Measurement of Polybrominated Diphenyl Ethers in Environmental Matrix Standard Reference Materials

Heather Stapleton[1], Michele Schantz[1], Stephen Wise[1]

[1]National Institute of Standards & Technology

Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of emerging contaminants of concern as many studies have now demonstrated that these compounds are bioaccumulative, persistent and increasing in concentration in the environment [1-3]. PBDEs are being detected in almost every environmental sample examined, and they have even been measured in samples collected in the Arctic [4], further demonstrating their persistence and potential for long range transport.
More and more studies are continuing to examine the fate and transport of these flame retardant compounds in environmental samples and as such, reference materials are needed to provide quality control on these measurements.

The National Institute of Standards and Technology (NIST) supports a national Standard Reference Material (SRM) program for measurement of organic contaminants such as PCBs, PAHs and chlorinated pesticides in environmental matrices. This current study was undertaken to provide reference measurements for PBDEs in selected SRMs that are currently used by various laboratories throughout the United States. These SRMs include matrices such as marine mammal blubber, lake trout tissue, mussel tissue, sediment, house dust and human serum. We report here reference values for 22 PBDE congeners that have been quantified in these seven types of SRMs.

Materials and Methods

Reference materials measured for PBDEs included: SRM 1945 (Organics in Whale Blubber), SRM 1946 (Lake Superior Fish Tissue), SRM 1974b (Organics in Mussel Tissue, *Mytilus edulis*), SRM 1944 (New York/ New Jersey Waterway Sediment), SRM 1589a (PCBs, Pesticides and Dioxins/Furans in Human Serum) and SRMs 2583 and 2584 (Trace Elements in Indoor Dust). All analyte standards used for quantification were purchased from either Cambridge Isotope Laboratories in Andover, MA or Wellington Laboratories in Guelph, Ontario (Canada). A ^{13}C labeled chlorinated diphenyl ether (2,2',3,4,5-pentachlorodiphenyl ether) was used as an internal standard to quantify the tri- through octaBDE congeners while ^{13}C labeled 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE 209L) was used as an internal standard for the quantification of the three nonaBDEs and BDE 209. All solvents used were HPLC-grade. Pressurized fluid extraction was used to extract the standard reference material using dichloromethane. The recovered extracts were concentrated to 1.0 mL and injected onto an HPLC for size exclusion chromatography to remove lipids (if necessary). Using dichloromethane as the carrier solvent, extracts were injected into the HPLC and eluted through a divinylbenzenepolystyrene column (10 µm particle size, 100 Å pore size, 2.5 cm i.d. x 60 cm, PL-Gel, Polymer Labs, Inc., Amherst, MA) at a flow rate of 10 mL/min. As a final clean up step, samples were eluted through silica solid phase extraction cartridges. Cartridges were pre-cleaned with 10 mL of hexane and eluted with 20 mL of hexane.

Instrumental Analysis

Extracts were analyzed for PBDEs by using gas chromatography (GC) with mass spectrometry detection, operated in negative chemical ionization (GC/NCI-MS). A 0.25 mm x 15 m fused silica capillary column coated with a 5% phenyl methylpolysiloxane (0.25 Φm film thickness) was used for the separation of PBDE congeners. On column injection was employed in the GC, and the injection port was set to track the oven temperature. The oven temperature program was held at 80 EC for 2 min followed by a temperature ramp of 12 EC/min to 140 EC and followed by a temperature ramp of 5EC/min to a final temperature of 280 EC which was held for an additional 20 min. The auxiliary temperature and transfer

line were maintained at 280 EC. Ions 79 and 81 (bromide ions) were monitored as quantitative and qualitative ions for the tri- through octaBDE analytes. However, the three nonaBDEs and BDE 209 were monitored through ions 487 and 409 (BDE 209) and 495 and 415 (BDE 209L).

