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Certification of a Frozen Mussel Tissue Standard Reference Material (SRM 1974a) for Trace Organic Constituents

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Abstract NIST SRM 1974a, Organics in Mussel Tissue (*Mytilus edulis*), has been issued as a frozen tissue homogenate with certified mass fractions for 15 polycyclic aromatic hydrocarbons (PAHs), 20 polychlorinated biphenyl (PCB) congeners, and 7 chlorinated pesticides. Noncertified mass fractions are provided for an additional 18 PAHs, 4 PCB congeners, 4 chlorinated pesticides, 28 inorganic constituents, 16 aliphatic hydrocarbons, and methylmercury. The mass fractions for the measured PAHs range from approximately 1 μg/kg to 164 μg/kg dry mass while the mass fractions for the measured PCB congeners range from approximately 3 μg/kg to 150 μg/kg dry mass.

Introduction

Many industrially synthesized organic contaminants are highly persistent within terrestrial and aquatic ecosystems and continue to be a public health issue years after production is banned [1]. Polychlorinated biphenyls (PCBs) and the DDT (dichloro-diphenyltrichloroethane) family of residues are familiar examples of such compounds that are a continuing concern in regions such as the Laurentian Great Lakes [2–4], the Canadian arctic archipelago [5], and in estuarine systems such as Buzzards Bay [6] and Chesapeake Bay [7] because the lipophilic nature of these compounds leads to their accumulation in aquatic food webs [8–10].

Marine biomonitoring programs often use the blue mussel (*Mytilus edulis*) as a possible indicator of pollution in the marine environment [11]. For example, blue mussels were recently utilized to monitor the levels of organic contaminants during a pilot dredging project in New Bedford Harbor, documenting the use of this species for quantifying bioavailable organic contaminats and for assessing ambient water quality [12]. The National Institute of Standards and Technology (NIST) issued in 1990 a frozen blue mussel tissue Standard Reference Material, SRM 1974, Organics in Mussel Tissue (*Mytilus edulis*), to assist researchers involved in marine biomonitoring programs in the validation of their organic contaminant measurements in this and similar sample matrices [13]. This material was issued as a frozen tissue homogenate with certified values for 9 polycyclic aromatic hydrocarbons (PAHs) and noncertified values for 19 additional PAHs, 13 PCB congeners, and 9 chlorinated pesticides [14]. The supply of SRM 1974 was depleted in 1994. As a result, the collection and preparation of a new material was initiated and a new mussel tissue, SRM 1974a, has been issued. To expand the usefulness of this new mussel tissue SRM, the goals were: (1) to provide sufficient quantities of material to extend the availability of this SRM to 7 to 8 years, (2) to provide certified values for a larger number of PAHs and for a number of the PCB congeners and chlorinated pesticides, and (3) to reduce the uncertainties associated with the certified values compared to the original mussel tissue SRM.

At the National Institute of Standards and Technology (NIST), the certification process for a natural-matrix SRM typically requires the use of two or more "chemically independent" analytical techniques, and the results of these analyses, if in agreement, are used to determine the certified values of the measured analytes. For organic analysis, there is a limit to the number of possible techniques for each analyte class. The

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techniques are chosen to be as independent as possible. Our approach makes use of different chromatographic systems with different selectivities and different detectors. This requirement of using two or more different techniques is based on the assumption that the agreement of results from independent methods implies that the results are unbiased. When only one analytical technique is used or there is insufficient agreement among results from the different techniques, the concentrations are generally reported as noncertified or information values. For the measurement of PAHs, Wise et al. [15] described the use of four different analytical techniques to provide certified values for 23 PAHs in a marine sediment SRM, SRM 1941a. This approach consisted of: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) for analysis of the total PAH fraction, (2) reversed-phase LC-FL analysis of isomeric PAH fractions isolated by normal-phase LC (i.e., multidimensional LC), (3) gas chromatography/mass spectrometry (GC/MS) analysis of the PAH fraction on a 5% phenyl-substituted methylpolysiloxane stationary phase, and (4) GC/MS of the PAH fraction on a smectic liquid crystalline stationary phase that provides excellent shape selectivity for the separation of PAH isomers. SRM 1974a was analyzed using these same four techniques to provide certified values for 15 PAHs and noncertified values for an additional 18 PAHs.

For the measurement of PCB congeners and chlorinated pesticides, the approach used for SRM 1974a was similar to that used for SRM 1945, Organics in Whale Blubber [16]. This approach consists of GC analyses with electron capture detection (GC-ECD) on a 5% phenyl-substituted methylpolysiloxane phase and on a dimethylpolysiloxane phase containing 50% methyl C_{18} and GC/MS analyses on a 5% phenyl-substituted methylpolysiloxane phase. Combined with the results from this approach were results from two interlaboratory comparison exercises.

The aliphatic hydrocarbons were determined in SRM 1974a using GC/MS on a 5% phenyl-substituted methylpolysiloxane phase. The trace elements were determined using instrumental neutron activation analysis (INAA). SRM 1974 was analyzed as a control sample for each of the techniques. Method blanks were also processed with each set and showed no significant concentration for any of the target analytes.

Experimental[1]

Sample collection

The mussels (*Mytilus edulis*) used for the preparation of SRM 1974a were collected on October 7, 1992 from Dorchester Bay within Boston Harbor, MA, following the same procedures as described previously for the collection of mussels for SRM 1974 [14]. Approximately 6000 individual mussels were collected by hand at low tide. The samples were transported to the Battelle Ocean Sciences Laboratory (Duxbury, MA) where the mussels were rinsed with water to remove rocks and other debris. The samples were bagged in Ziplock™ bags and placed in insulated, Teflon-lined wooden containers, frozen and transported to NIST on dry ice. The samples were transferred to Teflon bags and stored in a liquid nitrogen vapor freezer ($-120\,^{\circ}C$) until they were shucked.

Sample preparation

The mussel tissue was removed from the shell using the following procedure. The mussels were allowed to warm up to about 0 °C; the tissue was removed from the shell using a titanium knife and placed in Teflon bags (approximately 1 kg per bag) and immediately returned to a liquid nitrogen vapor freezer. Approximately 81 kg of mussel tissue were prepared for use as the SRM. Approximately 20 kg of the same frozen mussel homogenate were freeze-dried. The freeze-dried material will be issued as a separate material, SRM 2974.

The frozen mussel tissue was pulverized in batches of approximately 700 g each using a cryogenic procedure described previously [18]. The pulverized material was then homogenized in an aluminium mixing drum in 30 kg batches. The mixing drum was designed to fit inside the liquid nitrogen vapor freezer and to rotate in the freezer thereby mixing the frozen tissue powder. After mixing for 2 h, subsamples of approximately 15 g of the tissue homogenate were aliquoted into pre-cleaned, pre-cooled glass bottles fitted with screw caps containing Teflon liners.

Conversion to dry mass basis

The moisture content of SRM 1974a was determined by measuring the mass loss from freeze-drying. Twenty bottles of SRM 1974a were selected according to a stratified randomization scheme for the drying study. The entire contents of each bottle were transferred to a Teflon bottle and dried for 5 days at 1 Pa with a $-20\,^{\circ}C$ shelf temperature and a $-50\,^{\circ}C$ condenser temperature. The shelf temperature was gradually increased to 5 °C. The sample was considered dry when a stable mass was obtained. Based on these studies, a 95% confidence interval for the mean moisture content of SRM 1974a is $88.61\% \pm 0.08\%$. Analytical results for the organic constituents were determined on a wet basis and then converted to a dry basis by dividing by the conversion factor of 0.1139 kg dry mass/kg wet mass.

