

Analysis of Polybrominated Diphenyl Ether Flame Retardants by Gas Chromatography/Mass Spectrometry

Introduction

Polybrominated diphenyl ethers (PBDEs), commonly used flame retardants, are under scrutiny as a result of their global presence and rapid bioaccumulation. Recently, legislative and commercial groups have initiated programs to reduce or eliminate specific PBDE congeners as a result of their potential health threat. This application note will demonstrate a gas chromatography/mass spectrometry (GC/MS) analysis of common PBDE congeners. An optimized method and column will allow the PerkinElmer® Clarus® GC to provide ample separation and high yields of PBDE congeners. The extended mass range of the PerkinElmer Clarus MS and high mass calibration will produce mass spectra with very high levels of accuracy.

Experimental

A PerkinElmer Clarus GC/MS system was the analytical platform for this study. A summary of the instrumental conditions appears in Table 1 (Page 2). The GC separation was accomplished on a 15 meter x 0.25 mm ID x 0.1 µm film Elite 1

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column (PerkinElmer Part No. N9316006); the short column was chosen to minimize column-residence time and avoid analyte degradation¹. Resulting from the low vapor pressure and high boiling point of PBDEs, a temperature-programmed splitless injection was used, minimizing sample contact with hot, metal surfaces in the injector port¹; to further reduce injector-port activity, a deactivated glass liner with wool (PerkinElmer Part No. N6502001) was used. As you can see in Figure 1 (Page 2), the total run time of this analysis is less than 15 minutes; pictured here is an extracted ion chromatogram of a full-scan analysis of 14 PBDE congeners. The remaining GC/MS conditions are summarized in Table 1 (Page 2).

Table 1. Instrumental Conditions of the Clarus GC/MS.

GC Conditions		PSSI Temperature 1:	100 °C	MS Conditions	
GC Cycle Time:	13 min	PSSI Hold:	0 min	Source Temperature:	280 °C
GC Oven Temperature 1:	100 °C	PSSI Ramp Rate:	999 °C/min	GC Line Temperature:	280 °C
GC Temperature Hold:	1 min	PSSI Temperature 2:	320 °C	Photomultiplier:	450 V
GC Ramp Rate:	20 °C/min	Carrier Gas:	He	MS Function Type:	SIFI*
GC Temperature 2:	320 °C	Constant Flow:	1.5 mL/min		
Injection:	Splitless	Vacuum Compensation:	On		

* SIFI – Single ion and full ion scanning

High-molecular-weight detection by GC/MS requires a non-traditional calibration technique. The ions of the standard calibration gas PFTBA (FC-43, heptacosane) are limited to mass calibration fragments up to m/z 614. The mass range of the Clarus mass spectrometer is m/z 1-1200. To achieve accurate mass calibration in the upper half of this mass range (m/z 600-1200), it is necessary to use an alternate mass-calibration standard with known ions above m/z 600. This technique uses a GC injection of the calibration standard triazine (PerkinElmer Part No. N9311730), which produces ions up to m/z 1185. High mass calibration consistently produces experimental spectra with fragmentation very close to theoretical. Figure 2 (Page 3) shows the molecular ion cluster of deca-bromo diphenyl ether (BDE-209).

Along with GC optimization and high mass calibration, the data-acquisition functions of the mass spectrometer were optimized to achieve maximum sensitivity, while collecting scans sufficient to define each chromatographic

peak. Within the MS method, a combination of single ion recording (SIR) and scan functions were used. The simplicity of full-scan functions was preferred; however, when sensitivity dictated, 3-ion SIR data were collected.

Results

The PerkinElmer Clarus GC/MS used in this study provided excellent accuracy, precision and sensitivity in the analysis of PBDE congeners. The optimized experimental setup was used to analyze a calibration curve of 14 PBDE congeners. The tri- through hexa-BDEs were calibrated from extracted ions of full-scan functions, while SIR data were used to calibrate the hepta- through deca-BDEs. Figure 3 (Page 3) demonstrates a representative calibration from this analysis; BDE-028 is calibrated across a concentration range of 10 ppb to 1 ppm.

Even with a fully-optimized method, the routine analysis of PBDEs in polymers creates additional challenges as a result of the sample matrix. PBDEs are extracted from

