Standard Reference Materials Available from the National Institute of Standards and Technology for the Analysis of Brominated Flame Retardants

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Introduction

For 25 years, the U.S. National Institute of Standards and Technology (NIST) has provided Standard Reference Materials (SRMs) for the measurement of organic environmental contaminants. Recently, NIST has responded to the need for environmental SRMs with values for the polybrominated diphenyl ethers (PBDEs) and other brominated flame retardants. PBDE concentration values are now available for SRMs of many matrices, including house dust, sediment, fish tissue, mussel tissue, whale blubber, cod liver oil, and human serum. A collaborative project with the Centers for Disease Control is also in progress measuring PBDEs in a more recent collection of human serum (SRM 1957), a portion of this serum material fortified with elevated levels of several contaminants (SRM 1958), human milk (SRM 1953), and a portion of this milk fortified with elevated levels of several contaminants (SRM 1954). In addition, urban dust, air particulate, sewage sludge materials, and a new marine mussel tissue will be analyzed for PBDEs and other brominated flame retardants. Available PBDE concentrations measured in these SRMs are described in this presentation.

Materials and Methods

The status of the SRMs analyzed for PBDE congeners is summarized in Table 1. Many were analyzed by more than one laboratory and method details can be found on each SRM's Certificate of Analysis (http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm) or in the citations listed in Table 1.

Table 1. Certification Status of NIST SRMs for PBDE Concentrations.

SRM	Name	Status of PBDE Values[a]	Reference
2583	Trace Elements in Indoor Dust	Values available, but CoA update is not planned	Stapleton et al. 2006
2584	Trace Elements in Indoor Dust	Values available, but CoA update is not planned	Stapleton et al. 2006
2585	Organics in Indoor Dust	Values available on current CoA	Stapleton et al. 2006
1588b	Organics in Cod Liver Oil	Values available on current CoA	Stapleton et al. accepted
1945	Organics in Whale Blubber	CoA update in prep[b]	Stapleton et al. accepted
1946	Lake Superior Fish Tissue	CoA update in prep	Stapleton et al. accepted
1947	Lake Michigan Fish Tissue	CoA in prep	Stapleton et al. accepted
1974b	Organics in Mussel Tissue (*Mytilus edulis*)	CoA update in prep	Stapleton et al. accepted
2977	Mussel Tissue (Organic Contaminants and Trace Elements)	CoA update in prep	Stapleton et al. accepted
2978	Mussel Tissue (Organic Contaminants-Raritan Bay, NJ)	Values available, out of stock	Stapleton et al. accepted
1941b	Organics in Marine Sediment	Values available, but CoA update is not planned	Stapleton et al. accepted
1944	NewYork/New Jersey Waterway Sediment	Values available, but CoA update is not planned	Stapleton et al. accepted
1589a	PCBs, Pesticides, PBDEs, and Dioxins/Furans in Human Serum	Values available on current CoA	Schantz et al. in prep.
1957	Organics in Human Serum (Non-fortified)	Measuring now	Preliminarily presented here
1958	Organics in Human Serum (Fortified)	Measuring now	Preliminarily presented here
1953	Organics in Human Milk (Non-fortified)	Measuring now	
1954	Organics in Human Milk (Fortified)	Measuring now	
1649b	Urban Dust	Screening now	
1648a	Air Particulate	Screening now	
2781	Domestic Sludge	Screening now[b]	
2978a	Organics in Freeze-dried Mussel Tissue	Preparing material now	

[a] CoA = Certificate of Analysis; [b] Preliminary HBCD concentrations are also available by request.

Generalized methods used in the NIST laboratory are described here. All materials were spiked with either ^{13}C-PBDEs, fluorinated PBDEs, or ^{13}C-chlorinated diphenyl ethers as internal standards prior to extraction. Tissue, sediment, and dust SRMs were extracted with pressurized fluid extraction. The human serum SRMs were extracted with either liquid:liquid extraction, microwave-assisted extraction, or open-focused microwave extraction. Extracts were cleaned up using size exclusion chromatography and one of the following techniques: alumina columns, silica columns, or acidified silica columns. PBDEs were quantified using gas chromatography/mass spectrometry. Often two injections were performed, one used a 30 m or 60 m DB-5MS column and electron impact ionization (for lower-brominated congeners, especially when ^{13}C-PBDEs were used), and the other injection used a 15 m DB-5MS column and negative chemical ionization (for all congeners, except for lower-brominated congeners when ^{13}C-PBDEs were used). Calibration standards contained 27 PBDE congeners (17, 25, 28, 30, 33, 47, 49, 66, 71, 75, 85, 99, 100, 116, 119, 138, 153, 154, 155, 156, 181, 183, 190, 191, 203, 205, 206, and 209) were processed alongside each batch of SRMs along with procedural blanks.

