GC Analysis of Polybrominated Flame Retardants

Application

Environmental

Authors

Eberhardt Kuhn, Jason Ellis
Agilent Technologies, Inc.
91 Blue Ravine Rd,
Folsom, CA 95630
USA

Steve Wilbur
Agilent Technologies, Inc.
3380 146th Place SE
Suite 300
Bellevue, WA 98007
USA

Abstract

Polybrominated diphenyl ethers (PBDE) are used as flame retardants in such diverse products as textiles, circuit boards, and computer covers. Through the disposal of those products in landfills, PBDEs have found their way into the environment. Studies have shown that PBDEs have detrimental health effects.

Detection and quantitation of these compounds is complicated by their intrinsic properties: high boiling points and low thermal stability. This application note describes development of suitable gas chromatography/mass spectrometry, gas chromatography micro electron capture detection, and gas chromatography inductively coupled plasma mass spectrometry methods to analyze PBDEs. The Agilent DB-XLB is the column of choice for this demanding analysis. The detection limit with micro electron capture detector was 100 ppt for most congeners.

Introduction

The presence of polybrominated diphenyl ethers (PBDE) throughout the environment has attracted the attention of scientists around the world. PBDEs are used as flame retardants in many commercial products, such as textiles and furniture, and in circuit boards in consumer electronics, such as TVs and computers. As more and more of these abundant consumer products find their way into landfills, PBDEs have been found in our drinking water supplies [1]. One alarming study predicts that the levels found in human breast milk of North American women appear to double every 2 to 5 years [2]. Exposure of personnel working with computers is also a concern [3]. While the toxicology of PBDE is still under investigation, research has established that it is persistent, bioaccumulative, and toxic. There is evidence that

PBDE can cause neurotoxic effects similar to the now-banned polychlorinated biphenyls (PCB). As a result, California has just signed legislation banning the use of PBDEs [4]. Like PCBs, there are 209 PBDE congeners (Figure 1), and they are named in analogy to PCBs [5]. However, only seven congeners comprise about 95% of all detected peaks [6]. These major congeners are (by IUPAC number): 28, 47, 99, 100, 153, 154, and 209.

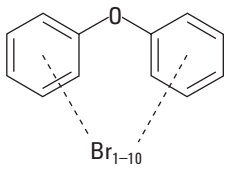


Figure 1. Structure of PBDE.

Until recently, the lack of available standards and individual congeners has made accurate quantitation difficult [7]. Now, practically all individual congeners are commercially available. For analysis by GC, several different stationary phases have been used. However, analysis times are generally quite long, and often not all critical congeners are sufficiently resolved. This study investigates two different columns and three detection modes. DB-XLB (Agilent Technologies, Folsom CA), a proprietary low-polarity stationary phase and DB-35ms (Agilent Technologies, Folsom CA), a mid-polarity phase, are both columns that have very low bleed and high thermal stability. DB-XLB has shown to be an excellent choice for detailed, high-resolution analysis of PCB congeners by GC/MS [8]. The structural similarities between PCBs and PBDEs suggest that DB-XLB should be an excellent choice for separation of PBDEs as well. DB-35ms has shown to be a suitable confirmatory column to DB-XLB [9]. The detection modes evaluated were mass selective detector (MSD), micro electron capture detector (μECD), and inductively coupled plasma mass spectrometry (ICP-MS). Method optimization efforts for speed, sensitivity, and resolution included different column dimensions, inlet conditions, detector settings, and temperature programs.

Results and Discussion

Baseline separation of all 14 critical congeners (Table 1) in a standard mixture including decabromodiphenylether (BDE-209) could be accomplished by DB-XLB in about 20 minutes with excellent peak shape and response of the decabromodiphenylether [10].

