Indoor Dust and Fish Tissue Standard Reference Materials Certified for Polybrominated Diphenyl Ethers

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Introduction

The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) program provides a number of environmental matrices with concentration values assigned for a number of organic contaminants such as PCBs, PAHs ,chlorinated pesticides, and inorganic compounds such as mercury, cadmium and lead. Reference values for polybrominatabteddiphenyl ethers (PBDEs) have previously been provided for several environmental matrix SRMs that included marine mammal blubber, fish tissue, mussel tissue, sediments, indoor dust and human serum[1,2]. The present study now provides certified values for PBDE congeners in three indoor dust SRMs and two fish tissue SRMs.

Materials and Methods

Reference materials measured for PBDEs included: SRM 1946, Lake Superior Fish Tissue, SRM 1947, Lake Michigan Fish Tissue, and SRMs 2583, 2584 and 2585, Indoor Dust. SRMs 2583 and 2584 have been certified previously for lead and other inorganic constituents. The third dust SRM, 2585, will be certified for organic compounds such as PCBs, PAHs and organochlorine pesticides. All PBDE analyte standards used for quantification were purchased from either Accustandard (New Haven, CT), 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 with dichloromethane was used to extract the SRMs. The fish 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. Both fish and dust extracts were eluted through silica solid phase extraction cartridges. Cartridges were pre-cleaned with 10 mL of hexane and eluted with 20 mL of hexane. The final extract was reduced in volume to 0.5mL in hexane for analysis of PBDEs.

Instrumental Analysis

Extracts were analyzed for PBDEs by using gas chromatography (GC) with mass spectrometry detection, operated in negative chemical ionization (GC/ECNI-MS) and in electron impact mode (GC/EI-MS). A 0.25 mm x 15 m fused silica capillary column coated with a 5% phenyl methylpolysiloxane (0.25 Fm 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, followed by a temperature ramp of 5EC/min to a final temperature of 280 EC which was held for an additional 20 min. The transfer line temperature was maintained at 280 EC.

Results and Discussion

Measurements were made for 30 individual PBDE congeners in the fish tissue and indoor dust SRMs. Lake trout from Lakes Superior and Michigan were used in the preparation of SRMs 1946 and 1947, respectively, and PBDE concentrations were higher in the Lake Michigan fish tissue SRM relative to the Lake Superior fish tissue. Concentrations of the primary PBDE congeners measured in the SRMs are presented in Table 1. The PBDE

congener pattern was comprised primarily of BDE 47 and BDE 99, similar to many environmental samples. However, despite the fact that both fish tissue SRMs are comprised of lake trout, significant differences were apparent in the relative distribution of individual congeners. For example, both SRM fish tissues had comparable levels of BDE 99 but significantly different levels of BDE 47. Lake Superior fish tissue was comprised of 43% BDE 47, whereas Lake Michigan fish tissue was comprised of 57% BDE 47.

Table 1. Certified Concentrations for Selected BDE Congeners in SRM 1946 (Lake Superior Fish Tissue) and SRM 1947 (Lake Michigan Fish Tissue) (µg/kg (wet-mass basis).

BDE Congener SRM 1946 SRM 1947

BDE 28 (2,4,4'-Tribromodiphenyl ether) 0.742 ± 0.027 2.26 ± 0.46[a]

33 (2',3,4-Tribromodiphenyl ether)

BDE 47 (2,2',4,4'-Tetrabromodiphenyl ether) 29.9 ± 2.3 73.3 ± 2.9

BDE 49 (2,2',4,5'-Tetrabromodiphenyl ether) 1.1 ± 0.3[a] 4.01 ± 0.10

BDE 66 (2,3',4,4'-Tetrabromodiphenyl ether) 1.35 ± 0.16 1.85 ± 0.13

BDE 99 (2,2',4,4',5-Pentabromodiphenyl ether) 18.5 ± 2.1 19.2 ± 0.8

BDE 100 (2,2',4,4',6-Pentabromodiphenyl ether) 8.57 ± 0.52 17.1 ± 0.6

BDE 153 (2,2',4,4',5,5'-Hexabromodiphenyl ether) 2.81 ± 0.41 3.83 ± 0.04

BDE 154 (2,2',4,4',5,6'-Hexabromodiphenyl ether) 5.77 ± 0.80 6.88 ± 0.52

BDE 155 (2,2',4,4',6,6'-Hexabromodiphenyl ether) 0.51 ± 0.05[a] 0.45 ± 0.10 [a]

[a] These values represent reference values and not a certified values.

Higher PBDE concentrations were measured in the house dust SRMs in which many PBDE congeners were detected ranging from tribromodiphenyl ethers to the fully brominateddiphenyl ether, BDE 209. Concentrations in the house dust SRMs were as high as 2510 ng/g dry mass for BDE 209 in SRM 2585. Table 2 presents the PBDE congeners measured in the various SRM matrices.

