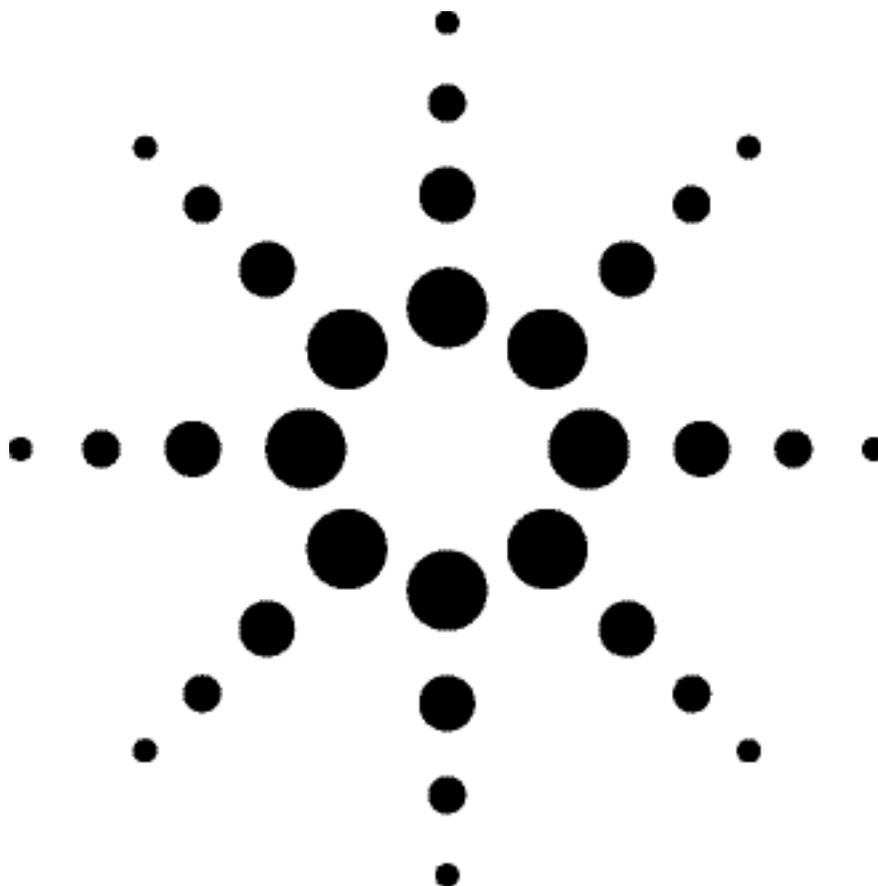


GC/MS Analysis of Polybrominated Flame Retardants

Pittcon 2003 Poster



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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 paper describes development of a suitable GC/MS method to analyze PBDEs. Agilent's DB-XLB was found to be the column of choice for this demanding analysis.

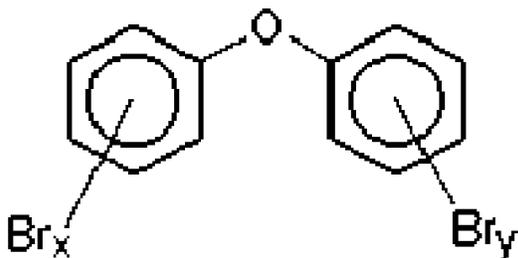
Introduction

The presence of polybrominated diphenyl ethers (PBDE) throughout the world environment has attracted the attention of scientists around the world. PBDEs are used as flame retardants in many commercial products, like textile and furniture, and in circuit boards in consumer electronics, like 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 level found in human breast milk of North American women appear to double every two to five 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).

Just like PCBs, there are 209 PBDE congeners (Fig. 1), and they are named in analogy to PCBs (4). However, only 7 congeners comprise about 95% of all detected peaks (5). These major congeners are (by IUPAC number): 28, 47, 99, 100, 153, 154, and 209.

