Newley Developed Standard Reference Materials for Organic Contaminant Analysis

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Introduction

Biota and Biological-related Standard Reference Materials (SRMs®). Since 1990, the National Institute of Standards and Technology (NIST) has issued a number of cryogenically homogenized marine-related tissue SRMs with certified and reference values assigned for organic contaminants (Table 1). The cryogenically homogenized materials are powder-like, as long as they are kept frozen, with the endogenous water retained. We recently reviewed the development and availability of mussel-tissue SRMs [1] and marine-related tissue SRMs [2]. The first of the natural-matrix biological materials was SRM 1974 Organics in Mussel Tissue (Mytilus edulis) prepared from mussels collected in Boston Harbor, MA. SRM 1974 had certified and reference values for a limited range of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides. After SRM 1974 was no longer available in 1995, SRM 1974a was issued with certified and reference values for an expanded list of organic contaminants. The certificate for SRM 1974a was later updated to include values for methylmercury, proximates, calories, and fatty acids. Since SRM 1974a is now no longer available, SRM 1974b has been developed as a replacement (Table 1). SRM 1974a and SRM 1974b were collected from the same location as SRM 1974. As analytical methods have improved, the number of certified and reference values for PAHs, PCB congeners, and chlorinated pesticides have increased with each new issue. SRM 1974b is described below. Two additional mussel tissue SRMs are also available for the determination of organic contaminants (Table 1). SRMs 2977 and 2978, are freeze-dried tissue homogenates prepared from mussels collected in Guanabara Bay, Brazil and Raritan Bay, New Jersey, respectively [1]. SRM 2978 contains contaminant levels similar to those of SRM 1974b. Organic contaminant levels in SRM 2977 are typically a factor of 2 to 4 lower than those in SRM 1974b and SRM 2978. In addition to the mussel tissue SRMs, a cryogenically homogenized fish tissue, SRM 1946 Lake Superior Fish Tissue, is now available and another, SRM 1947 Lake Michigan Fish Tissue, will soon be available [2]. Both fish tissues were prepared from filleted adult

Table 1. Recently developed environmental SRMs for the determination of trace pollutants.

SRM	SRM Name	Compound Classes Characterized
	Biota or Biological-related SRMs	
1588a	Organics in Cod Liver Oil	PCBs, pesticides
1589a	PCBs, Pesticides, and Dioxins/Furans in Human Serum	PCBs, pesticides, PCDDs/PCDFs
1945	Organics in Whale Blubber	PCBs, pesticides
1946	Lake Superior Fish Tissue	PCBs, pesticides, fatty acids, extractable fat, methyl-Hg, Hg, trace elements, proximates
1947	Lake Michigan Fish Tissue (*in preparation*)	PCBs, pesticides, trace elements
1974b	Organics in Mussel Tissue (*Mytilus edulis*)	PAHs, PCBs (1 non-*ortho* and total PCBs), pesticides, methyl-Hg, Hg, trace elements, total extractable organics
2977	Mussel Tissue (Organic Contaminants and Trace Elements	PAHs, PCBs, pesticides, methyl-Hg, Hg, trace elements
2978	Mussel Tissue (Organic Contaminants – Raritan Bay, New Jersey)	PAHs, PCBs, pesticides
	Sediment SRMs	
1939a	PCBs in River Sediment A	PCBs, pesticides
1941b	Organics in Marine Sediment	PAHs, PCBs, pesticides, mono-, di-, tributyl tin, total tin, total organic carbon, C, H, N
1944	NY/NJ Waterway Sediment	PAHs, PCBs, Pesticides, PCDDs/ PCDFs, trace elements
	Particle-related SRMs	
1649a	Urban Dust	PAHs, PCBs, pesticides, PCDDs/PCDFs,
1650b	Diesel Particulate Matter (*in preparation*)	PAHs, nitro-PAHs
1975	Diesel Particulate Extract	PAHs, nitro-PAHs
2585	Organic Contaminants in House Dust (*in preparation*)	PAHs, PCBs, pesticides, PBDEs
2975	Diesel Particulate Matter (Industrial Forklift)	PAHs, nitro-PAHs