Measurements of PAHs

SRM 1974a was analyzed for the determination of selected PAHs using GC/MS and LC-FL as shown in Figure 1. The general approach used for the determination of PAHs in SRM 1974a has been reported previously for the certification of a marine sediment material, SRM 1941a [15, 17].

Three sets of GC/MS results, designated as GC/MS (I), GC/MS (II), and GC/MS (Sm), were obtained using two columns with different selectivities for the separation of PAHs. For GC/MS (I) analyses, duplicate subsamples of 7 g to 9 g (wet basis) of the mussel homogenate from 12 randomly selected bottles were mixed with approximately 100 g of sodium sulfate, an internal standard (see below) was added to the sodium sulfate-tissue mixture, and then the mixture was Soxhlet extracted for 18 h using 250 mL of dichloromethane. The extract was concentrated, and size exclusion chromatography on a semi-preparative divinylbenzene-polystyrene

[1] Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are the best available for the purpose.

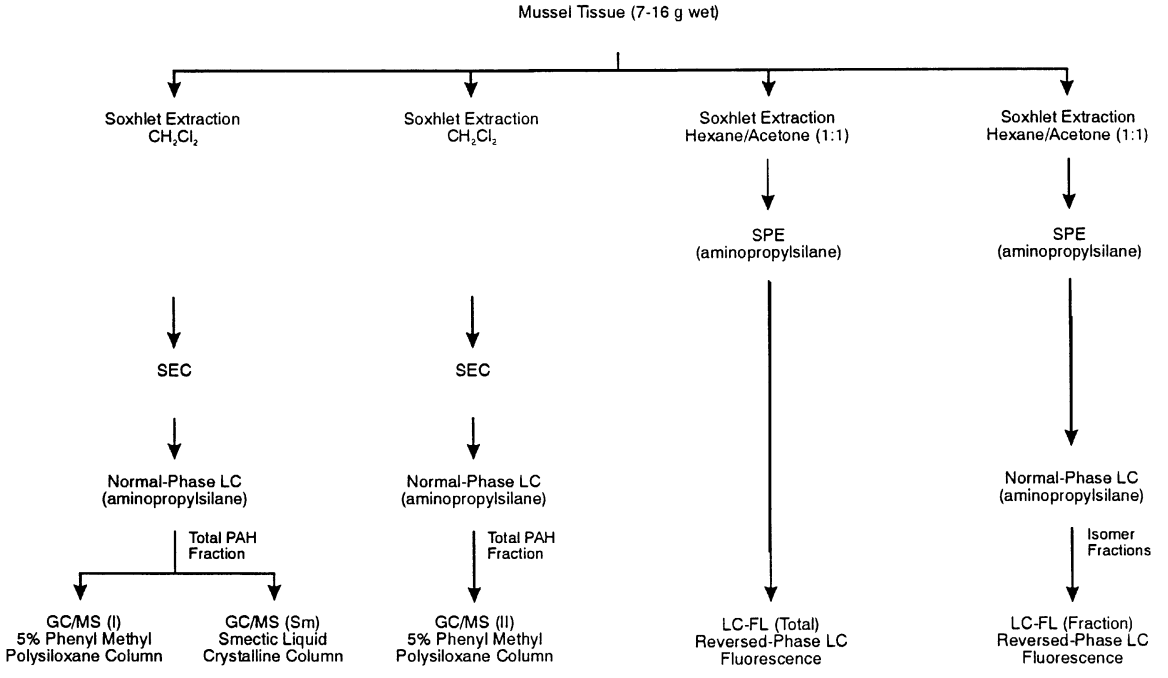

Fig. 1 Analytical scheme for the determination of PAHs in SRM 1974a

column (10 μm particle size, 100 Å pore size, 2.5 cm i.d. × 60 cm) was used to remove the majority of the lipid and biogenic materials. The eluant was concentrated and injected onto a semi-preparative aminopropylsilane column to isolate the PAH fraction by normal-phase LC [17]. The PAH fraction was then analyzed by GC/MS using a 0.25 mm × 60 m fused silica capillary column with a 5% phenyl-substituted methylpolysiloxane phase (0.25 μm film thickness, DB-5 MS, J&W Scientific, Folsom, CA).

For the GC/MS (II) analyses, subsamples of 14 g to 16 g (wet basis) from three bottles of SRM 1974a were extracted and one half of each extract was analyzed using the same procedure as described above for GC/MS (I). However, these extractions and analyses were performed as part of three different sample sets at different times using different calibrations, method blanks, and quality control samples for each set.

The GC/MS (Sm) results were obtained by analyzing seven of the sample extracts from the GC/MS (I) set using a 0.2 mm i.d. × 25 m (0.15 μm film thickness) smectic liquid crystalline stationary phase (SB-Smectic, Dionex, Lee Scientific Division, Salt Lake City, UT). The liquid crystalline phase provides significantly different selectivity based on molecular shape for the separation of PAH isomers when compared with the 5% phenyl-subst. methylpolysiloxane phase. The column has a limited temperature range.

Two sets of LC-FL results, designated as LC-FL (Total) and LC-FL (Fraction), were used in the certification process. For the LC-FL (Total) analyses, a subsample of approximately 15 g (wet basis) of the mussel homogenate from eight randomly selected bottles was mixed with approximately 100 g of sodium sulfate, an internal standard (see below) was added to the sodium sulfate-tissue mixture, and then the mixture was Soxhlet extracted for 20 h using 200 mL of 1:1 (volume ratio) hexane:acetone. The extract was concentrated and then passed through an aminopropylsilane solid phase extraction (SPE) column using 1:50 (volume ratio) dichloromethane in hexane to remove the lipid and more polar interferences. The eluant from the SPE column was concentrated and the SPE procedure was repeated five times on different SPE columns. The cleaned up extract was then analyzed by reversed-phase LC using a polymeric octadecylsilane (C_{18}) column (4.6 mm i.d. × 15 cm, 3 μm particle size, ChromSpher PAH, Chrompack, Middelburg, The Netherlands) with wavelength-programmed fluorescence detection [15, 19–21]. To quantify several PAHs that have low fluorescence sensitivity and /or selectivity, six additional samples of SRM 1974a were extracted and prepared as described above. The extract was then fractionated on a semi-preparative aminopropylsilane column to isolate isomeric PAH fractions as described previously [15, 20, 22]. These isomeric PAH fractions were analyzed by reversed-phase LC-FL on a similar C_{18} column; these results are designated as LC-FL (Fraction) in Table 1.

For both the GC/MS and LC-FL measurements, selected perdeuterated PAHs were added to the mussel tissue/sodium sulfate mixture immediately prior to Soxhlet extraction for use as internal standards for quantification purposes. For GC/MS analyses the following internal standards were used: naphthalene-d_8, acenaphthene-d_{10}, fluorene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, benz[*a*]anthracene-d_{12}, benzo[*e*]pyrene-d_{12}, dibenz[*a*,*h*]anthracene-d_{14}, and benzo[*ghi*]perylene-d_{12}. For the LC-FL analyses the following internal standards were used: naphthalene-d_8, phenanthrene-d_{10}, fluoranthene-d_{10}, and perylene-d_{12} for the LC-FL (Total) analyses and triphenylene-d_{12}, benz[*a*]anthracene-d_{12}, and benzo[*ghi*]perylene-d_{14} for the LC-FL (Fraction) analyses. Calibration response factors for the analytes relative to the internal standards were determined by analyzing aliquots of gravimetrically prepared mixtures of SRM 1491 and SRM 2260, Aromatic Hydrocarbons in Hexane/Toluene for the GC/MS analyses or SRM 1647b, Polycyclic Aromatic Hydrocarbons (in Acetonitrile) for the LC-FL analyses; gravimetrically prepared solutions of additional analytes not contained in SRMs 1491, 2260, or 1647b; and the internal standards.