Figure 1: Structure of Polybrominated diphenylethers (PBDE)



Until recently, the lack of available standards and individual congeners has made accurate quantitation difficult (6). Now, practically all individual congeners are commercially available. For analysis by GC, several different stationary phases have been used. However, run times are generally quite long, and often not all critical congeners are sufficiently resolved. This study investigates the use of the DB-XLB (Agilent Technologies, Folsom CA), a proprietary low-polarity, low-bleed stationary phase with high thermal stability. This column has been shown to be an excellent choice for detailed, high-resolution analysis of PCB congeners by GC/MS (7). The structural similarities between PCBs and PBDEs suggest that the DB-XLB should be an excellent choice for separation of PBDEs as well. Different column dimensions, injections modes, and temperature programs were evaluated to obtain an analysis method that was optimized for speed, sensitivity, and resolution.

Materials and Methods

The PBDE standards were purchased from Cambridge Isotope Labs (Andover, MA). Samples of commercial flame retardants were a generous gift from Dr. Mehran Alaei of Environment Canada.

GC Conditions for all chromatograms:

GC:	Agilent 6890 Gas Chromatograph with 7673 Autosampler and ChemStation Software
Column:	DB-XLB, 30 m x 0.25 mm I.D. x 0.1 µm (Agilent Part Number: 122-1231)
Carrier Gas:	Helium at 38 cm/sec at 100°C (1.2 mL/min), constant flow mode
Oven:	100°C for 1 min; 20°C/min to 340°C, hold 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 approx. 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.

Results and Discussion

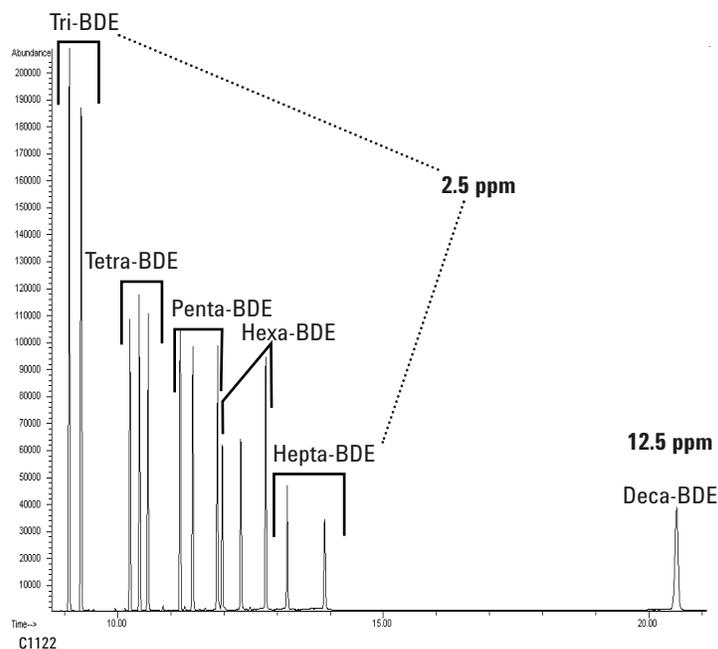
Baseline separation of all 14 critical congeners (Table 1) in a standard mixture including decabromodiphenylether (BDE-209) could be accomplished by DB-XLB in about 20 minutes (Fig. 2). This is much faster than run times typically reported with other columns. With a more demanding mixture at lower concentration, all 39 congeners (Table 2) were chromatographically resolved (Fig. 3), although two of the tetra isomers are very close. For baseline resolution of all congeners, as well as for separation of more complex mixture, a column with more theoretical plates and/or a lower phase ratio may be necessary. Using a DB-XLB, 30 m x 0.18 mm x 0.18 mm gave complete baseline separation of the tetra isomers, as did a DB-5ms, 60 m x 0.25 mm x 0.25 mm. 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.

Figures 4 and 5 show chromatograms of commercial flame retardant mixtures. While commercial samples are typically classified as "penta", "octa", or "deca", they contain other congeners as well. Again, the congeners in these mixtures are well resolved, and run times are very short (13 and 17 minutes, respectively).

It is worth noting the excellent peak shape and response of the decabromodiphenylether with cool-on-column injection (Fig. 2). While the overall peak shape remained the same,

response with splitless injections was lower. This is probably due to partial thermal degradation, particularly of BDE-209, in the hot inlet.

Figure 2: Polybrominated Diphenyl Ether Congener Mixture (EO-5103)



Analysis times may be reduced even further by using hydrogen carrier gas and an Electron Capture Detector (ECD). This combination would allow for faster flow rates, yet still provide good sensitivity. Research in this area is continuing, and those results, as well as confirmation of the peak identity, will be reported elsewhere.

