FIELD MODIFICATION FORM
FOR
LOWER PASSAIC RIVER RESTORATION PROJECT
THE LOUIS BERGER GROUP, INC.

DATE: April 13, 2010

DOCUMENT: Oversight Quality Assurance Project Plan (QAPP) for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing
Lower Passaic River Restoration Project

ACTIVITY: QAPP Field Modification No. 4 for the Oversight Program

REQUESTED MODIFICATION:
On behalf of the United States Army Corps of Engineers (USACE) and the United States Environmental Protection Agency (USEPA), The Louis Berger Group, Inc. is conducting oversight of the Cooperating Parties Group (CPG) biological sampling program to support the Remedial Investigation / Feasibility Study (RI/FS) for the Lower Passaic River Restoration Project. According to the Lower Passaic River Restoration Project "Oversight Quality Assurance Project Plan (QAPP) for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing" (Malcolm Pirnie, Inc., August 2009 and associated addenda), real-time modifications to the oversight project can be implemented by documenting the modification and obtaining approval from the Project Manager and Site Quality Control Officer or designee (refer to Worksheet #6).

The Oversight QAPP establishes quality control measures and performance criteria for the government split sample program to ensure that data are technically valid and legally defensible. The requested modification for "Field Modification No. 4" includes a performance audit for the split sample program to monitor laboratory accuracy. This performance audit will require laboratories to analyze a performance evaluation (PE) sample with the split samples. A PE sample, or quality control sample, is a material with a certified concentration (and an associated uncertainty on the mean certified value) that was determined by an independent third party. Laboratory results will then be compared to certified concentrations to assess the laboratory's accuracy.

The performance audit for the oversight program is described in Table 1 for sediment samples and Table 2 for tissue samples. In these tables, the data quality indicator is accuracy, and the measurement performance criteria evaluate laboratory percent recovery control limits. If the laboratory fails to achieve the performance criteria outlined in this audit, corrective action will be implemented once the source of the variance is identified, or the data will be appropriately flagged by the data validator. Where appropriate, corrective action may also include re-extracting and re-analyzing samples to generate reliable data. Worksheets #12, #20, and #28 will be updated with this performance audit in the next version of the Oversight QAPP.

RATIONALE:
At the request of the USEPA, a performance audit is being added to the split sample program to monitor a laboratory's accuracy via analysis of PE sample.

ATTACHMENTS:
Table 1: Performance Criteria for Sediment Split Samples
Table 2: Performance Criteria for Tissue Split Samples
Attachment 1: Certificates for Standard Reference Materials and Certified Reference Materials

Leonard J. Warner
The Louis Berger Group, Inc. Project Manager: ______________________________

AmyMarie Accardi-Dey
The Louis Berger Group, Inc.
Site Quality Control Officer Designee: ______________________________

Table 1: Performance Audit Criteria for Sediment Split Samples

Parameter	PE Sample [1]	Frequency of Audit [2]	Performance Criteria for Audit [3]
Polychlorinated Biphenyl (PCB) Congeners	NIST 1944	Minimum of 1 PE sample per 20 sediment split samples	65 percent of the PCB congeners will have reported laboratory concentrations within 25 percent difference of the certified value. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Polychloro-dibenzodioxin/ furan (PCDD/F) Isomers	NIST 1944	Minimum of 1 PE sample per 20 sediment split samples	Reported laboratory concentrations will be within 25 percent difference of the referenced value with two exceptions. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Polycyclic Aromatic Hydrocarbon (PAH) Compounds	NIST 1944	Minimum of 1 PE sample per 20 sediment split samples	Reported laboratory concentrations will be within 25 percent difference of the certified value with two exceptions. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Pesticide	NIST 1492 spiked into quartz sand NIST 1944	Minimum of 1 PE sample (primary and secondary) per 20 sediment split samples	For NIST 1492, reported laboratory concentrations will be within 25 percent difference of the certified values. And, for NIST 1944, reported laboratory concentrations will be within 30 percent difference of the certified and referenced values with four exceptions. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Metals	ERA-540	Minimum of 1 PE sample per 20 sediment split samples	Reported laboratory concentrations will be within ±10 percent of the certified value for each metal or within the acceptable range set by the provider.
Mercury	IAEA-405	Minimum of 1 PE sample per 20 sediment split samples	Reported laboratory concentration will be within 25 percent difference of the recommended value.
Methylmercury	IAEA-405	Minimum of 1 PE sample per 20 sediment split samples	Reported laboratory concentration will be within 25 percent difference of the recommended value.

Table 1 (continued)

1: **NIST 1944** is a standard reference material representing a New York/New Jersey Waterway Sediment (produced by the National Institute of Standards and Technology).
NIST 1492 is a standard reference material representing a chlorinated pesticide standard in hexane (produced by the National Institute of Standards and Technology). NIST 1492 will be spiked into quartz sand. The spike would be at a level equivalent to the middle calibration point of 80 nanograms per milliliter.
ERA-540 is a reference material representing metals in soil (produced by Environmental Resource Associates).
IAEA-405 is a reference material representing intertidal estuarine sediment from Portugal (produced by the International Atomic Energy Agency).
2: The oversight split sample program currently includes 10 split samples and a field duplicate.
3: Uncertainty values listed on the certificates represent the uncertainty on the mean value.

Table 2: Performance Audit Criteria for Tissue Split Samples

Parameter	PE Sample [1]	Frequency of Audit [2]	Performance Criteria for Audit [3]
Polychlorinated Biphenyl (PCB) Congeners	NIST 1946	Minimum of 1 PE sample per 20 tissue split samples	65 percent of the PCB congeners will have reported laboratory concentrations within 25 percent difference of the certified value. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Polychloro-dibenzodioxin/ furan (PCDD/F) Isomers	CARP-2	Minimum of 1 PE sample per 20 tissue split samples	Reported laboratory concentrations will be within 25 percent difference of the referenced value with one exception. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Polycyclic Aromatic Hydrocarbon (PAH) Compounds	NIST 1647e spiked into a clean salmon tissue matrix NIST 1974b (analyze one entire bottle)	Minimum of 1 PE sample set per 20 tissue split samples	For NIST 1647e, reported laboratory concentrations will be within 25 percent difference of the certified value parent PAH compounds. And, for NIST 1974b, reported laboratory concentrations will be within 25 percent difference of the certified value with four exceptions. No individual result will have more than a 50 percent difference. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.
Pesticide	NIST 1492 spiked into a clean salmon tissue matrix NIST 1946	Minimum of 1 PE sample set per 20 tissue split samples	For NIST 1492, reported laboratory concentrations will be within 25 percent difference of the certified values. And, for NIST 1946, reported laboratory concentrations will be within 30 percent difference of the certified values with three exceptions. Performance criteria will be applicable for certified values that are 3 times the concentration of the lowest calibration point within the initial calibration.

Table 2 (continued)

Parameter	PE Sample [1]	Frequency of Audit [2]	Performance Criteria for Audit [3]
Metals	DOLT-4	Minimum of 1 PE sample per 20 tissue split samples	Reported laboratory concentrations will be within 30 percent of the certified value for each metal. Performance criterion will be applicable for certified value that is 2 times the laboratory reporting limit.
Mercury	DORM-3	Minimum of 1 PE sample per 20 tissue split samples	Reported laboratory concentration will be within 30 percent difference of the certified value.
Methylmercury	DORM-3	Minimum of 1 PE sample per 20 tissue split samples	Reported laboratory concentration will be within 30 percent difference of the certified value.

NIST 1492 is a standard reference material representing a chlorinated pesticide standard in hexane (produced by the National Institute of Standards and Technology). NIST 1492 will be spiked into a clean salmon tissue matrix. The spike would be at a level equivalent to the middle calibration point.
NIST 1647e is a standard reference material representing a PAH standard in acetonitrile (produced by the National Institute of Standards and Technology). NIST 1647e will be spiked into a clean salmon tissue matrix. The spike would be at a level equivalent to the middle calibration point.
NIST 1946 is a standard reference material representing a Lake Superior fish tissue (produced by the National Institute of Standards and Technology).
NIST 1974b is a standard reference material representing mussel tissue (produced by the National Institute of Standards and Technology).
CARP-2 is a certified reference material representing a carp tissue matrix (produced by the National Research Council Canada).
DORM-3 is a certified reference material representing a fish protein matrix (produced by the National Research Council Canada).
DOLT-4 is a certified reference material representing a dogfish liver matrix (produced by the National Research Council Canada).
2: The oversight split sample program currently includes 9 blue crab tissue samples and a field duplicate. An additional 20 fish tissue samples are anticipated.
3: Uncertainty values listed on the certificates represent the uncertainty on the mean values.

Attachment 1

Certificates for Standard Reference Materials
and Certified Reference Materials

National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 1492

Chlorinated Pesticide in Hexane

This Standard Reference Material (SRM) is intended primarily for use in the calibration of chromatographic instrumentation used for the determination of the certified compounds. This SRM is a solution of 15 chlorinated pesticides in hexane, with certified concentrations for 14 of the 15 pesticides. A unit of SRM 1492 consists of five 2-mL ampoules, each containing approximately 1.2 mL of solution.

Certified Concentrations of Constituent Pesticides: The certified concentrations and estimated uncertainties for 14 of the 15 pesticides are given in Table 1. These values are based on results obtained from the gravimetric preparation of this solution and from the analytical results determined by using gas chromatography. Table 2 summarizes the calculated and chromatographically determined concentrations. Alternate names, Chemical Abstracts Service Nomenclature, and Registry Numbers of the certified components are listed in an appendix to the SRM 1492 Certificate of Analysis.

NOTICE AND WARNING TO USERS

Handling: This material contains chlorinated pesticide compounds, many of which have been reported to have toxic, mutagenic and/or carcinogenic properties, and should be handled with care. Use proper disposal methods.

Expiration of Certification: The certification of SRM 1492 is valid, within the measurement uncertainty(ies) specified, until **01 October 2003**, provided the SRM is handled in accordance with instructions given in this certificate. This certification is nullified if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures lower than 30 °C.

Instructions for Use: Sample aliquots for analysis should be withdrawn at 20 °C to 25 °C **immediately** after opening the ampoules and should be processed without delay for the certified values in Table 1 to be valid within the stated uncertainty. Because of the volatility of hexane, certified values are not applicable to material stored in ampoules that have been opened for more than three minutes, even if they are resealed.

Preparation and original analytical determinations were performed by R.M. Parris and F.R. Guenther of the NIST Analytical Chemistry Division.

The coordination of the technical measurements leading to the original certification was under the direction of S.N. Chesler and W.E. May of the NIST Analytical Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by R. Alvarez and B.S. MacDonald.

Gaithersburg, MD 20899
Certificate Issue Date: 1 December 1998*
17 Apr 89 (original certificate date); 20 Apr 92 (editorial revision)
*Removal of aldrin certification

Thomas E. Gills, Chief
Standard Reference Materials Program

Conformational analysis and coordination of stability measurements leading to updated certification in 1998 was under the direction of M.M Schantz of the NIST Analytical Chemistry Division.

Statistical consultations were provided by S.B. Schiller of the NIST Statistical Engineering Division.

Partial support for the preparation and certification of this Standard Reference Material was provided by the National Oceanographic and Atmospheric Administration, National Ocean Service, Office of Oceanography and Marine Assessment.

Table 1. Certified Concentrations of Chlorinated Pesticides in SRM 1492

Compound	Concentration μg /kg[a]	ng/mL[b]
Hexachlorobenzene	308 ± 2	205 ± 2
gamma-HCH	310 ± 2	207 ± 2
Heptachlor	299 ± 7	200 ± 5
Heptachlor epoxide	307 ± 7	204 ± 5
cis-Chlordane	305 ± 3	203 ± 2
trans-Nonachlor	297 ± 5	198 ± 4
Dieldrin	307 ± 4	205 ± 3
Mirex	306 ± 3	204 ± 2
2,4'-DDE	303 ± 3	202 ± 2
4,4'-DDE	306 ± 3	204 ± 2
2,4'-DDD	299 ± 4	200 ± 3
4,4'-DDD	296 ± 3	197 ± 2
2,4'-DDT	307 ± 3	205 ± 3
4,4'-DDT	302 ± 3	202 ± 2

[a]The certified value is the weighted average of the gravimetric and chromatographic concentrations. The uncertainty of the certified value is the half-width of an approximate 95 % confidence interval, plus an allowance for bias between analytical techniques.
[b]The concentrations. in ng/mL units, were obtained by multiplying the certified value by the measured density of the SRM solution at 22 °C (0.667 g/mL). These concentrations are for use over the temperature range of 20 °C to 25 °C.

PREPARATION AND ANALYSIS

Pesticides used in the preparation of this SRM were obtained from the U.S. EPA Pesticides & Industrial Chemicals Repository, Research Triangle Park, NC and the Office of Reference Materials, Laboratory of the Government Chemist, United Kingdom. The pesticide solution was prepared at NIST by weighing and mixing the individual pesticides and hexane. The weighed components were added to the hexane and mixed until completely dissolved and homogenized. The total mass of this solution was measured and the concentrations calculated from this gravimetric procedure are given in Table 2 for 14 of the components. These gravimetric concentrations were adjusted for the consensus purity estimation of each component, which was determined using flame ionization high resolution gas chromatography, differential scanning calorimetry, and the purity assay information from the component suppliers. This bulk solution was then chilled to approximately -5 °C and 1.2 mL aliquots were dispensed into 2 mL amber glass ampoules, which were then flame sealed.

Aliquots from twelve randomly selected ampoules were analyzed in duplicate by using electron capture capillary gas chromatography employing an immobilized non-polar stationary phase column. The four PCB internal standards added to each sample for quantification purposes were: PCB's 28, 66, 105, and 180(l). Calibration solutions consisting of weighed amounts of the pesticides (adjusted for the consensus purity estimation) and internal standard compounds in hexane were chromatographically analyzed to determine analyte response factors. The analytical values determined for 14 of the compounds also are given in Table 2.

During stability testing in August 1998, the aldrin content was found to be lower than originally certified. Therefore, the certified concentration of aldrin has been removed from the certificate and because of its observed instability, a new value is not provided. A representative chromatogram from the GC analysis of the original solution is shown in Figure 1.

Table 2. Summary of Results[a]

Compound	Concentrations Gravimetric[b] µg /kg	GC/ECD[c] µg /kg
Hexachlorobenzene	307	309 ± 2
gamma-HCH	310	310 ± 2
Heptachlor	297	301 ± 3
Heptachlor epoxide	306	307 ± 2
cis-Chlordane	304	306 ± 2
trans-Nonachlor	296	297 ± 2
Dieldrin	305	308 ± 4
Mirex	304	308 ± 4
2,4'-DDE	302	304 ± 2
4,4'-DDE	306	307 ± 3
2,4'-DDD	299	301 ± 3
4,4'-DDD	296	297 ± 3
2,4'-DDT	307	308 ± 2
4,4'-DDT	302	302 ± 2

[a]The summary of results given above is presented for use only as background information.
[b]Calculated concentration based on the mass of the pesticide added to the total mass of the solution.
[c]Concentrations determined by using gas chromatography with electron capture detection. The listed uncertainties represent one standard deviation of a single measurement for these results and recognize only the within-method variability.

REFERENCE

[1] Ballschmiter, K., and Zell, M., Fresenius Z. Anal. Chem. **302**, pp. 20-31 (1980).

Appendix to SRM Certificate
Standard Reference Material 1492

The following supplementary information may be of interest in connection with the use of this SRM and is supplied for the convenience of the user.

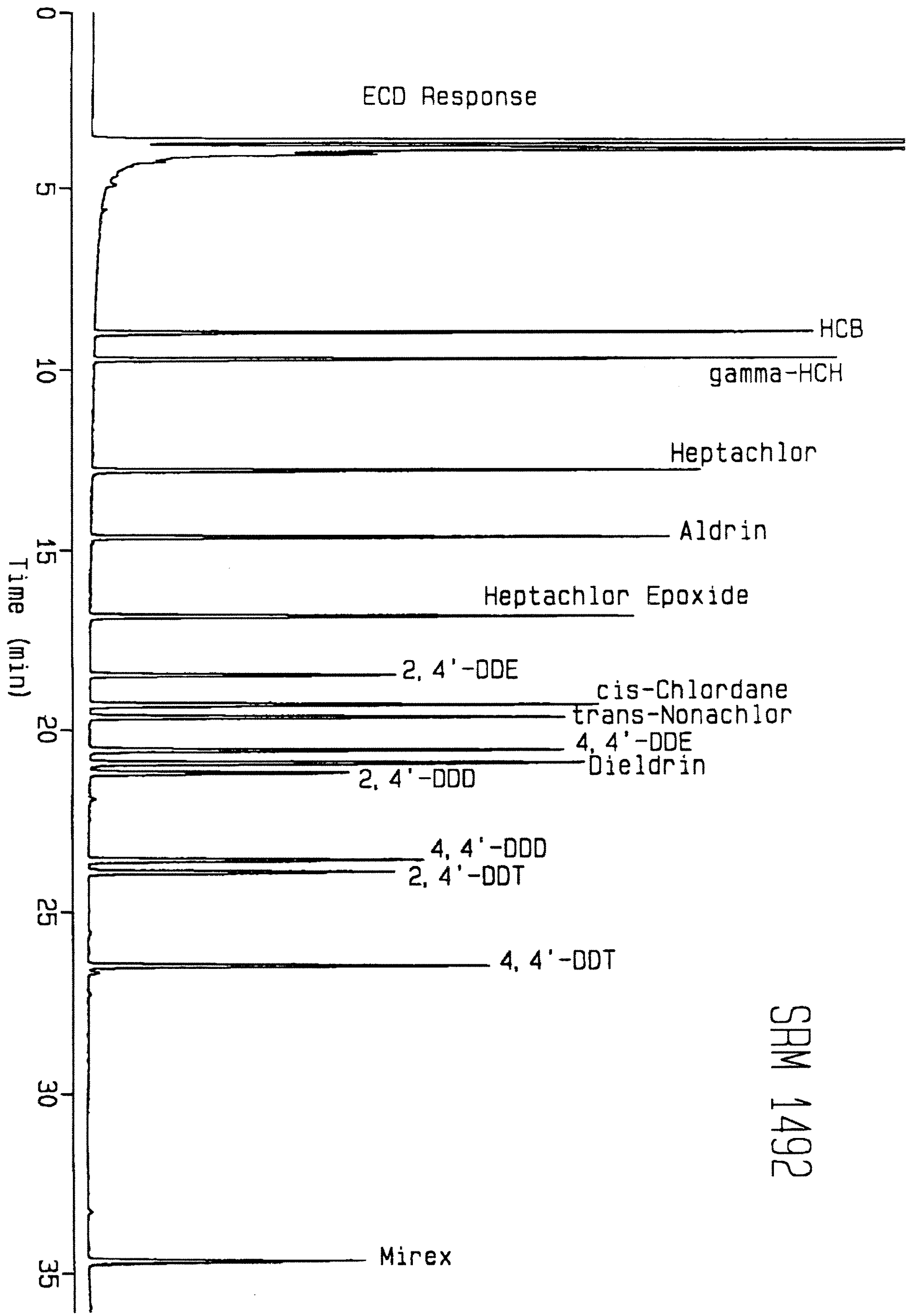
Table A-1. Name(s), Chemical Abstracts Service (CAS) Registry Numbers, and Nomenclature[a]

Compound (Alternative Name)	CAS Registry No.	CAS Nomenclature
Hexachlorobenzene (HCB)	118-74-1	hexachlorobenzene
gamma-HCH (gamma-BHC) (Lindane)	58-89-9	(1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane
Heptachlor	76-44-8	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene
Aldrin (HHDN)	309-00-2	(lα,4α,4aβ,5α,8α,8αβ)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene
Heptachlor epoxide	1024-57-3	(1aα,1bβ,2α,5α,5aβ,6aα)-2,3,4,5,6,7,7-heptachlor-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-ideno[1,2-b]oxirene

cis-Chlordane (alpha-Chlordane)	5103-71-9	(1α,2α,3aα,4β,7β,7aα)- 1,2,4,5,6,7,8,8-octachloro- 2,3,3a,4,7,7a-hexahydro-4,7-methano- 1H-indene
trans-Nonachlor	39765-80-5	(1α,2β,3α,3aα,4β,7β,7aα)- 1,2,3,4,5,6,7,8,8-nonachloro- 2,3,3a,4,7,7a-hexahydro-4,7-methano- 1H-indene
Dieldrin (HEOD)	60-57-1	(1aα,2β,2aα,3β,6β,6aα,7β,7aα)- 3,4,5,6,9,9-hexachloro- 1a,2,2a,3,6,6a,7,7a-octahydro- 2,7:3,6-dimethanonapth[2,3-b]oxirene
Mirex (Dechlorane) (Perchlordecone)	2385-85-5	1,1a,2,2,3,3a,4,5,5,5a,5b,6- dodecachlorooctahydro-1,3,4-metheno- 1H-cyclobuta[cd]pentalene
2,4'-DDE (o,p'-DDE)	3424-82-6	1-chloro-2-[2,2-dichloro-1-(4- chlorophenyl)ethenyl]benzene
4,4'-DDE (p,p'-DDE)	72-55-9	1,1'-(dichloroethenylidene)bis[4- chlorobenzene]
2,4'-DDD (o,p'-DDD) (o,p'-TDE)	53-19-0	1-chloro-2-[2,2,dichloro-1-(4- chlorophenyl)ethyl]benzene
4,4'-DDD (p,p'-DDD) (p,p'-TDE)	72-54-8	1,1'-(2,2,dichloroethylidene)bis[4- chlorobenzene]
2,4'-DDT (o,p'-DDT)	789-02-6	1-chloro-2-[2,2,2-trichloro-1-(4- chlorophenyl)ethyl]benzene
4,4'-DDT (p,p'-DDT)	50-29-3	1,1'-(2,2,2-trichloroethylidene)bis[4- chlorobenzene]

[a]Chemical Abstracts, Eleventh Collective Index. Index Guide, American Chemical Society, Columbus, Ohio, (1986).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet http://ts.nist.gov/srm.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Heptachlor Epoxide
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cis-Chlordane
trans-Nonachlor
4, 4'-DDE
Dieldrin
2, 4'-DDD
4, 4'-DDD
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4, 4'-DDT
Mirex
Time (min)
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SRM 1492

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1647e

Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)

This Standard Reference Material (SRM) is intended primarily as a calibration solution for use in chromatographic methods for the determination of polycyclic aromatic hydrocarbons (PAHs). One unit consists of five 2 mL ampoules, each containing approximately 1.2 mL of an acetonitrile solution of 16 PAHs. The PAHs are the 16 identified by the U.S. Environmental Protection Agency as priority pollutants. This SRM may also be useful in recovery studies for the addition of known amounts of these PAHs to a sample; because the solution is miscible with water, it can be used to fortify aqueous samples with known concentrations of PAHs.

Certified Values and Uncertainties: The certified values of the 16 PAHs are given in Table 1. Values are listed in units of mg/kg (mass fraction) and for user convenience mg/L (concentration). The volume fraction values were calculated from the mass fraction values using the density of acetonitrile at 23 °C (0.7789 g/mL). An allowance for the change in this density over the range 23 °C ± 2 °C is included in the uncertainty. The uncertainties are expanded uncertainties with a coverage factor of 2 (95 % confidence), calculated in accordance with the International Committee for Weights and Measures CIPM method [1]. They include uncertainty due to the calibration of the chromatographic method, measurement of selected samples using the chromatographic method, and purity of the reagents used to prepare the material.

Expiration of Certification: This certification is valid until **31 December 2015**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Storage and Use"). However, the certification will be nullified if the SRM is damaged, contaminated, or modified. NIST will monitor this SRM over the period of its certification. If changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the technical measurements leading to certification was under the direction of L.C. Sander and S.A. Wise of the NIST Analytical Chemistry Division.

Analytical determinations were performed by L.C. Sander of the NIST Analytical Chemistry Division.

Preparation and ampouling of SRM 1647e were carried out by L.C. Sander of the NIST Analytical Chemistry Division, and M.P. Cronise and C.N. Fales of the NIST Measurement Services Division.