Measurements of PCB congeners and chlorinated pesticides

SRM 1974a was analyzed for selected PCB congeners and chlorinated pesticides using GC-ECD on two columns with different selectivity and using GC/MS as shown in Figure 2. This same approach has been used previously at NIST for the certification of PCB congeners and chlorinated pesticides in other environmental matrices [16, 17, 23].

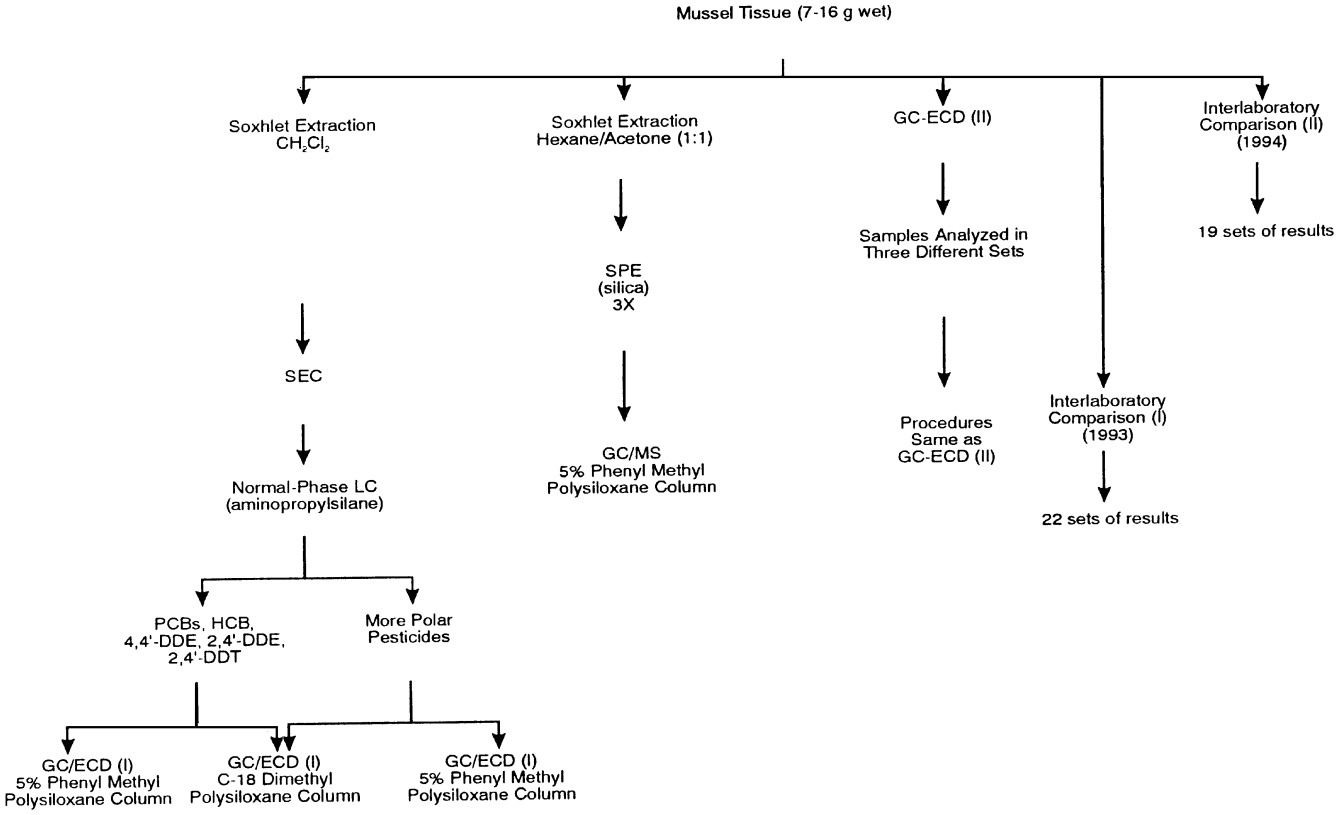

Fig. 2 Analytical scheme for the determination of PCB congeners and chlorinated pesticides in SRM 1974a

For SRM 1974a, two sets of GC-ECD analyses, designated as GC-ECD (I) and GC-ECD (II), were performed using similar procedures. For the GC-ECD (I) analyses, subsamples of 14 g to 16 g (wet basis) from eight bottles were mixed with 100 g of precleaned sodium sulfate and Soxhlet extracted for 18 h using 250 mL of dichloromethane. Size exclusion chromatography on a preparative-scale divinylbenzene-polystyrene column with dichloromethane as the mobile phase was used to remove the majority of the lipid and biogenic material. The concentrated eluant was then fractionated on a semi-preparative aminopropylsilane column to isolate two fractions containing (1) the PCB congeners and lower polarity pesticides using hexane as the mobile phase and (2) the more polar pesticides using 5:95 (volume ratio) dichloromethane in hexane. GC-ECD analyses of the two fractions were performed on two columns of different selectivities for PCB separations: 0.25 mm × 60 m fused silica capillary column with a 5% phenyl-substituted methylpolysiloxane phase (0.25 μm film thickness) DB-5, J&W Scientific, Folsom, CA) and a 0.32 mm × 100 m fused silica capillary column with a dimethylpolysiloxane phase containing 50% methyl C_{18} (0.1 μm film thickness) (CPSil 5 C18 CB, Chrompack International, Middelburg, The Netherlands). For the GC-ECD (II) analyses, subsamples of 14 g to 16 g (wet basis) from three bottles of SRM 1974a were extracted and one half of each extract was analyzed using the same procedure as described above for GC-ECD (I). However, these extractions and analyses were performed as part of three different samples sets at different times using different calibrations, method blanks, and quality control samples for each set.

For the GC/MS analyses of SRM 1974a, subsamples of 14 g to 16 g (wet basis) each from eight randomly selected bottles were Soxhlet extracted for 18 h using 1:1 (volume ratio) hexane:acetone. The extracts were concentrated and placed on a precleaned silica SPE column and eluted with 15 mL of 1:10 (volume ratio) dichloromethane in hexane. The SPE cleanup procedure was performed sequentially three times on separate SPE columns. The final fraction was analyzed by GC/MS on a 5% phenyl-substituted methylpolysiloxane phase as described above for PAH measurements.

For both the GC-ECD and GC/MS analyses, two PCB congeners that are not significantly present in the mussel tissue extract (PCB 103 and PCB 198 [24, 25]), octachloronaphthalene, 4,4′-DDT-d_8, and endosulfan-d_4 were added to the mussel tissue/sodium sulfate mixture prior to extraction for use as internal standards for quantification purposes. Calibration curves for the analytes relative to the internal standards were prepared by analyzing gravimetrically prepared mixtures of SRM 2261, Chlorinated Pesticides in Hexane (Nominal Concentration 2 μg/mL); SRM 2262, Chlorinated Biphenyl Congeners in 2, 2, 4-Trimethylpentane (Nominal Concentration 2 μg/mL); gravimetrically prepared solutions of additional analytes not contained in SRMs 2261 and 2262; and the internal standards.