Table 1. PBDE Congeners in Test Mix EO-5103 Elution Order on DB-XLB

Peak	Congener (2.5 mg/mL)
1	2,2',4-TriBDE (BDE-17)
2	2,4,4'-TriBDE (BDE-28)
3	2,3',4',6-TetraBDE (BDE-71)
4	2,2',4,4'-TetraBDE (BDE-47)
5	2,3',4,4'-TetraBDE (BDE-66)
6	2,2',4,4',6-PentaBDE (BDE-100)
7	2,2',4,4',5-PentaBDE (BDE-99)
8	2,2',3,4,4'-PentaBDE (BDE-85)
9	2,2',4,4',5,6'-HexaBDE (BDE-154)
10	2,2',4,4',5,5'-HexaBDE (BDE-153)
11	2,2',3,4,4',5'-HexaBDE (BDE-138)
12	2,2',3,4,4',5',6-HeptaBDE (BDE-183)
13	2,3,3',4,4',5,6-HeptaBDE (BDE-190)
14	DecaBDE (BDE-209) (12.5 mg/mL)

A more demanding mixture (Table 2a,b) containing 39 of the most common and important congeners at very low concentration could be separated by DB-XLB in about 14 minutes (Figure 2a, b). This is much faster than analysis times typically reported with other columns. Although two of the tetra isomers are very close with this column, they were baseline resolved with DB-35ms. By contrast, there were two co-elutions with the DB-35ms, which were both baseline resolved on DB-XLB. This demonstrates that these two stationary phases are an excellent choice as a pair of confirmation columns. For baseline resolution of all congeners on a single column, as well as for separation of more complex mixtures, a column with more theoretical plates and/or a higher phase ratio may be necessary. Using

a DB-XLB, 30 m × 0.18 mm × 0.18 µm gave complete baseline separation of the tetra isomers, as did a DB-5ms, 60 m × 0.25 mm × 0.25 µm. However, the higher substituted isomers, in particular BDE-209, showed relatively low response. The lower phase ratio results in longer retention times for all congeners. This longer residence time on the column at high temperature may lead to on-column break down of these thermally labile compounds.

Table 2a. PBDE Congeners in Test Mix EO-5113 Elution Order on DB-XLB

2-MonoBDE (#1)
3-MonoBDE (#2)
4-MonoBDE (#3)

2,6-DiBDE (#10)
2,4-DiBDE (#7)
3,3′-DiBDE (#11)
2,4′-DiBDE (#8)
3,4-DiBDE (#12)
3,4′-DiBDE (#13)
4,4'-DiBDE (#15)

2,4′,6-TriBDE (#32)
2,4,6-TriBDE (#30)
2,2',4-TriBDE (#17)
2,3′,4-TriBDE (#25)
2',3,4-TriBDE (#33)
2,4,4'-TriBDE (#28)
3,3′,4-TriBDE (#35)
3,4,4'-TriBDE (#37)

2,4,4′,6-TetraBDE (#75)
2,2',4,5'-TetraBDE (#49)
2,3′,4′,6-TetraBDE (#71)
2,2',4,4'-TetraBDE (#47)
2,3′,4,4′-TetraBDE (#66)
3,3',4,4'-TetraBDE (#77)

2,2',4,4′,6-PentaBDE (#100)
2,3′,4,4′,6-PentaBDE (#119)
2,2',4,4',5-PentaBDE (#99)
2,3,4,5,6-PentaBDE (#116)
2,3′,4,4′,5-PentaBDE (#118)

2,2',4,4',6,6'-HexaBDE(#155)

2,2′,3,4,4′-PentaBDE (#85)
3,3',4,4',5-PentaBDE (#126)

2,2',4,4',5,6′HexaBDE(#154)
2,2',4,4',5,5'-HexaBDE(#153)
2,2',3,4,4',5'-HexaBDE(#138)
2,3,4,4',5,6-HexaBDE (#166)

2,2',3,4,4',5',6-HeptaBDE (#183)
2,2',3,4,4',5,6-HeptaBDE(#181)
2,3,3',4,4',5,6-HeptaBDE (#190)