Statistical design of the experimental work and evaluation of the data were provided by S.D. Leigh of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 06 March 2006

Robert L. Watters, Jr., Chief
Measurement Services Division

Table 1. Certified Values for PAHs in SRM 1647e

Compound	CAS Registry No.[a]	Mass Fraction [b] (mg/kg)	Concentration [c] (mg/L) (at 23 °C ± 2 °C)
Naphthalene	91-20-3	25.48 ± 0.58	19.85 ± 0.45
Acenaphthylene	208-96-8	19.69 ± 0.47	15.34 ± 0.37
Acenaphthene	83-32-9	26.32 ± 0.60	20.50 ± 0.47
Fluorene	86-73-7	6.09 ± 0.14	4.74 ± 0.11
Phenanthrene	85-01-8	4.52 ± 0.11	3.52 ± 0.09
Anthracene	120-12-7	1.01 ± 0.02	0.79 ± 0.02
Fluoranthene	206-44-0	9.73 ± 0.21	7.58 ± 0.16
Pyrene	129-00-0	10.88 ± 0.22	8.47 ± 0.17
Benz[*a*]anthracene	56-55-3	5.25 ± 0.11	4.09 ± 0.09
Chrysene	218-01-9	4.62 ± 0.10	3.60 ± 0.08
Benzo[*b*]fluoranthene	205-99-2	5.38 ± 0.11	4.19 ± 0.09
Benzo[*k*]fluoranthene	207-08-9	6.02 ± 0.13	4.69 ± 0.10
Benzo[*a*]pyrene	50-32-8	6.25 ± 0.15	4.87 ± 0.12
Dibenz[*a*,*h*]anthracene	53-70-3	4.48 ± 0.26	3.49 ± 0.20
Benzo[*ghi*]perylene	191-24-2	4.71 ± 0.17	3.67 ± 0.13
Indeno[1,2,3-*cd*]pyrene	193-39-5	5.48 ± 0.17	4.27 ± 0.13

[a] Chemical Abstracts, Fourteenth Collective Index Guide, American Chemical Society, Columbus, Ohio, 2001.
[b] The results are expressed as the certified value ± the expanded uncertainty. The certified value is the mean of the concentrations determined by gravimetric and chromatographic measurements. The expanded uncertainty uses a coverage factor of 2 (95 % confidence) and includes both correction for estimated purity and allowance for differences between the concentration determined by gravimetric preparation and chromatographic measurements [1].
[c] The concentrations listed in mg/L units were obtained by multiplying the certified values in mg/kg by the density of acetonitrile at 23 °C (0.7789 g/mL). These concentrations are for use in the temperature range of 21 °C to 25 °C and an allowance for the change in density over this temperature range is included in the uncertainties.

NOTICE AND WARNING TO USER

Toxicity: This SRM contains acetonitrile. Acute and chronic health hazards have been documented from exposure through inhalation, ingestion, and skin absorption. This SRM also contains small amounts of PAHs, some of which have been reported to have mutagenic and/or carcinogenic properties; therefore, care should be exercised during handling and use. Use proper methods for disposal of waste.

INSTRUCTIONS FOR USE

Storage and Use: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C and 30 °C. Samples of the SRM for analysis should be withdrawn from ampoules and used without delay. The certified values listed in Table 1 apply only to aliquots removed at 23 °C ± 2 °C. Certified values are not valid for ampoules which have been stored after opening, even if resealed.

Preparation and Analysis: The acetonitrile solution of the 16 PAHs was prepared gravimetrically from individual compounds. Four of the compounds (acenaphthylene, acenaphthene, phenanthrene, anthracene), were obtained from J. Jacob (Ahrensburg, Germany), naphthalene and fluorene were from Fluka (Milwaukee, WI), and the other ten compounds were Certified Reference Materials (CRMs) produced by the Community Bureau of Reference (BCR) Brussels, Belgium and obtained from the Institute for Reference Materials and Measurements (IRMM) Geel, Belgium. The purities of all PAHs used to make this SRM were ≥ 99 %. Purities of the compounds obtained from J. Jacob and Fluka were determined at NIST by a combination of techniques including differential scanning calorimetry (DSC), gas chromatography with flame ionization detection (GC-FID), and liquid chromatography with absorbance detection. Purities of CRMs were certified by BCR. The SRM solution was aliquoted into 2-mL amber glass ampoules, which were purged with argon prior to addition of the solution. Samples representing early, middle, and final stages of ampouling were analyzed by liquid chromatography (LC). No evidence of sample inhomogeneity was observed.

Randomly selected ampoules were analyzed for all 16 PAHs by LC using an acetonitrile-water mobile phase. Concentrations for the 16 PAHs were determined from a calibration based on averaged response factors, which used gravimetric values and instrumental responses for four independently prepared calibration standards. Four previous issues of this SRM (1647a, b, c, and d) were used as control samples. An internal standard calibration approach was used in the certification, with triphenylene as the internal standard. A representative chromatogram and the separation conditions are shown in Figure 1.

Comments on Column Selection: Variations in C_{18} column selectivity for PAHs are known to result from different column manufacturing processes [2]. Columns prepared by reaction of monofunctional C_{18} silanes with silica (denoted monomeric C_{18} phases) differ from columns prepared with silica substrates using trifunctional C_{18} silanes in the presence of water (denoted polymeric C_{18} phases). The designation "polymeric C_{18} column" should not be confused with "polymer substrate columns" (nonsilica columns, often based on polystyrene particles). Better separations of PAH mixtures are often possible on polymeric C_{18} columns such as that used to produce the chromatogram shown in Figure 1, as compared to monomeric C_{18} columns. A chromatogram illustrating the separation of the components in the SRM solution using a monomeric C_{18} column is provided for comparison (Figure 2). Baseline resolution of all components was not achieved with the monomeric C_{18} column. The classification of monomeric and polymeric C_{18} columns for the separation of PAHs has been described [2-9] and may be accomplished using SRM 869a, *Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons*) [10]. Examples of various C_{18} columns as "monomeric" or "polymeric" are provided with SRM 869a.

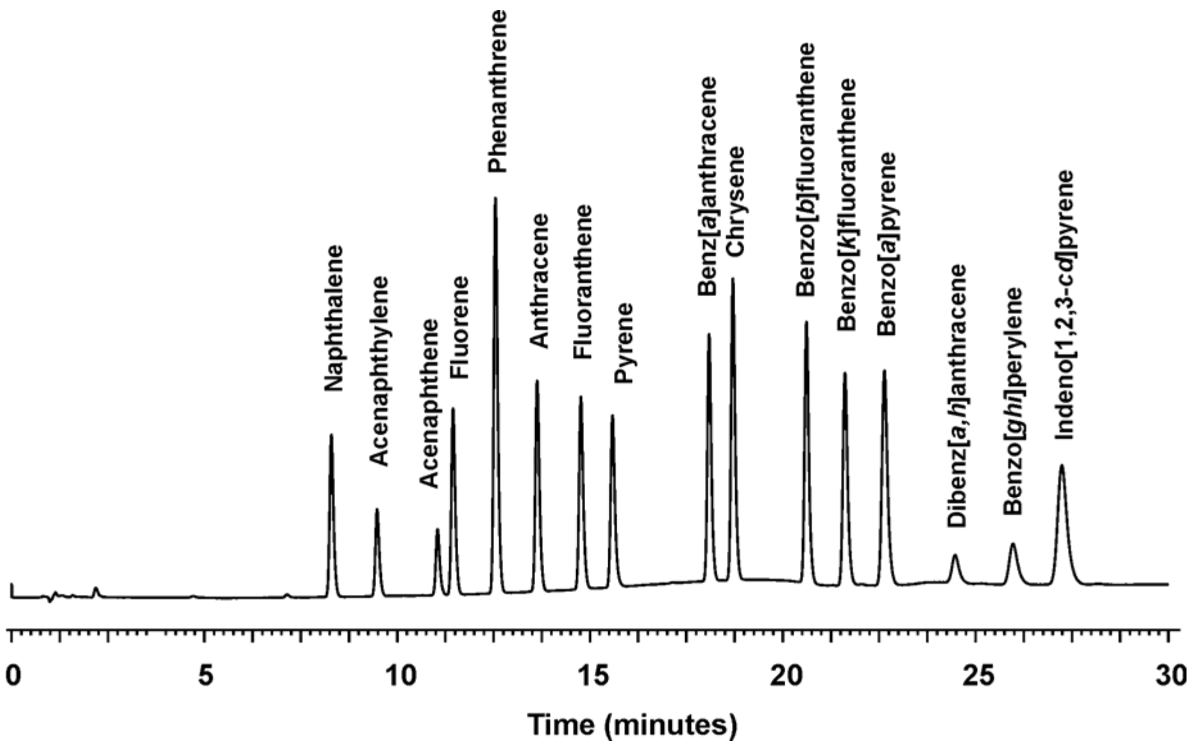

Figure 1. Reversed-phase LC separation of the 16 components of SRM 1647e. A polymeric C_{18} column (Pinnacle II PAH column, 5 µm, 0.46 cm × 25 cm; Restek, Bellefonte, PA) was used with a gradient elution program: 3 minutes hold at 50 % water: 50 % acetonitrile; 15 minutes linear gradient to 100 % acetonitrile; and 15 minutes hold at 100 % acetonitrile.

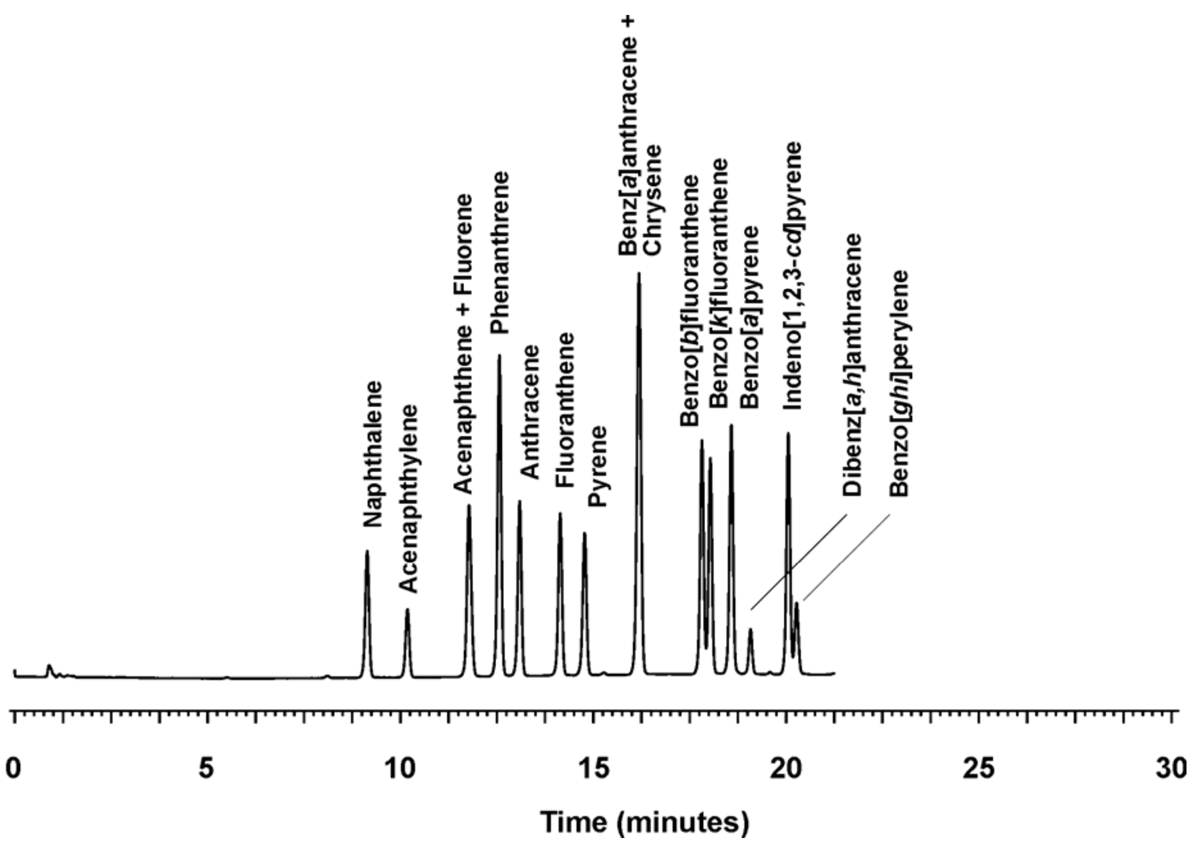

Figure 2. Reversed-phase LC separation of the 16 components of SRM 1647e using a monomeric C_{18} column (Zorbax ODS column, 5 µm, 0.46 cm × 25 cm; Mac-Mod Analytical Inc., Chadds Ford, PA) and the same gradient elution program as in Figure 1.

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[10] *Column Selectivity Test Mixture for Liquid Chromatography*; (*Polycyclic Aromatic Hydrocarbons*), *Certificate*; SRM 869a; NIST, U.S. Department of Commerce: Gaithersburg, MD (1998).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1944

New York/New Jersey Waterway Sediment

This Standard Reference Material (SRM) is a mixture of marine sediment collected near urban areas in New York and New Jersey. SRM 1944 is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, and trace elements in marine sediment and similar matrices. Reference values are also provided for selected dibenzo-*p*-dioxin and dibenzofuran congeners, total organic carbon, total extractable material, and particle-size characteristics. All of the constituents for which certified, reference, and information values are provided in SRM 1944 were naturally present in the sediment material before processing. A unit of SRM 1944 consists of a bottle containing 50 g of radiation sterilized, freeze-dried sediment material.

Certified Concentration Values: Certified values for concentrations, expressed as mass fractions, for 24 PAHs, 35 PCB congeners (some in combination), four chlorinated pesticides, and nine trace elements are provided in Tables 1-4. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified values for the PAHs, PCB congeners, and chlorinated pesticides are based on the agreement of results obtained at NIST from two or more chemically independent analytical techniques. The certified values for the trace elements are based on NIST measurements by one technique and additional results from several collaborating laboratories.

Reference Concentration Values: Reference values for concentrations, expressed as mass fractions, are provided for 32 additional PAHs (some in combination) in Table 5, seven additional chlorinated pesticides in Table 6, and 19 additional inorganic constituents in Tables 7 and 8. Reference values are provided in Table 9 for the 17 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners and total tetra-, penta-, hexa-, and hepta-congeners of polychlorinated dibenzo-*p*-dioxin and dibenzofuran. Reference values for particle-size characteristics are provided in Table 10. Reference values for total organic carbon and percent extractable mass are provided in Table 11. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. Explanations in support of each reference value are given as notes in Tables 5-11.

Information Concentration Values: Information values for concentrations, expressed as mass fractions, are provided in Table 12 for eight additional trace elements. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed.

Expiration of Certification: The certification of **SRM 1944** is valid, within the measurement uncertainty specified, until **31 March 2019**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the technical measurements leading to the certification was under the leadership of S.A. Wise of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 22 December 2008

Robert L. Watters, Jr., Chief
Measurement Services Division

See Certificate Revision History on Page17

Consultation on the statistical design of the experimental work and evaluation of the data were provided by M.G. Vangel and M.S. Levenson of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

The sediment material was collected with the assistance of the New York District of the U.S. Army Corp of Engineers (ACENYD), who provided the expertise in the site selection, the ship, sampling equipment, and personnel. L. Rosman of ACENYD and R. Parris (NIST) coordinated the collection of this sediment material. Collection and preparation of SRM 1944 were performed by R. Parris, M. Cronise, and C. Fales (NIST); L. Rosman and P. Higgins (ACENYD); and the crew of the *Gelberman* from the ACE Caven Point facility in Caven Point, NJ.

Analytical measurements for the certification of SRM 1944 were performed at NIST by E.S. Beary, D.A. Becker, R. Demiralp, R.R. Greenberg, M. Lopez de Alda, K.E. Murphy, B.J. Porter, D.L. Poster, L.C. Sander, M.M. Schantz, and L. Walton of the Analytical Chemistry Division. Measurements for percent total organic carbon measurements were provided by three commercial laboratories and T.L. Wade of the Geochemical and Environmental Research Group, Texas A&M University (College Station, TX). The particle-size distribution data were provided by Honeywell, Inc. (Clearwater, FL).

Analytical measurements for the polychlorinated dibenzo-*p*-dioxins and dibenzofurans were the results of an interlaboratory comparison study among 14 laboratories (see Appendix A) coordinated by S.A. Wise of the NIST Analytical Chemistry Division and R. Turle and C. Chiu of Environment Canada, Environmental Technology Centre, Analysis and Air Quality Division (Ottawa, Ontario, Canada). Analytical measurements for selected trace elements were provided by the International Atomic Energy Agency (IAEA, Seibersdorf, Austria) by M. Makarewicz and R. Zeisler. Results were also used from seven laboratories (see Appendix B) that participated in an intercomparison exercise coordinated by S. Willie of the Institute for National Measurement Standards, National Research Council Canada (NRCC, Ottawa, Ontario, Canada).

NOTICE AND WARNING TO USERS

Storage: SRM 1944 must be stored in its original bottle at temperatures less than 30 °C away from direct sunlight.

Handling: This material is naturally occurring marine sediment from an urban area and may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use.

INSTRUCTIONS FOR USE

Prior to removal of subsamples for analysis, the contents of the bottle should be mixed. The concentrations of constituents in SRM 1944 are reported on a dry-mass basis. The SRM, as received, contains approximately 1.3 % moisture. The sediment sample should be dried to a constant mass before weighing for analysis, or if the constituents of interest are volatile, a separate subsample of the sediment should be removed from the bottle at the time of analysis and dried to determine the concentration on a dry-mass basis.

PREPARATION AND ANALYSIS[1]

Sample Collection and Preparation: The sediment used to prepare this SRM was collected from six sites in the vicinity of New York Bay and Newark Bay in October 1994. Site selection was based on contaminant levels measured in previous samples from these sites and was intended to provide relatively high concentrations for a variety of chemical classes of contaminants. The sediment was collected using an epoxy-coated modified Van Veen-type grab sampler designed to sample the sediment to a depth of 10 cm. A total of approximately 2100 kg of wet sediment was collected from the six sites. The sediment was freeze-dried, sieved (nominally 250 µm to 61 µm), homogenized in a cone blender, radiation sterilized (^{60}Co), and then packaged in screw-capped amber glass bottles.

[1]Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify 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 necessarily the best available for the purpose.

Conversion to Dry-Mass Basis: The results for the constituents in SRM 1944 are reported on a dry-mass basis; however, the material "as received" contains residual moisture. The amount of moisture in SRM 1944 was determined by measuring the mass loss after freeze-drying subsamples of 1.6 g to 2.5 g for five days at 1 Pa with a -10 °C shelf temperature and a -50 °C condenser temperature. The moisture content in SRM 1944 at the time of the certification analyses was 1.25 % ± 0.03 % (95 % confidence level).

Polycyclic Aromatic Hydrocarbons: The general approach used for the value assignment of the PAHs in SRM 1944 was similar to that reported for the recent certification of several environmental matrix SRMs [1-5] and consisted of combining results from analyses using various combinations of different extraction techniques and solvents, cleanup/isolation procedures, and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction and pressurized fluid extraction (PFE) using dichloromethane (DCM) or a hexane/acetone mixture, cleanup of the extracts using solid phase extraction (SPE) or normal-phase liquid chromatography (LC), followed by analysis using the following techniques: (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 spectrometric (GC/MS) analysis of the PAH fraction on three stationary phases of different selectivity, i.e., a 5 % (mole fraction) phenyl-substituted methylpolysiloxane phase, a 50 % (mole fraction) phenyl-substituted methylpolysiloxane phase, and a smectic liquid crystalline stationary phase.

Six sets of GC/MS results, designated as GC/MS (I), GC/MS (II), GC/MS (III), GC/MS (IV), GC/MS (V), and GC/MS (Sm), were obtained using three columns with different selectivities for the separation of PAHs. For GC/MS (I) analyses, duplicate subsamples of 1 g from eight bottles of SRM 1944 were Soxhlet extracted for 24 h with DCM. Copper powder was added to the extract to remove elemental sulfur. The concentrated extract was passed through a silica SPE cartridge and eluted with 2 % DCM in hexane. The processed extract was then analyzed by GC/MS using a 0.25 mm i.d. × 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). The GC/MS (II) analyses were performed using 1 g to 2 g subsamples from three bottles of SRM 1944 and 2 g to 3 g subsamples from three bottles of SRM 1944 that had been mixed with a similar amount of water (i.e., a wetted sediment). These samples were Soxhlet extracted with DCM and processed through the silica SPE as described above; however, the extract was further fractionated using normal-phase LC on a semi-preparative aminopropylsilane column to isolate the PAH fraction [6-9]. The PAH fraction was then analyzed using the same column as described above for GC/MS (I); however, the subsamples were extracted, processed and analyzed as part of three different sample sets at different times using different calibrations for each set. For the GC/MS (III), 1 g to 2 g subsamples from six bottles of SRM 1944 were Soxhlet extracted for 18 h with 250 mL of a mixture of 50 % hexane/50 % acetone (volume fractions). The extracts were then processed and analyzed as described for GC/MS (II). For GC/MS (IV) analyses, 1 g to 2 g subsamples from six bottles of SRM 1944 were extracted using PFE with a mixture of 50 % hexane/50 % acetone as described by Schantz et al. [10], and the extracts were processed as described above for GC/MS (II). The GC/MS (V) results were obtained by analyzing three of the same PAH fractions that were analyzed in GC/MS (III) and three of the PAH fractions that were analyzed in GC/MS (IV) using a 50 % phenyl-substituted methylpolysiloxane stationary phase (0.25 mm i.d. × 60 m, 0.25 µm film thickness) (DB-17MS, J&W Scientific, Folsom, CA). For GC/MS (Sm) 1 g to 2 g subsamples from six bottles of SRM 1944 were Soxhlet extracted for 24 h with 250 mL of DCM. The extracts were processed as described above for GC/MS (I) using an aminopropylsilane SPE cartridge followed by GC/MS analysis using 0.2 mm i.d. × 25 m (0.15 µm film thickness) smectic liquid crystalline phase (SB-Smectic, Dionex, Lee Scientific Division, Salt Lake City, UT).

Two sets of LC-FL results, designated as LC-FL (Total) and LC-FL (Fraction), were used in the certification process. Subsamples of approximately 1 g from six bottles of SRM 1944 were Soxhlet extracted for 20 h using 200 mL of 50 % hexane/50 % acetone (volume fractions). The extracts were concentrated and then processed through two aminopropylsilane solid phase extraction (SPE) cartridges connected in series to obtain the total PAH fraction. A second 1 g subsample from the six bottles was Soxhlet extracted and processed as described above; the PAH fraction was then fractionated further on a semi-preparative aminopropylsilane column (µBondapak NH_2, 9 mm i.d. × 30 cm, Waters Associates, Milford, MA) to isolate isomeric PAH fractions as described previously [6-9]. The total PAH fraction and the isomeric PAH fractions were analyzed using a 5-µm particle-size polymeric octadecylsilane (C_{18}) column (4.6 mm i.d. × 25 cm, Hypersil-PAH, Keystone Scientific, Inc., Bellefonte, PA) with wavelength programmed fluorescence detection [7,8]. For all of the GC/MS and LC-FL measurements described above, selected perdeuterated PAHs were added to the sediment prior to solvent extraction for use as internal standards for quantification purposes.

Homogeneity Assessment for PAHs: The homogeneity of SRM 1944 was assessed by analyzing duplicate samples of 1 g from eight bottles selected by stratified random sampling. Samples were extracted, processed, and analyzed as described above for GC/MS (I). No statistically significant differences among bottles were observed for the PAHs at the 1 g sample size.

PCBs and Chlorinated Pesticides: The general approach used for the determination of PCBs and chlorinated pesticides in SRM 1944 was similar to that reported for the recent certification of several environmental matrix SRMs [2,4,11,12,13], and consisted of combining results from analyses using various combinations of different extraction techniques and solvents, cleanup/isolation procedures, and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction and PFE using DCM or a hexane/acetone mixture, cleanup/isolation using SPE or LC, followed by analysis using GC/MS and gas chromatography with electron capture detection (GC-ECD) on two columns with different selectivity.

Eight sets of results were obtained designated as GC-ECD (I) A and B, GC-ECD (II) A and B, GC/MS (I), GC/MS (II), GC/MS (III), and QA Exercise. For the GC-ECD (I) analyses, 1 g subsamples from four bottles of SRM 1944 were Soxhlet extracted with DCM for 18 h. Copper powder was added to the extract to remove elemental sulfur. The concentrated extract was passed through a silica SPE cartridge and eluted with 10 % DCM in hexane. The concentrated eluant was then fractionated on a semi-preparative aminopropylsilane column to isolate two fractions containing: (1) the PCBs and lower polarity pesticides, and (2) the more polar pesticides. 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 50 % (mole fraction) octadecyl (C-18) methylpolysiloxane phase (0.1 µm film thickness) (CPSil 5 C18 CB, Chrompack International, Middelburg, The Netherlands). The results from the 5 % phenyl phase are designated as GC-ECD (IA) and the results from the C-18 phase are designated as GC-ECD (IB). A second set of samples was also analyzed by GC-ECD (i.e., GC-ECD IIA and IIB). Subsamples of 1 g to 2 g from three bottles of SRM 1944 and 2 g to 3 g subsamples from three bottles of SRM 1944 that had been mixed with a similar amount of water (i.e., a wetted sediment) were extracted, processed, and analyzed as described above for GC-ECD (I); however, the subsamples were extracted, processed and analyzed as part of three different sample sets at different times using different calibrations for each set.

Three sets of results were obtained by GC/MS. For GC/MS (I), 1 g to 2 g subsamples from six bottles were Soxhlet extracted with a mixture of 50 % hexane/50 % acetone. Copper powder was added to the extract to remove elemental sulfur. The concentrated extract was passed through a silica SPE cartridge and eluted with 10 % DCM in hexane. The extract 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). The GC/MS (II) results were obtained in the same manner as the GC/MS (I) analyses except that the six subsamples were extracted using PFE as described by Schantz et al. [10]. The GC/MS (III) analyses were performed on the same extract fractions analyzed in GC-ECD (II) using the 5 % phenyl-substituted methylpolysiloxane phase describe above for GC/MS (I). For both the GC-ECD and GC/MS analyses, two PCB congeners that are not significantly present in the sediment extract (PCB 103 and PCB 198 [14,15]), and 4,4'-DDT-d_8 were added to the sediment prior to extraction for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1944 was used in an interlaboratory comparison exercise in 1995 as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment [16]. Results from 19 laboratories that participated in this exercise were used as the eighth data set in the determination of the certified values for PCB congeners and chlorinated pesticides in SRM 1944. The laboratories participating in this exercise used the analytical procedures routinely used in their laboratories to measure PCB congeners and chlorinated pesticides.

Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans: Value assignment of the concentrations of the 17 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners and the total tetra- through hepta-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans was accomplished by combining results from the analysis of SRM 1944 by 14 laboratories that participated in an interlaboratory comparison study (see Appendix A). Each laboratory analyzed three subsamples (typically 1 g) of SRM 1944 using their routine analytical procedures and gas chromatography with high resolution mass spectrometric detection (GC-HRMS).

The analytical procedures used by all of the laboratories included spiking with ^{13}C-labeled surrogates (internal standards); Soxhlet extraction with toluene; sample extract cleanup with acid/base silica, alumina, and carbon columns; and finally analysis of the cleaned up extract with GC-HRMS. Most of the laboratories used a 5 % phenyl-substituted methylpolysiloxane phase capillary column (DB-5), and about half of the laboratories confirmed 2,3,7,8-tetrachlorodibenzofuran using a 50 % (mole fraction) cyanopropylphenyl-substituted methylpolysiloxane capillary column (DB-225, J&W Scientific, Folsom, CA).

Analytical Approach for Inorganic Constituents: Value assignment for the concentrations of selected trace elements was accomplished by combining results of the analyses of SRM 1944 from NIST, NRCC, IAEA, and seven selected laboratories that participated in an interlaboratory comparison exercise coordinated by the NRCC [17] (see Appendix B). A similar approach was recently used to provide certified and reference concentration values for trace elements in two mussel tissue materials [18-20]. The analytical methods used for the determination of each element are summarized in Table 13. For the certified concentration values listed in Table 4, results were combined from: (1) analyses at NIST using isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) or instrumental neutron activation analysis (INAA), (2) analyses at NRCC using ID-ICPMS, graphite furnace atomic absorption spectrometry (GFAAS), and/or inductively coupled plasma atomic emission spectroscopy (ICPAES), (3) analyses at IAEA using INAA, and (4) the mean of the results from seven selected laboratories that participated in the NRC interlaboratory comparison exercise. The reference concentration values in Table 7 were determined by combining results from (1) analyses performed at NIST using INAA; (2) analyses at NRCC using ID-ICPMS, GFAAS, ICPAES, and/or cold vapor atomic absorption spectroscopy (CVAAS); (3) analyses at IAEA using INAA; and (4) the mean of the results from five to seven laboratories that participated in the NRCC interlaboratory comparison exercise. The information concentration values in Table 12 were determined by INAA at NIST and IAEA.

NIST Analyses using ID-ICPMS: Lead, cadmium, and nickel were determined by ID-ICPMS [21]. Subsamples (0.4 g to 0.5 g) from six bottles of the SRM were spiked with ^{206}Pb, ^{111}Cd, and ^{62}Ni and wet ashed using a combination of nitric, hydrochloric, hydrofluoric, and perchloric acids. Lead and cadmium were determined in the same sample; nickel was determined in a second sample set. A small amount of crystalline material remained after the acid dissolution. Lithium metaborate fusion was performed on this residue to confirm that the residue contained insignificant amounts of the analytes. Cadmium and nickel were separated from the matrix material to eliminate the possibility of spectral interferences, and concentrations were determined from the measurement of the $^{112}Cd/^{111}Cd$ and $^{62}Ni/^{60}Ni$ ratios, respectively. The $^{208}Pb/^{206}Pb$ ratios were measured directly because interferences at these masses are negligible.

NIST Analyses using INAA: Analyses were performed in two steps [22]. Elements with short-lived irradiation products (Al, Ca, Cl, K, Mg, Mn, Na, Ti, and V) were determined by measuring duplicate 300 mg samples from each of 10 bottles of SRM 1944. The samples, standards, and controls were packaged in clean polyethylene bags and were individually irradiated for 15 s in the NIST Reactor Pneumatic Facility RT-4. Reactor power was 20 megawatts which corresponds to a neutron fluence rate of about 8×10^{13} $cm^{-2} \cdot s^{-1}$. After irradiation, the samples, controls, and standards were repackaged in clean polyethylene bags and counted (gamma-ray spectrometry) three times at different decay intervals. A sample to detector distance (counting geometry) of 20 cm was used. Elements with long-lived irradiation products (Ag, As, Br, Co, Cr, Cs, Fe, Rb, Sb, Sc, Se, Th, and Zn) were determined by measuring one 300 mg sample from each of nine bottles of SRM 1944. The samples, standards, controls, and blank polyethylene bags were irradiated together for a total of 1 h at a reactor power of 20 megawatts. Approximately four days after irradiation, the polyethylene bags were removed, and each sample, standard, control, and blank was counted at 20 cm from the detector. The samples were then recounted at 10 cm from another detector. After an additional decay time of about one month, the samples, standards, controls, and blanks were counted a third time (at 10 cm) from the second detector.

Particle-Size Information: Dry particle-size distribution measurements for SRM 1944 were obtained as part of a collaborative effort with Honeywell's Particle and Components Measurements Laboratory (Clearwater, FL). A Microtrac particle analyzer, which makes use of light-scattering techniques, was used to measure the particle-size distribution of SRM 1944. Briefly, a reference beam is used to penetrate a field of particles and the light that scatters in the forward direction from the field is measured and the particle size as a volume distribution is derived via a computer-assisted analysis. From these data, the total volume, average size, and a characteristic width of the particle-size distribution are calculated. The system has a working range from 0.7 µm to 700 µm.

Total Organic Carbon and Percent Extractable Mass: Four laboratories provided results for Total Organic Carbon (TOC) using similar procedures. Briefly, subsamples of approximately 200 mg were reacted with 6 N hydrochloric acid and rinsed with deionized water prior to combustion in a gas fusion furnace. The carbon monoxide and carbon dioxide produced were measured and compared to a blank for calculation of the percent TOC. Each laboratory analyzed subsamples from six bottles of SRM 1944. For the determination of percent extractable mass, six subsamples of approximately 1 g to 2 g of SRM 1944 were extracted using Soxhlet extraction for 18 h with DCM. The extraction thimbles were allowed to air dry. After reaching constant mass, the difference in the mass before and after extraction was determined.

Table 1. Certified Concentrations for Selected PAHs in SRM 1944

PAHs	Mass Fractions in mg/kg (dry-mass basis)[a,b]		
Naphthalene[c,d,e,f,g]	1.65	±	0.31
Phenanthrene[c,d,e,f,g]	5.27	±	0.22
Anthracene[c,d,e,f,g]	1.77	±	0.33
Fluoranthene[c,d,e,f,g]	8.92	±	0.32
Pyrene[c,d,e,f,g]	9.70	±	0.42
Benzo[*c*]phenathrene[c,d,e,f,h]	0.76	±	0.10
Benz[*a*]anthracene[c,d,e,f,g,h]	4.72	±	0.11
Chrysene[h,k]	4.86	±	0.10[i]
Triphenylene[h,k]	1.04	±	0.27
Benzo[*b*]fluoranthene[g,h,j]	3.87	±	0.42
Benzo[*j*]fluoranthene[h,j]	2.09	±	0.44
Benzo[*k*]fluoranthene[c,d,e,f,g,h,j]	2.30	±	0.20
Benzo[*a*]fluoranthene[c,d,e,f,h,,j]	0.78	±	0.12
Benzo[*e*]pyrene[c,d,e,f,h,j]	3.28	±	0.11
Benzo[*a*]pyrene[c,d,e,f,g,h,j]	4.30	±	0.13
Perylene[c,d,e,f,g,h,j]	1.17	±	0.24
Benzo[*ghi*]perylene[c,d,e,f,j,k]	2.84	±	0.10
Indeno[1,2,3-*cd*]pyrene[c,d,e,f,j,k]	2.78	±	0.10
Dibenz[*a,j*]anthracene[c,d,e,f,j,k]	0.500	±	0.044
Dibenz[*a,c*]anthracene[j,k]	0.335	±	0.013
Dibenz[*a,h*]anthracene[j,k]	0.424	±	0.069
Pentaphene[c,d,e,f,j,k]	0.288	±	0.026
Benzo[*b*]chrysene[c,d,e,f,j,k,h]	0.63	±	0.10
Picene[c,d,e,f,j,k]	0.518	±	0.093

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.
[b] The results are expressed as the certified value ± the expanded uncertainty. Each certified value is a mean of the means from two or more analytical methods, weighted as described in Paule and Mandel [23]. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values within which the true value is believed to lie, at a level of confidence of approximately 95 %.
[c] GC/MS (I) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[d] GC/MS (II) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[e] GC/MS (III) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with 50 % hexane/50 % acetone.
[f] GC/MS (IV) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with 50 % hexane/50 % acetone.
[g] LC-FL of total PAH fraction after Soxhlet extraction with 50 % hexane/50 % acetone.
[h] GC/MS (Sm) using a smectic liquid crystalline phase after Soxhlet extraction with DCM.
[i] The uncertainty interval for chrysene was widened based on expert consideration of the analytical methods and analysis of the data for all PAHs, which suggests that the half-widths of the expanded uncertainties should not be less than 2 %.
[j] GC/MS (V) on 50 % phenyl-substituted methylpolysiloxane phase of extracts from GC/MS (III) and GC/MS (IV).
[k] LC-FL of isomeric PAH fractions after Soxhlet extraction with 50 % hexane/50 % acetone.

Table 2. Certified Concentrations for Selected PCB Congeners[a] in SRM 1944

PCB Congeners		Mass Fractions in µg/kg (dry-mass basis)[b,c]		
PCB 8	(2,4'-Dichlorobiphenyl)[d,e,f,g,h,i,j,k]	22.3	±	2.3
PCB 18	(2,2',5-Trichlorobiphenyl)[d,e,f,g,h,i,j,k]	51.0	±	2.6
PCB 28	(2,4,4'-Trichlorobiphenyl)[d,e,f,g,j,k]	80.8	±	2.7
PCB 31	(2,4',5-Trichlorobiphenyl)[d,e,f,g,j]	78.7	±	1.6[l]
PCB 44	(2,2',3,5'-Tetrachlorobiphenyl)[d,e,f,g,h,i,j,k]	60.2	±	2.0
PCB 49	(2,2',4,5'-Tetrachlorobiphenyl)[d,e,f,g,h,i,j,k]	53.0	±	1.7
PCB 52	(2,2',5,5'-Tetrachlorobiphenyl)[d,e,f,g,h,i,j,k]	79.4	±	2.0
PCB 66	(2,3',4,4'-Tetrachlorobiphenyl)[e,g,h,i,j]	71.9	±	4.3
PCB 87	(2,2',3,4,5'-Pentachlorobiphenyl)[d,e,f,g,h,i,j]	29.9	±	4.3
PCB 95	(2,2',3,5',6-Pentachlorobiphenyl)[e,g,h,i,j]	65.0	±	8.9
PCB 99	(2,2',4,4',5-Pentachlorobiphenyl)[d,e,f,g,h,i,j,k]	37.5	±	2.4
PCB 101	(2,2',4,5,5'-Pentachlorobiphenyl)[d,e,f,g,h,i,j,k]	73.4	±	2.5
90	(2,2',3,4',5-Pentachlorobiphenyl)			
PCB 105	(2,3,3',4,4'-Pentachlorobiphenyl)[e,f,g,h,i,j,k]	24.5	±	1.1
PCB 110	(2,3,3',4',6-Pentachlorobiphenyl)[g,h,i,j]	63.5	±	4.7
PCB 118	(2,3',4,4',5-Pentachlorobiphenyl)[d,e,f,g,h,i,j,k]	58.0	±	4.3
PCB 128	(2,2',3,3',4,4'-Hexachlorobiphenyl)[d,e,f,g,h,i,j,k]	8.47	±	0.28
PCB 138	(2,2',3,4,4',5'-Hexachlorobiphenyl)[d,e,f,g,h,i,j,k]	62.1	±	3.0
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)[d,e,f,g,h,i,j,k]	49.7	±	1.2
PCB 151	(2,2',3,5,5',6-Hexachlorobiphenyl)[d,e,f,g,h,i,j,k]	16.93	±	0.36
PCB 153	(2,2',4,4',5,5'-Hexachlorobiphenyl)[d,e,f,g,h,i,j,k]	74.0	±	2.9
PCB 156	(2,3,3',4,4',5-Hexachlorobiphenyl)[d,e,f,g,h,i,j]	6.52	±	0.66
PCB 170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)[d,e,f,g,h,i,j,k]	22.6	±	1.4
190	(2,3,3',4,4',5,5'-Heptachlorobiphenyl)			
PCB 180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)[d,e,f,g,h,i,j,k]	44.3	±	1.2
PCB 183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)[d,e,f,g,h,i,j]	12.19	±	0.57
PCB 187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)[d,e,f,g,h,i,j,k]	25.1	±	1.0
159	(2,3,3',4,5,5'-Hexachlorobiphenyl)			
182	(2,2',3',4,4',5,6'-Heptachlorobiphenyl)			
PCB 194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl)[d,e,f,g,h,i,j]	11.2	±	1.4
PCB 195	(2,2',3,3',4,4',5,6-Octachlorbiphenyl)[d,e,f,g,h,i,j,k]	3.75	±	0.39
PCB 206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl)[d,e,f,g,h,i,j,k]	9.21	±	0.51
PCB 209	Decachlorobiphenyl[d,e,f,g,h,i,j,k]	6.81	±	0.33

(a) PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [14] and later revised by Schulte and Malisch [15] 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 congener listed first is the major component; additional congeners may be present as minor components.

(b) Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.

(c) The results are expressed as the certified value ± the expanded uncertainty. Each certified value is a mean of the means from two or more analytical methods, weighted as described in Paule and Mandel [23]. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values within which the true value is believed to lie, at a level of confidence of approximately 95 %.

(d) GC-ECD (IA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

(e) GC-ECD (IB) on the 50 % C-18 dimethylpolysiloxane phase; same extracts analyzed as in GC-ECD (IA).

(f) GC-ECD (IIA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

(g) GC-ECD (IIB) on the 50 % octadecyl (C-18) methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IIA).

(h) GC/MS (I) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with 50 % hexane/50 % acetone.

(i) GC/MS (II) on 5 % phenyl-substituted methylpolysiloxane phase after PFE extraction with 50 % hexane/50 % acetone.

(j) GC/MS (III) on 5 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IIA).

(k) Results from 19 laboratories participating in an interlaboratory comparison exercise.

(l) The uncertainty interval for PCB 31 was widened based on expert consideration of the analytical methods and analysis of the data for all PCB congeners, which suggests that the half-widths of the expanded uncertainties should not be less than 2 %.

Table 3. Certified Concentrations for Selected Chlorinated Pesticides in SRM 1944

Chlorinated Pesticides	Mass Fractions in µg/kg (dry-mass basis)[a,b]		
Hexachlorobenzene[e,f,g,h,i,j]	6.03	±	0.35
cis-Chlordane (α-Chlordane) [c,d,e,f,g,h,i,j]	16.51	±	0.83
trans-Nonachlor[c,d,e,f,g,h,i,j]	8.20	±	0.51
4,4'-DDT[c,d,e,f,g,h,i,j]	119	±	11

(a) Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.
(b) The results are expressed as the certified value ± the expanded uncertainty. Each certified value is a mean of the means from two or more analytical methods, weighted as described in Paule and Mandel [23]. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values within which the true value is believed to lie, at a level of confidence of approximately 95 %.
(c) GC-ECD (IA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
(d) GC-ECD (IB) on the 50 % octadecyl (C-18) methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IA).
(e) GC-ECD (IIA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
(f) GC-ECD (IIB) on the 50 % octadecyl (C-18) methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IIA).
(g) GC/MS (I) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with 50 % hexane/50 % acetone.
(h) GC/MS (II) on 5 % phenyl-substituted methylpolysiloxane phase after PFE extraction with 50 % hexane/50 % acetone.
(i) GC/MS (III) on 5 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IIA).
(j) Results from 19 laboratories participating in an interlaboratory comparison exercise.

Table 4. Certified Concentrations for Selected Inorganic Constituents in SRM 1944

Elements	Degrees of Freedom	Mass Fractions in percent (dry-mass basis)[a,b]		
Aluminum[c,d,e]	4	5.33	±	0.49
Iron[c,d,e]	6	3.53	±	0.16
		Mass Fractions in mg/kg (dry-mass basis)[a,b]		
Arsenic[c,d,e,f,g]	10	18.9	±	2.8
Cadmium[c,f,h,i]	6	8.8	±	1.4
Chromium[c,d,f,g,i]	9	266	±	24
Lead[c,h,i]	5	330	±	48
Manganese[c,d,e]	8	505	±	25
Nickel[c,g,h,i]	6	76.1	±	5.6
Zinc[c,d,e,g,i]	9	656	±	75

(a) The results are expressed as the certified value ± the expanded uncertainty. The certified value is the mean of four results: (1) the mean of NIST INAA or ID-ICPMS analyses, (2) the mean of two methods performed at NRCC, and (3) the mean of results from seven selected laboratories participating in the NRCC intercomparison exercise, and (4) the mean results from INAA analyses at IAEA. The expanded uncertainty in the certified value is equal to $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor, both calculated according to the ISO and NIST Guides [24]. The value of u_c is intended to represent at the level of one standard deviation the combined effect of all the uncertainties in the certified value. Here u_c accounts for both possible method biases, within-method variation, and material inhomogeneity. The coverage factor, k, is the Student's t-value for a 95 % prediction interval with the corresponding degrees of freedom. Because of the material inhomogeneity, the variability among the measurements of multiple samples can be expected to be greater than that due to measurement variability alone.
(b) Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.
(c) Results from five to seven laboratories participating in the NRCC interlaboratory comparison exercise.
(d) Measured at NIST using INAA.
(e) Measured at NRCC using ICPAES.
(f) Measured at NRCC using GFAAS.
(g) Measured at IAEA using INAA.
(h) Measured at NIST using ID-ICPMS.
(i) Measured at NRCC using ID-ICPMS.

Table 5. Reference Concentrations for Selected PAHs in SRM 1944

NOTE: These concentrations are provided as reference values because either the results have not been confirmed by an independent analytical technique as required for certification or the agreement among results from multiple methods was insufficient for certification. Although bias has not been evaluated for the procedures used, the reference values should be useful for comparison with results obtained using similar procedures.

PAHs	Mass Fractions in mg/kg (dry-mass basis)[a,b]		
1-Methylnaphthalene[c,d,e,f]	0.52	±	0.03
2-Methylnaphthalene[c,d,e,f]	0.95	±	0.05
Biphenyl[c,d,e,f]	0.32	±	0.07
Acenaphthene[c,d,e,f]	0.57	±	0.03
Fluorene[c,d,e,f]	0.85	±	0.03
Dibenzothiophene[d,e,f]	0.62	±	0.01[g]
1-Methylphenanthrene[c,d,e,f]	1.7	±	0.1
2-Methylphenanthrene[c,d,e,f]	1.90	±	0.06
3-Methylphenanthrene[c,d,e,f]	2.1	±	0.1
4-Methylphenanthrene and 9-Methylphenanthrene[c,d,e,f]	1.6	±	0.2
2-Methylanthracene[c,d,e,f]	0.58	±	0.04
3,5-Dimethylphenanthrene[c]	1.31	±	0.04
2,6-Dimethylphenanthrene[c]	0.79	±	0.02[g]
2,7-Dimethylphenanthrene[c]	0.67	±	0.02[g]
3,9-Dimethylphenanthrene[c]	2.42	±	0.05[g]
1,6-, 2,9-, and 2,5-Dimethylphenanthrene[c]	1.67	±	0.03[g]
1,7-Dimethylphenanthrene[c]	0.62	±	0.02[g]
1,9- and 4,9-Dimethylphenanthrene[c]	1.20	±	0.03[g]
1,8-Dimethylphenanthrene[c]	0.24	±	0.01[g]
1,2-Dimethylphenanthrene[c]	0.28	±	0.01[g]
8-Methylfluoranthene[c]	0.86	±	0.02[g]
7-Methylfluoranthene[c]	0.69	±	0.02
1-Methylfluoranthene[c]	0.66	±	0.02[g]
3-Methylfluoranthene[c]	2.46	±	0.07
2-Methylpyrene[c]	1.81	±	0.04[g]
4-Methylpyrene[c]	1.44	±	0.03[g]
1-Methylpyrene[c]	1.29	±	0.03
Anthanthrene[h]	0.9	±	0.1

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.
[b] The reference value for each analyte is the equally-weighted mean of the means from two or more analytical methods or the mean from one analytical technique. The uncertainty in the reference value defines a range of values that is intended to function as an interval that contains the true value at a level of confidence of 95 %. This uncertainty includes sources of uncertainty within each analytical method, among methods, and from the drying study.
[c] GC/MS (I) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[d] GC/MS (II) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[e] GC/MS (III) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with 50 % hexane/50 % acetone.
[f] GC/MS (IV) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with 50 % hexane/50 % acetone.
[g] The uncertainty interval for this compound was widened in accordance with expert consideration of the analytical procedures, along with the analysis of the data as a whole, which suggests that the half-widths of the expanded uncertainties should not be less than 2 %.
[h] LC-FL of isomeric PAH fractions after Soxhlet extraction with 50 % hexane/50 % acetone.

Table 6. Reference Concentrations for Selected Chlorinated Pesticides in SRM 1944

NOTE: These concentrations are provided as reference values because either the results have not been confirmed by an independent analytical technique as required for certification or the agreement among results from multiple methods was insufficient for certification. Although bias has not been evaluated for the procedures used, the reference values should be useful for comparison with results obtained using similar procedures.

Chlorinated Pesticides	Mass Fractions in µg/kg (dry-mass basis)[a,b]
α-HCH[c,d,e,f]	2.0 ± 0.3
trans-Chlordane (γ-Chlordane)[c,d,e,f,g,h,i,j]	8 ± 2
cis-Nonachlor[d,e,f,i,j]	3.7 ± 0.7
2,4'-DDE[c,d,e,f,g,h,i,j]	19 ± 3
2,4'-DDD[e,f,g,h,i,j]	38 ± 8
4,4'-DDE[c,d,e,f,g,h,i,j]	86 ± 12
4,4'-DDD[c,d,e,f,g,h,i,j]	108 ± 16

[a] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.
[b] The reference value for each analyte is the equally-weighted mean of the means from two or more analytical methods or the mean from one analytical technique. The uncertainty in the reference value defines a range of values that is intended to function as an interval that contains the true value at a level of confidence of 95 %. This uncertainty includes sources of uncertainty within each analytical method, among methods, and from the drying study.
[c] GC-ECD (IA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[d] GC-ECD (IB) on the 50 % octadecyl (C-18) methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IA).
[e] GC-ECD (IIA) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.
[f] GC-ECD (IIB) on the 50 % octadecyl (C-18) methylpolysiloxane phase; same extracts analyzed as in GC-ECD (IIA).
[g] GC/MS (I) on 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with 50 % hexane/50 % acetone.
[h] GC/MS (II) on 5 % phenyl-substituted methylpolysiloxane phase after PFE extraction with 50 % hexane/50 % acetone.
[i] GC/MS (III) on 5 % phenyl-substituted methylpolysiloxane phase; same extracts anlayzed as in GC-ECD (IIA).
[j] Results from 19 laboratories participating in an interlaboratory comparison exercise.

Table 7. Reference Concentrations for Selected Inorganic Constituents in SRM 1944 as Determined by Multiple Laboratories

NOTE: These concentrations are provided as reference values because either the results have not been confirmed by an independent analytical technique as required for certification, the agreement among results from multiple methods was insufficient for certification, or insufficient analyses have been performed at NIST to confirm the results of the outside laboratories.

Elements	Degrees of Freedom	Mass Fraction in percent (dry-mass basis)[a,b]
Silicon[c,d]	81	31 ± 3
		Mass Fraction in mg/kg (dry-mass basis)[a,b]
Beryllium[c,h]	17	1.6 ± 0.3
Copper[c,d,f]	101	380 ± 40
Mercury[c,i]	18	3.4 ± 0.5
Selenium[c,e,f]	24	1.4 ± 0.2
Silver[c,d,e,g]	8	6.4 ± 1.7
Thallium[c,f]	12	0.59 ± 0.1
Tin[c,f]	22	42 ± 6

[a] The results are expressed as the reference value ± the expanded uncertainty. The reference value is the equally weighted mean of available results from: (1) NIST INAA analyses, (2) two methods performed at NRCC, (3) results from seven selected laboratories participating in the NRCC intercomparison exercise, and (4) results from INAA analyses at IAEA. The expanded uncertainty in the reference value is equal to $U = ku_c$ where u_c is the combined standard uncertainty and k is the coverage factor, both calculated according to the ISO and NIST Guides [24]. The value of u_c is intended to represent at the level of one standard deviation, the uncertainty in the value. Here u_c accounts for both possible method differences, within-method variation, and material inhomogeneity. The coverage factor, k, is the Student's t-value for a 95 % prediction interval with the

corresponding degrees of freedom. Because of material inhomogeneity, the variability among the measurements of multiple samples can be expected to be greater than that due to measurement variability alone.

[b] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.

[c] Results from five to seven laboratories participating in the NRCC interlaboratory comparison exercise.

[d] Measured at NRCC using GFAAS.

[e] Measured at NIST using INAA.

