Determination of Polybrominated Diphenylethers (PBDE) in Sediment and Sewage Sludge

Application

Environmental

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Abstract

Generally used as flame retardants, polybrominated diphenylethers (PBDE) have become chemicals of significant environmental concern. While little toxicological information is available, PBDEs have been determined to be persistent and bio-accumulative substances, similar to well-known environmental contaminants such as polychlorinated biphenyls (PCBs). Therefore, environmental laboratories are asked to analyze polybrominated diphenylethers (flame retardants) in sediment and sewage sludge. This application note describes the successful separation of all PBDEs, including the most difficult, decabrominated diphenylether. Examples include standards as well as real samples of sewage sludge with quantitative data.

Introduction

With increasing frequency, environmental laboratories are asked to analyze PBDEs (flame retardants) in sediment and sewage sludge. See Figure 1.

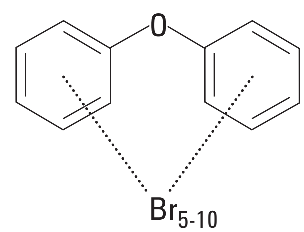

Figure 1. Structure of PBDEs.

Brominated flame retardants (BFRs) are a group of chemicals added to many products, including computers, TVs, and household textiles, in order to reduce fire risk. Two substances, decabromodiphenyl ether (DecaBDE) and tetrabromobisphenol A (TBBP-A), account for about 50% of world use of brominated flame retardants. Two other polybrominated diphenyl ethers (PolyBDE) - octabromodiphenyl ether (OctaBDE) and pentabromodiphenyl ether (PentaBDE) - are used commercially, but in much smaller quantities than DecaBDE.

Heating (for example, during manufacture of plastics) and burning of materials containing PBDEs and other BFRs can produce polybrominated dibenzo-p-dioxins and dibenzofurans, which have similar toxicological effects to chlorinated dioxins. Research has shown that low-level exposure of young mice to PBDEs causes permanent disturbances in behavior, memory, and learning (Eriksson et al., 1998) [1]. PBDEs have also been shown to disrupt the thyroid hormone system in rats and mice; these systems are a crucial part of the development of the brain and body (Darnerud and Thuvander, 1998 [2]; Hallgren and Darnerud, 1998) [3].

The release of these organic pollutants can be revealed by analyses of sewage sludge produced by municipal waste-water treatment plants. Therefore, the European community has given a directive (2000/60/CE) [4] for water to analyze four PBDEs (BDE-99, BDE-100, BDE-205, BDE-209) and is now working on an ISO norm ISO/CD 22032 to analyze eight PBDEs (BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-205, BDE-209).

This analysis starts with an extraction of brominated diphenyl ethers (BDEs) from the dried sample of sediment or sewage sludge by a solvent (for example, hexane or other solvents suitable to get high extraction rates). The extract is cleaned, with silica, for example, if necessary. After concentration, the BDEs are separated by capillary gas chromatography (GC) and detected with a suitable system. A calibration over the total procedure using an internal standard (ISTD) mix is used to calculate the concentration in the sample.

When analyzing PBDE with GC, a number of problems arise: [5]

- Adsorption to glass surfaces
- Discrimination of high molecular weight compounds
- Degradation of the heavier congeners
- Irreproducible results
- Disappearing peaks

This application note gives analysts the necessary tools to attempt low-level detection of PBDE by gas chromatography/mass spectrometry (GC/MS).

Materials and Methods

Samples

All sewage sludge and sediment samples were provided by municipal waste-water treatment plants. Ten grams of sediment or 1 g of sewage sludge is liquid extracted. The extract is cleaned on silica and the clean extract is concentrated in 1-mL hexane prior to GC analysis.

