.

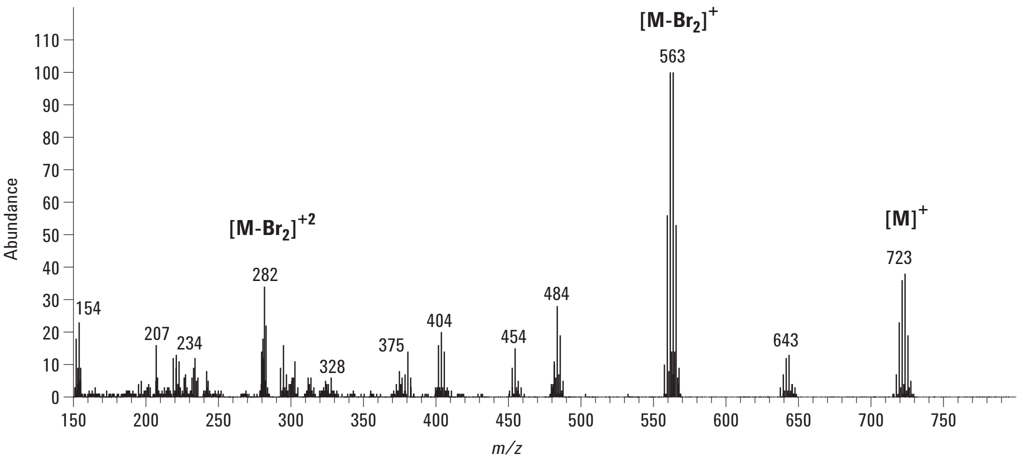

Figure 7 Normalized EI mass spectrum of a heptabrominated-DE obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.

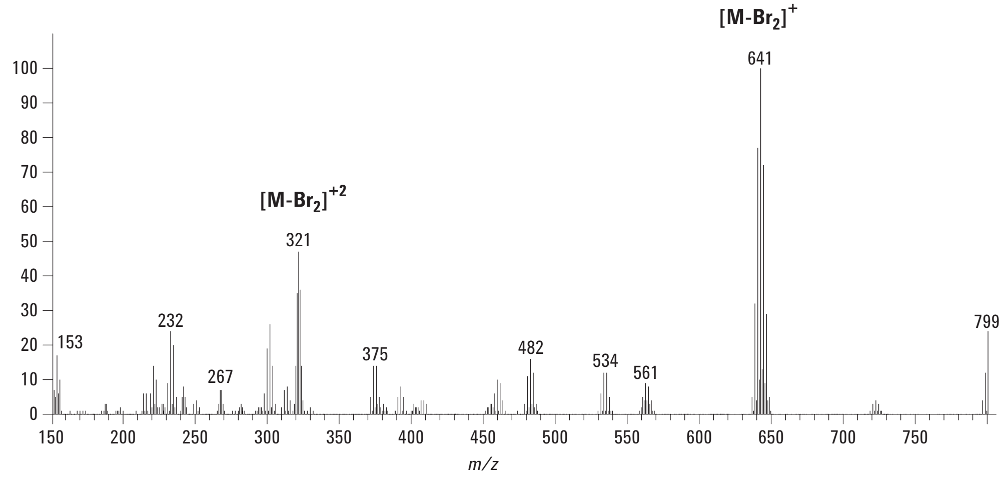

Figure 8 Normalized EI mass spectrum of a octabrominated-DE, PDBE-203, obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.