Results and Discussion

Measurements were made for 22 PBDE congeners in seven different natural matrix SRMs. The lowest PBDE concentrations were measured in the human serum SRM (1589a) which had a total PBDE concentration of 0.36 ng/g serum (60 ng/g lipid) in which only five congeners (BDE 47, BDE 99, BDE 100, BDE 154 and BDE 153) were detected. The highest concentrations were measured in the house dust SRMs in which many PBDE congeners were detected ranging from tribromodiphenyl ethers to the fully brominated diphenyl ether, BDE 209. Concentrations in the house dust SRMs were as high as 2230 ng/g dry mass for BDE 209 in SRM 2583. Table 1 displays a summary of some common PBDE congeners measured in the various SRM matrices. Concentrations of PBDEs measured in SRMs 1945, 1946 and 1974b are similar and in good agreement with recently published values for PBDEs in these SRMs reported by Zhu and Hites (2003)[5].

The four different biological matrix SRMs displayed similar PBDE congener patterns, which were dominated by PBDE congener 2,2',4,4'-tetrabromodipenyl ether (BDE 47), similar to patterns observed in most biological samples. However the abiotic samples, sediment and house dust, were dominated by the fully brominated diphenyl ether (BDE 209). The levels of BDE 209 observed in the house dust samples are comparable to levels reported in sewage sludge and industrially contaminated sediment [6-7]. SRM 2584 was originally produced as a reference material for high lead levels (1%) in house dust while SRM 2583 was produced as a reference material for nominal lead levels of 90 mg/kg. The high levels of PBDEs measured in these house dust samples (3000 ng/g) suggests that indoor environments may be an important route of exposure to PBDEs as was seen for lead exposure in the past.

Table 1. PBDE congener concentrations (ng/g wet mass for serum and biological tissues; ng/g dry mass for sediment and house dust) measured in select standard reference materials from NIST[a].

SRM	Matrix	BDE 28,33	BDE 47	BDE 99	BDE 153	BDE 183	BDE 209
1589a (n=10)	Human serum	<0.01	0.24 ± 0.03	0.04 ± 0.01	0.02 ± 0.001	<0.02	<1.0
1944 (n=5)	Sediment	<0.1	2.0 ± 0.3	2.7 ± 0.7	4.5 ± 0.8	17.5 ± 1.4	114 ± 14
1945 (n=5)	Whale blubber	20.2 ± 1.3	44.4 ± 5.0	17.9 ± 2.8	8.5 ± 0.6	6.1 ± 0.8	<1.0
1946 (n=4)	Fish Tissue	0.8 ± 0.2	31 ± 2.9	19.4 ± 1.8	5.1 ± 0.8	<0.4	<1.0
1974b (n=3)	Mussel Tissue	0.5 ± 0.2	5.8 ± 1.4	2.6 ± 0.6	0.6 ± 0.3	0.3 ± 0.2	<1.0
2583 (n=6)	House dust	12.3 ± 1.4	226 ±13	400 ± 27	52.7 ± 4.2	17.6 ± 1.6	2230 ± 190
2584 (n=6)	House dust	14.4 ± 1	205 ± 5.4	337 ± 7.7	46 ± 1.4	23.3 ±1.4	2050 ± 160

[a]- The uncertainties listed represent the standard deviation of the replicate values.

References

1 Betts K (2002) *Environ. Sci. Technol*., 36(3): 50A-52A.
2. Stapleton HM and Baker JE (2003) *Arch. Environ. Contam. Toxicol*., 45: 227-234.
3. Norstrom RJ, Simon M, Moisey J, Wakeford B, Weseloh DV (2002) *Environ. Sci. Technol*., 36(22): 4783-4789.
4. Ikonomou MG, Rayne S, and Addison RF (2002) *Environ. Sci. Technol*. 36(9): 1886-1892.
5. Zhu L, and Hites RA (2003). *Anal. Chem*. 75: 6696-6700
6. Hale RC, La Guardia MJ, Harvey EP, Gaylor MO, Matteson Mainor T, and Duff WH (2001) *Nature* 412: 140-141.
7. Sellstrom U, Kierkegaard A, De Wit C and Jansson B (1998) *Environ. Toxicol. Chem*. 17(6): 1065-1072.