Standards and ISTDs

The project for the European norm 22032 (2000/60/CE) is requesting analysis of four PDBE (BDE-99, BDE-100, BDE-205 and BDE-209) and recommends TetraBDE (BDE-77) as ISTD. (See Table 1.) These standards were purchased commercially and were of the highest grade available. A test mixture of pentaBDE (BDE-99, BDE-100), octaBDE (BDE-205), and decaBDE (BDE-209) was used for the evaluation in order to obtain a GC analysis with little or no discrimination. BDE-77 was used as ISTD. Standard solutions containing 0.01; 0.05; 0.1; 0.2; 0.25; 0.5 ng/µL of pentaBDE, 0.5; 1; 2; 3; 4; ng/µL of decaBDE and octaBDE, and 0.2 ng/µL of ISTD were prepared in hexane.

Table 1. Selected BDEs

Name	Formula	Abbreviation	Molar mass g/mol
3,3',4,4'-tetraBDE	$C_{12}H_6Br_4O$	BDE-77	481.715
2,2',4,4',5-pentaBDE	$C_{12}H_5Br_5O$	BDE-99	564.6911
2,2',4,4',6-pentaBDE	$C_{12}H_5Br_5O$	BDE-100	564.6911
2,3,3',4,4',5,5',6-octaBDE	$C_{12}H_2Br_8O$	BDE-205	801.3804
DecaBDE	$C_{12}Br_{10}O$	BDE-209	959.1714

GC Conditions

The selection of column and injection parameters is of great importance for the GC analysis of PBDE, especially for the high molecular weight congeners. See Table 2.

The temperature of the GC is of great importance since some congeners decompose at temperatures just above 300 °C. Thermal degradation is a function of temperature and time; thus, by choosing a column with as little retention for the BDE congeners as possible and shortening the column to the minimum length required for the separation, thermal degradation can be minimized. In addition, pulsed injection allows shorter injection time and also helps to minimize risk of thermal degradation.

A pulsed splitless injection and a DB-1 30 m, 0.32 mm, thin film, 0.1 µm, really minimizes the time each PDBE stays in both the injector and in the column and avoids degradation.

Table 2. Optimized Run Conditions

Column: **Part number:**	**DB-1** **123-1031**
Length:	30 m
Diameter:	0.32 mm
Film thickness:	0.1 µm
Carrier:	Helium at 58 cm/s Flow rate 2.5 mL/min
Injector:	2 µL Pulsed splitless at 250 °C
Oven:	60 °C for 2 minutes 60 °C–200 °C at 10 °C/min 200 °C for 2 minutes 200 °C–300 °C at 20 °C/min 300 °C for 25 minutes
Detector	MS
Agilent 5973 inert MSD	
SIM mode	Group 1 / 3 min / *m/z* 486; 484; 326 Group 2 / 20 min / *m/z* 406; 564; 566 Group 3 / 24 min / *m/z* 642; 644; 562 Group 4 / 28 min / *m/z* 799; 797
Quad temperature	150 °C
Source temperature	230 °C
Transfer line temperature	300 °C

Results and Discussion

The chromatograms (Figures 2 and 3) show very good peak shapes for each PBDE and a high response for the most critical decaBDE (BDE-209) (see Figure 4) using the optimized run conditions listed in Table 2.