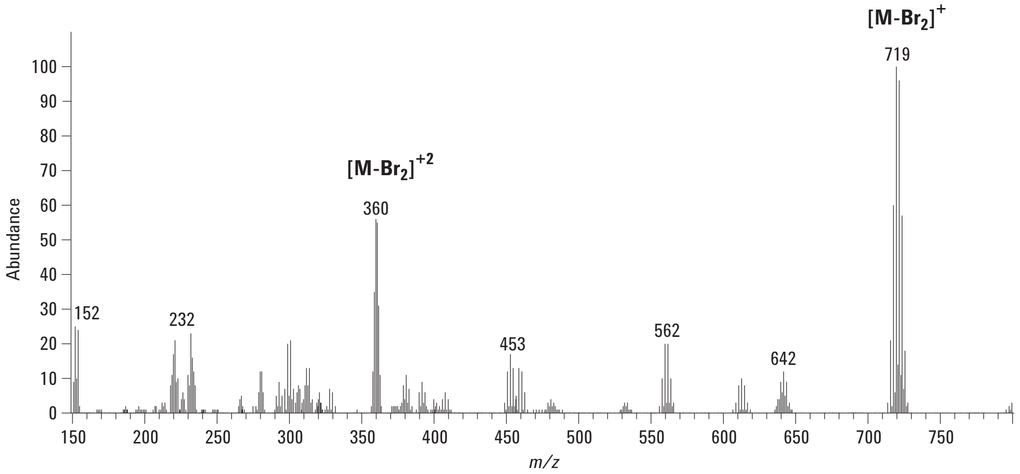

Figure 9 Normalized EI mass spectrum of a nonabrominated-DE, PDBE-208, obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.

In considering the EI spectrum of the decabromodiphenyl ether, PBDE-209, the same observations apply, Figure 10. Although the cluster of the molecular ion at 959 u, eludes the mass range limitation of the 5973N-MSD, the loss of Br_2 forms an intense isotope cluster at *m/z* 799, $[M\text{-}Br_2]^+$ and the doubly charged fragment(s) for the $[M\text{-}Br_2]^{+2}$ at *m/z* 400 (399.6) as shown in Figure 11. Other data has shown that the intensity of the molecular ion cluster (959 u) is far less than that of the fragments at *m/z* 799 as is the trend for the PBDEs.

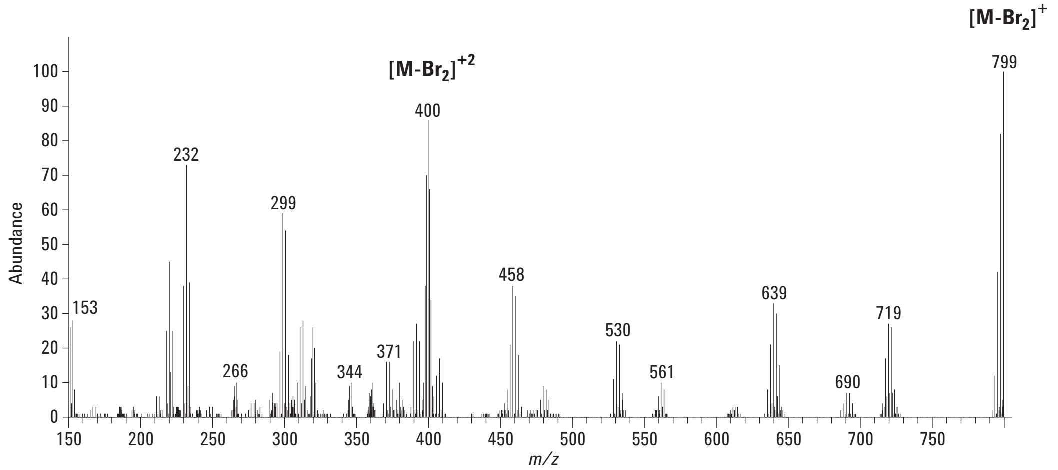

Figure 10 **Normalized EI mass spectrum of the decabrominated-DE, PDBE-209, obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.**

