Application Note: 10047

Quadrupole GC/MS Analysis of Polybrominated Diphenyl Ethers (PBDE) in Environmental Samples

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Key Words

- TRACE DSQ
- Environmental Analysis
- Flame Retardants (PBDE)
- PTV On-Column Injection
- SIM Analysis

Abstract

Ten PBDE congeners were selected across the mass range of Tri-BDE to Deca-BDE for quadrupole GC/MS analysis with the TRACE™ DSQ. To ensure good sample transfer to the column, a PTV injector configured for on-column injection was employed. The TRACE DSQ's capability to perform segmented scanning was used to customize tuning parameters to different segments of analytes eluting from the TRACE GC Ultra™. This approach allowed for a sensitive and linear detector response across the concentration and mass ranges of PBDE congeners tested.

For each compound being analyzed, full scan spectra were first obtained to assist in unknown identification and selection of SIM ions for quantitation. A SIM method was then developed and tested for sensitivity, stability and linearity over a chosen mass range. To demonstrate the use of this method in environmental analysis, a soil sample was collected and analyzed for the PBDE congeners.

Introduction

The use of PBDE congeners in flame retardants has increased the prevalence of these compounds in everyday living. They can be found in furniture, in dust particles in the air, and in human breast milk. Studies have shown one of the most widely used congeners, Penta-BDE, can lead to alterations in neurodevelopment in prenatal mice.[1] Legislation banning Penta- and Octa- BDE at a limit of one tenth of one percent by mass is scheduled to take effect in California on January 1, 2008.[2] Also, the European Union has passed a directive requiring that its member states ensure that "new electrical and electronic equipment put on the market does not contain...polybrominated diphenyl ethers".[3] As alarm over the health risks and the amount of PBDE congeners in the environment grow, so too will the need for identification and quantitation of these compounds. To help satisfy this need, the method described below was developed to demonstrate a fast, sensitive and reliable method for the analysis of PBDE congeners using the TRACE DSQ (Figure 1).

Figure 1: The TRACE DSQ

Method

The TRACE GC Ultra was equipped with a PTV inlet configured for on-column injections and programmed to track temperature closely with the oven during its temperature ramp. A megabore 0.53 mm ID deactivated fused silica pre-column, approximately 2 m in length, was connected to the inlet to facilitate on-column injection. This PTV configuration has been determined to be more effective at transferring the higher mass congeners to the analytical column than a straight split/splitless (SSL) configuration.[4] The GC conditions used for this method are listed in Table 1.

METHOD CONDITIONS

TRACE GC Ultra	
Oven Temp:	Initial Temp. of 80°C. Hold at 80°C for 0.10 min. Heat at 60°C/min to 275°C. No Hold. Heat at 45°C/min to 300°C. Hold for 12 min.
PTV Temp:	Initial Temp. of 80°C. Hold at 80°C 0.1 min. Heat at 1°C/sec to 300°C hold for 10 min.
Transferline Temp:	300°C
Flow Rate:	1 mL/min
Mode:	PTV Split
Split Flow (mL/min):	10
Injection Volume:	3 µL
Constant Purge:	On
TRACE DSQ	
Parameters set by autotune used except for the following manual adjustments:	
Electron Energy:	-130 eV
Prefilter Offset:	-17.10 V
For Tri- through Hexa-BDE segments:	Emission Current = 50 µA Detector Gain = 3 x 10^5
For Octa- through Deca-BDE segments:	Emission Current = 350 µA Detector Gain = 3 x 10^5

Table 1: Instrument conditions used in method

The TRACE DSQ and the Xcalibur™ software package allow separate scan segments to be implemented over the course of a single run. This gives the user the ability to customize the tuning parameters for each analyte being eluted from the column. The method developed for this study uses a lower emission current value for the more easily detected lower mass congeners. Later in the run, as the higher mass congeners are being detected, the emission current is elevated. This provides added sensitivity for the higher mass congeners.

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The prefilter offset was increased from its autotune value to -17.1 volts for the duration of the run. This value was chosen by isolating the cal gas ion m/z = 512 using SIM in the tune window after autotune was run. By varying the prefilter offset to maximize the intensity of this ion, the DSQ can be manually tuned to increase high mass sensitivity (Figure 2).

