Detecting "The New PCBs" Using GC–ICP-MS: Challenges of PBDE Analysis

Steve Wilbur and Emmett Soffey, Agilent Technologies

PBDEs are widely used as flame retardants in plastics used in computers, construction materials, furniture, and textiles. Structurally, they resemble PCBs, dioxins, and furans. This similarity in structure coupled with recent data showing significant concentrations in the environment and human and animal tissues have raised concern. Every day, the typical consumer comes in contact with dozens, if not hundreds of consumer goods that contain PBDEs. Since PBDEs are not covalently bound to the plastics in which they are incorporated, they are easily released into the environment. Products containing PBDEs typically contain from 5–20% of the product weight as PBDE. Because PBDEs are poorly soluble in water, but highly fat soluble, they are readily bioaccumulated in fatty tissues of animals and humans. Recent research on laboratory animals has shown that low-level exposure to PBDEs can cause permanent neurological and developmental damage. Those thought to be most at risk are pregnant women, developing fetuses and young children. Already levels of PBDEs found in some mothers and fetuses are approaching levels known to impair learning and development in mice (1).

Structure

The general structure of PBDEs is depicted in Figure 1. There are 10 possible sites for bromination, five on each ring. Similar to PCBs and dioxins, there are a large number of possible congeners depending on the number and location of bromine substitutions. In the case of PBDEs, there are 209 possible congeners, with the individual congeners named 1 through 209. The decabromo congener is PBDE-209.

Analytical Challenges

Typically, PBDEs are analyzed and detected similarly to PCBs or dioxins, using gas chromatography coupled to a halogen specific detector such as electron capture or to a mass spectrometer. However, unlike PCBs, PBDEs are much more difficult to chromatographically separate and detect. PBDEs are high molecular weight, high boiling point compounds which require high temperatures to elute from the GC column. However, unlike PCBs, which are very stable biphenyl compounds, the diphenyl ether structure makes PBDEs much more sensitive to degradation under high temperature GC conditions. Furthermore, since bromine elicits a much lower response by electron capture than does chlorine, the possibility of interferences from chlorinated compounds can be troublesome. Much work is ongoing to determine the optimum GC conditions for PBDE analysis. At present, the best inertness for the sensitive 209 congener has been shown to be a short, thin film 5 meter Agilent DB-5 MS column (2). Other columns tested show significant loss of the 209 congener (3). Worldwide, the deca product (PBDE-209), is the most widely used, making up 83% by weight of the total usage. This congener, is therefore the most important analytically. It is also the most difficult to measure.

GC–ICP-MS Analysis

Because the ICP-MS measures only the bromine, molecular weight is not an issue for detection. ICP-MS also exhibits extremely high sensitivity and selectivity for bromine, eliminating possible interferences from other halogenated polyaromatic compounds. In this work, a mixture of 14 PBDE congeners ranging from #17 to #209 were analyzed by a GC–ICP–MS system (an Agilent 6890 GC with ALS coupled to an Agilent 7500a ICP-MS). The chromatogram is depicted in figure 2. Congeners at 50 ng/mL in order of elution are as follows BDE: −17, −28, −71, −47, −66, −100, −99, −85, −154, −153, −138, −183, −190, and −209 (at 250 ng/mL).

Based on signal to noise measured in the 10 ppb standard (Figure 2), approximate detection limits are in the range of 100 ppt, comparable to those achievable by micro-ECD. Given that ICP-MS exhibits superior linearity, it does not suffer from non-analyte interferences and can definitively identify brominated compounds; GC–ICP-MS may be the method of choice for trace level analysis of PBDEs in a variety of samples.

References

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(3) E. Kuhn, J. Ellis, S. Wilbur, T. Trainor, and A. Gelbin, *GC Analysis of Polybrominated Flame Retardants Poster* presented at Dioxin 2003 Conference.

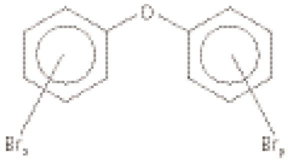

Figure 1: Basic structure of polybrominated diphenyl ethers.

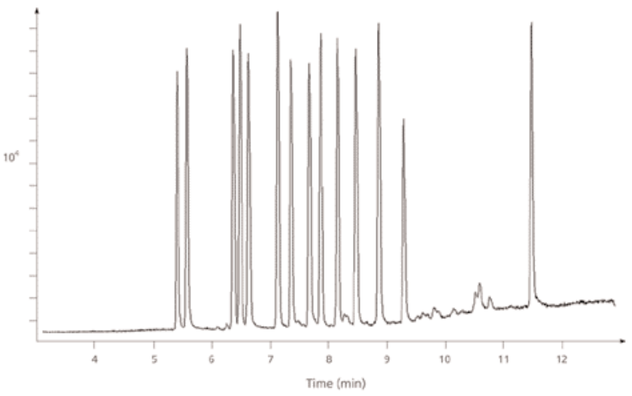

Figure 2: GC-ICP-MS chromatogram for ion 79 *m/z* of 14-compound PBDE standard mix. Column: Agilent DB-5MS, 30 m × 0.25 mm i.d. × 0.1 μ; Carrier gas: Hydrogen at 320 cm/s^{-1}, Constant flow mode; Oven: 80 °C for 1 min, 20 °C/min to 300 °C for 1 min; Injector: Programmable cool on-column in oven track mode.

Agilent Technologies
5301 Stevens Creek Blvd., Santa Clara, CA 95051
tel. (302) 993-5304, fax (302) 633-8901
www.agilent.com/chem

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