

RECENT DEVELOPMENTS IN ENVIRONMENTAL TISSUE STANDARD REFERENCE MATERIALS FOR THE DETERMINATION OF ORGANOHALOGEN COMPOUNDS

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Introduction and Background

The National Institute of Standards and Technology (NIST) provides a wide range of natural matrix environmental Standard Reference Materials (SRMs) that are characterized for a number of compounds in various contaminant classes including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, and most recently, brominated flame retardants (polybrominated diphenyl ethers, PBDEs).¹⁻⁴ Inorganic compounds such as mercury, cadmium, and lead, are characterized in selected materials as well. Environmental matrices include fossil fuels, air and diesel particulate matter, house dust, coal tar, sediment, mussel and fish tissue, fish oil, and whale blubber. Recent SRM developments for the determination of organic contaminants in the environment have focused largely on: (1) the production of new natural matrix materials and (2) examination of existing materials to update certified and reference values with contemporary or emerging contaminants (i.e., recertification) in an effort to increase the usefulness of the materials in modern analytical laboratories and environmental monitoring programs. These latest activities have included the determination of a range of PBDE congeners in up to 10 environmental natural matrix SRMs (7 biological materials, 2 marine sediments, and house dust) with several more in progress. The determination of PBDEs in mussel tissue and marine sediment SRMs is presented at this meeting in a paper by Poster et al.⁵

The latest new natural matrix material is a fish tissue SRM that consists of fillet lake trout collected from Lake Michigan (SRM 1947 Lake Michigan Fish Tissue). Recent recertifications of existing materials include the recertification of a cod liver oil (SRM 1588b Organics in Cod Liver Oil), a whale blubber (SRM 1945a Organics in Whale Blubber), and a human serum (SRM 1589b PCBs, Pesticides, PBDEs, and Dioxins/Furans in Human Serum). SRM 1588b has values assigned for 124 constituents, SRM 1945a for 89 constituents, and SRM 1589b has values assigned for 88 constituents. An overview of these recent SRM activities is provided below and selected organic contaminant values are presented. The recertification of SRM 1589b and the production of new human serum and human milk SRMs are presented at this meeting in a paper by Kucklick et al.⁶

Results and Discussion

Two new natural matrix materials have been issued recently for the determination of organic contaminants. These are a house dust SRM (SRM 2585 Organic Contaminants in House Dust) and a fish tissue SRM (SRM 1947 Lake Michigan Fish Tissue). The house dust SRM has been described by Stapleton et al.⁷ The new fish tissue SRM is described below.

SRM 1947 Lake Michigan Fish Tissue. SRM 1947 is a frozen fish tissue homogenate intended primarily for use in evaluating analytical methods for the determination of selected trace elements, including total mercury and methylmercury, PCB congeners, chlorinated pesticides, and PBDE congeners in fish tissue and similar matrices. The

material complements a second fish material collected from Lake Superior (SRM 1946, Lake Superior Fish Tissue). The two materials were prepared from filleted adult lake trout collected from Lake Michigan and Lake Superior. The fillets were cryogenically ground and homogenized as described by Poster et al.⁴ These two fish tissue SRMs are the most extensively characterized tissue SRMs with respect to organohalogen contaminants, with each having values assigned for approximately 70 PCBs, pesticides, and PBDEs. SRM 1947 has additionally been examined for selected synthetic musk fragrances.⁸ SRM 1947 has been issued this year while SRM 1946 was issued in 2003, although SRM 1946 has recently been updated to include PBDE congener concentrations. Concentrations of selected PBDE congeners in SRMs 1947 and 1946 are presented Figure 1. PBDE congeners 47, 99, 100, and 154 are the dominant congeners in the two fish tissue materials. The concentrations of PBDEs are generally 2 to 3 times greater in the Lake Michigan fish tissue relative to the Lake Superior fish tissue with the exception of PBDE congeners 99, 153, 154, and 155, which are about the same in both materials.