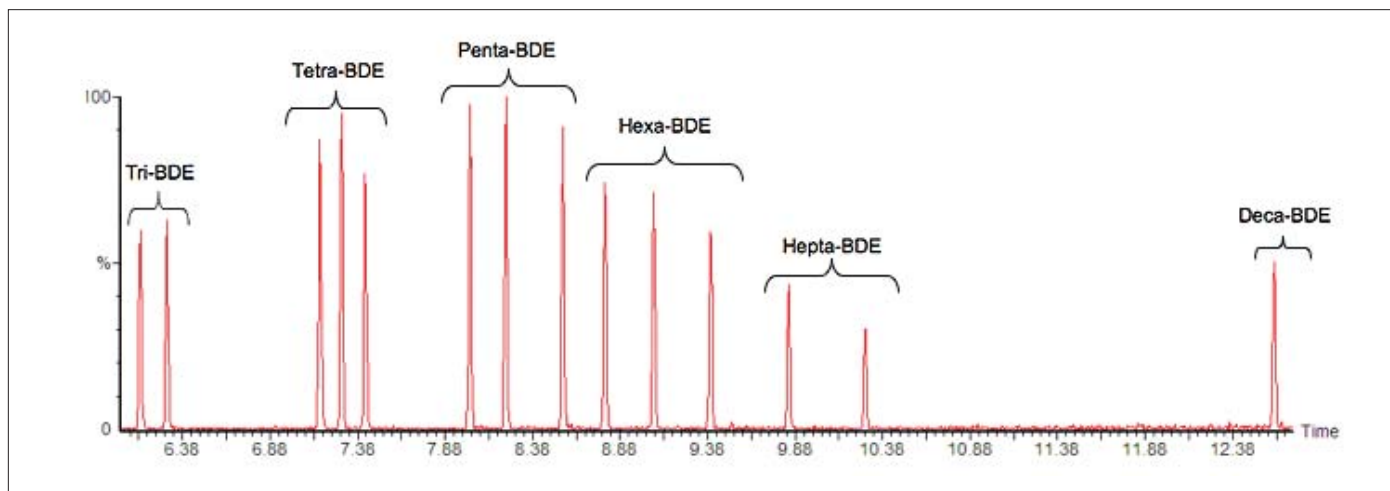


Figure 1. An extracted ion-composite chromatogram of a full-scan analysis of 14 PBDE flame retardants.

plastic materials with toluene or another non-polar solvent; the extraction process will yield not only analytes of interest, but also large amounts of plasticizers, additives and polymers. These extracts are cleaned with a combination of centrifugation, silica gel and GPC (gel permeation chromatography). Even with this extensive cleanup, much of the plastic matrix remains in the sample extract. Accumulation of this sample matrix in the injector-port liner and column head will, over time, degrade method performance. Periodic maintenance should be performed by the analyst to clean or replace the injector-port liner, removing any accumulated sample matrix. Additionally, the end of the capillary column should be clipped by about 2 cm – this will remove any matrix which may have accumulated. Routine maintenance of the injector-port liner and capillary column will preserve method performance over time.

Conclusion

Although GC/MS analysis of PBDEs is challenging, this study has demonstrated that the Clarus GC/MS provides a platform on which a fast and robust analytical technique is based. By using the appropriate combination of GC

column and analytical conditions, the chromatographic challenges of the method were met and runtimes of less than 15 minutes were achieved. SIFI MS data-collection functions provide necessary sensitivity and spectral identification across the full range of PBDE congeners. Instrument uptime is further optimized by developing the appropriate GC maintenance routine to keep the system clear of any sample-matrix accumulation.

References

1. J. Bjorklund, et al., "Influence of the injection technique and the column system on gas chromatographic determination of polybrominated diphenyl ethers", (2004) *Journal of Chromatography A*, 1041 (1-2) p. 201-210.

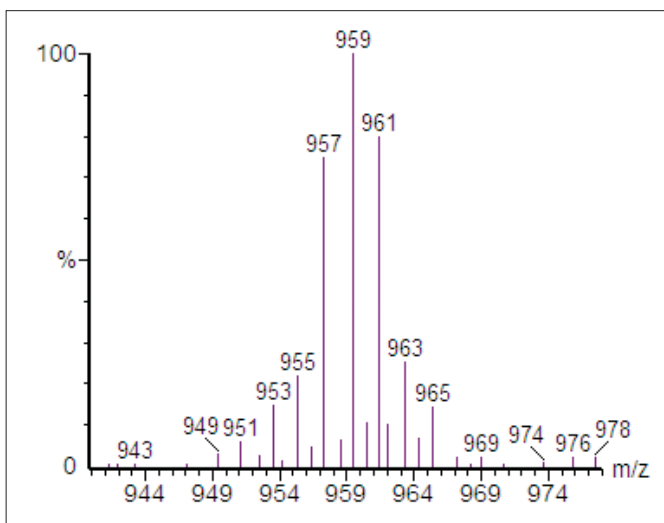


Figure 2. Mass spectrum of the molecular ion cluster of deca-bromo diphenyl ether (BDE-209).

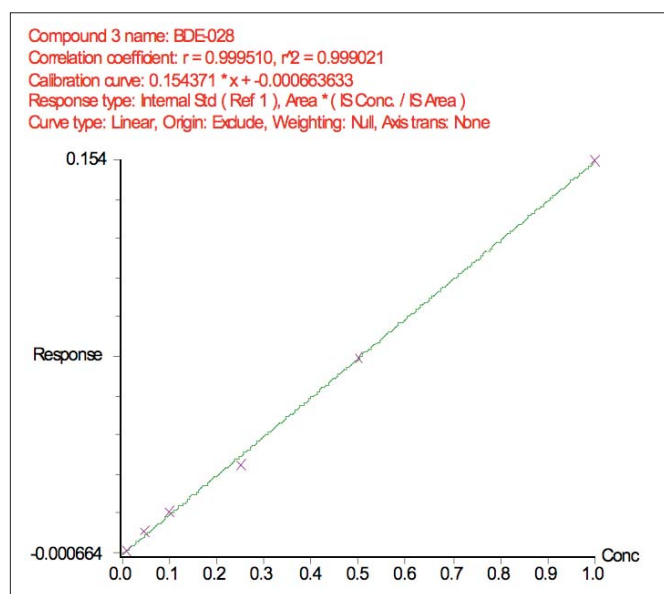


Figure 3. Calibration curves of tri-BDE (congener 028) across a concentration range of 10 ppb to 1 ppm.