Table 2b. PBDE Congeners in Test Mix EO-5113 Elution Order on DB-35ms

3-MonoBDE (#2)
2-MonoBDE (#1)
4-MonoBDE (#3)

2,6-DiBDE (#10)
2,4-DiBDE (#7)
3,3′-DiBDE (#11)
2,4′-DiBDE (#8)
3,4-DiBDE (#12)
3,4′-DiBDE (#13)
4,4'-DiBDE (#15)

2,4′,6-TriBDE (#32)
2,4,6-TriBDE (#30)
2,3′,4-TriBDE (#25)
2,2',4-TriBDE (#17)
2,4,4'-TriBDE (#28)
2',3,4-TriBDE (#33)
3,3′,4-TriBDE (#35)
3,4,4'-TriBDE (#37)

2,2',4,5'-TetraBDE (#49)
2,4,4′,6-TetraBDE (#75)
2,3′,4′,6-TetraBDE (#71)
2,2',4,4'-TetraBDE (#47)
2,3′,4,4′-TetraBDE (#66)
3,3',4,4'-TetraBDE (#77)

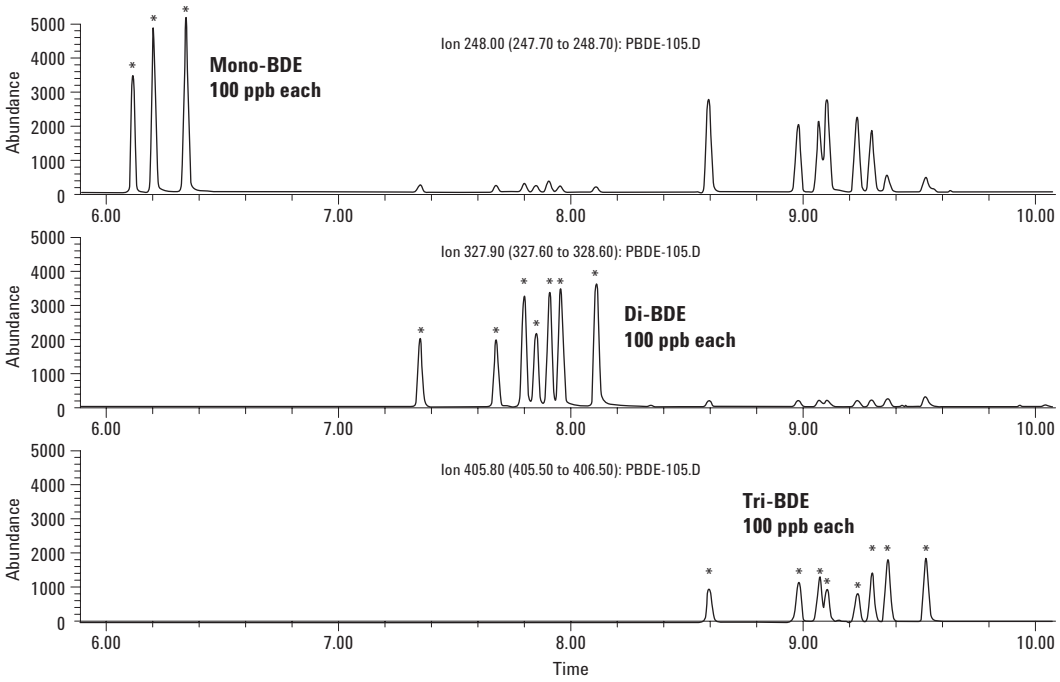
2,2',4,4′,6-PentaBDE (#100)
2,3′,4,4′,6-PentaBDE (#119)
2,2',4,4',5-PentaBDE (#99)
2,3′,4,4′,5-PentaBDE (#118)
2,3,4,5,6-PentaBDE (#116)

2,2',4,4',6,6'-HexaBDE(#155)

3,3',4,4',5-PentaBDE (#126)
2,2′,3,4,4′-PentaBDE (#85)