[f] Measured at NRCC using ID-ICPMS.

[g] Measured at IAEA using INAA.

[h] Measured at NRCC using ICPAES.

[i] Measured at NRCC using CVAAS.

Table 8. Reference Concentrations for Selected Inorganic Constituents in SRM 1944 as Determined by INAA

NOTE: These concentrations are provided as reference values because the results have not been confirmed by an independent analytical technique as required for certification; therefore, unrecognized bias may exist for some analytes in this matrix.

Element	Effective Degrees of Freedom	Mass Fraction in percent (dry-mass basis)[a,b]		
Calcium	21	1.0	±	0.1
Chlorine	21	1.4	±	0.2
Potassium	21	1.6	±	0.2
Sodium	25	1.9	±	0.1
		Mass Fraction in mg/kg (dry-mass basis)[a,b]		
Bromine	10	86	±	10
Cesium	11	3.0	±	0.3
Cobalt	10	14	±	2
Rubidium	14	75	±	2
Scandium	37	10.2	±	0.2
Titanium	21	4300	±	300
Vanadium	21	100	±	9

[a] The results are expressed as the reference value ± the expanded uncertainty. The reference value is based on the results from an INAA study. The associated uncertainty accounts for both random and systematic effects, but because only one method was used, unrecognized bias may exist for some analytes in this matrix. The expanded uncertainty in the reference value is equal to $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor, both calculated according to the ISO and NIST Guides [24]. The value of u_c is intended to represent at the level of one standard deviation, the uncertainty in the value. Here u_c accounts for within-method variation and material inhomogeneity. The coverage factor, k, is the Student's t-value for a 95 % prediction interval with the corresponding degrees of freedom. Because of material inhomogeneity, the variability among the measurements of multiple samples can be expected to be greater than that due to measurement variability alone.

[b] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.

Table 9. Reference Concentrations for Selected Dibenzo-*p*-dioxin and Dibenzofuran Congeners in SRM 1944

NOTE: These concentrations are provided as reference values because the results have not been confirmed by an independent analytical technique as required for certification. Although bias has not been evaluated for the procedures used, the reference values should be useful for comparison with results obtained using similar procedures.

Dibenzo-*p*-dioxin and Dibenzofuran Congeners	Mass Fraction in µg/kg (dry-mass basis)[(a,b)]		
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	0.133	±	0.009
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	0.019	±	0.002
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	0.026	±	0.003
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	0.056	±	0.006
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	0.053	±	0.007
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	0.80	±	0.07
Octachlorodibenzo-*p*-dioxin	5.8	±	0.7
2,3,7,8-Tetrachlorodibenzofuran[(c)]	0.039	±	0.015[(d)]
1,2,3,7,8-Pentachlorodibenzofuran	0.045	±	0.007
2,3,4,7,8-Pentachlorodibenzofuran	0.045	±	0.004
1,2,3,4,7,8-Hexachlorodibenzofuran	0.22	±	0.03
1,2,3,6,7,8-Hexachlorodibenzofuran	0.09	±	0.01
2,3,4,6,7,8-Hexachlorodibenzofuran	0.054	±	0.006[(e)]
1,2,3,7,8,9-Hexachlorodibenzofuran	0.019	±	0.018[(f)]
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.0	±	0.1
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.040	±	0.006[(e)]
Octachlorodibenzofuran	1.0	±	0.1
Total Toxic Equivalents (TEQ)[(g)]	0.25	±	0.01
Total Tetrachlorodibenzo-*p*-dioxins	0.25	±	0.05[(e)]
Total Pentachlorodibenzo-*p*-dioxins	0.19	±	0.06
Total Hexachlorodibenzo-*p*-dioxins	0.63	±	0.09
Total Heptachlorodibenzo-*p*-dioxins	1.8	±	0.2
Total Tetrachlorodibenzofurans	0.7	±	0.2
Total Pentachlorodibenzofurans	0.74	±	0.07
Total Hexachlorodibenzofurans	1.0	±	0.1
Total Heptachlorodibenzofurans	1.5	±	0.1
Total Dibenzo-*p*-dioxins[(h)]	8.7	±	0.9
Total Dibenzofurans[(h)]	5.0	±	0.5

[(a)] Each reference value is the mean of the results from up to 14 laboratories participating in an interlaboratory exercise. The expanded uncertainty in the reference value is equal to $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO and NIST Guides [24] and k is the coverage factor. The value of u_c is intended to represent at the level of one standard deviation, the combined effect of all the uncertainties in the reference value. Here u_c is the uncertainty in the mean arising from the variation among the laboratory results. The degrees of freedom is equal to the number of available results minus one (13 unless noted otherwise). The coverage factor, k, is the value from a student's t-distribution for a 95 % confidence interval.

[(b)] Concentrations reported on dry-mass basis; material as received contains approximately 1.3 % moisture.

[(c)] Confirmation results using a 50 % cyanopropyl phenyl polysiloxane or 90 % *bis*-cyanopropyl 10 % cyanopropylphenyl polysiloxane phase columns.

[(d)] Degrees of freedom = 7 for this compound.

[(e)] Degrees of freedom = 12 for this compound.

[(f)] Degrees of freedom = 9 for this compound.

[(g)] TEQ is the sum of the products of each of the 2,3,7,8-substituted congeners multiplied by their individual toxic equivalency factors (TEFs) recommended by the North Atlantic Treaty Organization (NATO) [25]. With regard to 2,3,7,8-tetrachlorodibenzofuran, the results of the confirmation column were used when available to calculate the TEQ.

[(h)] Total of tetra- through octachlorinated congeners.

Table 10. Reference Values for Particle-Size Characteristics for SRM 1944

NOTE: These results are provided as reference values because the results are method specific as defined by the procedures described in the Preparation and Analysis section. Although bias has not been evaluated for the procedures used, the reference values should be useful for comparison with results obtained using similar procedures.

Particle Measurement	Value[(a)]
Mean diameter (volume distribution, MV, µm)[(b)]	151.2 ± 0.4
Mean diameter (area distribution, µm)[(c)]	120.4 ± 0.1
Mean diameter (number distribution, µm)[(d)]	75.7 ± 0.3
Surface Area (m^2/cm^3)[(e)]	0.050 ± 0.013

(a) The reference value is the mean value of measurements from the analysis of subsamples from four bottles. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty. The expanded uncertainty defines a range of values for the reference value within which the true value is believed to lie, at a level of confidence of 95 %.
(b) The mean diameter of the volume distribution represents the center of gravity of the distribution and compensates for scattering efficiency and refractive index. This parameter is strongly influenced by coarse particles.
(c) The mean diameter of the area distribution, calculated from the volume distribution with less weighting by the presence of coarse particles than MV.
(d) The mean diameter of the number distribution, calculated using the volume distribution weighted to small particles.
(e) Calculated specific surface area assuming solid, spherical particles. This is a computation and should not be interchanged with an adsorption method of surface area determination as this value does not reflect porosity or topographical characteristics.

The following data show the percent of the volume that is smaller than the indicated size:

Percentile	Particle Diameter (µm)[(a)]
95	296 ± 5
90	247 ± 2
80	201 ± 1
70	174 ± 1
60	152 ± 1
50[(b)]	135 ± 1
40	120 ± 1
30	106 ± 1
20	91 ± 1
10	74 ± 1

(a) The reference value for particle diameter is the mean value of measurements from the analysis of subsamples from four bottles. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty. The expanded uncertainty defines a range of values for the reference value within which the true value is believed to lie, at a level of confidence of 95 %.
(b) Median diameter (50 % of the volume is less than 135 µm).

Table 11. Reference Values for Total Organic Carbon and Percent Extractable Mass in SRM 1944

NOTE: These results are provided as reference values because the results are method specific as defined by the procedures described in the Preparation and Analysis section. Although bias has not been evaluated for the procedures used, the reference values should be useful for comparison with results obtained using similar procedures.

Total Organic Carbon (TOC)	4.4 % ± 0.3 % mass fraction[a,b]
Extractable Mass[c]	1.15 % ± 0.04 % mass fraction[a,d]

[a] Concentration is reported on a dry-mass basis; material as received contains approximately 1.3% moisture.
[b] The reference value for total organic carbon is an equally weighted mean value from routine measurements made by three laboratories. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty. The expanded uncertainty defines a range of values for the reference value within which the true value is believed to lie, at a level of confidence of 95 %.
[c] Extractable mass as determined from Soxhlet extraction using DCM.
[d] The reference value for extractable mass is the mean value of six measurements. Each uncertainty, computed according to the CIPM approach as described in the ISO and NIST Guides [24], is an expanded uncertainty at the 95 % level of confidence, which includes random sources of uncertainty. The expanded uncertainty defines a range of values for the reference value within which the true value is believed to lie, at a level of confidence of 95 %.

Table 12. Information Values for Concentrations for Selected Inorganic Constituents in SRM 1944 as Determined by INAA

NOTE: These results are provided as information values only because insufficient information is available to assess adequately the uncertainty associated with the value or only a limited number of analyses were performed.

Elements	Mass Fractions in percent (dry-mass basis)[a]
Magnesium[b]	1.0
	Mass Fractions in mg/kg (dry-mass basis)[a]
Antimony[b,c]	5
Cerium[c]	65
Europium[c]	1.3
Gold[c]	0.10
Lanthanum[c]	39
Thorium[c]	13
Uranium[c]	3.1

[a] Concentration is reported on a dry-mass basis; material as received contains approximately 1.3 % moisture.
[b] Measured at NIST using INAA.
[c] Measured at IAEA using INAA.

Table 13. Analytical Methods Used for the Analysis of SRM 1944 for Inorganic Constituents

Elements	**Analytical Methods**
Aluminum	FAAS, ICPAES, INAA, XRF
Antimony	GFAAS, HGAAS, ICP-MS, ID-ICPMS, INAA
Arsenic	GFAAS, HGAAS, ICPMS, INAA, XRF
Beryllium	GFAAS, ICP-AES, ICPMS
Bromine	INAA
Cadmium	FAAS, GFAAS, ICPMS, ID-ICPMS
Calcium	INAA
Cerium	INAA
Cesium	INAA
Chlorine	INAA
Chromium	FAAS, GFAAS, ICPMS, ID-ICPMS, INAA, XRF
Cobalt	INAA
Copper	FAAS, GFAAS, ICPAES, ICPMS, ID-ICPMS, XRF
Europium	INAA
Gold	INAA
Iron	FAAS, ICPAES, ICPMS, ID-ICPMS, INAA, XRF
Lanthanum	INAA
Lead	FAAS, GFAAS, ICPMS, ID-ICPMS, XRF
Magnesium	INAA
Manganese	FAAS, ICPAES, ICPMS, INAA, XRF
Mercury	CVAAS, ICPMS
Nickel	GFAAS, ICPAES, ICPMS, ID-ICPMS, INAA, XRF
Potassium	INAA
Rubidium	INAA
Scandium	INAA
Selenium	GFAAS, HGAAS, ICPMS, INAA
Silicon	FAAS, ICPAES, XRF
Silver	FAAS, GFAAS, ICPMS, INAA
Sodium	INAA
Thallium	GFAAS, ICPAES, ICPMS, ID-ICPMS
Thorium	INAA
Tin	GFAAS, ICPMS, ID-ICPMS
Titanium	INAA
Uranium	INAA
Vanadium	INAA
Zinc	FAAS, ICPAES, ICPMS, ID-ICPMS, XRF, INAA

Methods

CVAAS	Cold vapor atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HGAAS	Hydride generation atomic absorption spectrometry
ICPAES	Inductively coupled plasma atomic emission spectrometry
ICPMS	Inductively coupled plasma mass spectrometry
ID-ICPMS	Isotope dilution inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
XRF	X-ray fluorescence spectrometry

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Certificate Revision History: 22 December 2008 (Extension of certification period); 14 May 1999 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX A

The analysts and laboratories listed below participated in the interlaboratory comparison exercise for the determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in SRM 1944.

W.J. Luksemburg, Alta Analytical Laboratory, Inc., El Dorado Hills, CA
L. Phillips, Axys Analytical Services Ltd., Sidney, British Columbia, Canada
M.J. Armbruster, Battelle Columbus Laboratories, Columbus, OH
G. Reuel, Canviro Analytical Laboratories Ltd., Waterloo, Ontario, Canada
C. Brochu, Environment Québec, Laval, Québec, Canada
G. Poole, Environment Canada Environmental Technology Centre, Ottawa, Ontario, Canada
B. Henkelmann, GSF National Research Center for Environment and Health, Neuherberg, Germany
R. Anderson, Institute of Environmental Chemistry, Umeå University, Umeå, Sweden
C. Lastoria, Maxxam Analytics, Inc., Mississauga, Ontario, Canada
E. Reiner, Ontario Ministry of Environment and Energy, Etobicoke, Ontario, Canada
J. Macaulay, Research and Productivity Council, Fredericton, New Brunswick, Canada
T.L. Wade, GERG, Texas A&M University, College Station, TX
C. Tashiro, Wellington Laboratories, Guelph, Ontario, Canada
T.O. Tiernan, Wright State University, Dayton, OH

APPENDIX B

The analysts and laboratories listed below participated in the interlaboratory comparison exercise for the determination of trace elements in SRM 1944.

A. Abbgy, Applied Marine Research Laboratory, Old Dominion University, Norfolk, VA
A. Scott, Australian Government Analytical Laboratories, Pymble, Australia
H. Mawhinney, Animal Research Institute, Queensland Department of Primary Industries, Queensland, Australia
E. Crecelius, Battelle Pacific Northwest, Sequim, WA
M. Stephenson, California Department of Fish and Game, Moss Landing, CA
B. Presley, Department of Oceanography, Texas A&M University, College Station, TX
K. Elrick, U.S. Geological Survey, Atlanta, GA

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1946

Lake Superior Fish Tissue

This Standard Reference Material (SRM) is a frozen fish tissue homogenate, which was prepared from lake trout (*Salvelinus namaycush namaycush*) collected from Lake Superior (U.S./Canada), and is intended primarily for use in evaluating analytical methods for the determination of polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, fatty acids (including omega-3 fatty acids), extractable fat, methylmercury, total mercury, and selected trace elements in fish tissue and similar matrices. Information is also provided for proximates and caloric content. All of the constituents for which certified, reference, and information values are provided, are naturally present in the fish tissue homogenate. A unit of SRM 1946 consists of five bottles, each containing approximately 7 g to 9 g (wet basis) of frozen tissue homogenate.

Certified Concentration Values: Certified concentration values are provided in Tables 1 and 2 for 30 PCB congeners and 15 chlorinated pesticides, respectively. The certified values for PCBs and chlorinated pesticides are based on results obtained from two or more independent analytical techniques [1,2]. Certified values are provided in Table 3 for extractable fat and 13 individual fatty acids. The certified values for fat and fatty acids are based on measurements made by NIST and by collaborating laboratories. Certified values for methylmercury, total mercury, arsenic, and iron are provided in Table 4. The certified values for methylmercury and these elements are based on results from two or more independent analytical techniques performed at NIST and collaborating laboratories. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [1].

Reference Concentration Values: Reference concentration values for 12 PCB congeners, 2 chlorinated pesticides, 12 fatty acids, proximates, caloric content, and nine elements are provided in Tables 5 through 8. Reference values are noncertified values, which represent the best estimate of the true values based on available data; however, the values **DO NOT** meet the NIST criteria for certification [1] and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Information Concentration Values: Information concentration values are provided for carbohydrates, two additional trace elements, and four additional fatty acids in Table 9. An information value is a value that may be of use to the SRM user, but insufficient information is available to assess adequately the uncertainty associated with the value.

Expiration of Value Assignment: The value assignment of this SRM is valid until **31 December 2012**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this report. Value assignment is nullified if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Value Assignment: NIST will monitor this SRM over the period of its value assignment. If substantive technical changes occur that affect the value assignment before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Coordination of the technical measurements leading to the certification of this SRM was performed by M.M. Schantz and S.A. Wise of the NIST Analytical Chemistry Division.

Willie E. May, Chief
Analytical Chemistry Division

John Rumble, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 29 September 2003
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Analytical measurements at NIST were performed by W.W. Brubaker, Jr., S.J. Christopher, J.R. Kucklick, S.E. Long, E.A. Mackey, C.S. Phinney, B.J. Porter, D.L. Poster, M.S. Rearick, and M.M. Schantz of the NIST Analytical Chemistry Division. Measurements from the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment were coordinated by M.M. Schantz of the NIST Analytical Chemistry Division (see Appendix A for participating laboratories). Measurements by the National Food Processors Association (NFPA) Food Industry Analytical Chemists Subcommittee were coordinated by K.E. Sharpless of the NIST Analytical Chemistry Division and H.B. Chin and D.W. Howell of the NFPA (Dublin, CA and Washington, DC, respectively) (see Appendix B for participating laboratories). Analytical measurements for mercury and methylmercury were also performed at the Institute of Applied Physical Chemistry, Research Centre Jülich (Jülich, Germany) by H. Emons and at the Jožef Stefan Institute (Lubljana, Slovenia) by M. Horvat and D. Gibičar.

Statistical analysis was provided by S.D. Leigh and B. Toman of the NIST Statistical Engineering Division.

The support aspects involved with the certification and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.C. Colbert and B.S. MacDonald of the NIST Measurement Services Division.

The fish used for SRM 1946 were collected with the assistance of the Wisconsin Department of Natural Resources (S. Schram and T. Gerrard), U.S. Geological Service (G. Cholwak), and the Bodine Fish House, Bayfield, WI (J. Bodine and T. Chaney). The coordination for the collection, field preparation of the fish fillets, and cryogenic homogenization of the fish tissue were performed by J.R. Kucklick, B.J. Porter, R.S. Pugh, and D.J. Struntz of the NIST Analytical Chemistry Division, and M.P. Cronise and C.N. Fales of the NIST Standard Reference Materials Program.

NOTICE AND WARNING TO USERS

Warning: For laboratory use only. NOT for human consumption.

Storage: SRM 1946 is packaged as a frozen tissue homogenate in glass bottles. The tissue homogenate should **NOT** be allowed to thaw prior to subsampling for analysis. This material has been stored at NIST at −80 °C (or lower) since it was prepared and should be stored by the user at this temperature for the certified values to be valid within the stated uncertainties.

INSTRUCTIONS FOR USE

This material is a frozen tissue homogenate. After extended storage at temperatures of −25 °C or higher, or if it is allowed to warm, the tissue homogenate will lose its powder-like form. For the handling of this material during sample preparation, the following procedures and precautions are recommended. If weighing relatively large quantities, remove a portion from the bottle and reweigh the bottle to determine the mass of the subsample. Avoid heavy frost buildup by handling the bottles rapidly and wiping them prior to weighing. For weighing, transfer subsamples to a pre-cooled, thick-walled glass container rather than a thin-walled plastic container to minimize heat transfer to the sample. If possible, use a cold work space, (e.g., an insulated container with dry ice or liquid nitrogen coolant on the bottom and pre-cooled implements, such as Teflon-coated spatulas, for transferring the powder). Normal biohazard safety precautions for the handling of biological tissues should be exercised. Subsamples of this SRM for analysis should be withdrawn from the bottle immediately after opening and used without delay for the certified values listed in Tables 1 through 4 to be valid within the stated uncertainties. The concentrations of constituents in SRM 1946 are reported on a wet-mass basis. The SRM tissue homogenate, as received, contains approximately 71 % moisture.

PREPARATION AND ANALYSIS[1]

Sample Collection: SRM 1946 was prepared from fillets from adult lake trout (*Salvelinus namaycush namaycush*) collected near the Apostle Islands in Lake Superior in October 1997. The fillets were removed from the fish using stainless steel knives and placed in Teflon bags. The tissue was placed on wet ice and transported to NIST where it was stored in liquid nitrogen vapor freezers (−120 °C) until processed and bottled. A total of 78 kg of fillets was obtained from approximately 70 fish. The frozen fillets were pulverized in batches of approximately 350 g using

[1] Certain commercial equipment, instruments, or materials are identified in this certificate in order to adequately specify 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 necessarily the best available for the purpose.

the cryogenic procedure described previously [3]. The pulverized fish tissue was then homogenized in an aluminum mixing drum in two batches of approximately 40 kg each [4]. The mixing drum was designed to fit inside a liquid nitrogen vapor freezer and to rotate in the freezer thereby mixing the frozen tissue powder. After mixing for 2 h, subsamples of approximately 10 g of fish tissue homogenate were aliquoted into pre-cooled glass bottles.

Moisture Content: The moisture content of the fish tissue homogenate was determined by measuring the mass loss from freeze drying. Twelve bottles (six from each batch) of SRM 1946 were selected according to a stratified randomization scheme for the drying study. The entire contents of each glass bottle were transferred to a Teflon bottle and dried for 8 days at 1 Pa with a −10 °C shelf temperature and a −50 °C condenser temperature. Based on these studies, the mean moisture content of SRM 1946 is 71.4 % ± 0.1 % (mass fraction expressed as percent ± expanded uncertainty with $k = 2$, approximately 95 % confidence). The concentration values are reported on a wet-mass (as-received) basis. If necessary, the results can be converted to a dry-mass basis by dividing by the conversion factor of 0.2863 (g dry mass per g wet mass).

PCBs and Chlorinated Pesticides: The general approach used for the value assignment of concentrations for PCBs and chlorinated pesticides in SRM 1946 was similar to that reported for the recent certification of several environmental matrix SRMs [5-8] and consisted of combining results from analyses at NIST using various combinations of different extraction techniques and solvents, cleanup/isolation procedures, and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction and pressurized fluid extraction (PFE) using dichloromethane (DCM) or a hexane/acetone mixture; cleanup/isolation using solid-phase extraction (SPE), size-exclusion chromatography (SEC), or normal-phase liquid chromatography (LC); followed by analysis using gas chromatography with electron capture detection (GC-ECD) or gas chromatography with mass spectrometric detection (GC/MS) on two columns with different selectivity for the separation of PCBs and chlorinated pesticides.

Three sets of results were obtained by GC-ECD and are designated as GC-ECD (I), GC-ECD (IIA), and GC-ECD (IIB). For the GC-ECD (I) analyses, duplicate subsamples of 1 g from 10 bottles of SRM 1946 were extracted using PFE with DCM [9]. SEC was used to remove the majority of the lipid material. The concentrated eluant was then fractionated on a semi-preparative aminopropylsilane column to isolate two fractions containing: (1) the PCBs and the less polar pesticides and (2) the more polar pesticides. GC-ECD analyses of the two fractions were performed on a 0.25 mm i.d. × 60 m fused silica capillary column with a 5 % (mole fraction) phenyl methylpolysiloxane phase (0.25 µm film thickness) (DB-5, J&W Scientific, Folsom, CA). For GC-ECD (IIA) and GC-ECD (IIB), 4 g subsamples from each of six bottles were extracted using PFE with DCM. The SEC and normal-phase LC cleanup steps were the same as for GC-ECD (I). GC-ECD (IIA) analyses were performed on a 5 % phenyl methylpolysiloxane phase as described above, and GC-ECD (IIB) analyses were on a 0.25 mm × 60 m fused silica capillary column with nonpolar proprietary phase (0.25 µm film thickness) (DB-XLB, J&W Scientific). For both GC-ECD analyses, two PCB congeners that are not significantly present in the fish extract (PCB 103 and PCB 198), and 4,4'-DDT-d_8, 4,4'-DDE-d_8, 4,4'-DDD-d_8, and endosulfan I-d_4 were added to the fish tissue prior to extraction for use as internal standards for quantification purposes.

Three sets of results were obtained by GC/MS. For GC/MS (I) and GC/MS (II), 3 g subsamples from six bottles were mixed with 50 g of sodium sulfate and Soxhlet extracted for 20 h with a mixture of hexane:acetone (1:1 volume fraction). The concentrated extract was treated with concentrated sulfuric acid to remove the majority of the lipid material, followed by additional cleanup on a silica solid-phase extraction cartridge with 10 % (volume fraction) DCM in hexane. The extract was then analyzed by GC/MS using the two different columns described above and using different ionization modes for the mass spectrometric detection. GC/MS (I) was performed using the nonpolar proprietary phase (DB-XLB) with electron impact ionization (EI) and GC/MS (II) was performed using the 5 % phenyl methylpolysiloxane phase with negative ion chemical ionization (NICI). For the GC/MS analyses, PCB 103, PCB 198, and ^{13}C-labeled 4,4'-DDT, lindane, PCB 28, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 169 were added to the fish tissue prior to extraction for use as internal standards for quantification purposes.

For GC/MS (III) analyses, 1.5 g subsamples from three bottles of SRM 1946 were mixed with sodium sulfate and Soxhlet extracted with DCM for 16 h. The concentrated extract was subjected to SEC to remove lipid material, followed by additional cleanup on a silica SPE cartridge with 10 % DCM in hexane. The GC/MS (III) analyses were performed using the same column and EI MS detection as in GC/MS (I). PCB 103, PCB 198, and 4,4'-DDT-d_8 were added to the fish tissue prior to extraction for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1946 was used in an interlaboratory comparison exercise in 1999 as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine

Environment [10]. Results from 30 laboratories that participated in this exercise (see Appendix A) were used as the seventh data set in the determination of the certified values for PCB congeners and chlorinated pesticides in SRM 1946. The laboratories participating in this exercise used the analytical procedures routinely used in their laboratories to measure these analytes.