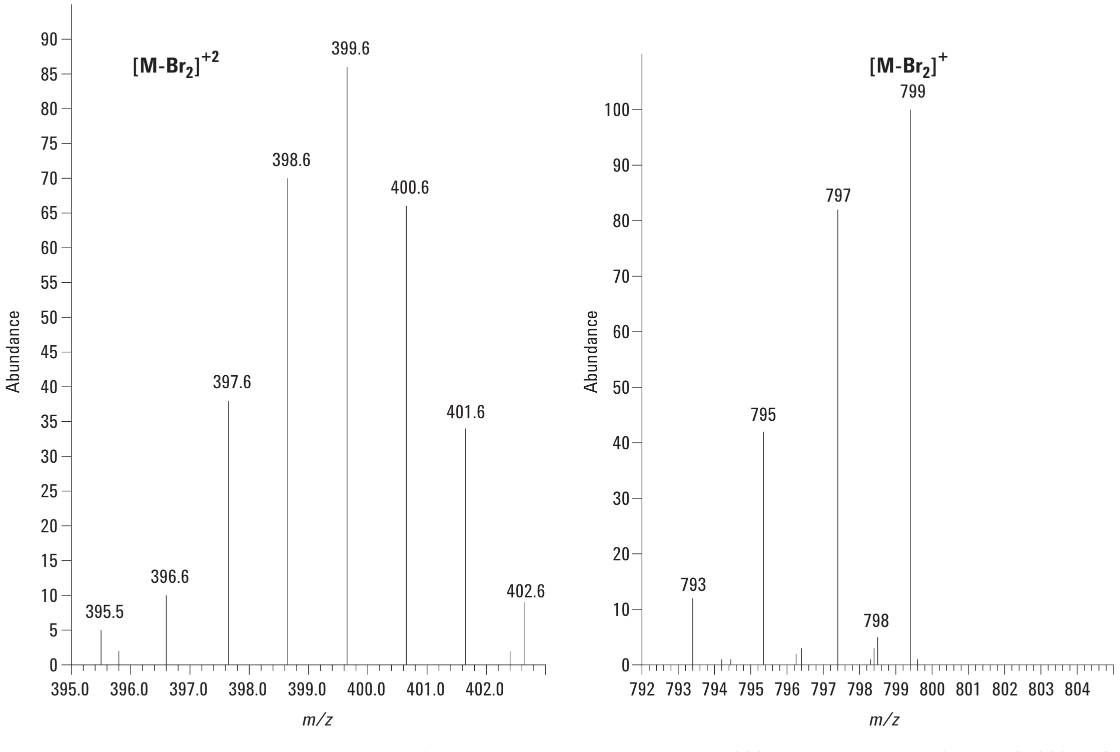

Figure 11 **Normalized EI mass spectrum of the decabrominated-DE, PDBE-209, obtained in scan from 150–800 *m/z* at a source temperature of 300 °C.**

Therefore these ions (that is, $[M\text{-}Br_2]^+$, $[M\text{-}Br_2]^{+2}$ and $[M]^+$ where available), and compound RTs, identify and allow determination of the deca-BDE and other PBDEs to the ability of the 15-m column to separate the isomers, which appears quite effective and sufficient for characterizing additives. The monitored ions are given in Table 3 with the ions for the internal standards used in this analysis. Obviously, the bromines provide other ions displaced in mass by two units (except for the doubly-charged ions) that offer other additional ions for quantitation or confirmation.

Using the ions listed in Table 3 to identify the PBDE isomers, the regions in the chromatograms presented in Figures 1, 2 and 3 were labeled with the isomer elution windows. These ions and their ratios were also used to characterize PBDEs not available in the standards but found to occur within the samples and technical mixtures (for example, PBDE 196).

Results for Polymeric Samples

Extracting PBDEs from polymers requires that the entrained PBDEs permeate the polymer into the extracting medium. Apparently "melting" the polymer closes the transport corridors in the polymer and impedes extraction. However, "swelling" the polymer with a proper solvent, greatly improves the kinetics of extraction. Beyond deciding the proper solvent, the optimal time of the extraction must be experimentally determined for each plastic based on its consistency and response to the solvent. For the polymer dissolution and soxhlet extraction methods used here, solvent contact times or the number of soxhlet cycles for near complete extraction was determined by serial extraction. Other concerns are described in the sample preparation protocols [3].