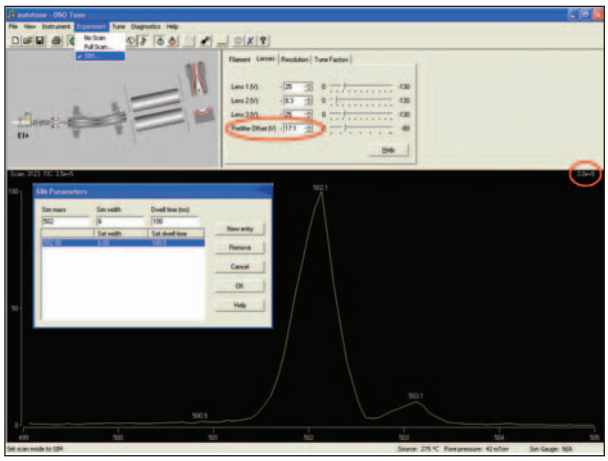

Figure 2: Maximizing the intensity of m/z = 502 by manually changing the prefilter voltage will increase high mass sensitivity. The prefilter voltage can be changed in the manual tune window and the base peak intensity, in this case m/z 502, is reported in the top right corner of the tune window. A prefilter value between -10 V and -25 V is recommended for this application.

Finally, the electron energy was changed from its default value of -70 eV to -130 eV. This value was chosen based on the observation that both peak intensity and signal to noise of Deca-BDE increased with electron energy up to -130 eV. The tuning parameters that were changed from their autotune or default values are listed in Table 1.

A 15 m TRACE TR-5 with a 0.25 mm diameter and a 0.1 µm film thickness was used as the analytical column. A short, thin-phased column was chosen so that the higher mass congeners could be passed through the column quickly at lower temperatures, minimizing their breakdown in the column. The analytical column was connected to the guard column using a glass connector.

The TRACE DSQ quadrupole mass spectrometer was used for the study. This instrument is well equipped for PBDE analysis because it has a scanning range which reaches 1,050 amu, which is high enough to obtain molecular spectra for even the heaviest congeners. Also, because of the instrument's fast scanning capabilities, the light, early eluting congers could be resolved even with a fast oven ramp. This gives the benefit of shorter run times and reduces the residence time of the congeners in the column, minimizing the loss of the higher mass congeners due to degradation in the column.

Ten samples of different PBDE congeners at 50 ng/µL in isooctane were purchased from Accustandard. These were mixed together in equal parts to obtain a 5 ng/µL mixture. Five point calibration curves were generated for each congener from 2 pg/µL to 5 ng/µL, with each concentration run in triplicate. Tetra-BDE (77) was used as the internal standard at a concentration of 500 pg/µL. Isooctane was used as the solvent throughout.

Analysis

Full scan spectra were obtained for each congener tested and used to determine retention times and to identify SIM ions. A typical spectrum obtained for deca-BDE is shown in Figure 3. This spectrum is taken over its molecular ion cluster and its fragment ion cluster formed by the loss of two bromine atoms.

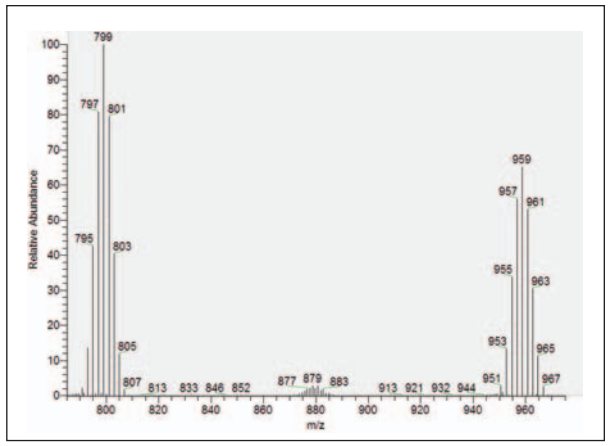

Figure 3: Full scan data for Deca-BDE (209)

For every congener tested, the highest intensity ion cluster was observed to be the one resulting from the loss of two bromine atoms. Therefore, the SIM ions chosen were the most intense ions in these clusters. A list of the SIM ions chosen can be found in Table 2.