lake trout (*Salvelinus namaycush namaycush*) collected either from Lake Superior for SRM 1946 or from Lake Michigan for SRM 1947. These two fish tissue SRMs are intended for use by both the environmental and food chemistry communities (Table 1). The materials have (or will have) certified, reference, and information values for PCB congeners, chlorinated pesticides, methylmercury, mercury and other trace elements, fatty acids, calories, and proximates. In the case of the PCB congeners and chlorinated pesticides, the concentrations in SRM 1947 Lake Michigan Fish Tissue are approximately two times higher than in SRM 1946 Lake Superior Fish Tissue. Two materials related to biological tissue SRMs are the cod liver oil SRM, SRM 1588a, and the human serum SRM, SRM 1589a (Table 1). SRM 1588a is a reissue of the original cod liver oil SRM 1588 with an expanded list of PCB congeners and chlorinated pesticides having certified concentrations. Kucklick et al. [3] have examined SRMs 1588a and 1945 for polybrominated

diphenyl ethers (PBDEs) 47, 99, 100, 153, and 154, total toxaphene, and toxaphene congeners 26, 50, and 62. SRM 1946 was also examined for total toxaphene and toxaphene congeners [3]. The human serum SRM, SRM 1589a, was certified in conjunction with the Centers for Disease Control (CDC) with certified concentrations for natural levels of selected PCB congeners and chlorinated pesticides along with reference values (determined using one method at CDC) of selected polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) congeners.

Sediment SRMs. Several sediment SRMs are available for the determination of organic contaminants (Table 1). The two newest marine sediment SRMs are SRM 1941b Organics in Marine Sediment and SRM 1944 New York/New Jersey Waterway Sediment. These are characterized for a range of PAHs, PCBs, and chlorinated pesticides [4]. SRM 1941b has certified concentrations for 24 PAHs, 29 PCB congeners, and 7 pesticides, and SRM 1944 has certified concentrations for 24 PAHs, 29 PCB congeners, and 4 pesticides. Reference concentrations are also provided for an additional 58 (SRM 1941b) and 39 (SRM 1944) PAHs, PCB congeners, and pesticides. SRM 1944, which was collected from multiple sites within New York/New Jersey coastal waterways, has concentrations of a factor of 10 to 20 greater than SRM 1941b, which was collected in the Baltimore (Maryland, USA) Harbor. SRM 1944 is additionally characterized for the 17 2,3,7,8-substituted PCDDs/PCDFs congeners and total tetra-, penta-, hexa-, and hepta-congeners of PCDD and PCDF [5]. These two SRMs represent the most extensively characterized marine sediment certified reference materials available.

Particle-related SRMs. Several particle-related SRMs are available for the determination of PAHs, PCBs, and pesticides that consist of actual particulate material. The newest particle-related material, SRM 1650b, Diesel Particulate Matter, has been characterized for a range of PAHs, including alkyl and nitrogen-substituted PAHs (Table 1). SRM 1650b is intended to replace its predecessor SRMs [6, 7]: SRM 1650 (originally issued in 1985 with an update provided in 1991) and SRM 1650a (issued in 2000). Both predecessors are no longer available. However, the diesel particulate material that was used to prepare SRMs 1650 and 1650a is the same as that used for the development of SRM 1650b. The material represents particles emitted from diesel engines (four-cycle) operated over a variety of conditions. It has been bottled (in units of 100 mg) and analyzed using multiple methods of analysis to provide a range of certified and reference values for PAHs. SRM 1650b complements two other diesel particulate-related SRMs that are currently available (Table 1): SRM 2975, Diesel Particulate Matter (Industrial Forklift) and SRM 1975, Diesel Particulate Extract which is a dichloromethane extract of the same material used to prepare SRM 2975. The second newest particle-related SRM, SRM 2585 (Organic Contaminants in House Dust), is composed of actual house dust and will be characterized for PAHs, PCBs, pesticides, and PBDEs. Stapelton et al. are presenting PBDE data for several environmental matrix SRMs including two house dusts [8]. These two new particle-related SRMs complement SRM 1649a, Urban Dust, which is characterized for a range of PAHs, PCBs , and PCDDs/PCDFs.

