Polybrominated Diphenyl Ether (PBDE) Analysis Using an Agilent J&W DB-5ms Ultra Inert Capillary GC Column

Application

Environmental

Authors

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Abstract

Trace and ultra trace-level polybrominated diphenyl ether (PBDE) analyses are important tools for understanding food supply and environmental quality worldwide. In this application, trace-level PBDE analysis is demonstrated using electron impact single quadrupole scanning mass spectrometry. For these challenging separations, knowing that each GC column has been thoroughly tested for column inertness gives the analyst higher confidence in the accuracy of the results.

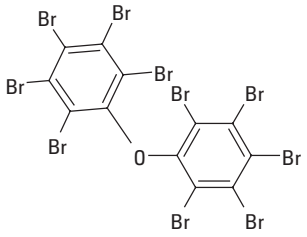
Agilent Technologies Inc. has implemented new testing procedures to more effectively evaluate GC column inertness performance. This new testing procedure employs deliberately aggressive probes to thoroughly investigate column inertness and quality. These extremely active probes, including 1-propionic acid, 4-picoline, and trimethyl phosphate, are used to verify each column's inertness performance.

Introduction

Polybrominated diphenyl ethers (PBDEs) are both persistent and increasingly common in the environment. These chemicals are typically used as flame retardants in textiles and electronic products such as televisions and computer equipment. There are 209 possible PBDE congeners that vary in the degree of bromination from mono to fully brominated decabromodiphenyl ether. Each of the individual congeners is assigned both an IUPAC name and bromodiphenyl ether (BDE) number, by convention. For example, fully brominated decabromodiphenyl ether is assigned the number BDE-209.

PBDEs as a class of molecules tend to undergo degradation on exposure to heat and light. BDE-209's long retention and susceptibility to thermal breakdown make it a particularly challenging analyte.

BDE-209 Structure



Unfortunately, these chemicals continue to find their way into food supplies and common house dust. [1–5] Similarities between PBDEs and polychlorinated biphenyl (PCBs) compounds include their tendency to persist in the environment and to bioaccumulate in adipose tissues.

The chief routes of human exposure to PBDEs appear to be ingestion of contaminated foods and inhalation of contaminated house dust. Measurable levels of PBDEs have been found in fish, meats,

dairy products, eggs, and vegetables. Higher levels of PBDEs are found more often in fish than in other food sources. House dust studies in the U.S., Belgium, and Singapore have all shown appreciable levels of PBDEs. The need for reliable, sensitive, and robust analytical methods for the analysis of PBDEs is of global concern.

Long-term human toxicities for PBDEs are not well understood, even though a number of studies have found appreciable levels in breast milk and human adipose tissue. These studies suggest a link between long-term exposure of the mother to specific BDEs and neurological effects in the growing fetus. Human heath concerns led to a ban on the use of penta-BDE and octa-BDE within the European Union in 2004.

This application highlights the value of using a 15-m Agilent J&W DB-5ms Ultra Inert capillary GC column for challenging PBDE analysis. Agilent Technologies Inc. has implemented new testing procedures to more effectively evaluate GC column inertness performance. This new testing procedure employs deliberately aggressive probes to thoroughly investigate column inertness and quality. These extremely active probes, including 1-propionic acid, 4-picoline, and trimethyl phosphate, are used to verify each column's inertness performance. Capillary GC column activity as a potential source of result uncertainty has been all but eliminated with the Ultra Inert series of columns.

Experimental

An Agilent 6890N GC/5975B MSD equipped with a 7683B autosampler was used for this series of experiments. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow-path consumable supplies used in these experiments.

Sample Preparation

A seven-level eight-component BDE calibration curve set was purchased from AccuStandard (New Haven, CT). These solutions were transferred directly to amber glass autosampler vials and used as supplied. Concentration ranges were 0.5 to 250 ng/mL for BDEs -47, -100, -99, -154, -153, -183, and -205. BDE-209 concentration ranged from 2.5 to 1,000 ng/mL. The isooctane used was Burdick and Jackson Ultra Resi Grade purchased through VWR International (West Chester, PA, USA). Isooctane was used as a reagent blank and syringe wash solvent.