In addition to the analyses performed at NIST described above, SRM 1974a was used in two interlaboratory comparison exercises as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment. The results from these two exercises, which were conducted in 1993 and 1994, and included results from 22 and 19 laboratories, respectively, were also used in the determination of the certified values for selected PCB congeners and chlorinated pesticides. The laboratories participating in these exercises used the analytical procedures routinely used in their laboratories to measure PCB congeners and chlorinated pesticides.

Measurements of aliphatic hydrocarbons

The fractions from SRM 1974a isolated for the measurement of PAHs by GC/MS (I) were analyzed on the same 5% phenyl-substituted methylpolysiloxane column by GC/MS for the determination of selected aliphatic hydrocarbons. Perdeuterated dodecane, eicosane, and triacontane were added prior to extraction as internal

standards for quantification purposes. Response factors for the analytes relative to the internal standards were determined by analyzing gravimetrically prepared mixtures of SRM 1494, "Aliphatic Hydrocarbons in 2,2,4-Trimethylpentane," and the internal standards.

Measurements of inorganic constituents

Selected inorganic constituents were determined in SRM 1974a using instrumental neutron activation analysis (INAA) procedures as described previously for the analysis of marine bivalves [26]. Samples from eight randomly selected bottles of SRM 1974a were freeze-dried and duplicate portions of approximately 20 mg (dry basis) each from each bottle were pelletized and analyzed.

Results and discussion

The analytical scheme for the analysis of SRM 1974a was similar to that used for SRM 1941a [17] with the addition of data from two interlaboratory comparison exercises for the PCB congeners and chlorinated pesticides. SRM 1974 was used as a control material for each of the techniques except for the first interlaboratory comparison exercise. The values determined for SRM 1974 by each of the techniques agreed with the certified and noncertified values listed on the Certificate of Analysis within the 95% confidence intervals.

PAHs

The results from each of the four analytical approaches used for the determination of 16 PAHs certified in SRM 1974a are summarized in Table 1. Results from GC/MS (I) and GC/MS (II) were considered as the same method for the purposes of certification. The results from all five data sets were in good agreement and were combined as equally weighted means to provide certified values for 15 PAHs in SRM 1974a (see Table 2). Each expanded uncertainty was computed according to the CIPM approach [27] at the 95% level of confidence, and includes within-method sources of uncertainty, such as instrument calibration and measurement variation. The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%. For some analytes, an additional allowance for differences between the methods was included in the total uncertainty.

Two of the goals for the reissue of the mussel tissue SRM were to increase the number of compounds with certified values and to reduce the uncertainties associated with the certified values compared to the original SRM 1974. In SRM 1974 certified values were determined for nine PAHs with relative uncertainties ranging from 11% to 28%. In SRM 1974a certified

Table 1 Summary of analytical results for PAHs in SRM 1974a

Compound	Mass Fractions (μg/kg dry mass basis)[a]				
	GC/MS (I)[b]	GC/MS (II)[c]	GC/MS (Sm)[d]	LC-FL (Total)[e]	LC-FL (Fraction)[f]
Naphthalene	21.7 ± 8.0	21.6 ± 2.6	–	27.3 ± 4.7	–
Phenanthrene	21.2 ± 5.9	21.5 ± 2.2	–	24.0 ± 3.0	–
Anthracene	7.26 ± 0.50	6.61 ± 0.40	–	4.34 ± 0.60	–
Fluoranthene	160.7 ± 10.4	158.3 ± 6.3	–	172.0 ± 5.8	–
Pyrene	145.9 ± 9.6	151.7 ± 7.1	–	157.0 ± 5.5	–
Benz[*a*]anthracene	29.3 ± 3.0	29.4 ± 2.4	34.3 ± 3.9	–	37.1 ± 2.3
Chrysene	85.2 ± 7.4[g]	90.2 ± 5.1[g]	42.8 ± 4.1	–	45.6 ± 3.4
Triphenylene	85.2 ± 7.4[g]	90.2 ± 5.1[g]	56.2 ± 4.1	–	45.2 ± 2.5
Benzo[*b*]fluoranthene	56.6 ± 5.1[h]	–	43.4 ± 2.7	49.4 ± 4.0	–
Benzo[*j*]fluoranthene	56.6 ± 5.1[h]	–	20.5 ± 1.8	–	–
Benzo[*k*]fluoranthene	19.5 ± 1.4	20.5 ± 3.7	20.3 ± 1.7	20.4 ± 1.7	–
Benzo[*e*]pyrene	84.6 ± 3.8	82.8 ± 4.7	84.5 ± 4.5	–	–
Benzo[*a*]pyrene	15.3 ± 1.0	15.36 ± 0.55	16.2 ± 1.9	–	–
Perylene	7.87 ± 0.60	7.65 ± 0.31	7.5 ± 1.0	7.64 ± 0.26	–
Benzo[*ghi*]perylene	22.1 ± 1.2	24.1 ± 1.2	–	20.85 ± 0.79	20.8 ± 1.7
Indeno[1,2,3-*cd*]pyrene	15.58 ± 0.99	15.62 ± 0.64	–	15.90 ± 0.75	11.37 ± 0.65

[a] Each uncertainty is an expanded uncertainty at the 95% level of confidence that incorporates only the individual method's within-method uncertainty. It defines a range of values within which the true method mean is believed to lie, at a level of confidence of approximately 95%.
[b] GC/MS(I) = GC/MS analysis on 5% phenyl-subst. methylpolysiloxane phase; duplicate samples from twelve bottles analyzed.
[c] GC/MS (II) = GC/MS analysis on 5% phenyl-subst. methylpolysiloxane phase; samples from three bottles analyzed on three different occasions.
[d] GC/MS (Sm) = GC/MS analysis using a smectic liquid crystalline phase; samples from eight bottles analyzed.
[e] LC-FL (Total) = LC-FL analysis of total PAH fraction; samples from eight bottles analyzed.
[f] LC-FL (Fraction) = LC-FL analysis of isomeric PAH fractions; samples from six bottles analyzed.
[g] Chrysene and triphenylene coeluted in GC/MS (I) and GC/MS (II); value represents the sum of the mass fractions of chrysene and triphenylene.
[h] Benzo[*b*]fluoranthene and benzo[*j*]fluoranthene coeluted in GC/MS (I) and GC/MS (II) analyses; value represents the sum of the mass fractions of benzo[*b*]fluoranthene and benzo[*j*]fluoranthene.