The dominant congener in all the house dust SRMs was BDE 209, the primary component of the decaBDE commercial mixture. This mixture is commonly used as a flame retardant for polymers such as high impact polystyrene. The levels of BDE 209 observed in the dust samples are comparable to levels reported in sewage sludge and industrially contaminated sediment [3,4]. Estimates of the relative composition of the commercial mixtures in the dust SRM can be made by assuming that the contribution of BDE 47, 99 and 100 are from a pentaBDE source, and that the levels of BDE 209 represent a pure decaBDE source. Based on these assumptions 32% of the dust SRM is from a pentaBDE source and 53% is associated with a decaBDE source (Figure 1).

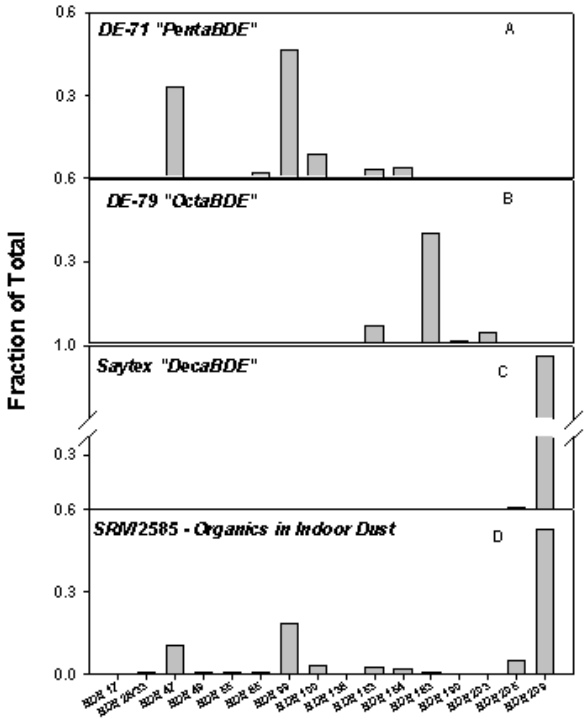

Figure 1. PBDE congener profile in the pentaBDE (A), octaBDE (B) and decaBDE (C) commercial mixtures and their comparition to the indoor dust SRM (2585).

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 (~3500 ng/g) suggests that indoor environments may be an important route of exposure to PBDEs as was seen for lead exposure in the past.

References

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Table 2. PBDE value assignments (ng/g dry; values corrected for moisture content) for indoor dust SRMs. Bold numbers indicate certified concentrations.

Congener	SRM 2583[a]	SRM 2584[b]	SRM 2585[c]
BDE 17	4.8 ± 2.9	4.5 ± 2.3	**11.5 ± 1.2**
BDE 25	<0.2	<0.2	<0.2
BDE 28, 33	20.1 ± 5.8	18.7 ± 3.3	**46.9 ± 4.7**
BDE 30	<0.2	<0.2	<0.2
BDE 47	**373 ± 58**	**363 ± 25**	**498 ± 46**
BDE 49	27.5 ± 3.1	26.2 ± 6.7	**53.5 ± 4.2**
BDE 66	14.9 ± 5.0	13.4 ± 2.5	29.5 ± 6.2
BDE 71	<0.2	<0.2	<0.2
BDE 75	<0.5	<0.5	4.5 ± 1.2
BDE 85	**34.6 ± 2.7**	**31.9 ± 2.5**	**43.8 ± 1.6**
BDE 99	**721 ± 94**	**671 ± 43**	**892 ± 53**
BDE 100	**117 ± 22**	**108.1 ± 6.3**	**145 ± 11**
BDE 116	<0.2	<0.2	<0.2
BDE 119	<0.2	<0.2	<0.2
BDE 138	**10.4 ± 1.5**	**10.9 ± 2.0**	**15.2 ± 2.0**
BDE 153	**90.5 ± 5.4**	**86.1 ± 5.7**	**119 ± 1.0**
BDE 154	69.5 ± 3.0	57.1 ± 2.7	**83.5 ± 2.0**
BDE 155	2.19 ± 0.18	2.20 ± 0.19	**3.94 ± 0.34**
BDE 156	<0.2	<0.2	<0.2
BDE 181	<0.3	<0.3	<0.3
BDE 183	**25.2 ± 2.7**	**31.9 ± 4.2**	**43.0 ± 3.5**
BDE 190	**1.35 ± 0.10**	1.98 ± 0.64	5.1 ± 2.9
BDE 191	<0.3	<0.3	<0.3
BDE 196	8 ± 1	9 ± 1	39 ± 4
BDE 197	10 ± 1	12 ± 1	29 ± 3
BDE 203	7.90 ± 0.44	10.8 ± 2.2	**36.7 ± 6.4**
BDE 205	<0.5	<0.5	<0.5
BDE 206	107.4 ± 8.9	82 ± 37	**270 ± 42**
BDE 209	**2290 ± 240**	**2330 ± 210**	**2510 ± 190**

[a] Moisture content in SRM 2583 was 2.70 % ± 0.07 % at time of measurement.

[b] Moisture content in SRM 2584 was 3.30 % ± 0.08 % at time of measurement.

[c] Moisture content in SRM 2585 was 2.11 % ± 0.007 % at time of measurement.