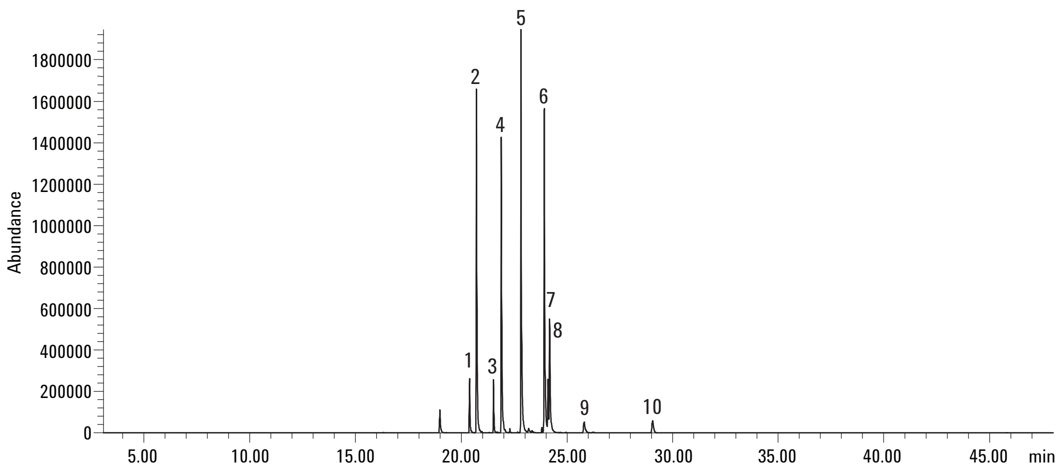

Figure 2. Total Ion Chromatogram (TIC) of a standard mixture at 2–20 ng/µL
1–2: pentaBDE
3–9: octaBDE
10: decaBDE

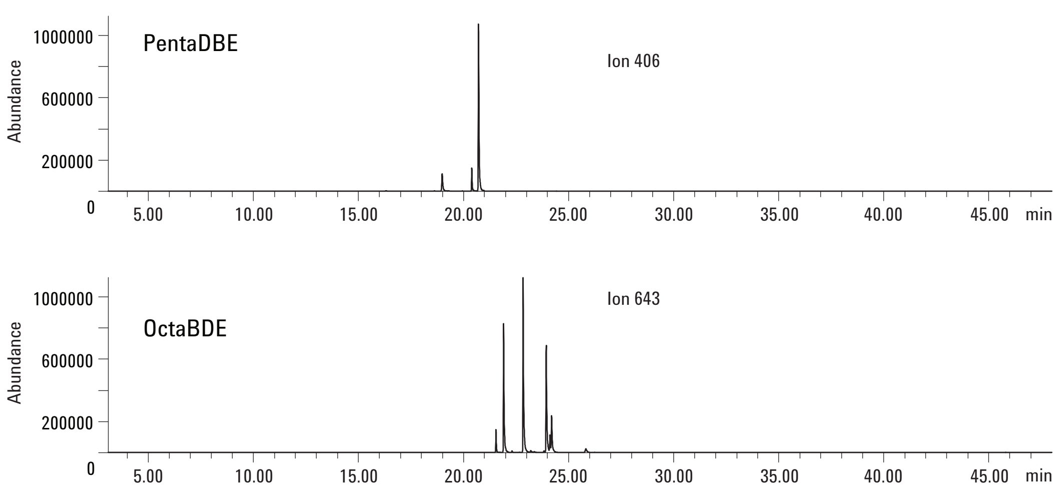

Figure 3. Selected Extracted Ion Chromatograms (EICs) of a standard mixture at 0.5–5 ng/µL.

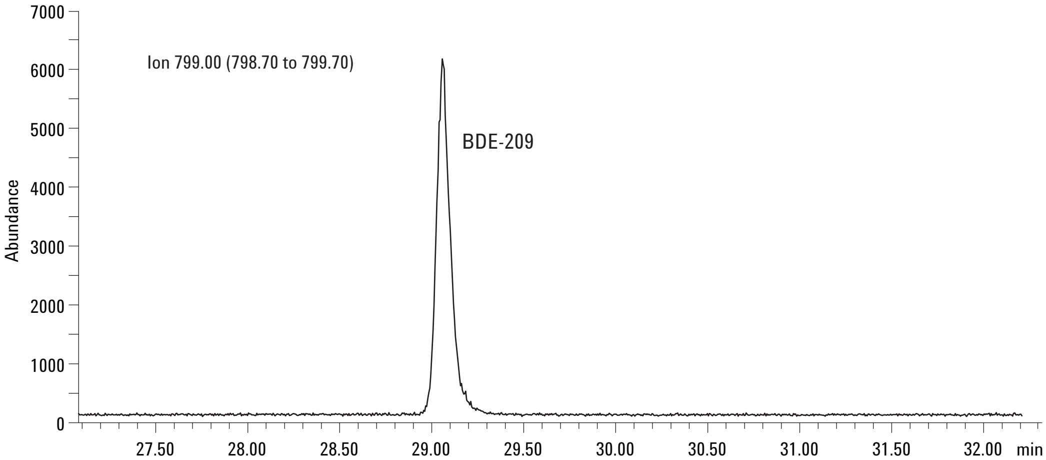

Figure 4. EIC of BDE-209 in a standard mixture at 5 ng/µL.