Figure 12 shows the chromatogram for an extracted HIPS (high-impact polystyrene) polymer sample supplied by an Agilent customer and Table 4 shows the results for replicate extractions and analysis. Note the chromatogram and its major components closely resembles the chromatogram for the OctaBDE technical mixture (Figure 2) and indicates the specificity of the selected ions and most importantly, the lack of polymeric interferences. The reproducibility of the component compositions is a testament to the reproducibility of the total method. A good portion of the variance is introduced by the high dilution factors used in the method to bring the polymer extract concentrations with the scale of the PBDE standards and therefore discriminates against the lower abundance components producing a higher degree of variation and absolute detection. A series of 25 replicate injections of an extracted sample showed negligible degradation in response or chromatography. The robust performance is largely due to the high MSD ion source and quadrupole operating temperatures of 300 °C and 150 °C, respectively. These high temperatures mitigate the effect of co-extracted polymeric residues on the ion source optics to render robust performance. The high operating temperature of the quadrupole provides a very long lifetime without cleaning or maintenance even when analyzing very dirty matrices such as these.

Table 3. Quantitation and Confirmation Ions for the PB_nDEs (n>2)

PBDE bromination	$[M]^+$	$[M\text{-}Br_2]^+$	$[M\text{-}Br_2]^{+2}$	Confirmation ion
3	405.8	246.0	123.0	403.8
4	485.7	325.9	162.9	483.7
5	563.6	403.8	201.9	561.6
6	643.5	483.7	241.9	641.5
7	721.5	561.6	(280.8 **)	563.6/719.4
8	799.4	641.5	320.8	643.5
9	–	719.4	360.7	721.5
10	–	799.4	399.7	–
PCB 207	463.7	461.7	–	–
PCB 209	497.7	499.7	–	–

**The 280.8 and 281.8 *m/z* ions can be compromised by column bleed interferences so these were not used in acquisition although they provide a useful diagnostic for column degradation.