2,2',4,4',5,6′HexaBDE(#154)
2,2',4,4',5,5'-HexaBDE(#153)
2,2',3,4,4',5'-HexaBDE(#138)
2,3,4,4',5,6-HexaBDE (#166)

2,2',3,4,4',5',6-HeptaBDE (#183)
2,2',3,4,4',5,6-HeptaBDE(#181)
2,3,3',4,4',5,6-HeptaBDE (#190)

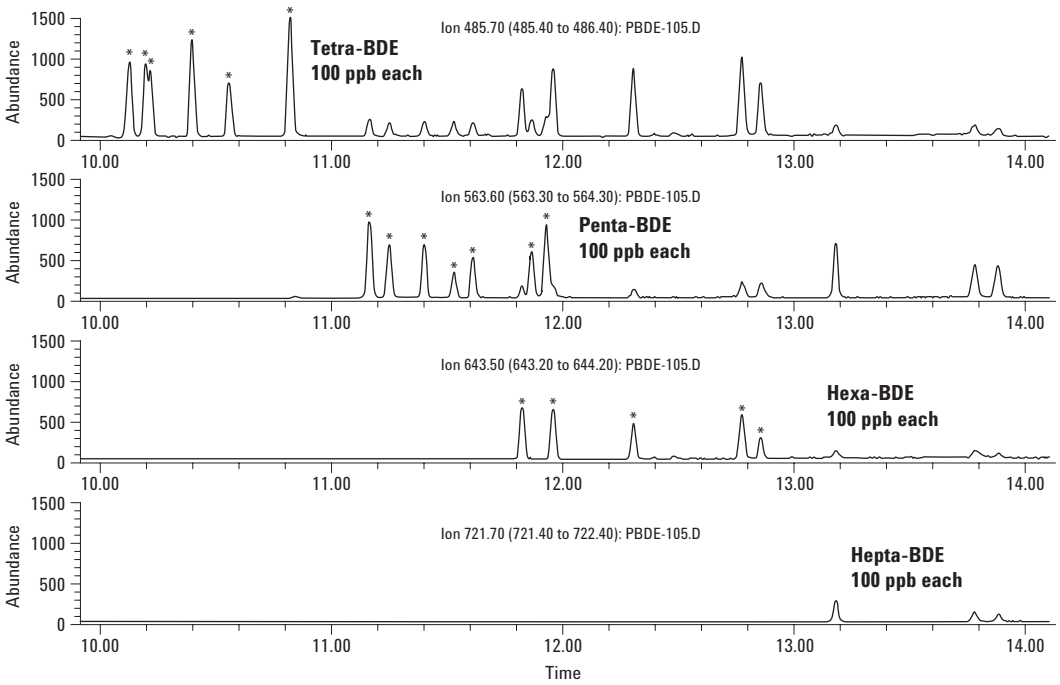


Instrument:	Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column:	DB-XLB, 30 m × 0.25 mm id × 0.1 µm (Agilent Technologies, part number 122-1231)
Carrier gas:	Helium at 38 cm/s at 100 °C (1.2 mL/min), constant flow mode
Oven:	100 °C for 1 min; 100 °C to 340 °C at 20 °C/min , 340 °C for 12 min
Injector:	Cool-on-column, oven-track mode, 0.5 µL
Detector:	Agilent 5973 MSD; transfer line at 325 °C, EI
SIM:	(Ions monitored: 231.8, 248.0, 327.9, 398.6, 400.5, 405.8, 845.7, 563.6, 643.5, 721.4, 799.3)

Note:

Mono-through octa-substituted homologs detected using selected ion monitoring (SIM) at the most intense of the M^+, $(M+2)^+$, $(M+4)^+$, $(M+6)^+$, or $(M+8)^+$ masses, with a data acquisition rate of approxroximately 3 cycles/second. Monitoring the molecular ion was not possible above octa-substituted PBDEs due to the limitations of the mass range of the Agilent 5973 instrument (maximum of *m/z* 800). Decabromodiphenylether was detected by monitoring significant fragments of high abundance: *m/z* 231.8, 398.6, 400.5, and 799.3.