In order to have a precise quantitation, five point calibration curves from 0.01 to 0.25 ng/µL for pentaBDE and from 0.5 to 4 ng/µL of octa and decaBDE were achieved with ISTD BDE-77 at 0.2 ng/µL. (See Figure 5.) For all components, the R^2 values range from 0.996 to 1, meeting the AFNOR requirements for valid quantitation (See Table 3).

Table 3. Calibration Curve Summary Using Optimized Analysis Conditions with GC/MS

Compound	Calibration range (ng/µL)	Target ion *m/z*	Qualifier ion *m/z*	R^2 value
BDE-77	*ISTD–0.2*	486.0	326.0	ISTD
BDE-99	*0.01–0.25*	405.8	563.6	1
BDE-100	*0.01–0.25*	405.8	563.6	1
BDE-205	*0.5–4*	641.6	643.6	0.990
BDE-209	*0.5–4*	799.4	797.4	0.996

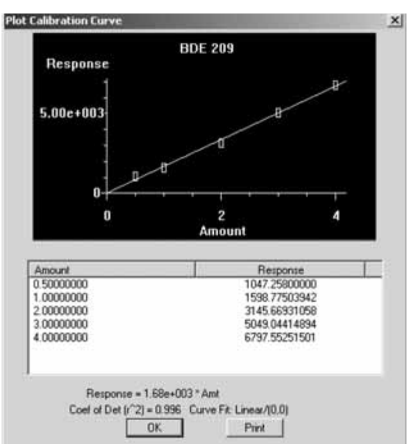

Figure 5. Calibration curve for decaBDE (BDE-209) by GC/MS.

Concerning the limit of detection (LOD), the lower level at 1 µg/kg (10 µg/kg for sewage sludge\) for pentaBDE and 50 µg/kg (500 µg/kg for sewage sludge) for octaBDE and decaBDE in sediment, which is 10 pg/µL of pentaBDE or 0.5 ng/µL of octa and decaBDE in solution, is easily achieved. This is the case even for decaBDE because a very good signal-to-noise ratio was achieved, as shown in Figure 6.

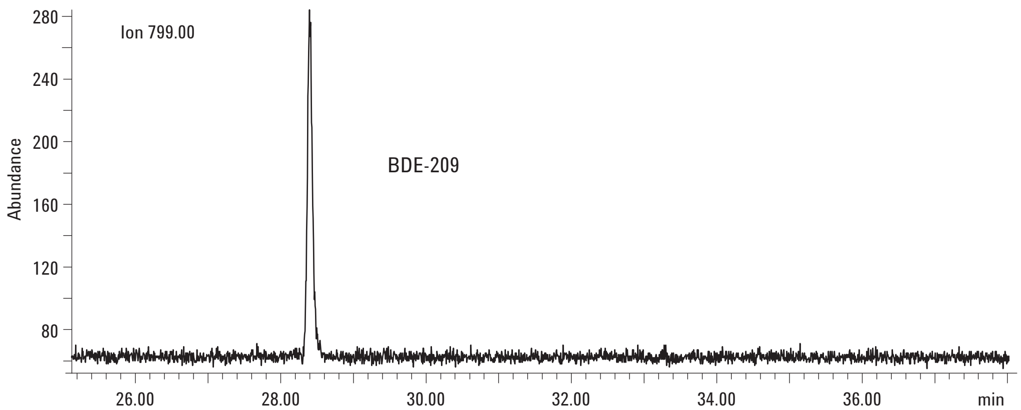

Figure 6. EIC of BDE-209 in a standard mixture at 0.5 ng/µL, which is the required LOD 50 µg/kg of sediment.