Results and Discussion

Concentrations of PBDE congeners measured in each SRM are shown in Tables 2 and 3.

Table 2. PBDE concentrations that are or will be listed on the Certificates of Analysis for NIST SRMs[a].

SRM number	2585	1588b	1945	1946	1947	1974b	1589a
Material type	House Dust	Fish Oil	Blubber	Fish	Fish	Mussel	Serum
Units	ng/g dry mass	ng/g wet mass	ng/g wet mass	ng/g wet mass	ng/g wet mass	ng/g wet mass	pg/g reconstituted serum
Congener							
PBDE 17	11.5 ± 1.2C						
PBDE 28, 33	46.9 ± 4.4C	1.08 ± 0.23R	2.67 ± 0.37R	0.742 ± 0.027C	2.26 ± 0.46R	0.13 ± 0.03R	11.9 ± 6.7R
PBDE 47	497 ± 46C	17.8 ± 2.0R	39.6 ± 0.2C	29.9 ± 2.3C	73.3 ± 2.9C	3.41 ± 0.21C	172 ± 10C
PBDE 49	53.5 ± 4.2C	2.25 ± 0.24R		1.10 ± 0.23R	4.01 ± 0.10C	0.75 ± 0.06C	
PBDE 66	29.5 ± 6.2R			1.35 ± 0.16C	1.85 ± 0.13C	0.11 ± 0.02C	
PBDE 75	4.5 ± 1.2R						
PBDE 85	43.8 ± 1.6C						
PBDE 99	892 ± 53C	0.56 ± 0.20R	18.9 ± 2.3C	18.5 ± 2.1C	19.2 ± 0.8C	1.50 ± 0.18C	39.9 ± 5.2C
PBDE 100	145 ± 11C	1.89 ± 0.45R	10.3 ± 1.1C	8.57 ± 0.52C	17.1 ± 0.6C	0.93 ± 0.07C	25.0 ± 3.2C
PBDE 138	15.2 ± 2.0C						
PBDE 153	119 ± 1C		8.34 ± 0.55C	2.81 ± 0.41C	3.83 ± 0.04C	0.08 ± 0.01R	18.5 ± 4.3R
PBDE 154	83.5 ± 2.0C	0.495 ± 0.069R	13.3 ± 1.7C	5.77 ± 0.80C	6.88 ± 0.52C	0.100 ± 0.02R	62.8 ± 7.5R
PBDE 155	3.94 ± 0.34C		4.75 ± 0.93R	0.51 ± 0.11R	0.45 ± 0.10R		
PBDE 183	43.0 ± 3.5C			0.235 ± 0.033R			4.65 ± 0.26C
PBDE 190	5.1 ± 2.9R						
PBDE 203	36.7 ± 6.4C						
PBDE 206	271 ± 42C						
PBDE 209	2510 ± 190C						

[a] Concentrations are means ± expected uncertainty as defined on the Certificate of Analysis. Values followed by a "C" are certified values, which are typically determined using two or more analytical methods (May et al. 2000). Those followed by an "R" are reference values, which are typically based on one analytical method.

The house dust and sediment SRMs were the only materials with detectable concentrations of PBDE 209, and it was the dominant congener in these materials. PBDE 47 was consistently the predominant

congener in biological tissues, which is typical for most wildlife and humans (reviewed by Hites, 2004). SRM 1947 (Lake Michigan Fish Tissue) and SRM 1945 (Whale Blubber) had the highest concentrations of PBDEs compared to other biological tissues. As expected based on temporal trends noted in North America (Hites, 2004), the levels in the more recently collected natural-level human serum (SRM 1957) had higher concentrations of the PBDEs than the human serum collected 10 years ago (SRM 1589a). Hexabromocyclododecane (HBCD) concentrations are also available for SRMs 1945 and 2781.

Table 3. PBDE concentrations that are preliminary or will not be listed on the Certificates of Analysis for NIST SRMs.