Materials and Methods

Environmental SRMs for the determination of organic contaminants are available from NIST (www.nist.gov). The methods used for the determination of concentration values are described in the corresponding Certificates of Analysis available from the Standard Reference Materials Program (http://ts.nist.gov/srm). The value assignment of organic contaminants is based on the combination of results from analyses using various methods. This includes independent extraction, isolation, and chromatographic techniques. Figure 1 provides an example of the multi-tiered analytical scheme used for the determination of PCBs and pesticides in the newest mussel tissue

SRM, SRM 1974b. Soxhlet and pressurized fluid extraction, cleanup of the extracts using size exclusion chromatography, solid phase extraction, or liquid chromatography, and analysis using GC/MS and GC-ECD on stationary phases with different selectivity for the separation of analytes are components of the analytical scheme. The results from up to eight methods of analysis were used for the determination of the concentrations of 38 PCB congeners and 13 pesticides in SRM 1974b (selected values; Table 2). Part of the SRM 1974b chlorinated contaminant analytical scheme included the use of carbon-13 labeled PCB internal standards (methods 1,2; Figure 1). Carbon-13 labeled PCB congener 77 was used for the determination of the concentration of PCB congener 77 (part of methods 4,5; Figure 1) [9]. Figure 2 provides GC-ECD chromatograms of SRM 1974b on a relatively non-polar column. The separation and determination of the individual PCB congener concentrations for the two pairs of PCB congeners: 66 and 95; and 110 and 77, can be facilitated with the use of this column. A unique aspect of SRM 1974b is that the sum of PCB congeners was determined as part of an intercomparison study (method 8; Figure 1). The methods used by four laboratories that reported data varied from GC/MS for the analysis of congeners to GC-ECD using various Aroclors as standards. These methods are described on the SRM 1974b Certificate of Analysis. The resulting reference value for total PCBs is 2020 ± 420 µg/kg dry mass.