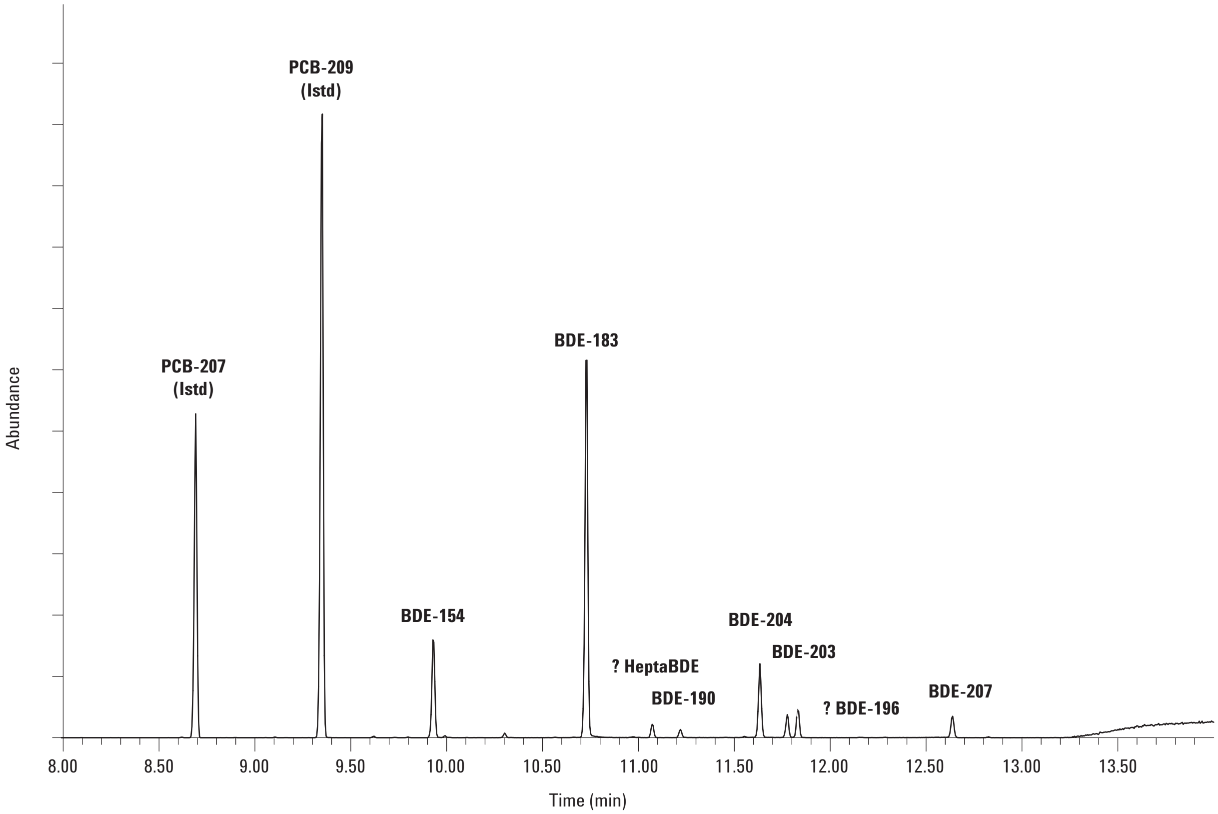

Figure 12 RIC of the GC/MS SIM acquisition of an extracted HIPS polymer sample.

Table 4. Extraction Results for Replicate Analysis of a Polymer Sample for PBDE Composition Using the Two Extraction and Sample Preparation Protocols [3]

Soxhlet polymer extraction protocol results

Sums	Replicate 1 (%)	Replicate 2 (%)	Replicate 3 (%)	Replicate 4 (%)	Replicate 5 (%)	SD
HexaBDEs	9.1	9.5	8.9	8.7	9.1	0.3
HeptaBDEs	53.3	52.5	51.7	53.1	53.1	0.7
OctaBDEs	29.5	29.5	30.7	29.5	29.8	0.5
NonaBDEs	8.0	8.4	8.6	8.7	8.1	0.3

Polymer Dissolution Extraction Protocol Results*

Sums	Replicate 1 (%)	Replicate 2 (%)	Replicate 3 (%)	SD
HexaBDEs	9.9	10.0	9.7	0.2
HeptaBDEs	55.3	56.2	55.9	0.5
OctaBDEs	34.8	33.8	34.4	0.5

SD standard deviation

No tri-DEs, tetraBDEs, pentaBDEs, or decaBDE were detected.

*A difference in analyte lists used to quantitate the soxhlet extracts slightly skews the results, specifically the addition of the nona-BDE analytes. Removing this group, the results agree within 3%.

Remarks

Figure 13 presents two overlaid reconstructed ion chromatograms of the SIM acquisitions of two splits of a single PBDE standard. One of the splits was contained in a clear vial and was exposed to laboratory light for about a week and the other split was stored in amber vial and in a freezer as a reference. The most impressive feature is the dramatic loss of the decaBDE and the possible appearance of another intense nonaBDE (around 11.8 minutes). Note the nonaBDEs in the standard showed no degradation while the octaBDEs and heptaBDEs showed varying degrees of loss in concentration. A number of small peaks appear in the baseline that suggest, on the basis of their fragments, ion ratios, and proximity to existing PBDEs in the standard, the presence of other BDE isomers. Assigning any identification in SIM without a standard reference compound to confirm RT and fragment ratios, or a full scan acquisition, must be considered highly speculative. However, the data does indicate a degradation of the decaBDE and some other PBDEs, and suggests possible isomerization of the some PBDEs under the influence of typical laboratory fluorescent lights. Time and resources do not allow us to pursue this matter, but we provide these observations since there are implications in sample handling and standard preparation and storage.