SRM number	2583[a]	2584[a]	2977[b]	2978[b]	1941b[c]	1944[c]	1957[d]	1958[d]
Material type	House Dust	House Dust	Mussel	Mussel	Sediment	Sediment	Serum	Serum
Units	ng/g dry mass	ng/g dry mass	ng/g dry mass	ng/g dry mass	ng/g dry mass	ng/g dry mass	pg/g reconstituted serum	pg/g reconstituted serum
Congener								
PBDE 17	4.8 ± 2.9	4.5 ± 2.3	<0.1	2.02 ± 0.31				
PBDE 28, 33	20.1 ± 5.8	18.7 ± 3.3	<1.2	0.77 ± 0.06	0.18 ± 0.07	0.26 ± 0.24		528 ± 16
PBDE 47	373 ± 58	363 ± 25	33.8 ± 1.9	19.7 ± 1.4	1.48 ± 0.51	1.63 ± 0.41	267 ± 27.2	638 ± 8
PBDE 49	27.5 ± 3.1	26.2 ± 6.7	1.02 ± 0.03	2.17 ± 0.15	0.23 ± 0.06	1.24 ± 0.55		
PBDE 66	14.9 ± 5.0	13.4 ± 2.5	0.38 ± 0.06	0.48 ± 0.04	0.06 ± 0.02	0.13 ± 0.08		426 ± 11
PBDE 75	<0.5	<0.5	0.17 ± 0.01	<1.6				
PBDE 85	34.6 ± 2.7	31.9 ± 2.5	<1.6	<1.6				433 ± 54
PBDE 99	721 ± 94	671 ± 43	4.11 ± 0.40	4.46 ± 0.29	0.62 ± 0.19	1.80 ± 0.35	81.7 ± 13.9	555 ± 19
PBDE 100	117 ± 22	108.1 ± 6.3	1.06 ± 0.18	3.13 ± 0.22	0.15 ± 0.06	0.46 ± 0.12	67.2 ± 23.6	511 ± 34
PBDE 138	10.4 ± 1.5	10.9 ± 2.0	<1.3	<1.4				
PBDE 153	90.5 ± 5.4	86.1 ± 5.7	<1.2	<1.2	0.09 ± 0.04	6.53 ± 1.32		305 ± 65
PBDE 154	69.5 ± 3.0	57.1 ± 2.7	<1.2	<1.2	0.09 ± 0.02	1.24 ± 0.58		385 ± 21
PBDE 155	2.19 ± 0.18	2.20 ± 0.19	<0.9	<0.9				
PBDE 183	25.2 ± 2.7	31.9 ± 4.2	<1.2	<1.2	0.05 ± 0.02	32.2 ± 7.9		
PBDE 190	1.35 ± 0.10	1.98 ± 0.64	<2.5	<1.1				
PBDE 203	7.90 ± 0.44	10.8 ± 2.2		<0.8				
PBDE 206	107.4 ± 8.9	82 ± 37		<1.2				
PBDE 209	2290 ± 240	2330 ± 210		<22.4	24.1 ± 14.1	128 ± 79		

[a] mean ± expanded uncertainty as defined in Stapleton et al. 2006 from one or more methods.

[b] mean ± standard deviation of 3 replicates analyzed by NIST (see Stapleton et al. accepted), these materials were also measured by Zhu and Hites 2003.

[c] geometric mean ± exercise standard deviation from an interlaboratory comparison exercise from up to ten laboratories (see Stapleton et al. accepted).

[d] mean ± standard deviation from preliminary measurements by NIST.

Recent studies have shown geographical differences in PBDE congener profiles within the same species (Keller et al. submitted; Streets et al. 2006). For example, lake trout from Lake Michigan had a lower proportion of PBDE 99 than trout from Lake Superior (Streets et al. 2006). This profile difference was also confirmed in the two fish tissue SRMs (Figure 1).

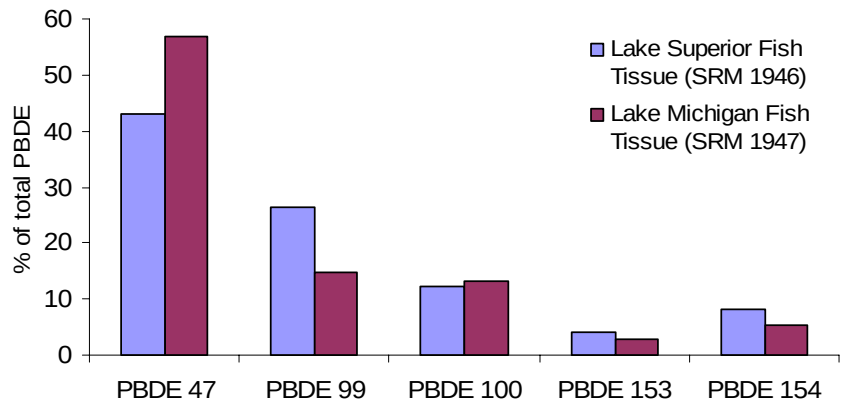

Figure 1. PBDE congener profiles from two fish tissue NIST SRMs.

Disclaimer: Certain commercial equipment or instruments are identified in the paper to specify adequately the experimental procedures. Such identification does not imply recommendations or endorsement by the NIST nor does it imply that the equipment or instruments are the best available for the purpose.

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