Table 2 Certified mass fractions for selected PAHs in SRM 1974a[a]

Compound	µg/kg wet mass basis[b]	µg/kg dry mass basis[b]
Naphthalene	2.68 ± 0.50[c]	23.5 ± 4.4[c]
Phenanthrene	2.53 ± 0.28	22.2 ± 2.4
Anthracene	0.69 ± 0.20[c]	6.1 ± 1.7[c]
Fluoranthene	18.6 ± 1.0[c]	163.7 ± 9.1[c]
Pyrene	17.26 ± 0.74[c]	151.6 ± 6.6[c]
Benz[*a*]anthracene	3.71 ± 0.54[c]	32.5 ± 4.7[c]
Chrysene	5.04 ± 0.26	44.2 ± 2.3
Triphenylene	5.77 ± 0.67	50.7 ± 5.9
Benzo[*b*]fluoranthene	5.28 ± 0.42[c]	46.4 ± 3.7[c]
Benzo[*k*]fluoranthene	2.30 ± 0.10	20.18 ± 0.84
Benzo[*e*]pyrene	9.56 ± 0.21	84.0 ± 1.9
Benzo[*a*]pyrene	1.780 ± 0.073	15.63 ± 0.65
Perylene	0.874 ± 0.030	7.68 ± 0.27
Benzo[*ghi*]perylene	2.50 ± 0.25[c]	22.0 ± 2.2[c]
Indeno[1,2,3-*cd*]pyrene	1.62 ± 0.32[c]	14.2 ± 2.8[c]

[a] Results reported on both wet and dry mass basis; SRM 1974a as received contains 88.61% ± 0.08% water.
[b] Each certified value is the mean of the equally weighted means from two or more independent analytical methods (see Table 1). Each uncertainty, computed according to the CIPM approach [27], is an expanded uncertainty at the 95% level of confidence that includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study (for the dry mass basis values). The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.
[c] An additional allowance for differences between methods was included in the total uncertainty for this analyte.

values were determined for 15 PAHs with relative uncertainties ranging from 1.0% to 28% with the majority in the 4% to 8% range. The increased number of certified values and the reduced uncertainties were achieved through the incorporation of two additional analytical techniques into the certification scheme, which were not used in the analysis of SRM 1974, i.e., the multidimensional normal-phase LC followed by LC-FL and the GC/MS on the liquid crystalline phase, and better agreement of the results among the different methods. A more detailed discussion of the certification of the PAHs in SRM 1974a is published elsewhere [28]. Noncertified values listed in Table 3 were determined for 18 additional PAHs in SRM 1974a. The noncertified values were determined from the equally weighted means of two analytical methods or the mean determined from one analytical method. The majority of the noncertified values were derived from the GC/MS (I) and GC/MS (II) data sets that were both determined using the 5% phenyl methylpolysiloxane column, and therefore were not considered to be independent methods.

PCB Congeners and Chlorinated Pesticides

Selected PCB congeners and chlorinated pesticides in SRM 1974a were determined by GC-ECD and GC/MS

Table 3 Noncertified mass fractions for selected PAHs in SRM 1974a[a]

Compound	µg/kg wet mass basis[b]	µg/kg dry mass basis[b]
1-Methylnaphthalene[c,d]	0.61 ± 0.20	5.3 ± 1.8
2-Methylnaphthalane[c,d]	1.16 ± 0.17[e]	10.2 ± 1.5[e]
Biphenyl[c,d]	0.582 ± 0.038	5.11 ± 0.33
Acenaphthylene[c,d]	0.598 ± 0.043[e]	5.25 ± 0.38[e]
Acenaphthene[c]	0.359 ± 0.038	3.15 ± 0.26
Fluorene[c,d]	0.65 ± 0.10[e]	5.72 ± 0.91[e]
1-Methylphenanthrene[c,d]	1.20 ± 0.55	10.5 ± 4.8
2-Methylphenanthrene[c]	2.34 ± 0.92	20.6 ± 8.0
3-Methylphenanthrene[c]	1.5 ± 1.1	13.5 ± 9.7
4-Methylphenanthrene/ 9-Methylphenanthrene[c]	1.7 ± 1.0	14.7 ± 9.2
Benzo[*c*]phenanthrene[c,f]	2.22 ± 0.76[e]	19.5 ± 6.7[e]
Benzo[*ghi*]fluoranthene[c]	3.22 ± 0.62	28.3 ± 5.5
Benzo[*a*]fluoranthene[c,d]	0.45 ± 0.22[e]	4.0 ± 1.9[e]
Benzo[*j*]fluoranthene[f]	2.33 ± 0.20	20.5 ± 1.7
Dibenz[*a,j*]anthracene[c]	0.142 ± 0.010	1.247 ± 0.075
Dibenz[*a,h*]anthracene/ Dibenz[*a,c*]anthracene[c,d]	0.342 ± 0.022	3.00 ± 0.20
Benzo[*b*]chrysene[c]	0.182 ± 0.016	1.60 ± 0.15
Anthanthrene[g]	0.131 ± 0.036	1.15 ± 0.31

[a] Results reported on both wet weight and dry weight basis, SRM 1974a as received contains 88.61% ± 0.08% water.
[b] Each noncertified value is the mean of the equally weighted means from two different analytical methods or the mean determined by one analytical method. Each uncertainty, computed according to the CIPM approach [27], is an expanded uncertainty at the 95% level of confidence that includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study (for the dry mass basis values). The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.
[c] GC/MS (I) = GC/MS analyses on 5% phenyl-subst. methylpolysiloxane phase; duplicate samples from twelve bottles analyzed.
[d] GC/MS (II) = GC/MS analysis on 5% phenyl-subst. methylpolysiloxane phase; samples from three bottles analyzed on three different occasions.
[e] An additional allowance for differences between methods was included in the total uncertainty for this analyte.
[f] GC/MS (Sm) = GC/MS analysis using a liquid crystalline phase; samples from eight bottles analyzed.
[g] LC-FL (Fraction) = LC-FL analysis of isomeric PAH fractions; samples from six bottles analyzed.

using an approach similar to that used for SRM 1945 [16] and for SRM 1941a [15] with the addition of data from two interlaboratory comparison exercises, conducted as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment. SRM 1974a was used in 1993 by 22 laboratories as an unknown exercise material and in 1994 by 19 laboratories as a known control material. The laboratories participating in these exercises used the analytical procedures routinely used in their laboratories to measure PCB congeners and chlorinated pesticides. The results used to determine the certified values are summarized in Table 4 for the PCB congeners and in Table 5 for the chlorinated pesticides.