Table 1: PBDE Congeners in Test Mix EO-5103

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

*Please note that peak assignments are based on elution order data on DB-5, and, while most likely correct, still should be confirmed by running individual congeners.

Table 2: PBDE Congeners in Test Mix EO-5113

Congener (BZ#)	Congener (BZ#)
2-MonoBDE (#1)	2,3',4,4'-TetraBDE (#66)
3-MonoBDE (#2)	2,3',4',6-TetraBDE (#71)
4-MonoBDE (#3)	2,4,4',6-TetraBDE (#75)
2,4-DiBDE (#7)	3,3',4,4'-TetraBDE (#77)
2,4'-DiBDE (#8)	2,2',3,4,4'-PentaBDE (#85)
2,6-DiBDE (#10)	2,2',4,4',5-PentaBDE (#99)
3,3'-DiBDE (#11)	2,2',4,4',6-PentaBDE (#100)
3,4-DiBDE (#12)	2,3,4,5,6-PentaBDE (#116)
3,4'-DiBDE (#13)	2,3',4,4',5-PentaBDE (#118)
4,4'-DiBDE (#15)	2,3',4,4',6-PentaBDE (#119)
2,2',4-TriBDE (#17)	3,3',4,4',5-PentaBDE (#126)
2,3',4-TriBDE (#25)	2,2',3,4,4',5'-HexaBDE(#138)
2,4,4'-TriBDE (#28)	2,2',4,4',5,5'-HexaBDE(#153)
2,4,6-TriBDE (#30)	2,2',4,4',5,6'-HexaBDE(#154)
2,4',6-TriBDE (#32)	2,2',4,4',6,6'-HexaBDE(#155)
2',3,4-TriBDE (#33)	2,3,4,4',5,6-HexaBDE (#166)
3,3',4-TriBDE (#35)	2,2',3,4,4',5,6-HeptaBDE(#181)
3,4,4'-TriBDE (#37)	2,2',3,4,4',5',6-HeptaBDE (#183)
2,2',4,4'-TetraBDE (#47)	2,3,3',4,4',5,6-HeptaBDE (#190)
2,2',4,5'-TetraBDE (#49)	

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.

For greatest sensitivity, cool-on-column injections or a PTV inlet are best. These injection techniques avoid thermal degradation of PBDEs

caused by hot inlets. Also, short columns with a high phase ratio (thin film) yield better response for the higher congeners. Shorter residence times on the column reduce the exposure to high temperatures, therefore reducing on-column break down.

Acknowledgements

Special thanks to Dr. Mehran Alaei and Ms. 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.

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Figure 3: Polybrominated Diphenyl Ether Congener Mixture (EO-5113)