Figure 2a. Gas chromatography/mass spectrometry (GC/MS) of PBDE congener mixture (EO-5113).



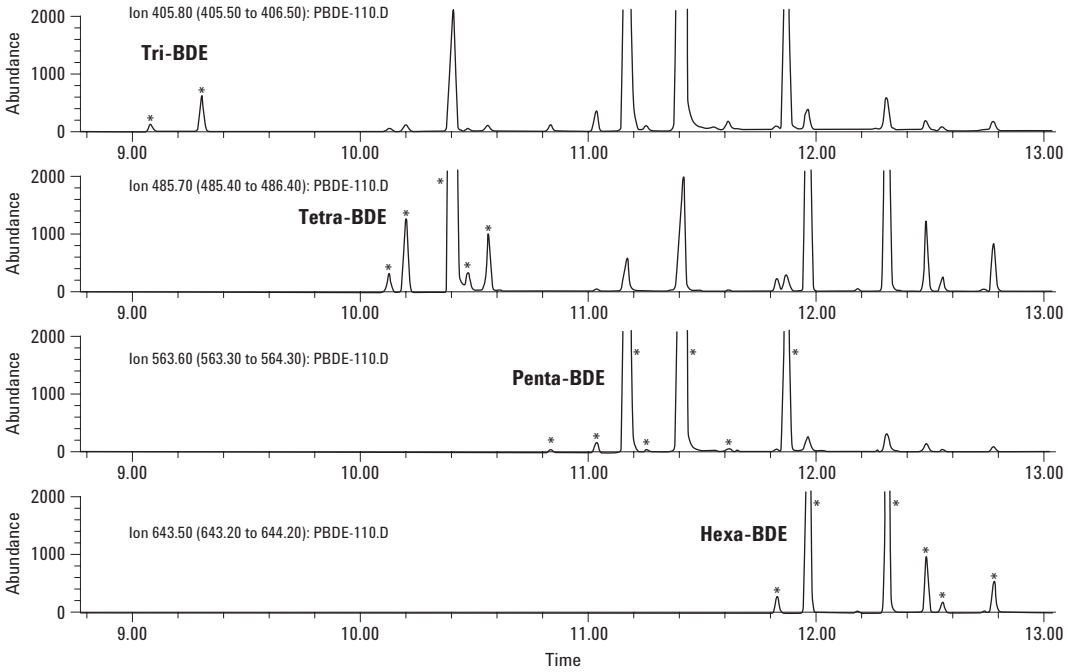
Instrument:	Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column:	DB-XLB, 30 m × 0.25 mm id × 0.1 µm (Agilent Technologies, part number 122-1231)
Carrier gas:	Helium at 38 cm/s at 100 °C (1.2 mL/min), constant flow mode
Oven:	100 °C for 1 min; 100 °C to 340 °C at 20 °C/min, 340 °C for 12 min
Injector:	Cool-on-column, oven-track mode, 0.5 µL
Detector:	Agilent 5973 MSD; transfer line at 325 °C, EI
SIM:	(Ions monitored: 231.8, 248.0, 327.9, 398.6, 400.5, 405.8, 845.7, 563.6, 643.5, 721.4, 799.3)

Note:

Mono-through octa-substituted homologs detected using SIM at the most intense of the M^+, $(M+2)^+$, $(M+4)^+$, $(M+6)^+$, or $(M+8)^+$ masses, with a data acquisition rate of approxroximately 3 cycles/second. Monitoring the molecular ion was not possible above octa-substituted PBDEs due to the limitations of the mass range of the 5973 instrument (maximum of *m/z* 800). Decabromodiphenylether was detected by monitoring significant fragments of high abundance: *m/z* 231.8, 398.6, 400.5, and 799.3.

Figure 2b. GC/MS of PBDE congener mixture (EO-5113).