Results

Figure 4 shows an example of a chromatogram for the ten congener mixture. The method provides an effective chromatographic separation of all ten congeners. Even while obtaining a full scan spectrum with a short runtime, multiple points across each peak are observed, as shown for Tri-BDE (28) in Figure 5.

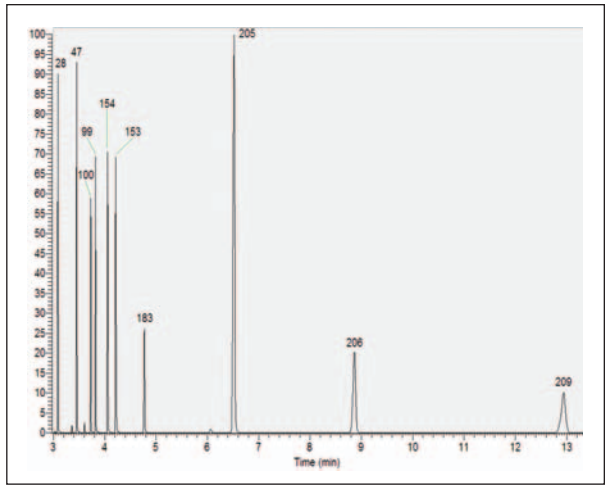

Figure 4: Chromatogram showing baseline separation of the 10 PBDE congeners tested

CONGENER	SIM PARAMETERS: (MASS, WIDTH, DWELL TIME) UNITS: amu, amu, msec	LINEAR CALIBRATION RANGE (pg/µL)	LIMIT OF DETECTION (fg/µL)	R^2 VALUE FOR CALIBRATION CURVE
Tri-BDE (28)	(246.1, 1.0, 75), (248.1, 1.0, 75)	2 – 5,000	62.5	0.9999
Tetra-BDE (47)	(224.0, 1.0, 50), (326.0, 1.0, 50), (328.0, 1.0, 50)	2 – 5,000	62.5	0.9999
Tetra-BDE (77) (Internal Standard)	(224.0, 1.0, 50), (326.0, 1.0, 50), (328.0, 1.0, 50)	N/A	N/A	N/A
Penta-BDE (99)	(403.9, 1.0, 75), (405.9, 1.0, 75)	2 – 5,000	31.3	0.9999
Penta-BDE (100)	(403.9, 1.0, 75), (405.9, 1.0, 75)	2 – 5,000	31.3	1.0000
Hexa-BDE (153)	(481.8, 1.0, 75), (483.8, 1.0, 75), (485.8, 1.0, 75)	2 – 5,000	31.3	1.0000
Hexa-BDE (154)	(481.8, 1.0, 75), (483.8, 1.0, 75), (485.8, 1.0, 75)	2 – 5,000	31.3	1.0000
Hepta-BDE (183)	(561.7, 1.0, 100), (563.1, 1.0, 100)	2 – 5,000	125	0.9998
Octa-BDE (205)	(639.6, 1.0, 150), (641.6, 1.0, 150), (643.6, 1.0, 150)	2 – 5,000	125	0.9979
Nona-BDE (206)	(719.6, 1.0, 400), (721.6, 1.0, 400)	2 – 5,000	1,000	0.9972
Deca-BDE (209)	(797.5, 1.0, 400), (799.5, 1.0, 400), (801.5, 1.0, 400)	2 – 5,000	2,000	0.9971