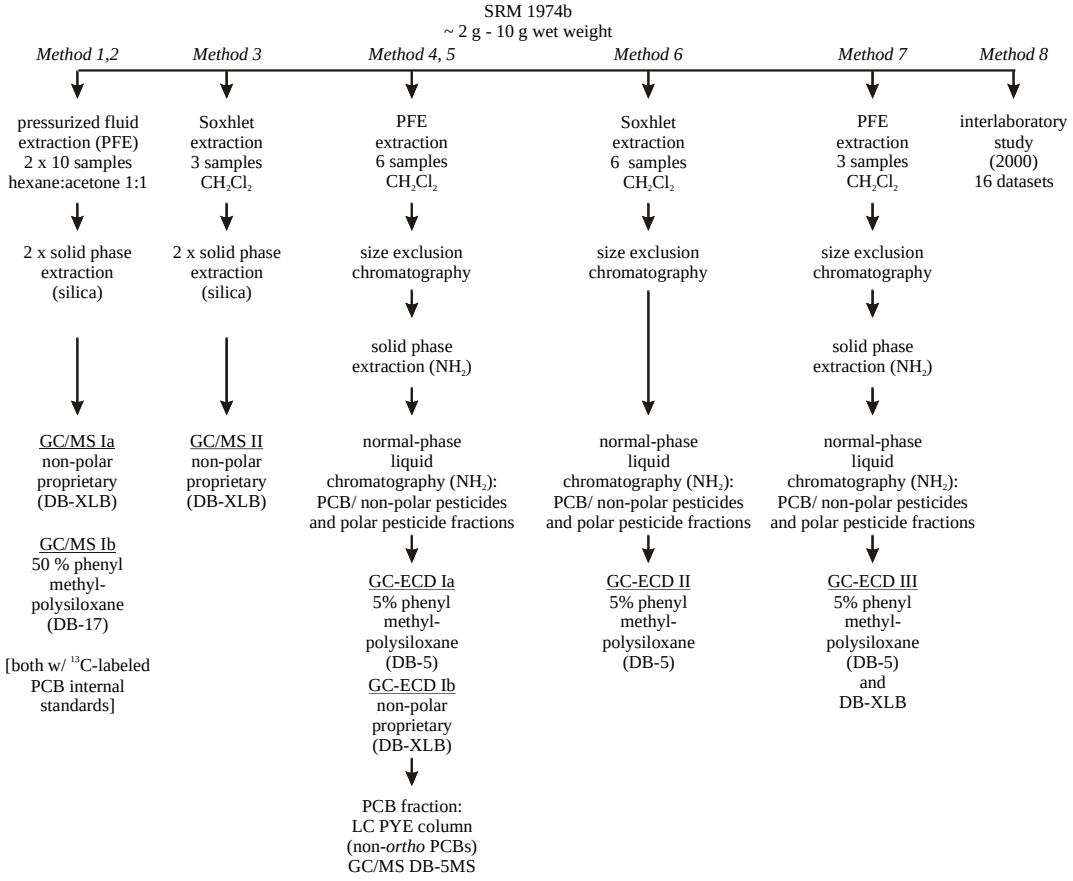

Figure 1. Analytical scheme for the determination of chlorinated contaminants in SRM 1974b.

Results and Discussion

Table 2 provides concentration values for selected PCB congeners and pesticides in three mussel tissue SRMs. Only a limited number of congeners and pesticides are shown in Table 2, but typically 20 to 25 PCB congeners and 5 to 10 pesticides have values listed in the Certificates of Analysis. Based on PCB concentrations obtained from each of the techniques described for mussel tissue SRMs 1974b (Figure 1), PCB congener concentrations range from (2.33 ± 0.24) µg/kg dry mass (PCB 157) to (121 ± 8) µg/kg dry mass (PCB 153). Pesticide concentrations range from (3.32 ± 0.43) µg/kg dry mass (2,4'-DDE) to (41.0 ± 3.8) µg/kg dry mass (4,4'-DDE).

Table 2. Concentrations (µg/kg dry mass) of selected PCBs and pesticides in three new mussel tissue SRMs[a,b]

Compound	SRM 1974b	SRM 2977	SRM 2978
PCB 28	33.9 ± 2.5	5.37 ± 0.44	7.91 ± 0.9
PCB 31	28.4 ± 2.3	3.92 ± 0.24	21.4 ± 0.43
PCB 44	38.0 ± 2.0	3.25 ± 0.63	11.8 ± 0.64
PCB 52	61.8 ± 3.7	8.37 ± 0.54	17.7 ± 2.8
PCB 66	62.9 ± 3.7	3.64 ± 0.32	18.4 ± 1.5
PCB 77	*5.56* ± *0.23*	--[a]	--[a]
PCB 95	59.6 ± 3.6	5.39 ± 0.59	20.8 ± 2.1
PCB 99	58.4 ± 2.7	1.59 ± 0.20	18.84 ± 0.44
PCB 105	39.5 ± 1.8	3.76 ± 0.49	10.85 ± 0.45
PCB 110	99.1 ± 7.1	4.03 ± 0.20	35.34 ± 0.71
PCB 118	102 ± 4	10.5 ± 1.0	35.1 ± 1
PCB 149	69.2 ± 2.8	9.23 ± 0.12	34.73 ± 0.69
PCB 153	121 ± 8	14.1 ± 1.0	56.9 ± 3.5
PCB 170	2.66 ± 0.34	2.95 ± 0.23	*2.4* ± *0.6*
PCB 180	11.5 ± 1.0	6.79 ± 0.67	7.81 ± 0.63
cis-chlordane	13.4 ± 1.0	1.42 ± 0.13	15.56 ± 0.83
trans-nonachlor	12.8 ± 1.4	1.43 ± 0.10	11.5 ± 1
dieldrin	*6.1* ± *1.3*	6.04 ± 0.52	6.30 ± 0.67
4,4'-DDE	41.0 ± 3.8	12.5 ± 1.6	37.5 ± 1.5
2,4'-DDD	10.8 ± 1.6	3.32 ± 0.29	10.5 ± 1
4,4'-DDD	33.0 ± 2.2	4.30 ± 0.38	38.8 ± 2.3
4,4'-DDT	*3.91* ± *0.94*	1.28 ± 0.18	3.84 ± 0.28