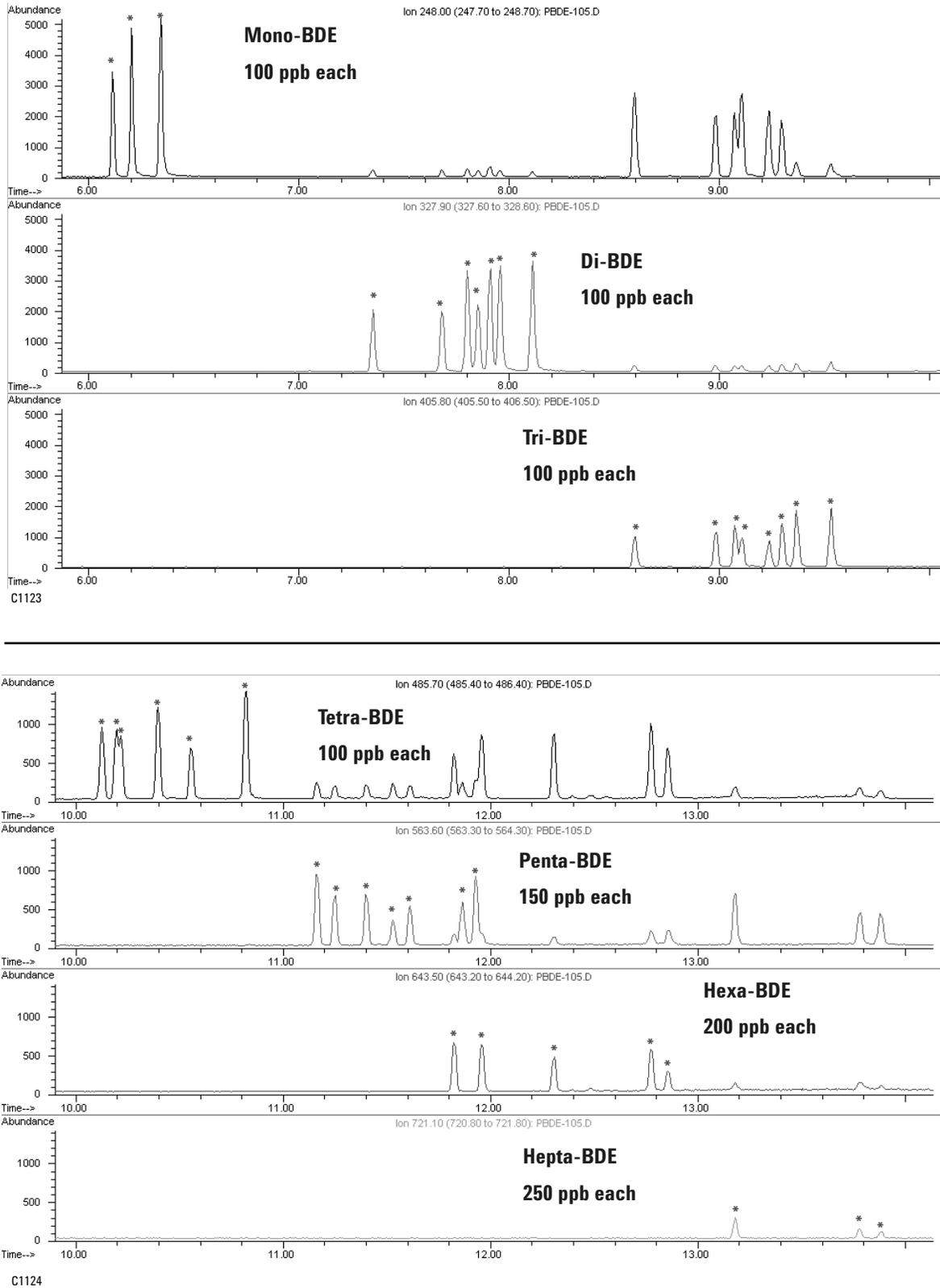


Figure 4: Commercial Flame Retardant Mixture DE71-R

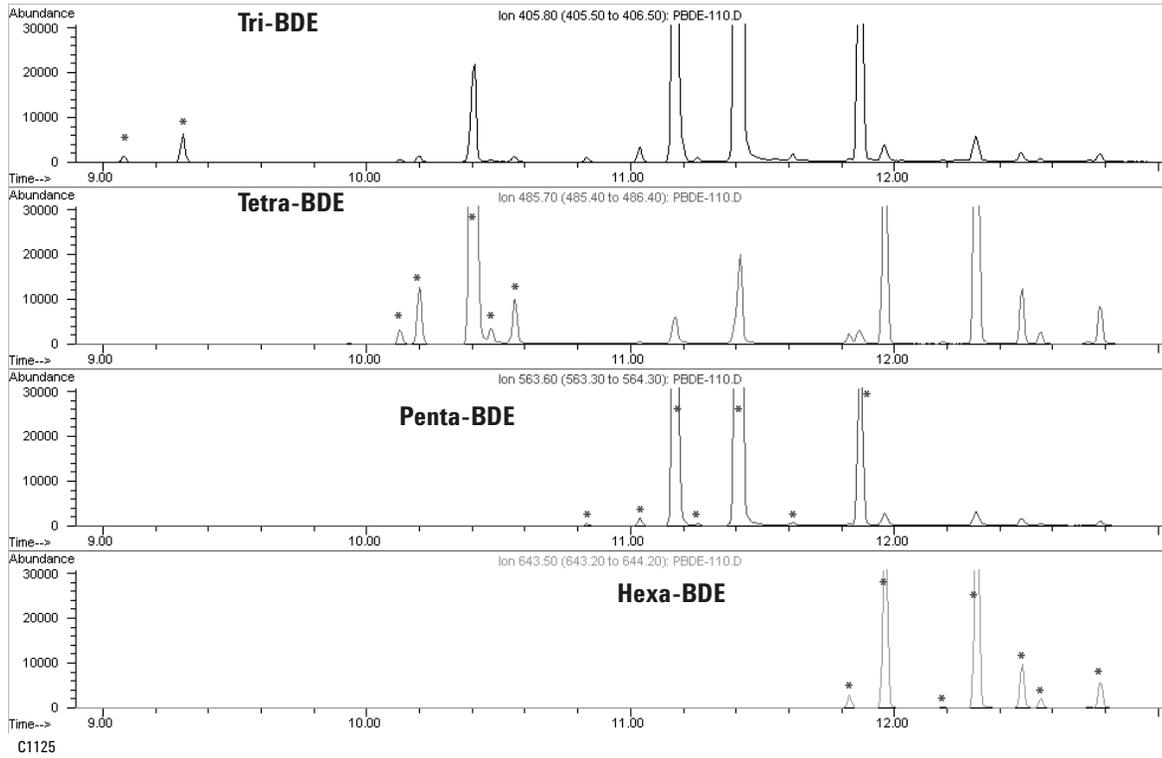