Conclusions

The 5973N inert MSD equipped with performance electronics allows a single SIM group to survey for PBDE isomers important to characterizing the technical formulations of the PBDEs. Using a single group has the advantages of allowing many formulations to be studied without regard to the particular elution of the congeners (which would require careful maintenance of SIM windows), simplified setup and very rapid analysis. Implementing RTL allows specific congeners to be characterized and quantitated with high confidence. The intense fragmentation of the PBDEs and their universal propensity to form [M-Br$_2$]$^+$ and [M-Br$_2$]$^{+2}$ ions provides a unique fingerprint for each degree of bromination. The 15-m column used here provides rapid analysis and sufficient class separation. The method is universally applicable regardless of the sample preparation scheme as demonstrated here by replicate polymer analysis by two techniques, soxhlet extraction and polymer dissolution.

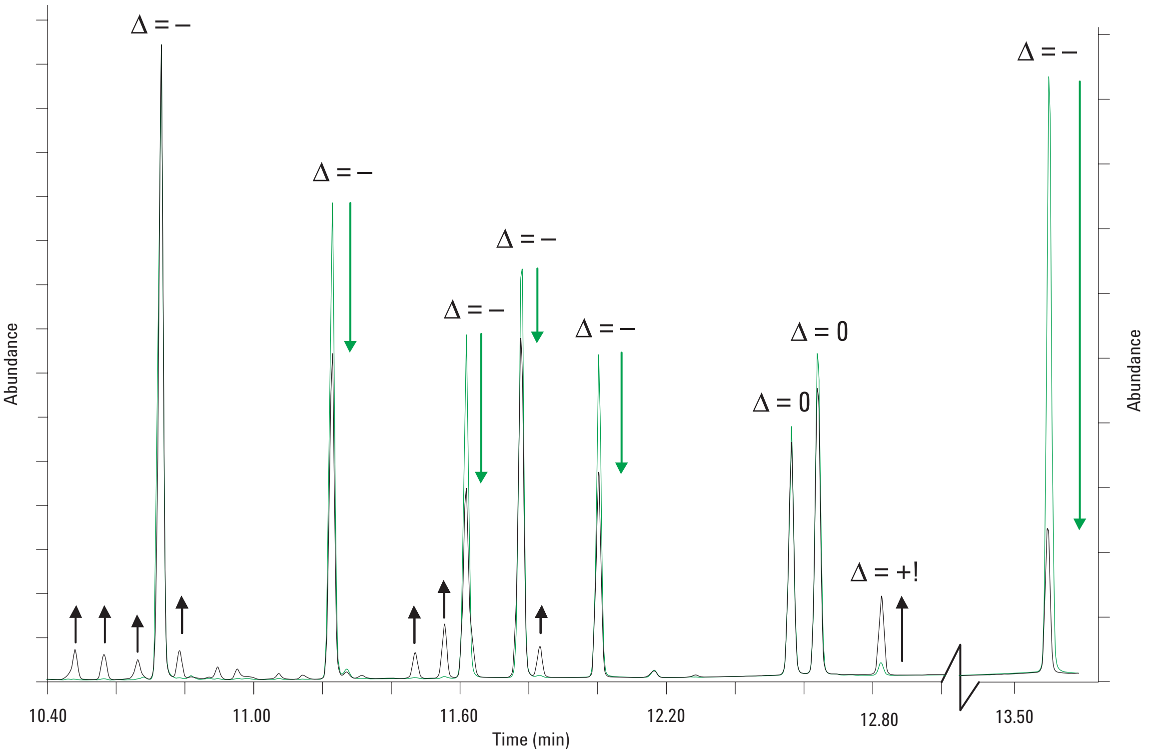

Figure 13. **PBDE standard unexposed (green) and exposed to laboratory light. Delta (Δ) indicates change in response as Exposed-Unexposed (with negative signs indicating loss in response and positive an increased response).**

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