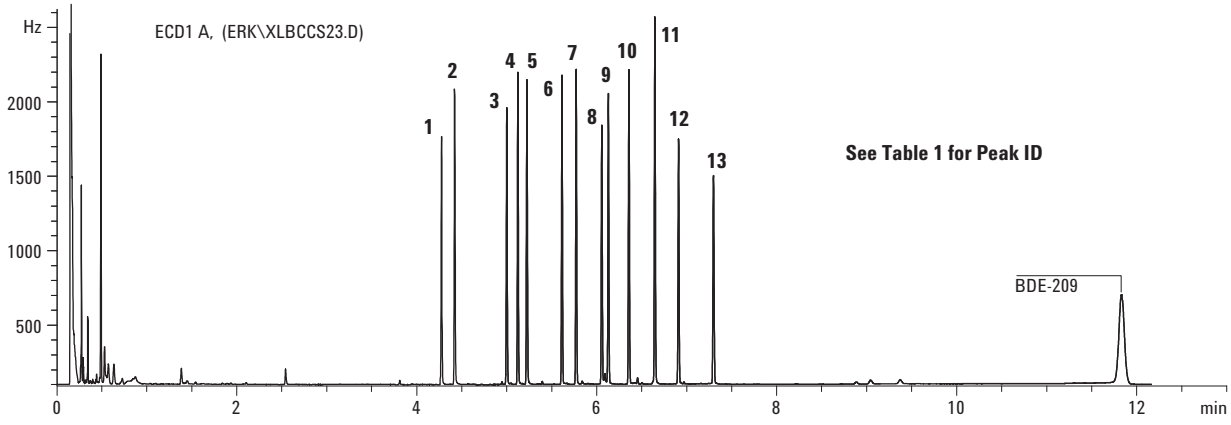
Figure 3 shows a chromatogram of a commercial flame retardant mixture. While commercial samples are typically classified as “penta”, “octa”, or “deca”, they contain other congeners as well. Again, the congeners in this mixture are well resolved, and the run time is very short (13 minutes).



Instrument:	Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column:	DB-XLB, 30 m × 0.25 mm id × 0.1 µm (Agilent Technologies, part number 122-1231)
Carrier gas:	Helium at 38 cm/s at 100 °C (1.2 mL/min), constant flow mode
Oven:	100 °C for 1 min; 100 °C to 340 °C at 20 °C/min , 34 °C for 12 min
Injector:	Cool-on-column, oven-track mode, 0.5 µL
Detector:	Agilent 5973 MSD; transfer line at 325 °C, EI
SIM:	(Ions monitored: 231.8, 248.0, 327.9, 398.6, 400.5, 405.8, 845.7, 563.6, 643.5, 721.4, 799.3)

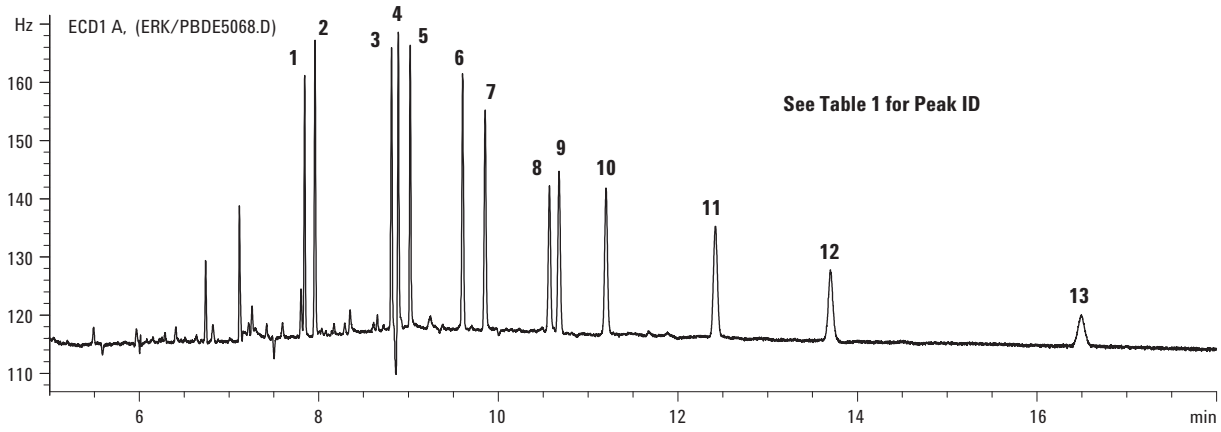
Figure 3. Commercial flame retardant penta DE71-R.