Non-*ortho*-Substituted PCBs: Three sets of results for non-*ortho*-substituted PCBs (NOPCBs) (PCB 77, PCB 126, and PCB169) were obtained using GC/MS after LC isolation of the NOPCB fraction [11]. For GC/MS (IV) and GC/MS (V), 1 g subsamples from nine bottles of SRM 1946 were mixed with sodium sulfate and extracted using PFE with DCM. The extracts were subjected to SEC to remove lipids followed by normal-phase LC on a semi-preparative aminopropylsilane column with hexane as the mobile phase to isolate the PCB fraction. The PCB fraction was then separated into a *ortho*-substitued PCB fraction and a NOPCB fraction using a 2-(pyrenyl)ethyldimethylsilylated silica (PYE) column (4.6 mm i.d. × 25 cm, 5 μm Comosil-PYE, Nacalai Tesque, Kyoto, Japan) with hexane as the mobile phase. The NOPCB fraction was then analyzed by GC/MS using NICI on a 0.25 mm i.d. × 30 m fused silica capillary column containing a 5 % (mole fraction) diphenyl dimethylpolysiloxane phase (HP-5, 0.25 μm film thickness, Hewlett-Packard, Palo Alto, CA) [denoted as GC/MS (IV)]. The same samples were also analyzed by GC with high resolution MS with EI on a 0.25 mm i.d. × 30 m fused silica capillary column containing a 5 % phenyl methylpolysiloxane phase (DB-5MS, 0.25 μm film thickness, J&W Scientific) [denoted as GC/MS (V)]. For GC/MS (VI) subsamples of 5 g from three bottles of SRM 1946 were extracted and the NOPCB fraction isolated as described above for GC/MS (IV) and (V). The NOPCB fractions were analyzed by GC/MS with NICI on a 0.25 mm i.d. × 60 m fused silica capillary column with a 5 % phenyl methylpolysiloxane phase (DB-5MS, 0.25 μm film thickness).

Homogeneity Assessment for PCB Congeners and Chlorinated Pesticides: The homogeneity of SRM 1946 was assessed by analyzing duplicate samples of 1 g from 10 bottles selected by stratified random sampling. Samples were extracted, processed, and analyzed as described above for GC-ECD (I). No statistically significant differences among bottles were observed for the PCB congeners and chlorinated pesticides at the 1 g sample size.

NFPA Interlaboratory Comparison Exercise: Results for proximates, extractable fat, fatty acids, and selected trace elements were obtained from an interlaboratory comparison exercise organized in 1999 by the National Food Processors Association (NFPA) Food Industry Analytical Chemists Subcommittee (FIACS; 11 participating laboratories, listed in Appendix B). The laboratories listed in Appendix B were asked to use AOAC methods or their equivalent, to make single measurements from each of two bottles, and to report the analytical method that was used. A summary of the methodological information and the number of laboratories using a particular analytical technique is provided in Appendix C. The methods used by NIST for these analytes are also included in this listing.

Extractable Fat Determination: The certified value for extractable fat was determined from the combination of results from analyses performed at NIST and the results from the NFPA interlaboratory comparison exercise as for previous food-matrix SRMs [12]. Two sets of results were obtained at NIST. Six samples were extracted with DCM using PFE and three samples were extracted with DCM using Soxhlet extraction. For both extraction sets, the extract was evaporatively concentrated to approximately 20 mL (known mass) and an aliquot of 90 μL was placed on an aluminum pan. The extract on the pan was air dried, and the mass of the dried extract determined. For the NFPA study, most of the laboratories used an acid digestion and ether extraction to obtain the extract and then determined the extractable fat by drying the extract and determining the mass of the remaining residue (see Appendix C).

Fatty Acids: The approach for value assignment of concentrations of individual fatty acids in SRM 1946 was similar to that reported for the recent certification of several food-matrix SRMs [12] and consisted of combining results from analyses at NIST using gas chromatography with flame ionization detection (GC-FID) with results from the NFPA interlaboratory comparison exercise.

For the NIST analyses, duplicate subsamples of approximately 2.5 g from each of nine bottles of SRM 1946 were analyzed in three sets of six samples over a three-day period. The fish tissue samples were mixed with diatomaceous earth and Soxhlet extracted for 18 h to 22 h with a mixture of 1:1 hexane:acetone. Prior to extraction a recovery standard, triheneicosanoin (C21 triglyceride), was added to the sample. Two fatty acid methyl esters (FAMEs), methyltridecanoate (C13:0 FAME) and methyltricosanoate (C23:0 FAME), were added to the extract for use as internal standards for quantification. The extract was then subjected to a two-step process employing methanolic sodium hydroxide and boron trifluoride to convert the fatty acids to their methyl esters (FAMEs). FAMEs were extracted into hexane, and analyzed by GC-FID on a 0.25 mm i.d. × 30 m fused capillary column with a 100 % poly(bis cyanopropylsiloxane) phase (SP-2340, 25 μm film thickness, Supelco, Bellefonte, PA).

Proximates: Results for proximates (solids, ash, protein, and fat) were obtained from the NFPA interlaboratory comparison exercise described above.

Methylmercury and Total Mercury: The general approach for the assignment of values for methylmercury and total mercury was similar to that used for these analytes in recent marine tissue SRMs [13,14]. The certified values for methylmercury and total mercury are based on results of analyses of SRM 1946 at NIST and two collaborating laboratories: the Institute of Applied Physical Chemistry, Research Centre Jülich (Jülich, Germany) and the Jožef Stefan Institute (Ljubljana, Slovenia). For the determination of methylmercury, SRM 1946 was analyzed at NIST using microwave digestion under acidic conditions, derivatization (phenylation), and preconcentration using solid-phase microextraction (SPME) followed by GC with atomic emission detection (GC-AED) [14,15]. The GC-AED analyses were performed using a nonpolar 0.32 mm × 25 m fused silica capillary column with a polydimethylsiloxane phase (0.17 µm film thickness) (HP-1, Hewlett Packard, Wilmington, DE). For detection, the emission lines of mercury at 254 nm and carbon at 264 nm were used. A total of 13 subsamples (0.5 g to 1 g) from 6 bottles of SRM 1946 were analyzed at NIST. At the Research Centre of Jülich the analytical procedure for methylmercury consisted of water steam distillation under acid conditions, anion exchange chromatographic separation of inorganic mercury and methylmercury, followed by cold vapor atomic absorption spectrometric (CVAAS) detection before and after ultraviolet radiation [16-18]. Triplicate subsamples (250 mg to 450 mg) from two bottles of SRM 1946 were analyzed. At the Jožef Stefan Institute, duplicate subsamples (≈500 mg) from six bottles of SRM 1946 were analyzed using solid-liquid extraction into toluene followed by GC-ECD [19,20].

For total mercury measurements at NIST, subsamples (300 mg to 500 mg) from six bottles of SRM 1946 were analyzed. The analytical procedure consisted of spiking with ^{201}Hg as an internal standard, microwave-assisted acid digestion of the tissue, followed by cold vapor generation coupled with inductively coupled plasma mass spectrometry (CV-ICP-MS) isotope ratio measurements as described by Christopher et al. [21]. For mercury determination at the Research Centre Jülich, triplicate subsamples of 350 mg to 600 mg from two bottles of SRM 1946 were digested with concentrated nitric acid in heated quartz vessels closed with a cap and then analyzed by CVAAS) [22]. At the Jožef Stefan Institute, duplicate subsamples (≈300 mg) from six bottles of SRM 1946 were digested with acid and analyzed by CVAAS [23,24].

Additional Trace Element Analyses: Value assignment of the concentrations of selected trace elements was accomplished by combining results of the analyses of SRM 1946 at NIST, U.S. Department of Agriculture (USDA) Food Composition Laboratory (Beltsville, MD), and one laboratory from the NPFA interlaboratory exercise. Analyses were performed at NIST using ICP-MS (cadmium, copper, iron, and selenium) and instrumental neutron activation analysis (INAA) (arsenic, iron, selenium, and zinc). For ICP-MS analyses, six subsamples (1 g) from one bottle were digested in 5 mL of concentrated nitric acid in closed vessels in a microwave oven. The digest was then analyzed by ICP-MS with rhodium as an internal standard. For INAA analyses, the contents of eight bottles of SRM 1946 were freeze-dried and ten subsamples (≈200 mg) were pelletized and analyzed as described previously [25].

USDA used inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, and zinc. One laboratory from the NFPA study provided results using ICP-OES (calcium, magnesium, and sodium) and flame atomic absorption spectrometry (FAAS) (copper, iron, manganese, potassium, and zinc).

Table 1. Certified Concentrations for Selected PCB Congeners

PCB Congener[a]			Mass Fraction µg/kg (wet-mass basis)[b]
PCB	44	(2,2',3,5'-Tetrachlorobiphenyl)[c,d,e,f,g,h]	4.66 ± 0.86
PCB	49	(2,2',4,5'-Tetrachlorobiphenyl)[c,d,e,f,g]	3.80 ± 0.39
PCB	52	(2,2',5,5'-Tetrachlorobiphenyl)[c,d,e,f,g,h]	8.1 ± 1.0
PCB	66	(2,3',4,4'-Tetrachlorobiphenyl)[f,g,h,i]	10.8 ± 1.9
PCB	70	(2,3',4',5-Tetrachlorobiphenyl)[c,e,f,i]	14.9 ± 0.6
PCB	74	(2,4,4',5-Tetrachlorobiphenyl)[c,e,f,i]	4.83 ± 0.51
PCB	77	(3,3',4,4'-Tetrachlorobiphenyl)[j,k,l]	0.327 ± 0.025[m]
PCB	87	(2,2',3,4,5'-Pentachlorobiphenyl)[c,d,f,g,i]	9.4 ± 1.4
PCB	95	(2,2',3,5',6-Pentachlorobiphenyl)[e,f,g,h]	11.4 ± 1.3
PCB	99	(2,2',4,4',5-Pentachlorobiphenyl)[c,d,e,f,g,i]	25.6 ± 2.3
PCB	101	(2,2',4,5,5'-Pentachlorobiphenyl)[c,d,f,g,h,i]	34.6 ± 2.6
PCB	105	(2,3,3',4,4'-Pentachlorobiphenyl) [c,d,e,f,g,h,i]	19.9 ± 0.9
PCB	110	(2,3,3',4',6-Pentachlorobiphenyl)[e,f,g,i]	22.8 ± 2.0
PCB	118	(2,3',4,4',5-Pentachlorobiphenyl)[c,d,e,f,g,h,i]	52.1 ± 1.0
PCB	126	(3,3',4,4',5-Pentachlorobiphenyl)[j,k,l]	0.380 ± 0.017[m]
PCB	128	(2,2',3,3',4,4'-Hexachlorobiphenyl)[c,e,f,g,h,i]	22.8 ± 1.9
PCB	138	(2,2',3,4,4',5'-Hexachlorobiphenyl)[d,f,g]	115 ± 13
PCB	146	(2,2',3,4',5,5'-Hexachlorobiphenyl[c,d,e,f,i]	30.1 ± 3.5
PCB	149	(2,2',3,4',5',6-Hexachlorobiphenyl)[c,d,e,f,g,i]	26.3 ± 1.3
PCB	153	(2,2',4,4',5,5'-Hexachlorobiphenyl)[c,d,e,f,g,h,i]	170 ± 9
PCB	156	(2,3,3',4,4',5-Hexachlorobiphenyl)[c,e,f,g,i]	9.52 ± 0.51
PCB	169	(2,2',3,4,4',5'-Hexachlorobiphenyl)[j,k,l]	0.106 ± 0.014[m]
PCB	170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)[c,d,e,f,g,h,i]	25.2 ± 2.2
PCB	180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)[c,d,e,f,g,h,i]	74.4 ± 4.0
PCB	183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)[c,d,f,g,i]	21.9 ± 2.5
PCB	187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)[c,d,f,g,h,i]	55.2 ± 2.1
PCB	194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl)[c,d,e,f,i]	13.0 ± 1.3
PCB	195	(2,2',3,3',4,4',5,6-Octachlorobiphenyl)[c,d,e,f,g,h,i]	5.30 ± 0.45
PCB	206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl)[c,d,e,f,g,h,i]	5.40 ± 0.43
PCB	209	(Decachlorobiphenyl)[c,d,e,f,g,h,i]	1.30 ± 0.21

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [26] and later revised by Schulte and Malisch [27] to conform with IUPAC rules; for the specific congeners listed in this table the Ballschmiter-Zell numbers correspond to those of Schulte and Malisch.

[b] The certified value is a weighted mean of the results from four to seven analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] incorporating inter-method bias with a pooled, within-method variance following the ISO/NIST Guides [2].

[c] GC-ECD (I) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.

[d] GC-ECD (IIB) on a proprietary nonpolar phase; same extracts analyzed as GC-ECD (IIA).

[e] GC-ECD (IIA) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.

[f] GC/MS (I) on a proprietary nonpolar phase after Soxhlet extraction with hexane/acetone mixture.

[g] GC/MS (III) on a proprietary nonpolar phase after Soxhlet extraction with DCM.

[h] Results from up to 30 laboratories participating in an interlaboratory comparison exercise.

[i] GC/MS (II) on a 5 % phenyl methylpolysiloxane phase; same extracts analyzed as GC/MS (I).

[j] GC/MS (IV) with NICI on 5 % diphenyl dimethylpolysiloxane phase.

[k] GC/HRMS (V) with EI on a 5 % phenyl methylpolysiloxane phase.

[l] GC/MS (VI) with NICI on a 5 % phenyl methylpolysiloxane phase.

[m] The certified value is an unweighted mean of the results from three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guides [2].

Table 2. Certified Concentrations for Selected Chlorinated Pesticides

	Mass Fraction[a] µg/kg (wet-mass basis)
Hexachlorobenzene[b,d,e,f,g,h]	7.25 ± 0.83
α-HCH[b,c,e,f,g]	5.72 ± 0.65[h]
γ-HCH[b,c,f,g]	1.14 ± 0.18
Heptachlor epoxide[b,c,e,f,g,i]	5.50 ± 0.23
Oxychlordane[b,d,e,f,g,i]	18.9 ± 1.5
cis-Chlordane (α-Chlordane)[b,c,e,f,g,i]	32.5 ± 1.8
trans-Chlordane[b,c,e,f,g,i]	8.36 ± 0.91
cis-Nonachlor[b,c,e,f,g,i]	59.1 ± 3.6
trans-Nonachlor[b,c,e,f,g,i]	99.6 ± 7.6
Dieldrin[b,c,f,g]	32.5 ± 3.5
Mirex[b,d,e,f,g]	6.47 ± 0.77
4,4'-DDE[b,c,e,f,g]	373 ± 48
2,4'-DDD[b,c,e,f,g]	2.20 ± 0.25
4,4'-DDD[b,c,e,f,g]	17.7 ± 2.8
4,4'-DDT[d,e,f,g]	37.2 ± 3.5

[a] The certified value is a weighted mean of the results from four to six analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] incorporating inter-method bias with a pooled, within-method variance following the ISO/NIST Guides [2].
[b] GC-ECD (I) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.
[c] GC-ECD (IIB) on a proprietary nonpolar phase; same extracts analyzed as GC-ECD (IIA).
[d] GC-ECD (IIA) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.
[e] GC/MS (I) on a proprietary nonpolar phase after Soxhlet extraction with hexane/acetone mixture.
[f] GC/MS (III) on a proprietary nonpolar phase after Soxhlet extraction with DCM.
[g] Results from up to 30 laboratories participating in an interlaboratory comparison exercise.
[h] The certified value is an unweighted mean of the results from five analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guides [2].
[i] GC/MS (II) on a 5 % phenyl methylpolysiloxane phase; same extracts analyzed as GC/MS (I).

Table 3. Certified Concentrations for Fat and Selected Fatty Acids

	Mass Fraction (%)[a] (wet-mass basis)
Fat (Extractable)	10.17 ± 0.48
Fat (Sum of Fatty Acids)[b]	8.76 ± 0.17

	Mass Fraction (%)[a] (as the triglyceride) (wet-mass basis)
Tetradecanoic Acid (C14:0) (Myristic Acid)	0.316 ± 0.009
Hexadecanoic Acid (C16:0) (Palmitic Acid)	1.22 ± 0.04
(Z)-9-Hexadecenoic Acid (C16:1) (Palmitoleic Acid)	0.816 ± 0.026
Octadecanoic Acid (C18:0) (Stearic Acid)	0.263 ± 0.011
(Z)-9-Octadecenoic Acid (C18:1) (Oleic Acid)[c]	2.64 ± 0.08
(Z,Z)-9,12-Octadecadienoic Acid (C18:2) (Linoleic Acid)	0.348 ± 0.023
(Z,Z,Z)-9,12,15-Octadecatrienoic Acid (C18:3) (Linolenic Acid)	0.221 ± 0.025
Eicosanoic Acid (C20:0) (Arachidic Acid)	0.0100 ± 0.0012
(Z)-11-Eicosenoic Acid (C20:1)	0.132 ± 0.012
(Z,Z)-11,14-Eicosadienoic Acid (C20:2)	0.0990 ± 0.0043
(Z,Z,Z,Z,Z)-5,8,11,14,17-Eicosapentaenoic Acid (C20:5) (EPA)	0.296 ± 0.019
(Z,Z,Z,Z,Z)-7,10,13,16,19-Docosapentaenoic Acid (C22:5) (DPA)	0.335 ± 0.026
(Z,Z,Z,Z,Z,Z)-4,7,10,13,16,19-Docosahexaenoic Acid (C22:6) (DHA)	0.92 ± 0.10

[a] The certified value is the unweighted mean of the mean of the average of results provided by laboratories listed in Appendix B and the mean of the NIST measurements. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guides [2].

[b] Fat as the sum of the fatty acids represents the sum of individual fatty acid concentrations reported in Tables 3, 7, and 9.

[c] Oleic acid is the major component measured; however, there may be minor contributions from other C18:1 fatty acids that coelute with the oleic acid.

Table 4. Certified Concentrations of Methylmercury, Total Mercury, Arsenic, and Iron

	Mass Fraction mg/kg (wet-mass basis)[a]
Methylmercury[b]	0.394 ± 0.015
Mercury (Total)	0.433 ± 0.009
Arsenic	0.277 ± 0.010
Iron	4.00 ± 0.32

[a] The certified value is an unweighted mean of the results from two or more analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[b] Results for methylmercury are reported as mg of mercury/kg.

Table 5. Reference Concentrations for Selected PCB Congeners and Pesticides

PCB Congeners[a]		Mass Fraction µg/kg (wet-mass basis)[b]
PCB 18	(2,2',5-Trichlorobiphenyl)[d,e]	0.84 ± 0.11
PCB 28	(2,4,4'-Trichlorobiphenyl)[d,e,f,g,h]	2.00 ± 0.24
PCB 31	(2,4',5-Trichlorobiphenyl)[c,d,f,g]	1.46 ± 0.20[i]
PCB 56	(2,3,3',4'-Tetrachlorobiphenyl)[c,d,f,j]	5.77 ± 0.93
PCB 63	(2,3,4',5-Tetrachlorobiphenyl)[c,e,f,j]	1.28 ± 0.19
PCB 107	(2,3,3',4',5-Pentachlorobiphenyl)[c,d,e,f,j]	8.86 ± 0.20
PCB 132	(2,2',3,3',4,6'-Hexachlorobiphenyl)[c,d,f,j]	5.83 ± 0.76
PCB 158	(2,3,3',4,4',6-Hexachlorobiphenyl)[c,d,f,j]	7.66 ± 0.88
PCB 163	(2,3,3',4',5,6-Hexachlorobiphenyl)[e,f,j]	31.8 ± 0.8[i]
PCB 174	(2,2',3,3',4,5,6'-Heptachlorobiphenyl)[c,d,e,f,j]	9.3 ± 1.3
PCB 193	(2,3',3,4',5,5',6-Heptachlorobiphenyl)[c,d,e,f,j]	5.78 ± 0.72
PCB 201	(2,2',3,3',4,5,5',6'-Octachlorobiphenyl)[f,j]	2.83 ± 0.13
Pesticides		
2,4'-DDE[c,f,g,h,j]		1.04 ± 0.29
2,4'-DDT[f,g,h]		22.3 ± 3.2

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [26] and later revised by Schulte and Malisch [27] to conform with IUPAC rules; for the specific congeners listed in this table, only PCB 107 and PCB 201 are different in the numbering systems. Under the Ballschmiter and Zell numbering system, the IUPAC PCB 107 is listed as PCB 108 and the IUPAC PCB 201 is listed as PCB 200.

[b] The reference value is a weighted mean of the results from two to five analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] incorporating inter-method bias with a pooled, within-method variance following the ISO/NIST Guides [2].

[c] GC-ECD (I) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.

[d] GC-ECD (IIB) on a proprietary nonpolar phase; same extracts analyzed as GC-ECD (IIA).

[e] GC-ECD (IIA) on 5 % phenyl methylpolysiloxane phase after PFE with DCM.

[f] GC/MS (I) on a proprietary nonpolar phase after Soxhlet extraction with hexane/acetone mixture.

[g] GC/MS (III) on a proprietary nonpolar phase after Soxhlet extraction with DCM.

[h] Results from up to 32 laboratories participating in an interlaboratory comparison exercise.

[i] Reference values are unweighted means of the results from three or four analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guides [2].

[j] GC/MS (II) on a 5 % phenyl methylpolysiloxane phase; same extracts analyzed as GC/MS (I).

Table 6. Reference Concentration Values for Fatty Acids

	Mass Fraction (%) (as the triglyceride) (wet-mass basis)
Dodecanoic Acid (C12:0) (Lauric Acid)	0.00555 ± 0.00051[a]
Pentadecanoic Acid (C15:0)	0.0285 ± 0.0016[b]
Heptadecanoic Acid (C17:0) (Margaric Acid)	0.0225 ± 0.0023[b]
(E)-9-Octadecenoic Acid (C18:1) (Elaidic Acid)	0.0098 ± 0.0010[c]
(Z)-11-Octadecenoic Acid (C18:1) (Vaccenic Acid)	0.373 ± 0.005[b]
(Z,Z,Z)-6,9,12-Octadecatrienoic Acid (C18:3) (gamma-linolenic Acid)	0.0149 ± 0.0031[b]
(Z,Z,Z,Z,)-6,9,12,15-Octadecatetraenoic Acid (C18:4) (Stearidonic Acid)	0.106 ± 0.013[b]
(Z,Z,Z)-11,14,17-Eicosatrienoic Acid (C20:3)	0.109 ± 0.018[b]
(Z,Z,Z,Z)-5,8,11,14-Eicosatetraenoic Acid (C20:4) (Arachidonic Acid)	0.212 ± 0.019[b]
(Z)-13-Docosenoic Acid (C22:1) (Erucic Acid)	0.0266 ± 0.0060[c]
(Z,Z)-13,16-Docosadienoic Acid (C22:2)	0.0369 ± 0.0011[b]
(Z)-15-Tetracosenoic Acid (C24:1) (Nervonic Acid)	0.0429 ± 0.0028[b]

[a] The reference value is the unweighted mean of the mean of the average of results provided by laboratories listed in Appendix B and the mean of the NIST measurements. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within method variance following the ISO/NIST Guides [2].

[b] The reference value is a weighted mean of the results provided by three to nine laboratories in Appendix B [29]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] incorporating inter-method bias with a pooled, within-method variance following the ISO/NIST Guides [2].

[c] Reference values are unweighted means of the results from three laboratories in Appendix B. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] with a pooled, within-method variance following the ISO/NIST Guides [2].

Table 7. Reference Concentration Values for Proximates and Caloric Content

	Mass Fraction (%)[a] (wet-mass basis)
Solids	28.6 ± 0.1
Ash	1.10 ± 0.04
Protein	17.8 ± 0.2
Calories[b]	(159 ± 4) kcal/100 g
Fat	(see Table 3)
Carbohydrates	(see Table 9)

[a] The reference value is a weighted mean of the results provided by the laboratories in Appendix B [29]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [28] incorporating inter-method bias with a pooled, within-method variance following the ISO/NIST Guides [2].

[b] The value for caloric content is the mean of individual caloric calculations from the laboratories listed in Appendix B. If the proximate values above are used for calculation, with caloric equivalents of 9, 4, and 4 for fat (as the sum of the fatty acids), protein, and carbohydrate, respectively, the mean caloric content is 154 kcal/100 g.

Table 8. Reference Concentration Values for Elements

	Mass Fraction (mg/kg)[a] (wet-mass basis)
Cadmium	0.00208 ± 0.00026[b]
Calcium	59.1 ± 1.5
Copper	0.476 ± 0.060
Magnesium	226 ± 18
Phosphorus	1980 ± 40
Potassium	3330 ± 180
Selenium	0.491 ± 0.043
Sodium	458 ± 25
Zinc	3.10 ± 0.18

[a] Reference values are unweighted means of the results from two or more analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance [29] with a pooled, within-method variance following the ISO/NIST Guides [2].

[b] The reference value for cadmium is the mean of results obtained by NIST using one analytical technique. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO/NIST Guides [2]. The coverage factor, k, is determined from the Student's t-distribution for the appropriate degrees of freedom to yield 95 % confidence.

Table 9. Information Concentration Values for Carbohydrates, Fatty Acids, and Elements

NOTE: Information values are typically provided with no uncertainty because of the lack of sufficient information to assess adequately the uncertainty associated with the value. It may be assumed that the uncertainty is relatively large.