Table 1. Chromatographic Conditions

GC	Agilent 6890N/5973B MSD
Sampler	Agilent 7683B, 5.0-µL syringe (Agilent p/n 5188-5246), 1.0-µL splitless injection, 5 ng each component on column
Carrier	Helium 72 cm/s, constant flow
Inlet	Pulsed splitless; 325 °C, 20 psi until 1.5 min, purge flow 50 mL/min at 2.0 min
Inlet liner	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Column	Agilent J&W DB-5ms Ultra Inert 15 m × 0.25 mm × 0.25 µm (Agilent p/n 122-5512UI)
Oven	150 to 325 °C (17 °C/min), hold 5 min
Detection	MSD source at 300 °C, quadrupole at 150 °C, transfer line at 300 °C, scan range 200–1000 amu
SIM program	

			SIM ions			
Time (min)	Group	PBDE bromination	$[M]^+$	$[M-Br_2]^+$	$[M-Br_2]^{+2}$	Confirmation ion
3.00	1	3	405.8	246		247.9
		4	485.7	325.8	162.9	
5.75	2	5	536.6	403.8		565.7
		6	643.6	483.7	241.8	
8.00	3	7	721.5	561.6		563.6
9.25	4	8	801.5	641.5	320.8	643.6
11.50	5	10	959.3	799.4	399.7	797

Table 2. Flow Path Supplies

Vials	Amber glass vials (Agilent p/n 5182-0716)
Vial caps	Blue screw cap (Agilent p/n 5282-0723)
Vial inserts	100 µL glass/polymer feet (Agilent p/n 5181-1270)
Syringe	5 µL (Agilent p/n 5181-1273)
Septum	Advanced Green (Agilent p/n 5183-4759)
Inlet liners	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Ferrules	0.4 mm id short; 85/15 Vespel/graphite (Agilent p/n 5181-3323)
20x magnifier	20x magnifier loupe (Agilent p/n 430-1020)

Results and Discussion

Baseline Inertness Profile for Ultra Inert Columns

The basic approach for inertness verification for the Agilent J&W Ultra Inert series of capillary GC columns is testing with highly active probes at low concentration and low temperature. [6] This is a new rigorous approach that establishes consistent baseline inertness profiles for each column in the Agilent J&W Ultra Inert GC column series. The baseline inertness profile then serves as a predictor for successful analysis of chemically active species that tend to adsorb onto the column's active sites, particularly at trace levels, like the BDEs in this application example. A detailed description of the test mix and additional application examples are available in references 7 through 9.

PBDE Analyses

PBDE-209 is a particularly challenging analyte due to its long retention and tendency to degrade with high-temperature exposure. High-temperature thermal stability is an issue for this class of compounds, but is more pronounced for BDE-209, as it is highly brominated and well retained. One key to successful BDE analysis is to limit the time that these compounds are exposed to high temperatures. A 15-m long column, as opposed to a typical 30-m long column was used in this case to limit residence time for BDE-209. [10,11] Fortunately, the BDEs resolve well, with symmetrical peak shapes, when using Agilent J&W DB-5ms phase, enabling successful separation on the shorter column. Figure 1 shows a total ion chromatogram of the eight BDEs investigated in this study.

In this application a seven-level eight-component BDE calibration curve set was evaluated over the concentration range of 0.5 to 250 ng/mL for BDEs -47, -100, -99, -154, -153, -183, and -205 and the range of 2.5 to 1,000 ng/mL BDE 209 on an Agilent J&W Ultra Inert DB-5ms 15 m × 0.25 mm × 0.25 µm (p/n 122-5512UI) column. Sensitivity was excellent, even for the more challenging BDE-209 with a 0.025 ng on-column loading, yielding a 3.28 signal-to-noise level. The exploded view of the BDE-209 peak in Figure 2 illustrates the sensitivity observed for a 0.025-ng on-column loading of BDE-209.