Analysis times could be reduced even further by using hydrogen carrier gas and an Electron Capture Detector (ECD). This combination allows for faster flow rates, while improving sensitivity and lowering the detection limit. With the same column dimensions as above, run times of around 15 minutes are possible. With a custom-made column (DB-XLB, 15 m × 0.18 mm id × 0.07 µm) the run time was less than 12 minutes (Figure 4), with no signs of degradation of the 209 congener. Break down of the higher congeners was, however, dependent on the run conditions. An inlet temperature of 250 °C worked best, while the µECD gave best results at 300 °C. At higher detector temperature, degradation was noticeable, while lower ECD temperatures resulted in tailing peaks (likely due to cold trapping). As expected, sensitivity for PBDEs with a µECD is excellent (Figure 5). In the splitless injection mode, the detection limit under those run conditions for the tri and higher substituted PBDEs was around 100 ppt, with a signal-to-noise ratio of >20. The calibration curve for 2,2',4,4',6-PentaBDE (BDE-100) was linear from 1 ppm to 100 ppt.



Instrument:	Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column:	DB-XLB, 15 m × 0.18 mm id × 0.07 µm (Agilent Technologies, custom column)
Carrier gas:	Hydrogen at 72 cm/s at 100 °C (4.0 mL/min), constant flow mode
Oven:	100 °C for 0.5 min; 100 °C to 300 °C at 30 °C/min, 300 °C for 5 min
Injector:	250 °C, split 20:1, 1 µL
Detector:	ECD at 300 °C

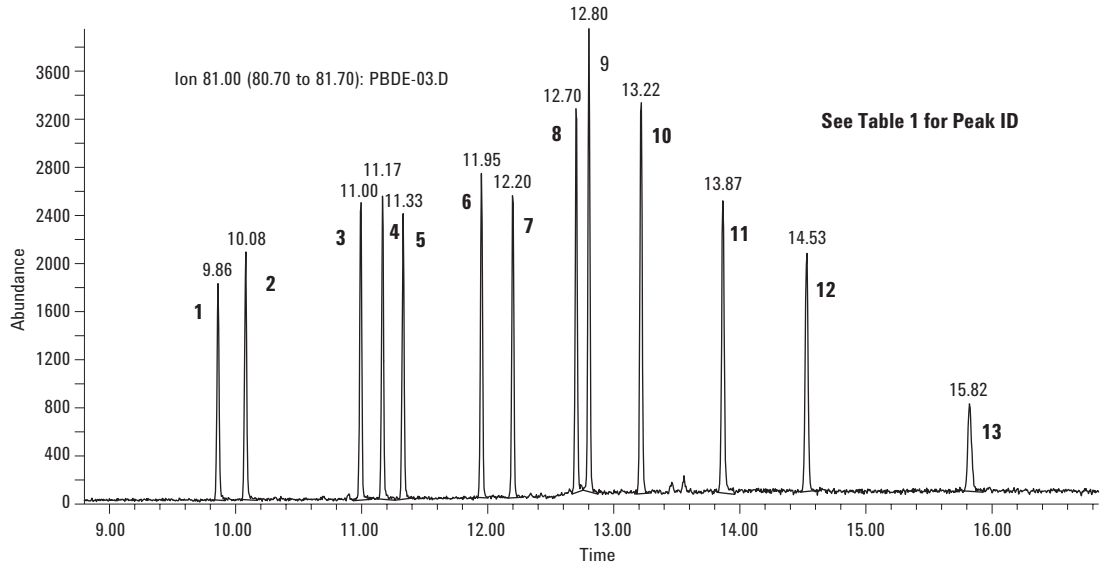
Figure 4. GC-µECD of PBDE congener mixture (EO-5103).



