

CURRENT ACTIVITIES IN ENVIRONMENTAL STANDARD REFERENCE MATERIALS FOR TRACE HALOGENATED ORGANIC POLLUTANTS

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Introduction

Since 1980, the National Institute of Standards and Technology (NIST) has issued a number of Standard Reference Materials (SRMs) for use in the determination of the concentrations of organic contaminants in environmental samples. Many of these are simple calibration solutions that contain a number of analytes and are useful for calibrating the measurement system. In addition, environmental natural matrix materials are available and are useful for validating complete analytical procedures and providing quality control of organic contaminant analyses.

Calibration solutions with 28 polychlorinated biphenyl (PCB) congeners and 15 chlorinated pesticides have been developed at two concentration levels that are approximately an order of magnitude different. Other calibration solutions available include one containing 11 additional PCB congeners and one containing 9 additional chlorinated pesticides. In addition, NIST is preparing a number of calibration solutions in support of the externalization of U.S. EPA's Water Proficiency Testing Studies. These solutions include Aroclors in methanol and transformer oil, and chlorinated pesticides in methanol.

Current activities in the area of environmental natural matrix materials include updating the Certificates of Analysis (COAs) for a number of existing SRMs and issuing several new materials. These activities are summarized in Table 1.

In addition to those SRMs listed in Table 1, a second fish tissue material is in preparation, SRM 1947, Lake Michigan Fish Tissue, as well as a household dust material for pesticides. SRM 1947 has been prepared from lake trout fillets collected from Lake Michigan and will be issued as a fresh frozen homogenate.

Materials and Methods

The SRMs mentioned in this abstract are available from the Standard Reference Materials Program (SRMP), NIST (Gaithersburg, MD, www.nist.gov). The methods used for certification are described in detail in the corresponding Certificates of Analysis available from SRMP¹.

Results and Discussion

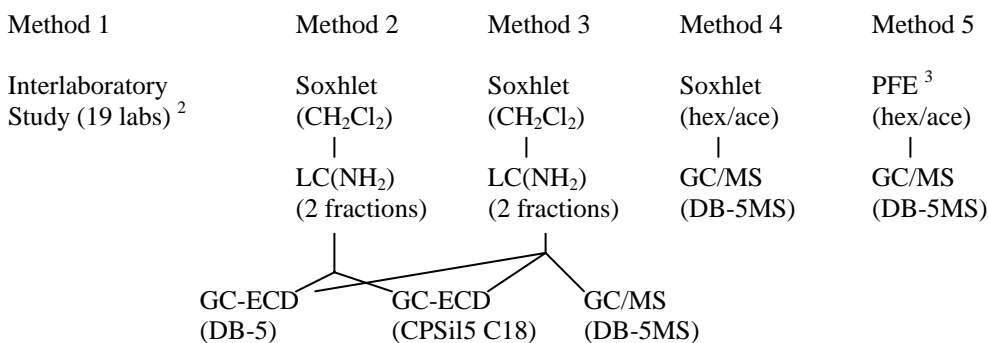
During the certification of SRMs at NIST, the results from at least two "chemically independent" analytical techniques are typically used to determine the certified concentrations of the analytes. This includes independent extraction, isolation, and chromatographic techniques. An example is

given in Figure 1 for the certification of the PCBs and chlorinated pesticides in SRM 1944, a marine sediment material.

Table 1. Recently released natural matrix SRMs for trace organic halogenated pollutants

<u>SRM number</u>	Compound classes with certified values <u>and reference values</u>
1588a Organics in Cod Liver Oil	PCBs, Pesticides, PCDDs/ PCDFs
1589a Polychlorinated Biphenyls / Pesticides in Human Serum	PCBs, Pesticides, PCDDs/PCDFs
1649a Urban Dust	PAHs, PCBs, Pesticides, PCDDs/PCDFs, trace elements
1939a Polychlorinated Biphenyl (Congeners) in River Sediment A	PCBs, Pesticides
1941b Organics in Marine Sediment	PAHs, PCBs, Pesticides, Trace Elements
1944 NY/NJ Waterway Sediment	PAHs, PCBs, Pesticides, PCDDs/ PCDFs, trace elements
1945 Organics in Whale Blubber	PCBs, Pesticides
1946 Lake Superior Fish Tissue	PCBs, Pesticides, Fatty Acids, Extractable Fat, Methyl-Hg, Hg, elements, proximates
1974b Organics in Mussel Tissue (<i>Mytilus edulis</i>)	PAHs, PCBs, Pesticides, Methyl-Hg, Hg trace elements
2977 Mussel Tissue (Organic Contaminants and Trace Elements)	PAHs, PCBs, Pesticides, Methyl-Hg, trace elements
2978 Mussel Tissue (Organic Contaminants – Raritan Bay, New Jersey)	PAHs, PCBs, Pesticides

Figure 1. Methods used for the determination of PCB congeners and pesticides in SRM 1944



For the SRM in Figure 1, data from an interlaboratory exercise (Method 1) coordinated by NIST and the National Oceanic and Atmospheric Administration (NOAA) were used along with data from four methods of analyses conducted at NIST. For these four methods, both Soxhlet extraction and pressurized fluid extraction (PFE), using either dichloromethane or hexane/acetone (1:1, v:v), were used followed by the isolation of two fractions, one containing PCBs and lower polarity pesticides and the other the more polar pesticides. Samples fractionated in this manner were used for the two methods where gas chromatography with electron capture detection was used as the final analysis step.