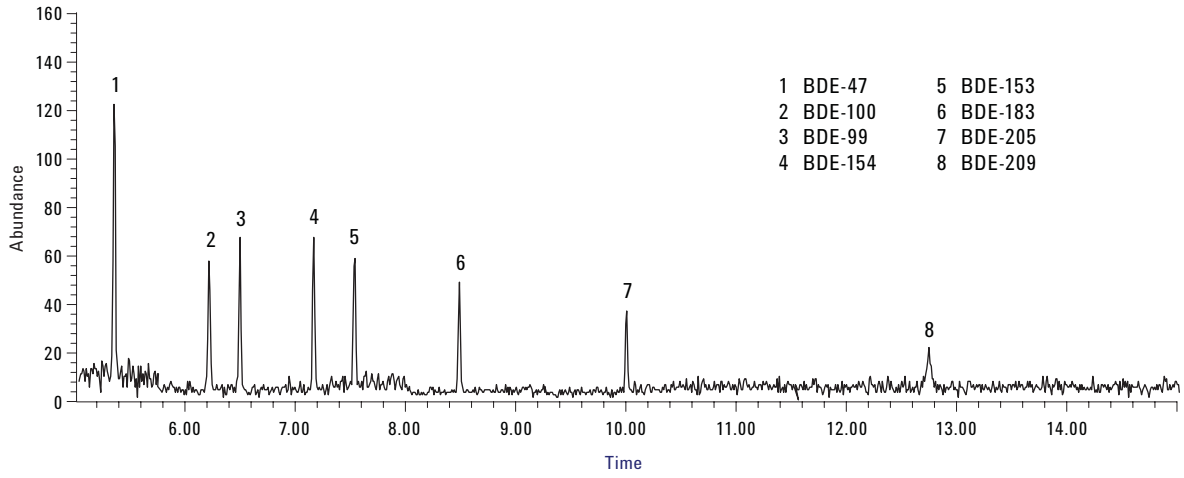


Figure 1. Total ion chromatogram (SIM mode) of a 0.005-ng (BDEs -47, -100, -99, -154, -153, -183, -205, and -209) and 0.025-ng (BDE-209) on-column loading on an Agilent J&W DB-5ms Ultra Inert 15 m × 0.25 mm × 0.25 µm capillary GC column (p/n 122-5512UI).