Table 4 Summary of analytical results for PCB congeners in SRM 1974a

PCB Congener[b]	Mass fraction (μg/kg dry mass basis)[a]						
	GC-ECD (I)[c] (5% Phenyl)	GC-ECD (I)[c] (C-18)	GC-ECD (II)[d] (5% Phenyl)	GC-ECD (II)[d] (C-18)	GC/MS[e] (5% Phenyl)	Interlaboratory exercise (I)[f]	Interlaboratory exercise (II)[g]
PCB 18	36.2 ± 8.7	45 ± 53			25.3 ± 2.5	30.7 ± 4.7	24.9 ± 2.8
PCB 28	84.9 ± 7.4	104 ± 23	76.4 ± 3.0	78.6 ± 3.3	145.1 ± 8.6[h]	66 ± 12	67 ± 10
PCB 31	66 ± 10	96 ± 19	70.6 ± 8.6	71.6 ± 8.0	145.1 ± 8.6[h]	–	–
PCB 44	67.5 ± 9.1	–	75.2 ± 3.3	77.7 ± 4.1	81.1 ± 6.1	62 ± 14	73.3 ± 7.5
PCB 49	84.4 ± 7.3	–	89.3 ± 4.6	92.2 ± 4.6	89.5 ± 5.1	–	–
PCB 52	103 ± 10	127 ± 24	116 ± 11	117 ± 11	127.0 ± 6.1	104 ± 18	110.1 ± 8.9
PCB 66	168 ± 16[i]	–	174 ± 16[i]	101.1 ± 8.8	101.7 ± 2.7	103 ± 16	159 ± 18
PCB 87	–	66 ± 13	45.2 ± 5.7	52.0 ± 5.6	51.5 ± 3.7	–	–
PCB 95	168 ± 16[i]	95 ± 42	174 ± 16[i]	76.4 ± 8.3	77.8 ± 4.2	–	–
PCB 99	65.3 ± 6.8	72 ± 18	72.5 ± 8.0	73.6 ± 7.6	71.8 ± 2.9	–	–
PCB 101	114 ± 15	149 ± 65	125 ± 15	125 ± 13	128.2 ± 2.9	129 ± 21	127 ± 11
PCB 105	56 ± 11	56.5 ± 3.5	46.4 ± 5.7	50.1 ± 3.4	54.1 ± 3.5	55.6 ± 9.2	52.7 ± 3.7
PCB 110	94 ± 28[j]	123 ± 37	122.6 ± 9.6[j]	128 ± 14	131.1 ± 5.7	–	–
PCB 118	132 ± 28	135 ± 17	124.1 ± 7.4	128.3 ± 3.0	133.9 ± 4.9	133 ± 16	129 ± 11
PCB 128	28.6 ± 4.1	20.5 ± 1.3	20.3 ± 2.5	20.3 ± 3.0	20.66 ± 0.87	21.7 ± 3.3	20.2 ± 1.6
PCB 138	136 ± 21	145 ± 12	121.2 ± 8.5	121.3 ± 8.6	135 ± 10	147 ± 19	129 ± 12
PCB 149	88 ± 22	88 ± 57	88.8 ± 6.4	84.3 ± 5.2	87.8 ± 4.3	–	–
PCB 151	30.4 ± 9.2	24.9 ± 8.0	23.0 ± 2.1	24.3 ± 2.5	25.1 ± 1.2	–	–
PCB 153	131 ± 23	136 ± 11	151 ± 10	150 ± 15	152 ± 10	147 ± 18	148 ± 17
PCB 156	–	6.5 ± 2.1	7.92 ± 0.80	7.7 ± 1.3	7.59 ± 0.23	–	–
PCB 170	7.1 ± 1.6	6.5 ± 1.0	3.96 ± 0.48	5.0 ± 2.7	6.36 ± 0.32	4.4 ± 1.3	5.52 ± 0.89
PCB 180	23.8 ± 4.9	17.8 ± 3.2	16.7 ± 2.1	17.2 ± 2.2	15.76 ± 0.79	13.2 ± 2.0	15.4 ± 2.6
PCB 183	15.4 ± 2.4	14.2 ± 1.4	17.6 ± 2.1	17.9 ± 2.8	16.62 ± 0.71	–	–
PCB 187	37.9 ± 7.1	36.9 ± 3.1	33.2 ± 6.7	34.3 ± 4.5	31.9 ± 1.3	32.2 ± 4.4	31.6 ± 5.0

[a] Each uncertainity is an expanded uncertainty at the 95% level of confidence which incorporates only the individual method's within-method uncertainty. It defines a range of values within which the true method mean is believed to lie, at a level of confidence of approximately 95%.
[b] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [24] and later revised by Schulte and Malisch [25] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, the Ballschmiter-Zell numbers correspond to those of Schulte and Malisch. When two or more congeners are known to coelute, the PCB congener listed first is the major component and the additional congeners may be present as minor components. The quantitative results are based on the response of the congener listed first.
[c] Samples from six bottles analyzed by GC-ECD on 5% phenyl-subst. methylpolysiloxane phase and on 50% C-18 dimethylpolysiloxane phase.
[d] Samples from three bottles analyzed on three different occasions.
[e] Samples from six bottles analyzed by GC/MS on 5% phenyl-subst. methylpolysiloxane phase.
[f] Interlaboratory exercise using SRM 1974a as an unknown sample; 22 sets of results obtained. For individual congeners the number of results ranged from 13 to 20.
[g] Interlaboratory exercise using SRM 1974a as a control sample; 19 sets of results obtained. For individual congeners the number of results ranged from 9 to 16.
[h] PCB 28 and PCB 31 coeluted in these analyses; results not used to determine the certified value.
[i] PCB 66 and PCB 95 coeluted in the analyses on the 5% phenyl-subst. methylpolysiloxane phase; results not used to determine the certified value.
[j] PCB 110 and PCB 77 (not quantified) coeluted in the analyses on the 5% phenyl-subst. methylpolysiloxane phase; results not used to determine the certified value.

At NIST the samples were analyzed using GC-ECD with two stationary phases that have differing properties for the separation of the PCB congeners. The 50% C_{18} dimethylpolysiloxane phase separated several congeners that are not separated using the 5% phenyl-subst. methylpolysiloxane phase, e.g., PCB 66 from PCB 95 [29]. Two different sets of results for each stationary phase were obtained, i.e., GC-ECD (I) and GC-ECD (II). Samples were also analyzed using GC/MS with the 5% phenyl-subst. methylpolysiloxane phase where coeluting congeners with different levels of chlorination could be quantified, e.g. PCB 66 and PCB 95.

The results from the 7 data sets (see Tables 4 and 5) are generally in good agreement and are combined as equally weighted means to provide certified values for 20 PCB congeners (Table 6) and 7 chlorinated pesticides (Table 7). A 95% confidence interval, based on the seven data set means, was computed to determine the expanded uncertainty for each analyte. In the original mussel tissue SRM, SRM 1974, the PCB congeners and chlorinated pesticides were listed as noncertified values because of limited data from independent techniques. Noncertified values listed in Table 8 were determined for four PCB congeners and four chlorinated pesticides in SRM 1974a.

Table 5 Summary of analytical results for chlorinated pesticides in SRM 1974a

	Mass fraction (μg/kg dry mass basis)[a]						
	GC-ECD (I)[b] (5% Phenyl)	GC-ECD (I)[b] (C-18)	GC-ECD (II)[c] (5% Phenyl)	GC-ECD (II)[c] (C-18)	GC/MS[d] (5% Phenyl)	Interlaboratory exercise (I)[e]	Interlaboratory exercise (II)[f]
cis-Chlordane	24.0 ± 6.0	17.0 ± 3.6	16.1 ± 2.7	15.2 ± 3.1	16.22 ± 0.66	15.6 ± 1.8	16.2 ± 1.4
trans-Chlordane	–	18.6 ± 6.3	16.8 ± 2.8	16.3 ± 3.5	16.72 ± 0.78	–	–
cis-Nonachlor	7.0 ± 1.9	6.5 ± 2.2	–	–	7.00 ± 0.31	–	–
trans-Nonachlor	–	24.4 ± 6.5	18.6 ± 2.7	16.5 ± 3.2	15.4 ± 1.2	17.5 ± 3.2	15.3 ± 1.3
Dieldrin	–	6.7 ± 1.9	6.37 ± 0.46	4.34 ± 0.77	–	6.8 ± 1.7	6.8 ± 1.5
2,4′-DDE	–	–	5.22 ± 0.50	5.32 ± 0.48	5.24 ± 0.67	–	4.61 ± 0.91
4,4′-DDE	–	61 ± 25	49.5 ± 5.2	50.7 ± 5.5	48.8 ± 2.4	50.5 ± 6.4	46.5 ± 9.8
2,4′-DDD	15.4 ± 3.4	18.8 ± 9.2	11.5 ± 1.1	9.3 ± 2.1	12.69 ± 0.77	14.4 ± 2.5	14.0 ± 2.1
4,4′-DDD	40.2 ± 6.0	33 ± 10	49.9 ± 7.7	48.9 ± 9.6	45.8 ± 3.3	42.1 ± 6.6	47.6 ± 7.9
2,4′-DDT	9.5 ± 5.6	11.4 ± 2.1	5.66 ± 0.41	8.7 ± 1.0	9.14 ± 0.47	6.0 ± 2.6	8.8 ± 1.0
4,4′-DDT	4.3 ± 2.4	4.9 ± 2.3	4.11 ± 0.35	4.07 ± 0.61	3.74 ± 0.21	3.05 ± 0.70	3.23 ± 0.62