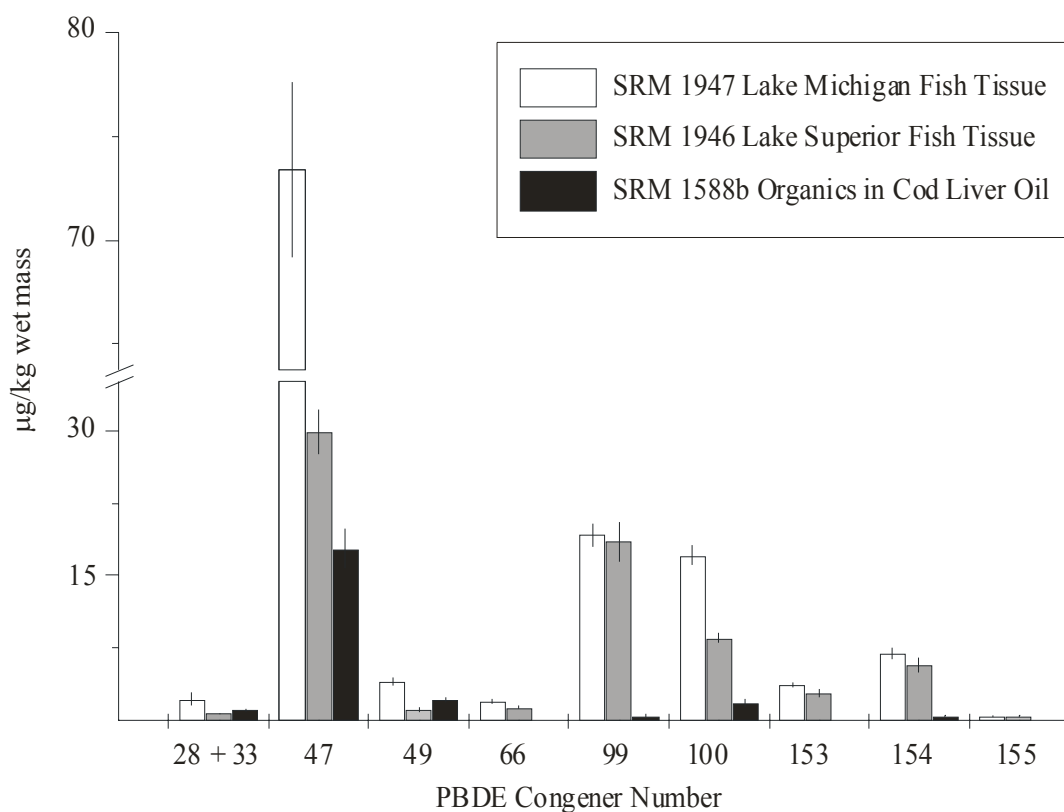


Figure 1. Concentrations of selected PBDE congeners in fish tissue and cod liver oil SRMs.

Polychlorinated naphthalenes (PCNs) have also been examined in SRMs 1947 and 1946. PCNs are a class of halogenated compounds that are similar to the polychlorinated biphenyls (PCBs) as they were at one time widely used in applications ranging from dielectrics to fabric water repellents. While both PCBs and PCNs have been largely banned, the high dioxin-like toxicity of certain PCNs and coplanar PCBs has led to the continued analysis of these compounds in environmental matrices. SRMs 1947 and 1946 have been analyzed for PCN congeners or congener groups and three non-ortho substituted PCB congeners 77, 126, and 169. Specifically, samples were analyzed by gas chromatography/mass spectrometry in the electron capture negative chemical ionization mode (GC/MS ECNCI) following the cleanup and separation using planar-selective liquid chromatography. These compounds have been

Analytical quality control and assurance

determined in additional environmental matrix SRMs: SRM 1588b Organics in Cod Liver Oil, SRM 1974b Organics in Mussel Tissue, SRM 1649a Urban Dust, and SRM 1944 New York/New Jersey Waterway. Results of Brubaker et al.⁹ have been combined with these additional measurements to provide values for the non-*ortho* substituted PCB congeners.

Recertification of SRM 1588a Organics in Cod Liver Oil. In 1989, a cod liver oil SRM, SRM 1588 Organics in Cod Liver Oil, was issued for the determination of selected organic contaminants (Table 1) and alpha-tocopherol.¹⁰ In 1988, SRM 1588 was updated as SRM 1588a with the certified and reference values expanded to 75 constituents to increase the usefulness of this material (Table 1). This year, SRM 1588a was updated to SRM 1588b and now has values assigned for 124 constituents (Table 1). In addition to expanding the number of PCB congeners (74 congeners) and chlorinated pesticides (18 pesticides), two additional groups of contaminants were added: PBDE congeners (6 congeners) and toxaphene (3 congeners) (total of 101 organic contaminants, Table 1). PBDE concentrations in SRM 1588b are plotted in Figure 1 and compared to the concentrations in the two fish tissue SRMs. SRM 1588b is the first SRM with values for toxaphene congeners assigned. Because of the importance of fatty acids, particularly omega-3 fatty acids, in human nutrition assessment, values were also assigned for 20 individual fatty acids. These values were added partly in response to reference material needs expressed by the food industry and government regulators with regard to proper food labeling requirements.^{11,12}

Table 1. Constituent values in the SRM 1588 Organics in Cod Liver Oil series.

	<i>Date Released</i>	<i>Certified Values</i>	<i>Reference Values</i>	<i>Information values</i>
SRM 1588	1989	10 pesticides 10 PCB congeners alpha-tocopherol	none	6 PCDDS octaCDF
SRM 1588a	1998	14 pesticides 24 PCB congeners	3 pesticides 34 PCB congeners alpha-tocopherol	6 PCDDS octaCDF
SRM 1588b	2006	15 pesticides 27 PCB congeners 14 fatty acids	3 pesticides 47 PCB congeners 6 PBDE congeners 3 toxaphene congeners 6 fatty acids alpha-tocopherol	6 PCDDS octaCDF

Recertification of SRM 1945 Organics in Whale Blubber. SRM 1945 Organics in Whale Blubber consists of blubber that was collected in 1991 from a stranded female pilot whale. Approximately 15 kg of blubber from the animal was cryohomogenized and divided into 10-15 g portions and stored at or below -80 °C. SRM 1945 was developed in response to the need for a control material to use for the determination of persistent organic pollutants in marine mammal blubber.¹³ The material was certified in 1994¹⁴ for 27 polychlorinated biphenyl congeners (PCBs), 15 organochlorine pesticides including DDT and metabolites, hexachlorobenzene, chlordane and related compounds, mirex, hexachlorocyclohexanes isomers, and total extractable organic material (TEO, mainly lipid). Since the original certification, SRM 1945 has been used as a control material in five international quality assurance exercises administered by the National Institute of Standards and Technology (NIST) and as a laboratory control material by NIST in the routine analysis of marine mammal blubber samples. Hence, a number of new measurements exist for previously certified compounds and for compounds not previously reported in SRM 1945. New compounds measured in SRM 1945 include the non-*ortho* substituted PCBs, PBDE congeners, hexabromocyclododecane isomers, additional PCB congeners, toxaphene, and fatty acids. More than 60 PCB congener concentrations have been determined in SRM 1945, now denoted as SRM 1945a.

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