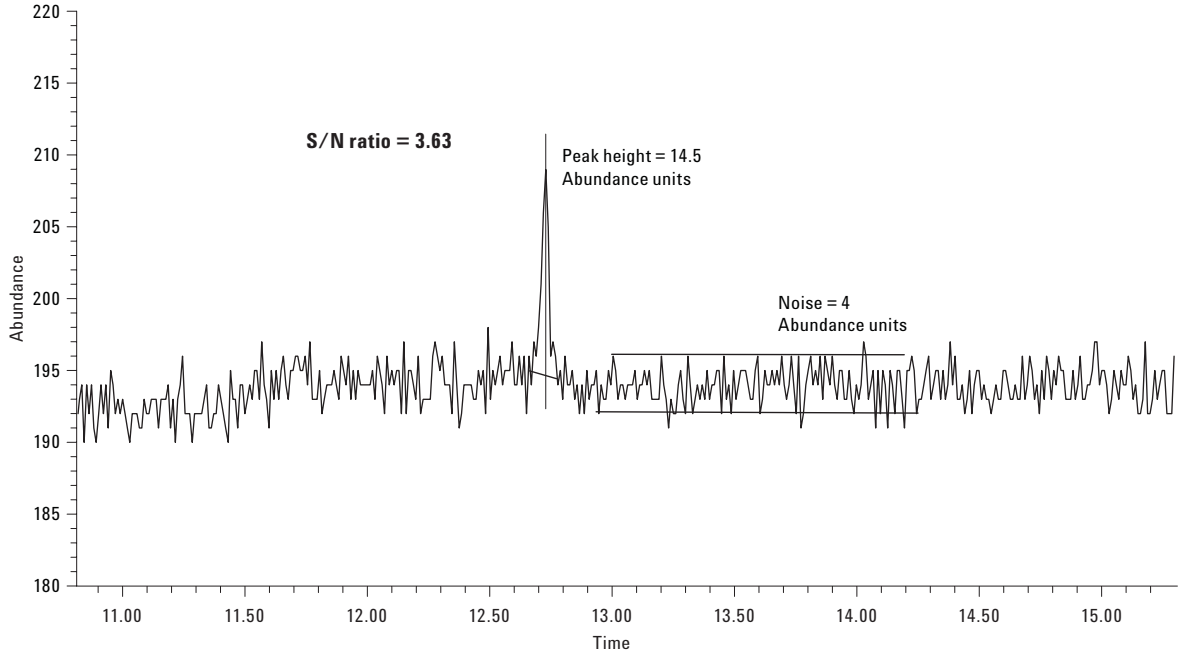


Figure 2. **Enlarged section of the total ion chromatogram (SIM mode) of a 0.025-ng BDE-209 on-column loading. The large peak in the figure is BDE-209, a particularly challenging BDE due to its long retention and thermal instability.**

Linearity was excellent across the range studied, giving R^2 values of 0.997 or greater in all cases. Figure 3 indicates the correlation coefficients for each of the individual analytes and shows an example linear regression plot for BDE-209.

BDR	R^2
47	0.999
100	0.999
99	0.999
154	0.999
153	1.000
183	0.999
205	0.999
209	0.997

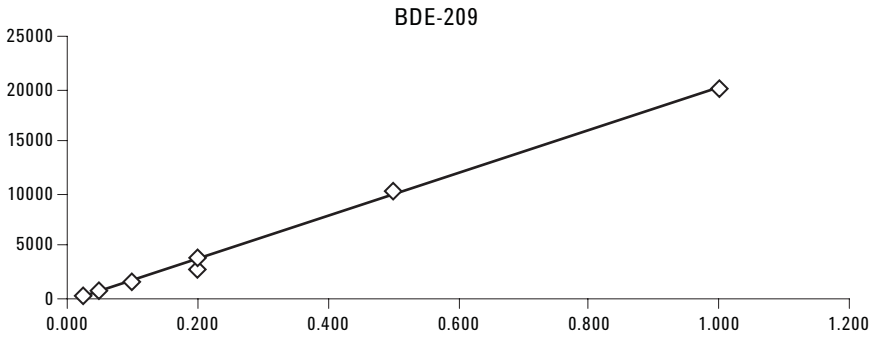


Figure 3. **Correlation coefficients for the eight components over the 0.5 ng / mL to 1,000 ng / mL concentration range (BDE-209 2.5 to 1,000 ng / mL) used in this study. An example linear regression plot of particularly challenging BDE-209 is also shown.**

Conclusions

This application successfully demonstrates the use of a 15-m Agilent J&W DB-5ms Ultra Inert capillary GC column for trace-level BDEs in a 15-minute analysis. Linearity was excellent for all eight BDEs studied, yielding 0.997 or greater R^2 values down to a 0.005 ng (0.025 ng for BDE-209) on-column loading of each component. One of the reasons for the excellent linearity and high R^2 values is the highly inert surface of the column. The lack of chemically active sites makes these columns an excellent choice for trace-level applications.

The Agilent 6890/5975B GC/MSD (SIM mode) equipped with an inert electron impact source had excellent sensitivity with even the most challenging BDE in this set, PBD-209. The signal-to-noise ratio for a 0.025-ng on-column loading of BDE-209 was greater than three to one with this system. This result shows clearly the power of using an Agilent J&W DB-5ms Ultra Inert column for trace-level BDE analysis. Lower limits of quantification are expected when using one of Agilent's latest GC/MS offerings, such as the 7890/5975C GC/MSD Triple-Axis Detector coupled with an Agilent J&W DB-5ms Ultra Inert GC capillary column.

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Printed in the USA
August 27, 2008
5989-9571EN

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