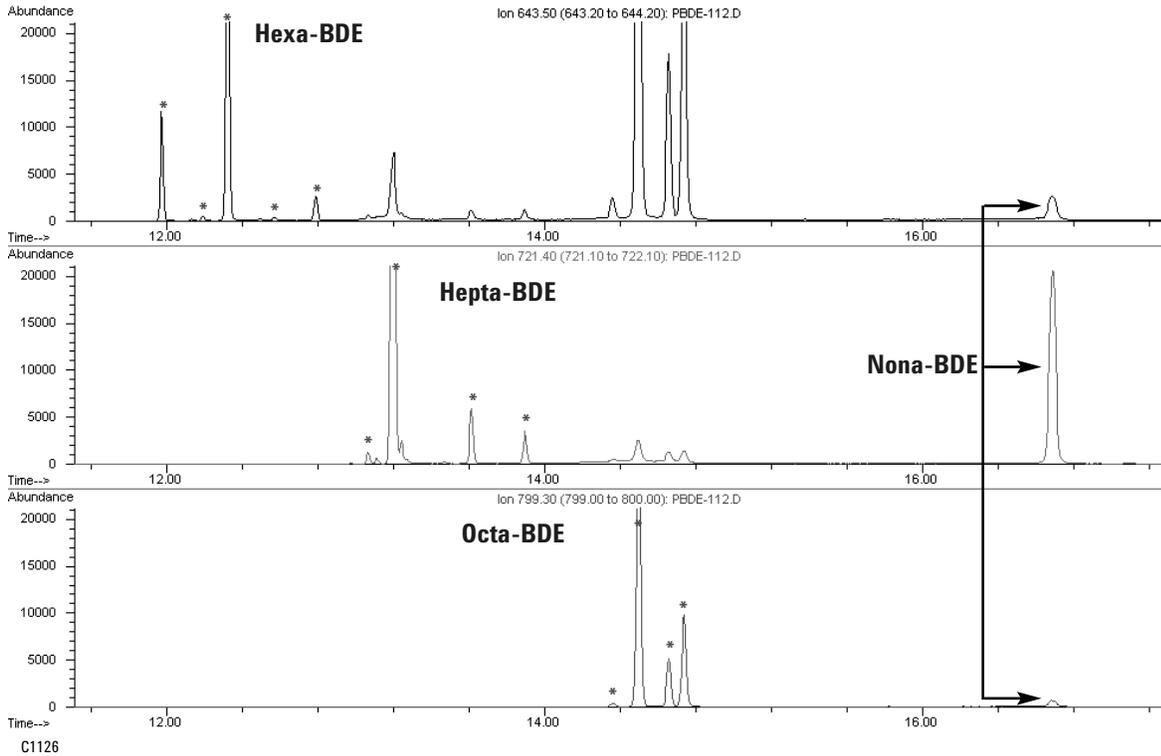


Figure 5: Commercial Flame Retardant Mixture DE79-R



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