Real sewage sludge samples were analyzed using the run conditions listed in Table 2. Figure 7 shows one example. The EICs of the different PDBE show that only one pentaBDE and the decaBDE are present in this sample, and they were quantified in a quantitation report showed on Table 4.

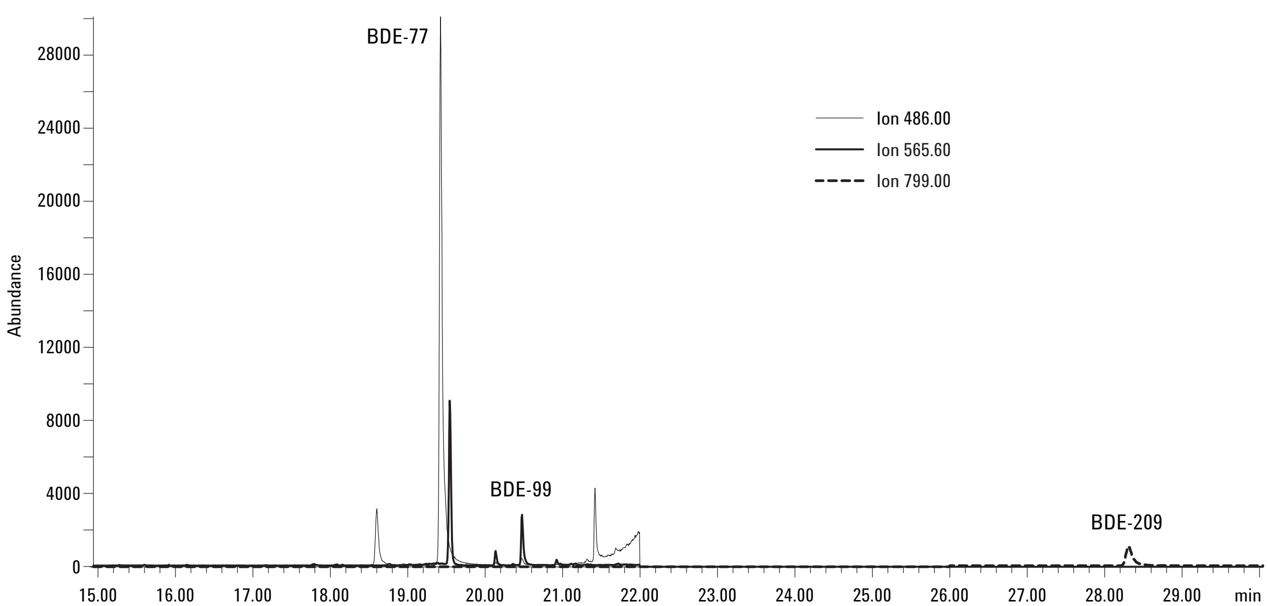

Figure 7. Overlaid EICs for BDE-77, 99, and 209 from sewage sludge.

Table 4. Quantitation Report of Real Sewage Sludge

ISTDs	RT	QIon	Response	Conc units	Dev(min)
BDE 77	19.43	486	823207	0.20 ng/µL	0.02
Target compounds					**Qvalue**
BDE 100	20.14	406	22687	0.0072 ng/µL	11
BDE 99	20.48	406	107372	0.0405 ng/µL	87
BDE 205	23.91	642	17336	0.3417 ng/µL	57
BDE 209	28.31	799	64526	5.2530 ng/µL	90

Summary

By combining the highly inert thin film DB-1 with the Agilent 6890 gas chromatograph and the Agilent 5973 inert MSD, laboratories can achieve accurate quantitation of PBDE in sediments and sewage sludge.

References

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5. E. Kuhn, J. Ellis, and S. Wilbur, GC Analysis of Polybrominated Flame Retardants, Agilent Technologies publication 5989-0094EN www.agilent.com.chem

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