Instrument: Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column: DB-XLB, 30 m × 0.25 mm id × 0.1 µm (Agilent Technologies, part number 122-1231)
Carrier gas: Hydrogen at 72 cm/s at 100 °C (4.0 mL/min), constant flow mode
Oven: 100 °C for 1 min; 100 °C to 300 °C at 25 °C/min, 300 °C for 10 min
Injector: 300 °C, splitless, 1 µL
Detector: ECD at 300 °C

Figure 5. GC-µECD of PBDE mixture EO-5103 at 500 ppt.

The same sensitivity could be achieved with GC-ICP-MS. Figure 6 shows congener mixture EO-5103 diluted to 10 ppb. Calibration curves of individual congeners from 1 ppm to 1 ppb were linear (R^2 = 1.000), and the lower detection limit is calculated at 150 ppt. The system setup conditions for the ICP-MS, such as torch position, may not be fully optimized yet, so detection limits may be even lower.



Instrument: Agilent 6890 Gas Chromatograph with ALS and ChemStation Software
Column: DB-XLB, 30 m × 0.25 mm id × 0.1 µm (Agilent Technologies, part number 122-1231)
Carrier Gas: Helium at 36 cm/s at 100 °C (1.5 mL/min), constant flow mode
Oven: 100 °C for 1 min; 100 °C to 300 °C at 20 °C/min, 320 °C for 13 min
Injector: 320 °C, splitless, 1 µL
Detector: Agilent 7500cs ICP-MS, monitoring Br at *m/z* = 81

Figure 6. GC-ICP-MS of PBDE mixture EO-5103 at 10 ppb.

Conclusions

DB-XLB is the column of choice for GC analysis of PBDEs. The high upper temperature limit and very low bleed characteristics of this column make it ideal for this class of large molecules. While the high upper temperature limit allows for fast run times - complete analyses, including BDE-209, can be run in about 20 minutes, the extremely low bleed at those temperatures increases sensitivity, thus providing lower detection limits. The DB-35ms is an excellent secondary column that has the same outstanding bleed and thermal properties as DB-XLB, yet a different selectivity required for a confirmation column. In general, short columns with a high phase ratio (thin film) yield better response for the higher congeners, since the shorter residence times on the column reduce the exposure to high temperatures, therefore reducing on-column break down.

Due to the high bromine content of PBDEs, sensitivity on an ECD is very high. With splitless injection, the lower detection limit that we achieved is approximately 100 ppt. This limit might be pushed even lower with a programmable temperature vaporization (PTV) inlet, where larger injection volumes are possible. However, in real samples, for example, marine wildlife, other halogenated compounds, like PCBs, may be present. Since an ECD cannot distinguish between halogens, it is impossible to determine if a PCB co-elutes with a PBDE, thus quantitation may not be accurate. GC/MS offers secondary confirmation of the identity of the eluted peak, but sensitivity is not as great. In SIM mode, the detection limit for PBDEs is estimated at about 10 ppb. GC-ICP-MS offers both – high sensitivity and ion selectivity. It can be tuned for Cl or Br. Thus, by monitoring for example *m/z* 81, only PBDE would be detected, and PCB would not interfere with quantitation.

Acknowledgements

Individual PBDE congeners were a generous gift from AccuStandard (New Haven, CT). Special thanks to Mehran Alaee and Ivy D'Sa of the Aquatic Ecosystem Protection Research Branch, National Water Research Institute, Burlington, Canada, for helpful discussions, sharing of data, and providing samples of industrial brominated flame retardants. Thanks also to Harry Prest and Emmett Soffey of Agilent Technologies and Robert Trengrove of Murdoch University for helpful discussions and providing data.

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Printed in the USA
September 11, 2003
5989-0094EN

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