	Mass Fraction (%) (wet-mass basis)
Carbohydrates	0.93

	Mass Fraction (%) (as the triglyceride) (wet-mass basis)
Hexadecadienoic Acid (C16:2)	0.032
(E)-9-Hexadecenoic Acid (C16:1) (Palmitelaidic Acid)	0.066
Heptadecenoic Acid (C17:1)	0.041
(E,E)-9,12-Octadecadienoic Acid (C18:2) (Linoelaidic Acid)	0.011

	Mass Fraction (mg/kg) (wet-mass basis)
Lead	0.7
Manganese	0.07

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Certificate Revision History: 29 September 2003 (Change in grams per bottle); 20 February 2003 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.

APPENDIX A

The laboratories listed below performed measurements that contributed to the value assignment for PCBs and pesticides in SRM 1946.

Arthur D. Little, Inc.; Cambridge, MA, USA
Axys Analytical Services; Sidney, BC, Canada
B & B Laboratories; College Station, TX, USA
Battelle Ocean Sciences; Duxbury, MA, USA
California Department of Fish and Game; Rancho Cordova, CA, USA
Central Contra Costa Sanitary District; Martinez, CA, USA
Chesapeake Biological Laboratory; Solomons, MD, USA
Centro de Investigaciones Energetices Medioambientales y Tecnologicas (CIEMAT); Madrid, Spain
City of Los Angeles, Environmental Monitoring Division; Playa del Rey, CA, USA
City of San Jose, Environmental Sciences Department; San Jose, CA, USA
Columbia Analytical Services; Kelso, WA
Environment Canada, Environmental Sciences Centre; Moncton, New Brunswick, Canada
U.S. Environmental Protection Agency (EPA), Atlantic Ecology Division; Narragansett, RI, USA
Florida Department of Environmental Protection; Tallahassee, FL, USA
Murray State University; Murray, KY, USA
Massachusetts Water Resources Authority Central Laboratory; Winthrop, MA, USA
National Oceanic and Atmospheric Administration, National Marine Fisheries Service (NOAA/NMFS), Center for Coastal Environmental Health and Biomolecular Research (CCEHBR); Charleston, SC, USA
NOAA/NMFS, Sandy Hook Marine Laboratory; Highlands, NJ, USA
NOAA/NMFS, Northwest Fisheries Science Center; Seattle, WA, USA
Orange County Sanitation District; Fountain Valley, CA, USA
Philip Analytical Services; Burlington, Ontario, Canada
Serv de Hidrografia Naval; Buenos Aires, Argentina
Skidaway Institute of Technology; Savannah, GA, USA
Southwest Laboratory of Oklahoma; Broken Arrow, OK, USA
Texas A & M University, Geochemical and Environmental Research Group (GERG); College Station, TX, USA
Texas Parks and Wildlife Department; San Marcos, TX, USA
University of Connecticut, Environmental Research Institute; Storrs, CT, USA
University of Rhode Island, Graduate School of Oceanography; Narragansett, RI, USA
U.S. Geological Survey, National Water Quality Laboratory; Denver, CO, USA
Wright State University; Dayton, OH, USA

APPENDIX B

The laboratories listed below performed measurements that contributed to the value assignment for proximates, caloric content, nutrients, extractable fat, and fatty acids in SRM 1946.

Covance Laboratories; Madison, WI, USA
Dionex Corporation; Salt Lake City, UT, USA (extractable fat only)*
General Mills, Inc.; Minneapolis, MN, USA
Hormel Foods Corporation; Austin, MN, USA
Kraft Foods, Glenview; IL, USA
Nabisco, Inc.; East Hanover, NJ, USA
Nestlé USA; Dublin, OH, USA
Novartis Nutrition Corporation; St. Louis Park, MN, USA
Pillsbury; St. Paul, MN, USA
Ralston Purina Company; St. Louis, MO, USA
U.S. Department of Agriculture, Food Composition Laboratory; Beltsville, MD, USA
Woodson-Tenent Laboratories; Memphis, TN, USA

* Not an NFPA FIACS laboratory

APPENDIX C

The methodological information reported by laboratories whose results were used for value assignment of proximates, caloric content, fatty acids, and trace elements is summarized below. The number of laboratories using a particular method is provided in parentheses.

Proximates, Fatty Acids, and Calories

Solids	Moisture determined by mass loss after oven-drying: Forced-air oven (3) Vacuum oven (7)
Ash	Mass loss after ignition in muffle furnace (10)
Extractable Fat	Acid digestion, ether extraction (8) Soxhlet extraction (2 + NIST) Pressurized-fluid extraction (1 + NIST)
Fatty Acids	Hydrolysis followed by gas chromatography (10 + NIST)
Nitrogen	Kjeldahl (5) Thermal conductivity (2) Pyrolysis, gas chromatography (1) Combustion (2)
Protein	Calculated; a factor of 6.25 was used to calculate protein from nitrogen results
Carbohydrates	Calculated; [solids – (protein + fat + ash)]
Calories	Calculated; [9(fat) + 4(protein) + 4(carbohydrates)]

Elements

Methods

FAAS	Flame atomic absorption spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ID-ICP-MS	Isotope dilution inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
CVAAS	Cold vapor atomic absorption spectrometry

Arsenic	ICP-MS (NIST), INAA (NIST)
Calcium	ICP-OES (2)
Cadmium	ICP-MS (NIST)
Copper	FAAS (1), ICP-OES (1), ICP-MS (NIST)
Iron	FAAS (1), ICP-OES (1), ICP-MS (NIST), INAA (NIST)
Magnesium	ICP-OES (2)
Manganese	FAAS (1), ICP-OES (1)
Mercury	ID-ICP-MS (NIST), CVAAS (2)
Phosphorus	ICP-OES (2)
Potassium	FAAS (1), ICP-OES (1)
Selenium	ICP-MS (NIST), INAA (NIST)
Sodium	ICP-OES (2)
Zinc	FAAS (1), ICP-OES (1), ICP-MS (NIST)

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1974b

Organics in Mussel Tissue (*Mytilus edulis*)

Standard Reference Material (SRM) 1974b is a frozen mussel tissue homogenate intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in marine bivalve mollusk tissue and similar matrices. All of the constituents for which certified and reference values are provided in SRM 1974b were naturally present in the tissue material before processing. A unit of SRM 1974b consists of five bottles each containing approximately 8 g to 10 g (wet basis) of frozen tissue homogenate.

Certified Concentration Values: Certified values for concentrations, expressed as mass fractions, for 22 PAHs, 31 PCB congeners, and 7 chlorinated pesticides are provided in Tables 1 to 3. The certified values for the PAHs, PCB congeners, and chlorinated pesticides are based on the agreement of results obtained at NIST from two or more chemically independent analytical techniques along with results from an interlaboratory comparison study [1,2]. A certified value for the concentration of total mercury, based on results from NIST and collaborating laboratories, is provided in Table 4. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

Reference Concentration Values: Reference values for concentrations, expressed as mass fractions, are provided for 16 additional PAHs (some in combination), 8 additional PCB congeners plus total PCBs, 6 additional chlorinated pesticides, total extractable organics (TEO), methylmercury, and 11 trace elements in Tables 4 to 8. Reference values are noncertified values that are the best estimate of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Expiration of Certification: The certification of this SRM lot is valid until **01 March 2013**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification is invalid if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive changes occur which affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to the certification of this material was under the leadership of M.M. Schantz and S.A. Wise of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.C. Colbert and B.S. MacDonald of the NIST Measurement Services Division.

Willie E. May, Chief
Analytical Chemistry Division

John Rumble, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 01 July 2003

Consultation on the statistical design of the experimental work and evaluation of the data were provided by S.D. Leigh of the NIST Statistical Engineering Division.

Collection and preparation of SRM 1974b were performed by M.P. Cronise and C.N. Fales of the NIST Standard Reference Materials Program and P.R. Becker, E.A. Mackey, B.J. Porter, R.S. Pugh, and W.D.J. Struntz of the NIST Analytical Chemistry Division. The mussels were collected with the assistance of W. Truly of Battelle Ocean Sciences Laboratory in Duxbury, MA.

Analytical measurements for the certification of SRM 1974b were performed at NIST by J.R. Kucklick, S.E. Long, B.J. Porter, D.L. Poster, and M.M. Schantz of the NIST Analytical Chemistry Division. Results were also used from laboratories that participated in the 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] coordinated by M.M. Schantz and from selected laboratories that participated in the 14th Intercomparison for Trace Elements in Marine Sediments and Biological Tissues [4] coordinated by S. Willie of the National Research Council (NRC) of Canada (see Appendix A for participating laboratories). Measurements for selected trace elements were performed at NRC Canada by J.W.H. Lam, C. Scriver, S. Willie, and L. Yang. Measurements for total mercury and methylmercury were performed at the Jožef Stefan Institute (Ljubljana, Slovenia) by M. Horvat, D. Gibiĉar, and Z. Kljakovic.

NOTICE AND WARNING TO USERS

Storage: SRM 1974b is packaged as a frozen tissue homogenate in glass bottles. The tissue homogenate should not be allowed to thaw prior to subsampling for analysis. If the tissue homogenate does thaw, the entire bottle should be used for analysis. This material has been stored at NIST at -80 °C (or lower) since it was prepared and should be stored by the user at this temperature, if possible, since the validity of the certified values is unknown when stored at higher temperatures.

Handling: This material is a frozen tissue homogenate. After extended storage at temperatures of -25 °C or higher, or if allowed to warm, the tissue homogenate will lose its powder-like form. For the handling of this material during sample preparation, the following procedures and precautions are recommended. If weighing relatively large quantities, remove a portion from the bottle and reweigh the bottle to determine the weight of the subsample. (Avoid heavy frost buildup by handling the bottles rapidly and wiping them prior to weighing.) For weighing, transfer subsamples to a pre-cooled thick-walled glass container rather than a thin-walled plastic container to minimize heat transfer to the sample. If possible, use a cold work space, e.g., an insulated container with dry ice or liquid nitrogen coolant on the bottom and pre-cooled implements, such as Teflon© coated spatulas, for transferring the powder. Normal biohazard safety precautions for the handling of biological tissues should be exercised.

Instructions for Use: Subsamples of this SRM for analysis should be withdrawn from the bottle immediately after opening and used without delay for the certified values listed in Tables 1 to 3 to be valid within the stated uncertainties. The concentrations of constituents in SRM 1974b are reported on both a wet-mass and a dry-mass basis for user convenience. The SRM tissue homogenate, as received, contains approximately 90 % moisture. A separate subsample of the SRM should be removed from the bottle at the time of analysis and dried to determine the concentration on a dry-mass basis.

PREPARATION AND ANALYSIS[1]

Sample Collection and Preparation: The mussels (*Mytilus edulis*) used for the preparation SRM 1974b were collected October 27, 1999 from Dorchester Bay within Boston (MA) Harbor (42°18.25'N and 72°02.31'W) following the same procedures as described previously for the collection of mussels for SRM 1974 and SRM 1974a [5,6]. Approximately 6300 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 placed in insulted 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 °C) until they were shucked.

[1] Certain commercial equipment, instruments, or materials are identified in this certificate in order 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 necessarily the best available for the purpose.

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 0.5 kg per bag) and immediately returned to a liquid nitrogen freezer. Approximately 59 kg of mussel tissue was prepared for use as the SRM. The frozen mussel tissue was pulverized in batches of approximately 700 g each using a cryogenic procedure described previously [7]. The pulverized material was then homogenized in an aluminum mixing drum in two batches of approximately 30 kg each. 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 (approximately 8 g to 10 g) of the mussel tissue homogenate were aliquoted into cleaned, pre-cooled glass bottles.

Conversion to Dry-Mass Basis: The moisture content of the mussel homogenate was determined by measuring the mass loss after freeze drying. Ten bottles of SRM 1974b were selected according to a stratified randomization scheme for the drying study. The entire contents of each glass bottle were transferred to a Teflon© bottle and dried for seven days at 1 Pa with a -20 °C shelf temperature and a -50 °C condenser temperature. The moisture content in SRM 1974b at the time of the certification analyses was 89.87 % ± 0.05 % (95 % confidence level). Analytical results for the organic constituents were determined on a wet-mass basis and then converted to a dry-mass basis by dividing by the conversion factor of 0.1013 (g dry mass/g wet mass). The trace elements, other than mercury, were determined on a dry-mass basis and then converted to a wet-mass basis by multiplying by the conversion factor of 0.1013 (g dry mass/g wet mass).

Polycyclic Aromatic Hydrocarbons: The general approach used for the value assignment of the PAHs in SRM 1974b was similar to that reported for the recent certification of several environmental matrix SRMs [6,8,9,10] and consisted of combining results from analyses using various combinations of different extraction techniques and solvents, cleanup/isolation procedures, and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction and pressurized fluid extraction (PFE) using dichloromethane (DCM) or a hexane/acetone mixture, cleanup of the extracts using size exclusion chromatography (SEC) and/or solid phase extraction (SPE), followed by analysis using gas chromatography/mass spectrometry (GC/MS) analysis of the PAH fraction on two stationary phases of different selectivity, i.e., a 50 % (mole fraction) phenyl-substituted methylpolysiloxane phase and a relatively non-polar proprietary phase.

Six sets of GC/MS results, designated as GC/MS (I) through GC/MS (V) were obtained using two columns with different selectivities for the separation of PAHs. For GC/MS (I) analyses, duplicate subsamples of between 2 g and 3 g from 10 bottles of SRM 1974b were extracted using PFE with 50 % hexane and 50 % acetone (volume fraction) [11]. The concentrated extract was passed through a silica SPE cartridge and eluted with 10 % DCM in hexane. Following concentration, the silica SPE step was repeated. The processed extract was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a relatively non-polar proprietary phase (0.25 µm film thickness) (DB-XLB, J&W Scientific, Folsom, CA). This method is designated as GC/MS (Ia). For GC/MS (1b), the same extracts were analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with 50 % (mole fraction) phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-17MS, J&W Scientific, Folsom, CA). The GC/MS (II) analyses were performed using subsamples of 8 g to 10 g from six bottles of SRM 1974b. These samples were extracted using PFE with DCM. The high molecular mass compounds (i.e, lipids and biogenic material) were removed from the extracts using SEC with a preparative-scale divinylbenzene-polystyrene column (10 µm particle size with 100 Å diameter pores), and the concentrated extract was passed through an aminopropyl SPE cartridge and eluted with 10 % DCM in hexane. GC/MS analysis was performed using a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-17MS). For the GC/MS (III) analyses, approximately 10 g subsamples from six bottles of SRM 1974b were Soxhlet extracted for 18 h with 250 mL of DCM. The extracts was cleaned up using SEC as described above, and the concentrated extract was passed through a silica SPE cartridge and eluted with 2 % DCM in hexane. The processed extract was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a relatively non-polar proprietary phase (0.25 µm film thickness) (DB-XLB) and a 50 % phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-17 MS). The GC/MS (IV) method used 9 g subsamples from three bottles of SRM 1974b with the same clean-up and analysis method as GC/MS (Ia) while the GC/MS (V) method used 9 g subsamples from three bottles of SRM 1974b with the same clean-up and analysis method as GC/MS (II). For the GC/MS measurements described above, selected perdeuterated PAHs were added to the mussel tissue homogenate prior to solvent extraction for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1974b was used in an interlaboratory comparison exercise in 2000 as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment [3]. Results from 16 laboratories that participated in this exercise were used as the seventh data set in the determination of the certified values for PAHs in SRM 1974b. The laboratories participating in this exercise employed the analytical procedures routinely used in their laboratories to measure PAHs.

Homogeneity Assessment for PAHs: The homogeneity of SRM 1974b was assessed by analyzing duplicate samples of between 2 g and 3 g from 10 bottles selected by stratified random sampling. Samples were extracted, processed, and analyzed as described above for GC/MS (Ia and Ib). No statistically significant differences among bottles were observed for the PAHs at this sample size.

PCBs and Chlorinated Pesticides: The general approach used for the determination of PCBs and chlorinated pesticides in SRM 1974b was similar to that reported for the recent certification of several environmental matrix SRMs [6,8-10,12-14], and consisted of combining results from analyses using various combinations of different extraction techniques and solvents, cleanup/isolation procedures, and chromatographic separation and detection techniques. This approach consisted of Soxhlet extraction and PFE using DCM or a hexane/acetone mixture, cleanup/isolation using SEC, SPE or liquid chromatography (LC), followed by analysis using GC/MS and gas chromatography with electron capture detection (GC-ECD) on three columns with different selectivity for the separation of PCBs and chlorinated pesticides.

Eight sets of results were obtained designated as GC/MS (Ia and Ib), GC/MS (II), GC-ECD (Ia and Ib), GC-ECD (II), GC-ECD (III), and Interlaboratory Comparison Exercise. For GC/MS (Ia and Ib), duplicate subsamples of between 2 g and 3 g from 10 bottles of SRM 1974b were extracted using PFE with 50 % hexane and 50 % acetone (volume fraction). The concentrated extract was passed through a silica SPE cartridge and eluted with 10 % DCM in hexane. Following concentration of the extract, the silica SPE step was repeated. The processed extract was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a relatively non-polar proprietary phase (0.25 µm film thickness) (DB-XLB). This method is designated as GC/MS (Ia). For GC/MS (1b), the same extracts were analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with 50 % (mole fraction) phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-17MS). For GC/MS (II), subsamples of 9 g from three bottles of SRM 1974b were extracted using Soxhlet extraction with DCM. The concentrated extracts were processed as described above for GC/MS I and then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a relatively nonpolar proprietary phase (0.25 µm film thickness) (DB-XLB, J&W Scientific, Folsom, CA). For the GC/MS analyses, selected carbon-13 labeled PCB congeners and chlorinated pesticides were added to the mussel tissue homogenate prior to extraction for use as internal standards for quantification purposes.

For GC-ECD (Ia and Ib), subsamples of between 8 g and 10 g from six bottles of SRM 1974b were extracted using PFE with DCM, followed by SEC, as described above for the PAHs, to remove the high molecular mass compounds. The concentrated extracts were then passed through an aminopropyl SPE cartridge and eluted with 10 % DCM in hexane. The concentrated extract was fractionated on a semi-preparative aminopropylsilane LC column to isolate two fractions containing: (1) the PCBs and lower polarity pesticides and, (2) the more polar pesticides. 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 0.25 mm × 60 m fused silica capillary column with a nonpolar proprietary phase (0.25 µm film thickness) (DB-XLB). The results from the 5 % phenyl phase are designated as GC-ECD (Ia) and the results from the proprietary phase are designated as GC-ECD (Ib). The GC-ECD (II) analyses used Soxhlet extraction with DCM followed by SEC to remove the high molecular mass compounds and fractionation of the extract using the semi-preparative aminopropylsilane LC column described for GC-ECD (I). The GC-ECD analysis used a 0.25 mm × 60 m fused silica capillary column with a 5 % phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-5). The GC-ECD (III) method used 9 g subsamples from three bottles of SRM 1974b extracted, processed, and analyzed as described above for GC-ECD (I). For the GC-ECD analyses, two PCB congeners that are not significantly present in the mussel tissue extract (PCB 103 and PCB 198 [25,26]), and endosulfan I-d_4, 4,4'-DDE-d_8, 4,4'-DDD-d_8, and 4,4'-DDT-d_8 were added to the mussel tissue homogenate prior to extraction for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1974b was used in an interlaboratory comparison exercise in 2000 as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment [3]. Results from 16 laboratories that participated in this exercise were used as the eighth data set in the determination of the certified values for PCB congeners and chlorinated pesticides in SRM 1974b. The laboratories participating in this exercise employed the analytical procedures routinely used in their laboratories to measure PCB congeners and chlorinated pesticides.

The reference value for PCB 77 (3,3',4,4'-tetrachlorobiphenyl) was determined from the GC-ECD (I) samples. The first fraction (PCBs and lower polarity pesticides) from the semi-preparative aminopropylsilane column was further fractionated using a Cosmosil PYE column (5 µm particle size, 4.6 mm i.d. × 25 cm, Phenomenex, Torrance, CA) [15].

Three fractions were collected: the first fraction contained the pesticides and multi-*ortho* PCBs, the second fraction contained the polychlorinated naphthalenes, non-*ortho* PCB congeners, and some mono-*ortho* PCB congeners, and the third fraction removed the residual planar compounds from the column. The second fraction was 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-5MS, J&W Scientific, Folsom, CA). Carbon-13 labeled PCB 77 was used as an internal standard for quantification purposes.

Homogeneity Assessment for PCBs and Chlorinated Pesticides: The homogeneity of SRM 1974b was assessed by analyzing duplicate samples of between 2 g and 3 g from 10 bottles selected by stratified random sampling. Samples were extracted, processed, and analyzed as described above for GC/MS (Ia and Ib). No statistically significant differences among bottles were observed for the chlorinated analytes at this sample size.

Total PCBs and Total Extractable Organics: A subset of laboratories participated in an interlaboratory comparison study for total PCBs and total extractable organics (TEO) in SRM 1974b. The methods used by the four laboratories reporting total PCBs were: sum of congeners using GC/MS; determination of 112 congeners using GC-ECD; calibration of GC-ECD using Aroclors 1242, 1248, 1254, and 1260; and use of an individual congener for each homolog group to calibrate the GC/MS and then summing the homolog groups.

The TEO values were determined gravimetrically by six laboratories after extraction using the following conditions: PFE with DCM (2 laboratories), Soxhlet extraction with DCM (2 laboratories), Soxhlet extraction with hexane (1 laboratory), and PFE with a DCM/acetone mixture (1 laboratory).

Methylmercury and Total Mercury: The certified value for total mercury is based on results of analyses of SRM 1974b at NIST, the Jožef Stefan Institute (Ljubljana, Slovenia), NRC Canada, and selected participants in an interlaboratory comparison exercise coordinated by NRC Canada. For total mercury measurements at NIST, subsamples of ≈500 mg from six bottles of SRM 1974b were analyzed. The analytical procedure consisted of spiking with ^{201}Hg as an internal standard, microwave-assisted acid digestion of the tissue, followed by cold vapor generation coupled with inductively coupled plasma mass spectrometry (CV-ICP-MS) isotope ratio measurements as described previously [16]. At the Jožef Stefan Institute triplicate subsamples (≈500 mg) from six bottles of SRM 1974b were digested with acid and analyzed by cold vapor atomic absorption spectrometry (CVAAS) [17,18]. At NRC Canada, total mercury was determined by analyzing five subsamples (≈250 mg dry mass) using microwave-assisted acid digestion followed by CVAAS. Results from four selected laboratories participating in the NRC Canada intercomparison exercise [4] (see below) were also used in the value assignment for total mercury.

The reference value for methylmercury is based on results from two methods performed at the Jožef Stefan Institute. For the first method, triplicate subsamples (≈500 mg) from six bottles of SRM 1974b were analyzed using solid-liquid extraction into toluene followed by GC-ECD [19,20]. The second analytical method for methylmercury (subsamples of ≈500 mg from six bottles) consisted of acid digestion, anion exchange chromatographic separation of inorganic mercury and methylmercury, followed by CVAAS detection before and after ultraviolet radiation [21,22].

Additional Trace Element Analyses: SRM 1974b was freeze-dried and used in an interlaboratory comparison study coordinated by the NRC Canada [4]. The laboratories participating in this exercise employed the analytical procedures routinely used in their laboratories to measure the selected trace elements. Value assignment for the concentrations of the trace elements was accomplished by combining the results from the analyses of the freeze-dried sample of SRM 1974b from (1) NRC Canada using isotope dilution ICP-MS, graphite furnace atomic absorption spectrometry (GFAAS), and/or inductively coupled plasma atomic emission spectroscopy (ICP-AES) and (2) the mean of the results from six selected laboratories that participated in the NRC Canada interlaboratory study [4] using a variety of analytical techniques (laboratories listed in Appendix A).