There are currently three sediment SRMs available: two harbor sediments (SRM 1941b and SRM 1944) differing in concentration by about an order of magnitude and a river sediment (SRM 1939a) which is representative of a PCB spill. There is an urban dust, SRM 1649a, with certified concentrations for selected PCB congeners and chlorinated pesticides.⁴ Four marine tissue materials are available, three provided as fresh frozen materials (whale blubber SRM 1945, mussel tissue SRM 1974b, and fish tissue SRM 1946⁵) and two as freeze-dried materials (SRM 2977 and SRM 2978). SRM 1588a, a cod liver oil, was reissued with an expanded list of PCB congeners and chlorinated pesticides having certified concentrations. The human serum 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 PCDD and PCDF congeners.

Table 2 shows the relative concentrations of selected PCB congeners and chlorinated pesticides in five of the above mentioned materials. Only a limited number of congeners and pesticides are shown in this table, but typically 20 to 25 PCB congeners and 5 to 10 pesticides have values listed in the Certificates of Analysis¹.

Acknowledgements

The authors acknowledge the help of Donald Patterson and Wayman Turner at CDC on the certification of SRM 1589a.

References

1. Certificates of Analysis available from <http://ts.nist.gov/srm>
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Table 2. Concentrations (ng/g dry mass) of Selected PCB Congeners and Chlorinated Pesticides in Sediment, Urban Dust, and Mussel Tissue SRMs and (ng/g wet mass) in a Fish Tissue SRM

Compound	SRM 1941b (sediment)	SRM 1944 (sediment)	SRM 1939a (sediment)	SRM 1649a (urban dust)	SRM 1974b (mussel tissue)	SRM 1946 (fish tissue)
PCB 28	4.52 ± 0.57	80.8 ± 2.7	461 ± 78	18.5 ± 1.2	33.9 ± 2.5	2.00 ± 0.24
PCB 52	5.24 ± 0.28	79.4 ± 2.0	4320 ± 130	24.65 ± 0.97	61.8 ± 3.7	8.1 ± 1.0
PCB 99	2.90 ± 0.36	37.5 ± 2.4	380 ± 96	9.58 ± 0.69	58.4 ± 2.7	25.6 ± 2.3
PCB 101	5.11 ± 0.34			52.9 ± 1.0	106 ± 11	34.6 ± 2.6
PCB 101/90		73.4 ± 2.5				
PCB 105	1.43 ± 0.10	24.5 ± 1.1	201 ± 28	8.63 ± 0.80	39.5 ± 1.8	19.9 ± 0.9
PCB 118	4.23 ± 0.19	58.0 ± 4.3	423 ± 88	25.7 ± 1.5	102 ± 4	52.1 ± 1.0
PCB 138	3.60 ± 0.28			91 ± 14		115 ± 13
PCB 138/163/164		62.1 ± 3.0	258.1 ± 6.9	69.7 ± 7.5		
PCB 153	5.47 ± 0.32	74.0 ± 2.9	297 ± 19	82.5 ± 8.0	121 ± 8	170 ± 9
PCB 170	1.35 ± 0.09			2.66 ± 0.34		25.2 ± 2.2
PCB 170/190		22.6 ± 1.4	107 ± 17	30.8 ± 2.2		
PCB 180	3.24 ± 0.51	44.3 ± 1.2	140.3 ± 6.1	78.7 ± 8.2	11.5 ± 1.0	74.4 ± 4.0
<i>cis</i> -chlordane	0.85 ± 0.11	16.51 ± 0.83	4.8 ± 1.3	34.88 ± 0.42	13.4 ± 1.0	32.5 ± 1.8
<i>trans</i> -nonachlor	0.438 ± 0.073	8.20 ± 0.51		27.6 ± 1.6	12.8 ± 1.4	99.6 ± 7.6
4,4'-DDE	3.22 ± 0.28	86 ± 12		40.4 ± 1.7	41.0 ± 3.8	373 ± 48
4,4'-DDD	4.66 ± 0.46	108 ± 16	5.50 ± 0.97	34.01 ± 0.48	33.0 ± 2.2	17.7 ± 2.8
4,4'-DDT	1.12 ± 0.42	119 ± 11	2.72 ± 0.42	212 ± 15	3.91 ± 0.94	37.2 ± 3.5
Total Certified Values	60	72	23	65	60	63
Total Reference Values	63	78	4	50	43	37

^a Concentrations are the certified concentrations or *reference concentrations* as determined by statistically combining the data from the different methods used for certification. For each SRM the method used for combining data and the definition of the associated uncertainties are given in the Certificates of Analysis[1].