Table 2: Quantitative data for the PBDE congeners analyzed

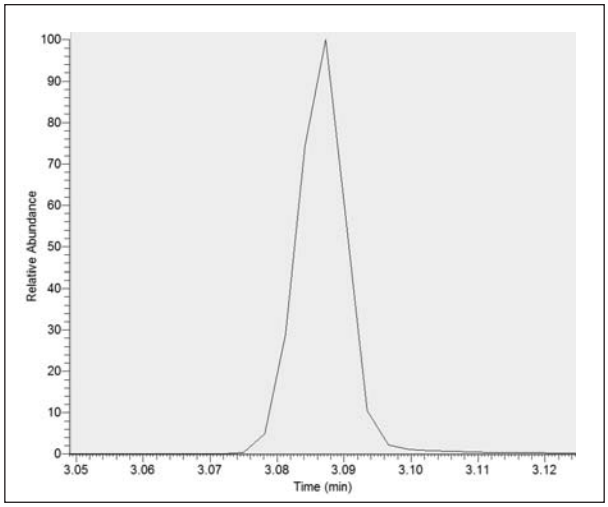

Figure 5: Chromatographic peak of Tri-BDE (28), which is the first congener to elute. Six points across it's peak are observed providing good peak definition.

The instrumentation and method also provided good quantitative data. Listed in Table 2 are the ranges of linearity successfully tested and the limits of detection (LOD) for each of the congeners analyzed. The LOD for each congener was determined by making successive 50% dilutions of the lowest level standard until the peak for each congener was no longer observable. Figure 6 shows an example of a calibration curve from which this data was obtained. The percent RSD for the internal standard, Tetra-BDE (77), was calculated over the 15 runs used to generate the calibration curves. The result was a 6.3% RSD, showing that the method is precise and stable over consecutive runs.

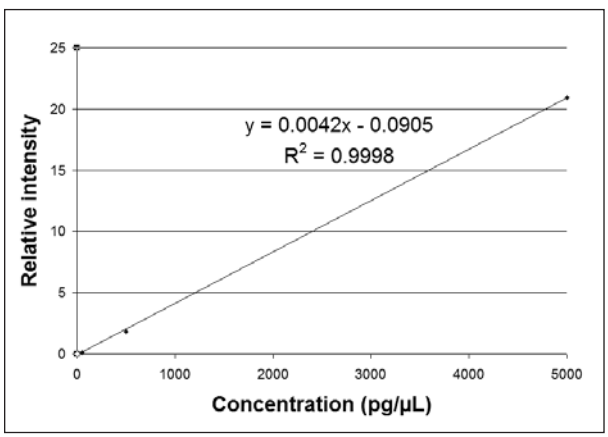

Figure 6: Calibration curve for Hepta-BDE (183)

A soil sample obtained from the grounds nearby was extracted and analyzed for PBDEs. The simple extraction consisted of stirring and then sonicating fine dirt granules for ten minutes in methylene chloride. The resulting liquid extract was poured over glass wool to filter out the soil. A solvent exchange with isooctane was then performed by blowing off the methylene chloride under low heat (~ 60°C). 5 mL of isooctane were added to the resulting residue.

14.306 g of soil were extracted. The sample was run according to the method described above, and it was discovered that the soil contained Deca-BDE.

To determine the concentration of Deca-BDE, four aliquots of the extracted soil solution were spiked with between 5 pg/µL and 500 pg/µL of Deca-BDE. Additionally, each was spiked with 500 pg/µL of Tetra-BDE (77) used as an internal standard. The samples were run, and a calibration curve was generated which had a linear fit with $R^2 = 1.0000$. The equation for the resulting line follows:

$$I = m * (C + C_o),$$

where "I" is the peak intensity, "m" is the response factor, "C" is the spiked concentration and "C_o" is the concentration present in each sample from the extracted soil. By determining the response factor and the peak intensity at C=0 from the calibration curve, the concentration of Deca-BDE in the original 5 mL isooctane solution can be determined, which in turn can be used to calculate the concentration extracted from the original soil sample. This calculation was made, and it was determined that Deca-BDE was extracted at a concentration of 36.5 ppb from the soil.

Conclusion

The TRACE DSQ proved to be an excellent choice of instrumentation for quadrupole analysis of each PBDE congener tested. The TRACE DSQ's ability to scan up to 1050 amu allows molecular spectra to be obtained for every PBDE congener. Coupled with the TRACE TR-5 column and the method described above, the instrument was able to detect 2 pg/µL or below for each congener tested.

Good chromatographic separation and peak shapes were observed during the runs with the last compound, Deca-BDE, eluting from the column at 13 minutes. Furthermore, the instrument performed admirably identifying and quantitating the PBDE contents of an unknown sample in a common environmental matrix.

References

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