[a] Each uncertainty is an expanded uncertainty at the 95% level of confidence which incorporates only the individual method's within-method uncertainty. It defines a range of values within which the true method mean is believed to lie, at a level of confidence of approximately 95%.
[b] Samples from six bottles analyzed by GC-ECD on 5% phenyl-subst. methylpolysiloxane phase and on 50% C-18 dimethylpolysiloxane phase.
[c] Samples from three bottles analyzed on three different occasions.
[d] Samples from six bottles analyzed by GC/MS on 5% phenyl-subst. methylpolysiloxane phase.
[e] Interlaboratory exercise using SRM 1974a as an unknown sample; 24 sets of results obtained. For individual congeners the number of results ranged from 8 to 20.
[f] Interlaboratory exercise using SRM 1974a as a control sample; 20 sets of results obtained. For individual congeners the number of results ranged from 5 to 17.

Table 6 Certified mass fractions for selected PCB congeners in SRM 1974a[a]

Chlorinated biphenyls[b]		μg/kg wet mass basis[c]	μg/kg dry mass basis[c]
PCB 44	(2,2′,3,5′-Tetrachlorobiphenyl)	8.28 ± 0.84	72.7 ± 7.4
PCB 49	(2,2′,4,5′-Tetrachlorobiphenyl)	10.12 ± 0.59	88.8 ± 5.0
PCB 52	(2,2′,5,5′-Tetrachlorobiphenyl)	13.1 ± 1.3	115 ± 11
PCB 66	(2,3′,4,4′-Tetrachlorobiphenyl)	11.54 ± 0.50	101.4 ± 4.4
PCB 95	(2,2′,3,5′,6-Pentachlorobiphenyl)	9.5 ± 1.9	83 ± 17
PCB 99	(2,2′,4,4′,5-Pentachlorobiphenyl)	8.08 ± 0.46	70.9 ± 4.0
PCB 101	(2,2′,4,5,5′-Pentachlorobiphenyl)	14.6 ± 1.1	128.3 ± 9.7
PCB 105	(2,3,3′,4,4′-Pentachlorobiphenyl)	6.04 ± 0.39	53.0 ± 3.4
PCB 110	(2,3,3′,4′,6-Pentachlorobiphenyl)	14.5 ± 1.0	127.3 ± 8.6
PCB 118	(2,3′,4,4′,5-Pentachlorobiphenyl)	14.90 ± 0.40	130.8 ± 3.6
PCB 128	(2,2′,3,3′,4,4′-Hexachlorobiphenyl)	2.50 ± 0.39	22.0 ± 3.4
PCB 138	(2,2′,3,4,4′,5′-Hexachlorobiphenyl)	15.2 ± 1.1	133.5 ± 9.5
163	(2,3,3′,4′,5,6-Hexachlorobiphenyl)		
164	(2,3,3′,4′,5′,6-Hexachlorobiphenyl)		
PCB 149	(2,2′,3,4′,5′,6-Hexachlorobiphenyl)	9.98 ± 0.27	87.6 ± 2.3
PCB 151	(2,2′,3,5,5′,6-Hexachlorobiphenyl)	2.91 ± 0.40	25.6 ± 3.5
PCB 153	(2,2′,4,4′,5,5′-Hexachlorobiphenyl)	16.54 ± 0.86	145.2 ± 7.6
PCB 156	(2,3,3′,4,4′,5-Hexachlorobiphenyl)	0.85 ± 0.11	7.43 ± 0.99
PCB 170	(2,2′,3,3′,4,4′,5-Heptachlorobiphenyl)	0.63 ± 0.12	5.5 ± 1.1
PCB 180	(2,2′,3,4,4′,5,5′-Heptachlorobiphenyl)	1.95 ± 0.43	17.1 ± 3.8
PCB 183	(2,2′,3,4,4′,5′,6-Heptachlorobiphenyl)	1.82 ± 0.27	16.0 ± 2.4
PCB 187	(2,2′,3,4′,5,5′,6-Heptachlorobiphenyl)	3.87 ± 0.27	34.0 ± 2.3
159	(2,3,3′,4,5,5′-Hexachlorobiphenyl)		
182	(2,2′,3′,4,4′,5,6′-Heptachlorobiphenyl)		

[a] Results reported on both wet and dry mass basis; the sample as received contains 88.61% ± 0.08% water.
[b] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [24] and later revised by Schulte and Malisch [25] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, the Ballschmiter-Zell numbers correspond to those of Schulte and Malisch. When two or more congeners are known to coelute under the conditions used, the PCB congener listed first is the major component and the additional congeners may be present as minor components. The quantitative results are based on the response of the congener listed first.
[c] Each certified value is the mean of the equally weighted means from four to seven different analytical methods (see Table 4). Each uncertainty, computed according to the CIPM approach [27], is an expanded uncertainty at the 95% level of confidence that incorporates within- and between-method uncertainty as well as uncertainty due to the drying study (for the dry mass basis values). The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.

Table 7 Certified mass fractions for selected chlorinated pesticides in SRM 1974a[a]

Chlorinated pesticides	µg/kg wet mass basis[b]	µg/kg dry mass basis[b]
cis-Chlordane (α-Chlordane)	1.96 ± 0.32	17.2 ± 2.8
trans-Chlordane	1.89 ± 0.19	16.6 ± 1.7
cis-Nonachlor	0.78 ± 0.10	6.84 ± 0.90
trans-Nonachlor	2.05 ± 0.41	18.0 ± 3.6
4,4′-DDE	5.84 ± 0.63	51.2 ± 5.5
4,4′-DDD	4.90 ± 0.72	43.0 ± 6.3
4,4′-DDT	0.445 ± 0.067	3.91 ± 0.59

[a] Results reported on both wet and dry mass basis; the sample as received contains 88.61% ± 0.08% water.
[b] Each certified value is the mean of the equally weighted means from four to seven different analytical methods (see Table 5). Each uncertainty, computed according to the CIPM approach [27], is an expanded uncertainity at the 95% level of confidence that incorporates within- and between-method uncertainty as well as uncertainty due to the drying study (for the dry mass basis values). The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.