[a] SRM 1974b is a frozen homogenate with (89.7 % ± 0.05) % water (as received); SRMs 2977 and 2978 are freeze-dried materials; PCB 77 not determined in SRMs 2977 and 2978.

[b] Certificates of Analyses provide descriptions of values and uncertainities; values in italics are reference values (available at http://ts.nist.gov/srm). See review by Poster et al. [1].

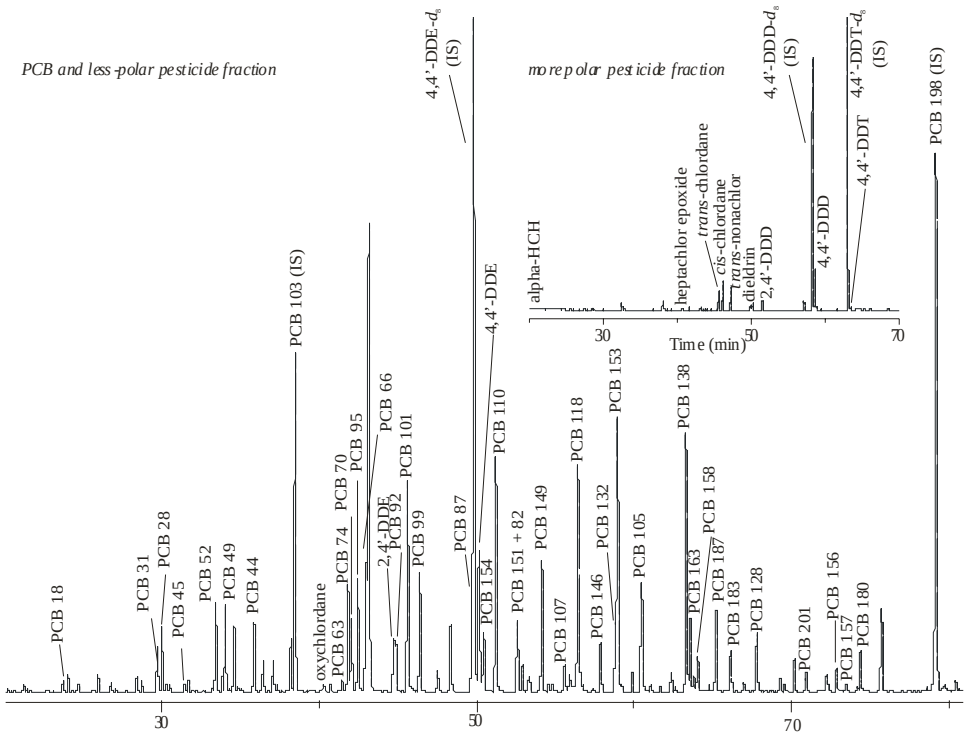

Figure 2. GC-ECD analyses (relatively non-polar column) of fractions isolated from SRM 1974b.

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