Table 1. Certified Concentrations for Selected PAHs in SRM 1974b

	Mass Fractions in µg/kg[a]	
	Wet-Mass Basis	Dry-Mass Basis
Naphthalene[d,e,f,g,h,i,j]	2.43 ± 0.12[b]	24.0 ± 1.2[b]
Fluorene[d,e,f,g,h,i,j]	0.494 ± 0.036[b]	4.88 ± 0.36[b]
Phenanthrene[d,e,f,g,h,i ,j]	2.58 ± 0.11[b]	25.5 ± 1.1[b]
Anthracene[d,e,f,g,h,i,j]	0.527 ± 0.071[c]	5.20 ± 0.71[c]
1-Methylphenanthrene[d,e,f,g,h,i,j]	0.98 ± 0.13[c]	9.66 ± 1.3[c]
2-Methylphenathrene[d,e,f,g]	1.28 ± 0.31[b]	24.0 ± 1.2[b]
3-Methylphenanthrene[d,e,g]	1.27 ± 0.04[c]	12.5 ± 0.4[c]
Fluoranthene[d,e,f,g,h,i,j]	17.1 ± 0.7[b]	169 ± 7[b]
Pyrene[d,e,f,g,h,i,j]	18.04 ± 0.6[b]	178 ± 6[b]
Benz[*a*]anthracene[d,e,f,g,h,i,j]	4.74 ± 0.53[b]	46.8 ± 5.2[b]
Chrysene[d,g,h]	6.3 ± 1.0[b]	62.2 ± 9.9[b]
Triphenylene[d,g,h]	4.33 ± 0.72[b]	42.7 ± 7.1[b]
Benzo[*b*]fluoranthene[e,f,g,h,i,j]	6.46 ± 0.59[b]	63.8 ± 5.8[b]
Benzo[*j*]fluoranthene[e,f,g,h,i]	2.99 ± 0.29[b]	29.5 ± 2.9[b]
Benzo[*k*]fluoranthene[d,e,f,g,h,i,j]	3.16 ± 0.18[b]	31.2 ± 1.8[b]
Benzo[*a*]fluoranthene[d,e,f,g]	0.634 ± 0.074[b]	6.26 ± 0.73[b]
Benzo[*e*]pyrene[d,e,f,g,h,i,j]	10.3 ± 1.1[b]	102 ± 11[b]
Benzo[*a*]pyrene[d,e,f,g,h,i,j]	2.80 ± 0.38[b]	27.6 ± 3.8[b]
Perylene[d,e,f,g,h,i,j]	0.99 ± 0.14[b]	9.8 ± 1.4[b]
Benzo[*ghi*]perylene[d,e,f,g,h,i,j]	3.12 ± 0.33[b]	30.8 ± 3.3[b]
Indeno[1,2,3-*cd*]pyrene[d,e,f,g,h,i,j]	2.14 ± 0.11[b]	21.1 ± 1.1[b]
Dibenz[*a,h*]anthracene[e,f,g,h,i]	0.327 ± 0.031[c]	3.23 ± 0.31[c]

[a] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[b] Certified values are weighted means of the results from three to seven analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[c] The certified value is an unweighted mean of the results from three to seven analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2]. Note for anthracene and 1-methylphenanthrene the within method variance for the interlaboratory study was not used for the calculation of the expanded uncertainty.

[d] GC/MS (Ia) on a relatively nonpolar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[e] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[f] GC/MS (II) on 50 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[g] GC/MS (III) on a relatively nonpolar proprietary phase and 50 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[h] GC/MS (IV) on a relatively nonpolar proprietary phase after Soxhlet extraction with DCM.

[i] GC/MS (V) on 50 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[j] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

Table 2. Certified Concentrations for Selected PCB Congeners[a] in SRM 1974b

		Mass Fractions in µg/kg[b]	
		Wet-Mass Basis	Dry-Mass Basis
PCB 18	(2,2',5-Trichlorobiphenyl)[e,f,g,h,i,j,k,l]	0.84 ± 0.13[c]	8.30 ± 1.3[c]
PCB 28	(2,4,4'-Trichlorobiphenyl)[e,f,g,h,j.k.l]	3.43 ± 0.25[c]	33.9 ± 2.5[c]
PCB 31	(2,4',5-Trichlorobiphenyl)[e,f,g,h,i,j,k,l]	2.88 ± 0.23[c]	28.4 ± 2.3[c]
PCB 44	(2,2'3,5'-Tetrachlorobiphenyl)[e,f,g,h,i,j,k,l]	3.85 ± 0.20[c]	38.0 ± 2.0[c]
PCB 49	(2,2'4,5'-Tetrachlorobiphenyl)[e,f,g,h,i,j,k,l]	5.66 ± 0.23[c]	55.9 ± 2.3[c]
PCB 52	(2,2',5,5'-Tetrachlorobiphenyl)[e,f,g,h,i,j,k,l]	6.26 ± 0.37[c]	61.8 ± 3.7[c]
PCB 66	(2,3',4,4'-Tetrachlorobiphenyl)[e,f,g,h,j,k,l]	6.37 ± 0.37[c]	62.9 ± 3.7[c]
PCB 70	(2,3',4',5-Tetrachlorobiphenyl)[e,f,h,i]	6.01 ± 0.22[d]	59.3 ± 2.2[d]
PCB 74	(2,4,4',5-Tetrachlorobiphenyl)[e,f,h,i]	3.55 ± 0.23[c]	35.0 ± 2.3[c]
PCB 82	(2,2',3,3',4-Pentachlorobiphenyl)[e,f,g,i]	1.16 ± 0.14[c]	11.5 ± 1.4[c]
PCB 87	(2,2',3,4,5'-Pentachlorobiphenyl)[e,f,i]	4.33 ± 0.36[d]	42.7 ± 3.6[d]
PCB 95	(2,2',3,5',6-Pentachlorobiphenyl)[e,f,g,h,j,k,l]	6.04 ± 0.36[c]	59.6 ± 3.6[c]
PCB 99	(2,2',4,4',5-Pentachlorobiphenyl)[e,f,g,h,i,j,k,l]	5.92 ± 0.27[c]	58.4 ± 2.7[c]
PCB 101	(2,2',4,5,5'-Pentachlorobiphenyl)[e,f,h,i,j,k,l]	10.7 ± 1.1[c]	106 ± 11[c]
PCB 105	(2,3,3',4,4'-Pentachlorobiphenyl)[e,f,g,h,i,j,k,l]	4.00 ± 0.18[c]	39.5 ± 1.8[c]
PCB 107	(2,3,3',4,5'-Pentachlorobiphenyl)[e,f,g,h,i]	1.03 ± 0.12[c]	10.2 ± 1.2[c]
PCB 110	(2,3,3',4',6-Pentachlorobiphenyl)[e,f,h]	10.0 ± 0.7[c]	99.1 ± 7.1[c]
PCB 118	(2,3',4,4',5-Pentachlorobiphenyl)[e,f,g,h,i,j,k,l]	10.3 ± 0.4[c]	102 ± 4[c]
PCB 128	(2,2',3,3',4,4'-Hexachlorobiphenyl)[e,f,g,h,i,j,k,l]	1.79 ± 0.12[c]	17.7 ± 1.2[c]
PCB 132	(2,2',3,3',4,6'-Hexachlorobiphenyl)[e,f,g,h,i]	2.43 ± 0.25[c]	24.0 ± 2.5[c]
PCB 138	(2,2',3,4,4',5'-Hexachlorobiphenyl)[e,f,h,j,k,l]	9.2 ± 1.4[c]	91 ± 14[c]
PCB 146	(2,2',3,4',5,5'-Hexachlorobiphenyl)[e,f,g,h]	1.92 ± 0.16[c]	19.0 ± 1.6[c]
PCB 149	(2,2',3,4',5',6-Hexachlorobiphenyl)[e,f,h,i,j,k,l]	7.01 ± 0.28[c]	69.2 ± 2.8[c]
PCB 151	(2,2',3,5,5',6-Hexachlorobiphenyl)[e,f,g,i]	1.86 ± 0.16[c]	18.4 ± 1.6[c]
PCB 153	(2,2',4,4',5,5'-Hexachlorobiphenyl)[e,f,g,h,i,j,k,l]	12.3 ± 0.8[c]	121 ± 8[c]
PCB 156	(2,3,3',4,4',5-Hexachlorobiphenyl)[e,f,h,j,k,l]	0.718 ± 0.080[c]	7.09 ± 0.79[c]
PCB 158	(2,3,3',4,4',6-Hexachlorobiphenyl)[e,g,h,i]	0.999 ± 0.096[c]	9.86 ± 0.95[c]
PCB 170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)[e,f,h,j,k,l]	0.269 ± 0.034[c]	2.66 ± 0.34[c]
PCB 180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)[e,f,g,h,i,j,k,l]	1.17 ± 0.10[c]	11.5 ± 1.0[c]
PCB 183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)[e,f,g,h,i]	1.25 ± 0.03[c]	12.3 ± 0.3[c]
PCB 187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)[e,f,g,h,i,j,k,l]	2.94 ± 0.15[c]	29.0 ± 1.5[c]

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [25] and later revised by Schulte and Malisch [26] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, only PCB 107 is different in the numbering systems. Under the Ballschmiter and Zell numbering system, the IUPAC PCB 107 is listed as PCB 108.

[b] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[c] Certified values are weighted means of the results from three to eight analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[d] The certified value is an unweighted mean of the results from three analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[e] GC/MS (Ia) on a relatively nonpolar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[f] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[g] GC-ECD (Ia) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[h] GC-ECD (Ib) on a relatively nonpolar proprietary phase; same extracts as GC-ECD (Ia).

[i] GC-ECD (II) on a 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[j] GC/MS (II) on a relatively nonpolar proprietary phase after Soxhlet extraction with DCM.

[k] GC-ECD (III) on a 5 % phenyl-substituted methylpolysiloxane phase and a relatively non-polar proprietary phase after PFE with DCM.

[l] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

Table 3. Certified Concentrations for Selected Chlorinated Pesticides in SRM 1974b

	Mass Fractions in µg/kg[a,b]					
	Wet-Mass Basis			Dry-Mass Basis		
cis-Chlordane[c,d,e,f,g,h,i,j]	1.36	±	0.10	13.4	±	1.0
trans-Chlordane[c,d,e,f,g,h,i,j]	1.14	±	0.17	11.3	±	1.7
trans-Nonachlor[c,d,e,f,g,h,i,j]	1.30	±	0.14	12.8	±	1.4
2,4’-DDE[c,d,h,i,j]	0.336	±	0.044	3.32	±	0.43
4,4’-DDE[c,d,e,f,g,h,i,j]	4.15	±	0.38	41.0	±	3.8
2,4’-DDD[c,d,e,f,h,i,j]	1.09	±	0.16	10.8	±	1.6
4,4’-DDD[c,d,e,f,g,h,i,j]	3.34	±	0.22	33.0	±	2.2

[a] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[b] Certified values are weighted means of the results from five to eight analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[c] GC/MS (Ia) on a relatively non-polar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[d] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[e] GC-ECD (Ia) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[f] GC-ECD (Ib) on a relatively non-polar proprietary phase; same extracts as GC-ECD (Ia).

[g] GC-ECD (II) on a 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[h] GC/MS (II) on a relatively non-polar proprietary phase after Soxhlet extraction with DCM.

[i] GC-ECD (III) on a 5 % phenyl-substituted methylpolysiloxane phase and a relatively non-polar proprietary phase after PFE with DCM.

[j] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

Table 4. Certified and Reference Concentrations for Total Mercury and Methylmercury in SRM 1974b

	Mass Fraction in µg/kg[a]					
	Wet-Mass Basis			Dry-Mass Basis		
Total Mercury[b]	17.0	±	1.1[b]	167	±	11[b]
Methylmercury[c]	7.05	±	0.44[c]	69.6	±	4.3[c]

[a] The concentrations are reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[b] The certified value for total mercury is the weighted mean of four results [23] from the following: (1) ICP-MS analyses performed at NIST, (2) ICP-MS analyses performed at NRC Canada, (3) the mean of results from four selected laboratories participating in the NRC Canada 14th Intercomparison for Trace Elements in Marine Sediments and Biological Tissues [4], and (4) results from CV-AAS performed at the Jožef Stefan Institute. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[c] The reference value for methylmercury is an unweighted mean of the results from CV-AAS and GC-ECD performed at the Jožef Stefan Institute. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

Table 5. Reference Concentrations for Selected PAHs in SRM 1974b

	Mass Fractions in μg/kg[a]	
	Wet-Mass Basis	Dry-Mass Basis
1-Methylnaphthalene[e,f,g,h,i,j,k]	0.614 ± 0.050[b]	6.06 ± 0.49[b]
2-Methylnaphthalene[e,f,g,h,i,j,k]	1.25 ± 0.09[b]	12.3 ± 0.9[b]
2,6-Dimethylnaphthalene[e,f,g,h,i,j,k]	0.33 ± 0.16[b]	3.3 ± 1.6[b]
2,3,5-Trimethylnaphthalene[e,f,g,h,i,j,k]	0.400 ± 0.032[b]	3.95 ± 0.32[b]
Biphenyl[e,f,g,h,i,j,k]	0.61 ± 0.14[b]	6.0 ± 1.4[b]
Acenaphthylene[e,f,g,h,i,j,k]	0.48 ± 0.12[b]	4.7 ± 1.2[b]
Acenaphthene[e,f,g,h,i,j,k]	0.274 ± 0.054[b]	2.70 ± 0.53[b]
4-Methylphenanthrene and 9-Methylphenanthrene[g,h]	1.60 ± 0.18[b]	15.8 ± 1.8[b]
2-Methylanthracene[e,f]	0.232 ± 0.004[c]	2.29 ± 0.04[c]
Cyclopenta[*cd*]pyrene[h]	0.227 ± 0.010[d]	2.24 ± 0.10[d]
Benzo[*c*]phenanthrene[e,f,h]	1.85 ± 0.21[b]	18.3 ± 2.1[b]
Benzo[*b*]chrysene[h]	0.507 ± 0.030[d]	5.00 ± 0.30[d]
Benzo[*c*]chrysene[g,h]	0.318 ± 0.042[b]	3.14 ± 0.42[b]
Dibenz[*a,c*]anthracene[f,g]	0.212 ± 0.013[c]	2.09 ± 0.13[c]
Dibenz[*a,j*]anthracene[g,h]	0.467 ± 0.048[b]	4.61 ± 0.47[b]
Picene[g,h]	0.75 ± 0.16[b]	7.4 ± 1.6[b]

[a] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[b] The reference value is a weighted mean of the results from two to seven analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[c] The reference value is an unweighted mean of the results from two analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[d] The reference value is the mean of results obtained by NIST using one analytical technique. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO Guide [2]. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

[e] GC/MS (Ia) on a relatively nonpolar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[f] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[g] GC/MS (II) on 50 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[h] GC/MS (III) on a relatively nonpolar proprietary phase and 50 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[i] GC/MS (IV) on a relatively nonpolar proprietary phase after Soxhlet extraction with DCM.

[j] GC/MS (V) on 50 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[k] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

Table 6. Reference Concentrations for Selected PCB Congeners[a] and Total PCBs in SRM 1974b

		Mass Fractions in µg/kg [b] Wet-Mass Basis	Dry-Mass Basis
PCB 8	(2,4'-Dichlorobiphenyl)[f,g]	0.37 ± 0.11[c]	3.7 ± 1.1[c]
PCB 45	(2,2',3,6-Tetrachlorobiphenyl)[f,h,i,j]	0.50 ± 0.18[d]	4.9 ± 1.8[d]
PCB 56	(2,3,3',4-Tetrachlorobiphenyl)[f,h,i,k]	2.82 ± 0.56[d]	27.8 ± 5.5[d]
PCB 63	(2,3,4',5-Tetrachlorobiphenyl)[f,h,j,k]	0.46 ± 0.14[d]	4.5 ± 1.4[d]
PCB 77	(3,3',4,4'-Tetrachlorobiphenyl)[l]	0.563 ± 0.023[e]	5.56 ± 0.23[e]
PCB 92	(2,2',3,5,5'-Pentachlorobiphenyl)[f,h,i,k]	2.76 ± 0.58[d]	27.2 ± 5.7[d]
PCB 157	(2,3,3',4,4',5'-Hexachlorobiphenyl)[f,h,i]	0.236 ± 0.024[d]	2.33 ± 0.24[d]
PCB 163	(2,3,3',4',5,6-Hexachlorobiphenyl)[f,h,i]	2.02 ± 0.05[c]	19.9 ± 0.5[c]
Total PCBs[m]		205 ± 42	2020 ± 420

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [25] and later revised by Schulte and Malisch [26] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, only PCB 107 (Table 2) is different in the numbering systems. Under the Ballschmiter and Zell numbering system, the IUPAC PCB 107 is listed as PCB 108.

[b] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[c] The reference value is an unweighted mean of the results from two to three analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[d] The reference value is a weighted mean of the results from three to four analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[e] The reference value is the mean of results obtained by NIST using one analytical technique. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO Guide [2]. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for the analyte.

[f] GC-ECD (Ib) on a relatively nonpolar proprietary phase; same extracts as GC-ECD (Ia).

[g] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

[h] GC/MS (Ia) on a relatively nonpolar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[i] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[j] GC-ECD (Ia) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[k] GC-ECD (II) on a 5% phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[l] GC/MS on a 5 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC-ECD (I) fractionated using a PYE column.

[m] Interlaboratory comparison study with four laboratories submitting data (See Preparation and Analysis for definition of total PCBs.). The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO Guide [2]. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for the total PCBs.

Table 7. Reference Concentrations for Selected Chlorinated Pesticides and Total Extractable Organics in SRM 1974b

	Mass Fractions in µg/kg[a] Wet-Mass Basis	Mass Fractions in µg/kg[a] Dry-Mass Basis
Heptachlor[d,e]	0.212 ± 0.084[b]	2.09 ± 0.83[b]
Oxychlordane[d,e]	0.362 ± 0.072[b]	3.57 ± 0.71[b]
Dieldrin[d,e,f,g,h,i]	0.62 ± 0.13[c]	6.1 ± 1.3[c]
cis-Nonachlor[d,e,f,g,h,i,j]	0.64 ± 0.16[c]	6.3 ± 1.6[c]
2,4'-DDT[e,h,i]	0.894 ± 0.057[b]	8.83 ± 0.56[b]
4,4'-DDT[d,e,f,g,h,i,j,k]	0.396 ± 0.096[c]	3.91 ± 0.94[c]
	Percent	
Total Extractable Organics (TEO)[l]	0.64 ± 0.13	6.3 ± 1.3

[a] Concentrations reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water.

[b] The reference value is an unweighted mean of the results from two to three analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[c] The reference value is a weighted mean of the results from six to eight analytical methods [23]. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95 % confidence), calculated by combining a between-method variance incorporating inter-method bias with a pooled within-source variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurements [2].

[d] GC-ECD (Ib) on a relatively nonpolar proprietary phase; same extracts as GC-ECD (Ia).

[e] GC-ECD (III) on a 5 % phenyl-substituted methylpolysiloxane phase and a relatively non-polar proprietary phase after PFE with DCM.

[f] GC/MS (Ib) on 50 % phenyl-substituted methylpolysiloxane phase; same extracts analyzed as in GC/MS (Ia).

[g] GC-ECD (Ia) on 5 % phenyl-substituted methylpolysiloxane phase after PFE with DCM.

[h] GC/MS (II) on a relatively nonpolar proprietary phase after Soxhlet extraction with DCM.

[i] 2000 NIST Intercomparison Exercise for Organic Contaminants in the Marine Environment [3] with 16 laboratories submitting data.

[j] GC/MS (Ia) on a relatively nonpolar proprietary phase after PFE with 50 % hexane/50 % acetone mixture.

[k] GC-ECD (II) on a 5 % phenyl-substituted methylpolysiloxane phase after Soxhlet extraction with DCM.

[l] Interlaboratory comparison study with six laboratories submitting data. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO Guide [2]. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for the TEO.

Table 8. Reference Concentrations for Additional Trace Elements in SRM 1974b

	Mass Fraction in mg/kg[a,b] Wet-Mass Basis	Mass Fraction in mg/kg[a,b] Dry-Mass Basis
Arsenic[c]	0.796 ± 0.049	7.86 ± 0.48
Cadmium[c,d]	0.155 ± 0.005	1.53 ± 0.05
Chromium[c]	0.233 ± 0.010	2.30 ± 0.10
Copper[c,d]	0.967 ± 0.016	9.55 ± 0.16
Iron[e]	55.1 ± 3.4	544 ± 34
Lead[d]	0.752 ± 0.026	7.42 ± 0.26
Nickel[c,d]	0.109 ± 0.005	1.08 ± 0.05
Selenium[c]	0.224 ± 0.015	2.21 ± 0.15
Silver[c,d]	0.028 ± 0.003	0.280 ± 0.033
Tin[d]	0.028 ± 0.002	0.273 ± 0.018
Zinc[c,d]	12.3 ± 0.3	121 ± 3

[a] The concentrations are reported on both wet- and dry-mass basis; material as received contains 89.87 % ± 0.05 % (95 % confidence level) water. These elements were determined in freeze-dried samples on a dry-mass basis.

[b] The reference values are the means of results obtained from NRC Canada using one or two analytical techniques and the consensus mean from six laboratories participating in the NRC Canada 14th Intercomparison for Trace Elements in Marine Sediments and Biological Tissues [4]. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance [24] with a pooled, within method variance following the ISO/NIST Guide to the Expression of Uncertainty in Measurement [2].

[c] Determined at NRC Canada using GFAAS.

[d] Determined at NRC Canada using ID-ICP-MS.

[e] Determined at NRC Canada using ICP-AES.

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Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.

APPENDIX A

The laboratories listed below performed measurements that contributed to the certification of SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*).

Arthur D. Little, Inc; Cambridge, MA, USA
Australian Nuclear Science and Technology Organization; Menai, NSW, Australia
B & B Laboratories; College Station, TX, USA
BWPC Laboratory; San Francisco, CA, USA
Battelle Pacific Northwest; Sequim, WA, USA
California Department of Fish and Game; Rancho Cordova, CA, USA
City of San Jose Environmental Services Department Laboratory; San Jose, CA, USA
Environment Canada; Moncton, New Brunswick, Canada
Manchester Environmental Laboratory; Port Orchard, WA, USA
NOAA, National Ocean Service, Center for Coastal Environmental Health and Biomolecular Research; Charleston, SC, USA
NOAA, NMFS, Sandy Hook Marine Laboratory; Highlands, NJ, USA
NOAA, NMFS, Northwest Fisheries Science Center; Seattle, WA, USA
Orange County Sanitation District; Fountain Valley, CA, USA
Resource Sciences Centre Department of Natural Resources; Indooroopillly, Queensland, Australia
STL Sacramento; Sacramento, CA, USA
Texas Parks and Wildlife Department; San Marcos, TX, USA
Texas A&M University College of Veterinary Medicine; College Station, TX, USA
University of Connecticut Environmental Research Institute; Storrs, CT, USA
University of Rhode Island Graduate School of Oceanography; Narragansett, RI, USA
US Department of Agriculture, Environmental Chemistry Laboratory; Beltsville, MD, USA
US Geological Survey, National Water Quality Laboratory; Denver, CO, USA
Wright State University; Dayton, OH, USA

Certified Reference Material

National Research Council Canada

Conseil national de recherches Canada

CARP-2

Ground Whole Carp Reference Material for Organochlorine Compounds

This reference material replaces CARP-1, supplies of which have been exhausted. Each unit of CARP-2 contains six individually sealed ampoules.

This reference material is primarily intended for use in the calibration of procedures and the development of methods used for the determination of PCB's, PCDD's, PCDF's and pesticides in biological materials.

Preparation of CARP-2

The material was prepared from ground whole carp (*Cyprinus carpio*), harvested in March 1994 near the warm water discharge of the Consumer's Power Plant, Saginaw Bay, Lake Huron. It was frozen to -30°C and shipped to the Canadian Institute for Fisheries Technology for further processing. It was comminuted four times, an antioxidant (ethoxyquin powder) was added followed by distilled water to increase the moisture content to 85%. The slurry was passed four times through a high pressure homogenizer and aliquoted in 10 g quantities into nitrogen flushed glass ampoules and sealed. The vials were thermally sterilized in a steam retort at 118°C for 11 minutes.

Except for the addition of some water and an antioxidant, CARP-2 is a natural biological material.

A lipid content of approximately 7% was determined by pressurized fluid extraction (PFE).

Storage

It is recommended that the reference material be stored in a cool, clean location. The ampoules should only be opened immediately prior to use. This material has been stored at 22°C since packaging.

Handling of the Material Prior to Extraction

The following procedure is recommended for weighing and transferring CARP-2 quantitatively for extraction. Weigh the ampoule. Sonicate it in an ultrasonic bath for fifteen minutes. Break the seal at the neck and transfer as much material as possible out of the ampoule. Wash the inside of the ampoule and the top with a small amount of the extraction solvent and transfer the wash quantitatively. Weigh the empty ampoule, the top and any glass slivers. Calculate the CARP-2 slurry weight by difference. Use the whole ampoule contents for analysis.

NRC · CNRC

Certified Concentrations for Selected Polychlorinated biphenyl (PCB) Congeners in CARP-2.

Congener (IUPAC No.)	µg/kg, (wet weight basis)		
18	27.3	±	4.0
28	34.0	±	7.2
44	86.6	±	25.9
52	138	±	43
118	148	±	33
128	20.4	±	4.4
153	105	±	22
180	53.3	±	13.0
194	10.9	±	3.1
206	4.4	±	1.1

The certified results are expressed as the mean value ± the expanded uncertainty. These results were derived from four contributions: (1) the NRC analysis, (2) the mean of three methods performed at NIST, (3) the recommended value arising from the NIST/NOAA intercomparison [3], (4) the mean from three results performed by an external laboratory.

Reference Concentrations for Selected Polychlorinated biphenyl (PCB) Congeners and Pesticides in CARP-2.

These concentrations are provided as reference values because (1) the variance from multiple methods was greater than desired for certified values or (2) in the case of PCBs, limited data were available concerning the relative amounts of co-eluting congeners.

Congener (IUPAC No.)	µg/kg, (wet weight basis)		
8	4.8	±	1.8
66/95	174	±	52
101/90	145	±	48
105	53.2	±	15.6
138/163/164	103	±	30
170/190	20.6	±	2.9
187/182	37.1	±	6.3
209	4.6	±	2.0

Pesticides	µg/kg (wet weight basis)		
gamma-chlordane	4.5	±	0.7
2,4'-DDE	2.9	±	0.5
trans-nonachlor	11.0	±	0.9
dieldrin	8.3	±	0.8
4,4'-DDE	158	±	14
2,4'-DDD	21.8	±	0.7
4,4'-DDD	90.9	±	8.5

The results are expressed as the mean value ± the expanded uncertainty. The PCB reference results were derived from four contributions: (1) the NRC analysis, (2) the mean of three methods performed at NIST, (3) the recommended value arising from the NIST/NOAA intercomparison[3] and (4) the mean of three results performed by an external laboratory. The pesticide reference results were derived from process 1,2 and 3 only.