Table 8 Noncertified mass fractions for selected PCB congeners and chlorinated pesticides in SRM 1974a[a]

PCB congener[b]	µg/kg wet mass basis[c]	µg/kg dry mass basis[c]
PCB 18 (2,2′,5-Trichlorobiphenyl)	3.7 ± 1.2	33 ± 11
PCB 28 (2,4,4′-Trichlorobiphenyl)	9.0 ± 1.7	79 ± 15
PCB 31 (2,4′,5-Trichlorobiphenyl)	8.6 ± 2.4	76 ± 21
PCB 87 (2,2′,3,4,5′-Pentachlorobiphenyl)	6.1 ± 1.6	54 ± 14
Chlorinated Pesticides		
Dieldrin	0.70 ± 0.15	6.2 ± 1.3
2,4′-DDE	0.599 ± 0.031	5.26 ± 0.27
2,4′-DDD	1.56 ± 0.32	13.7 ± 2.8
2,4′-DDT	0.96 ± 0.21	8.5 ± 1.9

[a] Results reported on both wet and dry mass basis; the sample as received contains 88.61% ± 0.08% water.
[b] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [24] and later revised by Schulte and Malisch [25] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, the Ballschmiter-Zell numbers correspond to those of Schulte and Malisch.
[c] Each noncertified value is the mean of the equally weighted means from four to seven different analytical methods (see Tables 4 and 5). Each uncertainty, computed according to the CIPM approach [27], is an expanded uncertainty at the 95% level of confidence that incorporates within- and between-method uncertainty as well as uncertainty due to the drying study (for the dry mass basis values). The expanded uncertainty defines a range of values for the certified value within which the true value is believed to lie, at a level of confidence of approximately 95%.

Aliphatic hydrocarbons and trace elements

Aliphatic hydrocarbons were determined in SRM 1974a by GC/MS and the results are reported in Table 9 as noncertified values. Even though SRM 1974a is intended primarily for the determination of organic contaminants, concentrations have been determined for selected trace elements. The noncertified values for 28 trace elements in SRM 1974a are listed in Table 10 as determined by INAA. In addition, methylmercury measurements have been completed for SRM 1974a and are reported elsewhere [30, 31].

Table 9 Noncertified mass fractions for selected aliphatic hydrocarbons in SRM 1974a[a,b]

Compound	µg/kg wet mass basis	µg/kg dry mass basis
n-Tetradecane (*n*-C_{14})	9.54 ± 0.35	83.8 ± 3.0
n-Pentadecane (*n*-C_{15})	12.4 ± 1.4	108 ± 12
n-Hexadecane (*n*-C_{16})	18.4 ± 3.2	161 ± 28
n-Heptadecane (*n*-C_{17})	31.8 ± 6.5	280 ± 57
Pristane (2,6,10,14-Tetramethylpentadecane)	8.44 ± 0.67	74.1 ± 5.8
n-Octadecane (*n*-C_{18})	17.4 ± 2.0	153 ± 17
Phytane (2,6,10,14-Tetramethylpentadecane)	6.48 ± 0.78	56.9 ± 6.8
n-Nonadecane (*n*-C_{19})	4.60 ± 0.11	40.4 ± 1.1
n-Eicosane (*n*-C_{20})	7.41 ± 0.69	65.1 ± 6.0
n-Docosane (*n*-C_{22})	5.32 ± 0.22	46.7 ± 1.9
n-Tetracosane (*n*-C_{24})	6.51 ± 0.66	57.2 ± 5.7
n-Hexacosane (*n*-C_{26})	5.61 ± 0.72	49.3 ± 6.3
n-Octacosane (*n*-C_{28})	7.34 ± 0.39	64.5 ± 3.3
n-Triacontane (*n*-C_{30})	5.44 ± 0.84	47.8 ± 7.3
n-Dotriacontane (*n*-C_{32})	6.36 ± 0.48	55.9 ± 4.2
n-Tetratriacontane (*n*-C_{34})	3.25 ± 0.22	28.5 ± 1.9

[a] Results reported on both wet and dry mass basis; the sample as received contains 88.61% ± 0.08% water.
[b] Each noncertified value is the mean value determined by GC/MS. Each uncertainty is an expanded uncertainty at the 95% level of confidence that incorporates within-method uncertainty as well as uncertainty due to the drying study (for the dry mass basis values). Duplicate subsamples from 12 bottles were extracted and analyzed.

Comparison of SRM 1974a with SRM 1974

SRMs 1974 and 1974a were collected at the same site in 1987 and 1992, respectively. The concentrations of the PAHs, PCB congeners, and pesticides in the two materials are similar, but some changes are observed. For example, fluoranthene and pyrene concentrations in SRM 1974a are about 40% lower than in SRM 1974 whereas the higher molecular weight PAHs are nearly identical. The concentrations of the PCB congeners are typically 10% to 20% higher in SRM 1974a, while the concentrations of the chlorinated pesticides tend to be lower in SRM 1974a, especially for 2,4′-DDD and 4,4′-DDD, which are about 35% lower. The concentrations of the inorganic constituents are very similar in the two materials.

Conclusions

SRM 1974a has certified values for 15 PAHs, 20 PCB congeners, and 7 chlorinated pesticides, which are naturally present in the material. Noncertified values have

Table 10 Noncertified mass fractions for selected inorganic constituents in SRM 1974a[a,b]

Element	Percent wet mass basis	Percent dry mass basis
Chlorine	0.85 ± 0.02	7.5 ± 0.2
Magnesium	0.057 ± 0.002	0.51 ± 0.02
Sodium	0.52 ± 0.01	4.6 ± 0.1
Potassium	0.131 ± 0.004	1.15 ± 0.04
	mg/kg wet mass basis	mg/kg dry mass basis
Aluminium	51 ± 2	450 ± 20
Antimony	0.0038 ± 0.0005	0.033 ± 0.004
Arsenic	1.26 ± 0.04	11.0 ± 0.3
Bromine	36 ± 1	318 ± 9
Cerium	0.066 ± 0.006	0.58 ± 0.05
Cesium	0.0032 ± 0.0002	0.028 ± 0.002
Chromium	0.24 ± 0.02	2.1 ± 0.1
Cobalt	0.038 ± 0.001	0.33 ± 0.01
Europium	0.00153 ± 0.00007	0.0134 ± 0.0006
Gold	0.0027 ± 0.0002	0.024 ± 0.002
Hafnium	0.0043 ± 0.0005	0.038 ± 0.004
Iron	57 ± 1	500 ± 10
Lanthanum	0.028 ± 0.002	0.24 ± 0.01
Manganese	1.21 ± 0.06	10.6 ± 0.5
Mercury	0.023 ± 0.02	0.20 ± 0.02
Samarium	0.0034 ± 0.0004	0.030 ± 0.004
Scandium	0.0103 ± 0.0004	0.090 ± 0.003
Selenium	0.235 ± 0.007	2.06 ± 0.06
Silver	0.068 ± 0.002	0.59 ± 0.02
Strontium	9.1 ± 0.6	80 ± 5
Tantalum	0.0029 ± 0.0004	0.025 ± 0.003
Thorium	0.0071 ± 0.0009	0.062 ± 0.008
Vanadium	0.17 ± 0.02	1.5 ± 0.2
Zinc	11.9 ± 0.4	105 ± 4

[a] Results reported on both wet and dry mass basis; the sample as received contains 88.61% ± 0.08% water. Duplicate subsamples of 200 mg (dry) from eight bottles were analyzed.
[b] Each uncertainty is an expanded uncertainty at the 95% level of confidence that incorporates within-method uncertainty.

also been determined for 18 additional PAHs, 4 additional PCB congeners, 4 additional chlorinated pesticides, 16 aliphatic hydrocarbons, 28 trace elements, and methylmercury. SRM 1974a greatly expands the number of certified analytes as compared to the original issue of SRM 1974 and in general provides smaller un certainties for the PAHs that were certified in both materials.

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