Reference Concentrations for Selected PCDF's and PCDD's in CARP-2.

The following table lists the polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congeners for which reference values have been established for CARP-2. These concentrations are provided as reference values because limited data were available to permit certification.

Congener	ng/kg, (wet weight basis)
Polychlorinated dibenzofuran (PCDF)	
2,3,7,8-Tetrachlorodibenzofuran	18.2 ± 1.6
1,2,3,7,8-Pentachlorodibenzofuran	5.6 ± 0.3
Polychlorinated dibenzo-*p*-dioxin (PCDD)	
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	7.4 ± 0.7
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	5.3 ± 1.3
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	1.6 ± 0.3
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	5.8 ± 0.8
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	0.78 ± 0.12
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	6.4 ± 0.9
Octachlorodibenzo-*p*-dioxin	9.4 ± 1.7

The results are expressed as the mean value ± the expanded uncertainty. The reference result is the mean of five independent analyses performed at NRC.

The results used to calculate both certified and reference values in CARP-2 were judged to be independent measurements. The uncertainty in these values is equal to $U = ku_c$ where u_c is the combined standard uncertainty calculated according to the ISO Guide [2] and k is the coverage factor. The value of u_c is intended to represent at the level of one standard deviation the combined effect of all the uncertainties in the certified or reference value. Here u_c is given by the standard error of the mean of the analyses. The coverage factor, k , is the Student's t-value for a 95% confidence interval with the appropriate degrees of freedom.

Analytical Methods used at NRC

PCBs: (Method1a, b) Soxhlet extraction using 1:1 acetone/hexane followed by Florisil and alumina column cleanup. Measurement by both GC-ECD and GC/MS using a DB5 fused silica column (30m x 0.25mm id x 0.25µm film).

PCBs and Chlorinated Pesticides: (Method 2) Pressurized fluid extraction using dichloromethane solvent with alumina in the extraction cell. Glass Silica SPE tubes were used for the final cleanup step. Samples were spiked with selected Carbon-13 labelled PCBs and selected Carbon-13 or Deuterium labelled pesticides prior to extraction. Final analysis was by GC/HRMS using an HT8 fused silica column (50m x 0.22mm id x 0.25µm film).

PCDDs and PCDFs: Carp-2 was analysed using five combinations of different extraction/cleanup techniques followed by GC/HRMS. Carp-1 samples were analysed concurrently using the same techniques to validate the methods. The extraction steps consisted of either Soxhlet (1:1 acetone/hexane) [4], shaking with acetonitrile or sonication with HCl. A sulphuric acid shake step was used for bulk lipid removal when required. The final cleanup steps were completed using either in house prepared glass columns (acid-base silica, Florisil, carbon) or commercially available glass SPE tubes (C-18, SCX, SAX, SiOH, Florisil, alumina). In all of these methods, the samples were spiked with a mixture of Carbon-13 labelled PCDDs and PCDFs prior to the extraction step. GC/HRMS was performed at a resolution of 5000 or 10000. A DB5 fused silica column (50m x 0.25mm id x 0.1µm film) was used for the determination of these compounds.

Further details concerning any of these methods are available upon request.

Homogeneity and Stability

CARP-1 was monitored at NRC for a period of twelve years. No signs of inhomogeneity or instability were evident and CARP-2 is expected to be similarly stable with respect to its organochlorine contents.

Certification

The bulk of the analytical and certification work was performed at the Institute for National Measurement Standards, National Research Council of Canada. Results for selected analytes were also used from twenty-one laboratories that participated in an intercomparison exercise coordinated by R. Parris and S. Wise [3] of the National Institute of Standards and Technology , Gaithersburg, MD.

Acknowledgements

The following members of staff of the Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario participated in the analyses and certification: C.A. Fraser, G.J. Gardner, R. Guevremont, P.S. Maxwell and S.N. Willie.

T. Kubiak and L. Williams of the U.S. Fish and Wildlife Service, East Lansing, Michigan, donated the harvested carp.

The cooperation of the following in the preparation and analysis of this material is gratefully acknowledged:

S.A. Wise, R.M. Parris, M.M. Schantz and W. E. May, National Institute of Standards and Technology, Gaithersburg, MA, USA.

C. Hotton, I.J. Britt, D.S. Singer and T.A. Gill, Canadian Institute of Fisheries Technology, Technical University of Nova Scotia, Halifax, Nova Scotia.

J. McAnally, City of San Diego,
EMTS Laboratory, La Mesa, CA.

Canada

References

[1] C.A. Fraser, G.J. Gardner, P.S. Maxwell, C. Kubwabo, R. Guevremont, K.W.M. Siu and S.S. Berman, "Preparation and certification of a biological reference material (CARP-1) for polychlorinated dibenzo-p-dioxin and dibenzofuran congeners," Fresenius J Anal Chem, 352, 143-147,1995.

[2] Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993).

[3]1995 NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment, Fish Homogenate III, QA95FSH3. R. Parris, S. Wise, M. Schantz.

[4] J.J. Ryan, P.Y. Lau, J.C. Pilon, D. Lewis, H.A. McLeod, and A. Gervais; Incidence and Levels of 2,3,7,8-TCDD in Lake Ontario Commercial Fish., Environ. Sci. Technol., 18, 719-721, 1984.

Date of issue: July 1, 2001
Date of expiry: July 30, 2013

It is expected that as more data becomes available, the reference values may be updated and/or certified, and values assigned to additional compounds. These updates will be forwarded to all users of this reference material.

Comments, information and inquiries should be addressed to:

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Certified Reference Material

National Research Council Canada
Conseil national de recherches Canada

DORM-3

Fish Protein Certified Reference Material for Trace Metals

The following table shows those elements for which certified values have been established for this reference material. Certified values are based on unweighted mean results from data generated at NRCC as well as results submitted by laboratories participating in an annual intercomparison. The expanded uncertainty (U_{CRM}) in the certified value is equal to U = ku_c where u_c is the combined standard uncertainty calculated according to the ISO Guide [1] and k is the coverage factor. The value of u_c is calculated from the combined uncertainties of the various methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}).

It is intended that U_{CRM} accounts for every aspect that reasonably contributes to the uncertainty of the measurand [2]. A coverage factor of 2 was applied for all elements. The table below lists certified values for DORM-3 expressed on a dry mass basis.

TRACE ELEMENTS (milligram/kilogram)

Arsenic (d,g,h)	6.88	±	0.30
Cadmium (d,g,i,p)	0.290	±	0.020
Copper (d,i,p)	15.5	±	0.63
Chromium (d,g,i)	1.89	±	0.17
Iron (d,i)	347	±	20
Lead (d,g,p)	0.395	±	0.050
Mercury (c,d,p)	0.382	±	0.060
Nickel (d,g,i,p)	1.28	±	0.24
Tin (d,p)	0.066	±	0.012
Zinc (d,i,p)	51.3	±	3.1
Methylmercury (as Hg) (q,s,t)	0.355	±	0.056

Coding

The coding refers only to the instrumental method used for quantitation.

c - Cold vapour atomic absorption spectrometry.
d - Inductively coupled plasma mass spectrometry.
g - Electrothermal vaporization atomic absorption spectrometry.
h - Hydride generation atomic absorption, fluorescence or emission spectrometry.
i - Inductively coupled plasma atomic emission spectrometry.
p - Isotope dilution inductively coupled plasma mass spectrometry
q - Isotope dilution gas chromatography inductively coupled plasma mass spectrometry
s - Isotope dilution gas chromatography mass spectrometry
t - Cold vapour atomic fluorescence spectrometry.

NRC · CNRC

Intended Use

This reference material is primarily intended for use in the calibration of procedures and the development of methods for the analysis of marine fauna and materials of similar matrix.

Storage and Sampling

This material should be stored in a cool and dark location. Prior to use, the bottle should be rotated and shaken to ensure the contents are well mixed. The bottle should be tightly closed thereafter. Certified values are based on a minimum 0.250 g sub-sample from the bottle.

Instructions for Drying

Determination of dry mass should be performed on a separate sample to avoid contamination. DORM-3 can be dried to constant weight by:

(1) drying at reduced pressure (e.g., 50 mm Hg) at room temperature in a vacuum desiccator over magnesium perchlorate for 24 hours;

(2) vacuum drying (about 0.5 mm Hg) at room temperature for 24 hours.

Expiry

Based on sample stability noted on page 3, the certified values for DORM-3 are considered valid until September, 2016, provided the CRM is handled and stored in accordance with instructions herein.

Preparation of DORM-3

This reference material was prepared from a fish protein homogenate. A uniform material was produced using an enzyme hydrolysis procedure subsequent to removal of the bones and the majority of the oil. The protein hydrolysate was spray dried, sieved to pass a 297 µm screen, blended and bottled.

After bottling the material was sterilized by subjecting it to a minimum dose of 25 kGy gamma irradiation at the Canadian Irradiation Centre, Laval, Québec.

Information values

Due to the scatter of results, certified values for Ag and Se were not calculated. A lack of independent values precluded the determination of a certified value for Al and Mn. Information values for these analytes are thus given below.

Ag	0.04	mg/kg
Se	3.3	mg/kg
Al	1700	mg/kg
Mn	4.6	mg/kg

Updates

It is anticipated that as more data become available, the established values may be updated and reliable values assigned to more elements. Our web site at http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html will contain any new information.

Uncertainties

The uncertainties associated with the various methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}) are listed in Table 2. The principles used to calculate these values are described on page 3.

Table 2. Statistical Data for DORM-3

	data sets	u_{char}, (mg/kg)	u_{hom}, (mg/kg)
As	6	0.05	0.14
Cd	8	0.006	0.008
Cu	7	0.20	0.26
Cr	5	0.04	0.07
Fe	5	5	9
Pb	5	0.015	0.020
Hg	7	0.009	0.029
Ni	6	0.08	0.08
Sn	5	0.004	0.005
Zn	7	1.1	1.0
MeHg	3	0.009	0.027

Certified value

DORM-3 was provided as an unknown sample to a group of laboratories participating in an annual intercomparison for trace metals in marine samples sponsored by NRCC [3]. Data generated by NRCC were also included in the pool of intercomparison results.

Laboratories were requested to provide triplicate dry weight values using an analytical method of choice based on total digestion of the sample.

Data were returned to NRCC for evaluation. The results from a select sub-group of participants were used for the certification of DORM-3. Such laboratories were selected based on their performance history in previous intercomparisons. NIST SRM 2976, Mussel Tissue served as a quality control sample.

The certified values were calculated from the unweighted means of the results of the selected laboratories [4]. Data were first examined for outliers using the Dixon and Grubb's Tests. Testing of variances was conducted using the Cochran and Bartletts Tests.

Included in the overall uncertainty estimate are uncertainties in the batch characterisation (u_{char}), uncertainties related to possible between-bottle variation (u_{hom}) as well as instability derived from effects relating to long-term storage and transport (u_{stab}). Expressed as standard uncertainties these components can be combined as:

$$u^2_{c(CRM)} = u^2_{char} + u^2_{hom} + u^2_{stab} \qquad (1)$$

Results for the various statistics used to calculate the certified values are shown in Table 2.

Characterisation

The characterisation uncertainties (u_{char}) were calculated in accordance with equation 2, where s is the standard deviation of the means and p is the number of mean results included in the calculation [4].

$$u_{char} = \frac{s}{\sqrt{p}} \qquad (2)$$

Homogeneity

The homogeneity components of the uncertainties in the certified values were derived according to the recommendation of an international study group [4]. The material was tested for homogeneity at NRCC using ICP-MS. Results from sub-samples (0.250 g) from twelve bottles were evaluated using ANOVA.

In certain situations the inhomogeneity contribution to uncertainty, u_{hom}, was set to the experimentally determined between-unit standard deviation ($s_{between}$) as the best estimate of the uncertainty due to between-unit heterogeneity. However, if the situation depicted in equation 3 occurred:

$$s^2_{between} < \frac{s^2_{meas}}{n} \qquad (3)$$

where s_{meas} is the repeatability standard deviation for the method used in the homogeneity assessment and n is the number of replicates per unit, then u_{hom} was calculated according to:

$$u_{hom} = \sqrt{\frac{s^2_{meas}}{n}} \qquad (4)$$

It is recognized that this is not an ideal situation, as it represents a worst case scenario by suggesting the homogeneity could be as poor as the precision of the measurement technique selected for homogeneity assessment.

Stability

The predecessor CRM, DORM-2, has been periodically analyzed for more than nine years and found to be both physically and chemically stable over this time interval. We expect similar results for DORM-3. The stability of this CRM will continue to be monitored and customers will be notified if any significant irregularity occurs prior to the expiry date. Uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Acknowledgements

The following staff members of the Institute for National Measurement Standards, National Research Council Canada, participated in the certification: V.J. Boyko, C. Scriver, P. Maxwell, R. Sturgeon, L. Yang and S. Willie.

The following laboratories participated in the certification of DORM-3:

Australian Institute of Marine Sciences
Queensland, 4810, Australia
Frank Tirendi, Cassie Payn and Stephen Boyle

Australian Nuclear Science and Technology Organisation
Environment Laboratory
Lucas Heights, NSW, Australia
David Hill, Henri Wong

Battelle Pacific Northwest
Sequim, WA
Eric Crecelius, Laurie Niewolny, Mary Ann Deuth, and Brenda Lasorsa

NOAA, National Ocean Service
Hollings Marine Laboratory
Charleston, SC
Dan Bearden, Aaron Dias

Texas A. & M.
College of Veterinary Medicine
Trace Element Research Laboratory
College Station, TX
Robert Taylor, Gerald Bratton and Bryan Brattin

Texas Parks and Wildlife
Environmental Contaminants Laboratory
San Marcos, TX
Gary Steinmetz

U.S. Customs Laboratory
Savannah, GA
Ralph Smith

References

[1] Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993).

[2] J. Pauwels, A. van der Veen, A. Lamberty, H. Schimmel, Evaluation of uncertainty of reference materials.
Accred Qual Assur (2000) 5:95-99.

[3] S. Willie, Fifteenth Intercomparison for Trace Elements in Marine Sediments and Biological Tissues, NRC No. 46670, June 2004.

[4] S.L.R. Ellison, S.Burke, R.F.Walker, K. Heydorn, M.Månsson, J.Pauwels, W.Wegscheider, B.te Nijenhuis, Uncertainty for reference materials certified by interlaboratory study.
Accred Qual Assur (2001) 6:274–277.

Certificate issued February 2007
Total Hg revised January 2008
MeHg added January 2008

The results listed in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such, they serve as suitable reference materials for laboratory quality assurance programs, as outlined in ISO/IEC 17025. This CRM is registered at the Bureau International des Poids et Mesures (BIPM) in Appendix C of the Comité International des Poids et Mesures database listing Calibration and Measurement Capabilities accepted by signatories to the Mutual Recognition Arrangement of the Metre Convention.

Comments, information and inquiries should be addressed to:

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Certified Reference Material

National Research Council Canada

Conseil national de recherches Canada

DOLT-4

Dogfish Liver Certified Reference Material for Trace Metals

This reference material is primarily intended for use in the calibration of procedures and the development of methods for the analysis of marine fauna and materials with a similar matrix.

Elements for which certified values have been established for this dogfish (*Squalus acanthias*) liver CRM, along with their expanded uncertainty ($U_{CRM} = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO Guide [1] and k=2 is the coverage factor) are listed in Table 1. It is intended that U_{CRM} encompasses every aspect that reasonably contributes to the uncertainty of the certified mass fraction [2]. Values are based on dry mass.

Table 1. Certified Values for DOLT-4

Element	Mass Fraction (mg/kg)
Arsenic (d,e,h)	9.66 ± 0.62
Cadmium (d,e,i,p)	24.3 ± 0.8
Copper (d,e,i,p)	31.2 ± 1.1
Iron (d,i)	1833 ± 75
Lead (d,e,p)	0.16 ± 0.04
Mercury (c,d,p)	2.58 ± 0.22
Nickel (d,e,i,p)	0.97 ± 0.11
Selenium (e,h)	8.3 ± 1.3
Silver (d,e,p)	0.93 ± 0.07
Zinc (d,i,p)	116 ± 6
CH_3Hg (as Hg)(g,s,t)	1.33 ± 0.12

Coding

The coding refers only to the instrumental method of determination of the measurand.

- c - Cold vapour atomic absorption spectrometry.
- d - Inductively coupled plasma mass spectrometry.
- e - Electrothermal vaporization atomic absorption spectrometry (ETAAS).
- g - Solid phase microextraction (SPME) isotope dilution gas chromatography mass spectrometry.
- h - Hydride generation atomic absorption spectrometry.
- i - Inductively coupled plasma atomic emission spectrometry.
- p - Isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS).
- s - SPME isotope dilution gas chromatography ICPMS.
- t - Ethylation cold vapor atomic fluorescence spectrometry.

NRC · CNRC

Preparation of DOLT-4

This reference material was processed at the Guelph Food Technology Center, Guelph Ontario. The preparation sequence is illustrated below.

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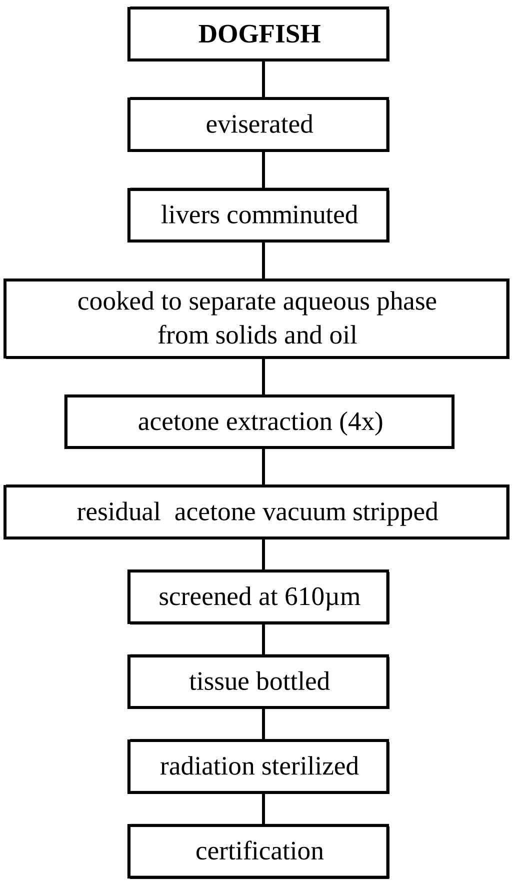

The material was sterilized by gamma irradiation (miminimum dose of 25 kGy) at the Canadian Irradiation Centre, Laval, Québec

Sampling

A sample mass of 250 mg of material (dry mass basis) is the minimum sample intake for which the established uncertainty is valid.

Instructions for Drying

Moisture content should be determined using a separate sub-sample. DOLT-4 can be dried to contant mass by:
(1) drying at reduced pressure (e.g., 50 mm Hg) at room temperature in a vacuum desiccator over magnesium perchlorate for 24 hours;

(2) vacuum drying (about 0.5 mm Hg) at room temperature for 24 hours.

Information Values

Table 2 presents information values for elements which could not be certified because of insufficient information to accurately assess uncertainties.

Table 2. Information Values for DOLT-4

Element	Mass Fraction, (mg/kg)
Na	6800
Mg	1500
Al	200
K	9800
Ca	680
V	0.6
Cr	1.4
Co	0.25
Sr	5.5
Mo	1
Sn	0.17

Storage and Handling

This material should be kept in the original bottle tightly closed and stored in a cool location, away from any significant radiation sources such as ultraviolet lamps and sunlight. The contents should be well mixed by rotation and shaking prior to use, and the bottle tightly closed immediately after sampling.

Calculation of Certified Values

DOLT-4 was provided as an unknown sample to a group of laboratories participating in an annual intercomparison for trace metals in marine samples coordinated by NRCC [3]. Data generated by NRCC were also included in the pool of intercomparison results.

Laboratories were requested to provide triplicate results using an analytical method of choice based on total digestion of the sample. DOLT-3 was provided as a quality control sample.

Data were returned to NRCC for evaluation. Results from a select sub-group of participants were used for the certification of DOLT-4. Such laboratories were selected based on their performance history in previous intercomparisons.

The certified values were calculated from the unweighted means of the results. Data were first examined for outliers using the Dixon and Grubb's Tests. Testing of variances was conducted using the Cochran and Bartletts Tests.

Included in the overall uncertainty estimate are uncertainties in the batch characterisation (u_{char}) and uncertainties related to possible between-bottle variation (u_{hom}). Expressed as standard uncertainties these components can be combined as:

$$u^2_{c(CRM)} = u^2_{char} + u^2_{hom}$$

Based on NRC's experience with similar materials, uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Results for the various uncertainty components used to calculate the certified values are summarized in Table 3.

Table 3. Statistical Data for DOLT-4

Element	data sets	u_{char}, (mg/kg)	u_{hom}, (mg/kg)
As	10	0.22	0.21
Cd	12	0.25	0.31
Cu	10	0.31	0.46
Fe	10	22	30
Pb	8	0.016	0.013
Hg	8	0.014	0.11
Ni	9	0.024	0.049
Se	9	0.18	0.63
Ag	8	0.017	0.028
Zn	11	2	2
CH_3Hg	3	0.016	0.057

Expiration of Certificate

A predecessor CRM, DOLT-2, has been periodically analyzed for more than nine years and found to be both physically and chemically stable over this time interval. We expect similar characteristics from DOLT-4. The stability of this CRM will continue to be monitored and any significant irregularity will be posted on our web site.

The certified values for DOLT-4 are considered valid until April 2014, provided the CRM is handled and stored in accordance with instructions herein.

References

[1] Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993).

[2] ISO Guide 35:2006, Reference materials — General and statistical principles for certification Geneva, Switzerland (2006)

[3] S. Willie, Twentieth Intercomparison for Trace Elements in Marine Sediments and Biological Tissues, NRC No. 50099, October 2007.

Acknowledgements

The following staff members of the Institute for National Measurement Standards, National Research Council Canada, participated in the certification: P. Maxwell, C. Scriver, L. Yang and S. Willie.

The cooperation of I. Britt and A. Mannen of the Guelph Food Technology Centre, Guelph, ON, Canada in the preparation of this material is gratefully acknowledged.

The following laboratories participated in the certification of DOLT-4:

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Menai, N.S.W., Australia

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Central Laboratory, Winthrop, MA 02152

NOAA, National Ocean Service,
Hollings Marine Laboratory, Charleston, SC 29412

San Francisco Public Utilities Commission
Southeast Laboratory, Sn Francisco, CA,

Texas A. & M.
College of Veterinary Medicine
Trace Element Research Laboratory
College Station, TX 77843-4458

Texas Parks and Wildlife
Environmental Contaminants Laboratory
San Marcos, TX 78666

U.S. Customs Laboratory
Savannah, GA 31408

USGS-WRD
3039 Amwiler Road, Atlanta, GA 30360-2824

Updates

Users of this material should ensure that the certificate in their possession is current. Please consult our web site at http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html for any new information.

As additional data become available, the certified values may be updated and reliable values assigned to additional measureands.

Certificate issued May 2008.

The results presented in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such, they serve as suitable reference materials for laboratory quality assurance programs, as outlined in ISO/IEC 17025. NRCC CRM's are registered at the Bureau International des Poids et Mesures (BIPM) in Appendix C of the Comité International des Poids et Mesures database listing Calibration and Measurement Capabilities accepted by signatories to the Mutual Recognition Arrangement of the Metre Convention.

Comments, information and inquiries should be addressed to:

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Catalog No. 540
Issue Date: May 1, 2008
Revision Date: Original

Certification

Parameter	Total Concentration [1] (mg/kg)	Certified Value [2] (mg/kg)	Uncertainty [3]	QC PALs™ [4] (mg/kg)	PT PALs™ [5] (mg/kg)
aluminum	61800	10600	5.1%	5750 - 15400	4880 - 16300
antimony	267	126	1.6%	63.3 - 189	26.5 - 317
arsenic	253	225	3.8%	181 - 270	160 - 290
barium	1160	565	4.6%	461 - 669	422 - 709
beryllium	178	162	5.4%	134 - 190	122 - 202
boron	129	107	9.3%	74.3 - 139	63.1 - 151
cadmium	79.5	69.1	6.3%	58.1 - 80.1	50.6 - 87.6
calcium	18100	10000	7.1%	8310 - 11700	7540 - 12400
chromium	356	124	5.4%	101 - 147	86.7 - 161
cobalt	132	115	6.2%	95.6 - 135	85.7 - 145
copper	78.8	66.7	5.3%	53.9 - 79.5	48.8 - 84.6
iron	34400	17600	2.4%	8930 - 26400	7320 - 28000
lead	272	223	3.6%	183 - 264	168 - 279
magnesium	7440	4260	5.6%	3290 - 5230	2980 - 5540
manganese	695	368	4.8%	304 - 433	279 - 458
mercury	5.20	5.15	20.1%	3.69 - 6.61	2.63 - 7.67
molybdenum	136	107	6.2%	83.8 - 130	75.0 - 141
nickel	202	172	7.0%	140 - 204	127 - 218
potassium	24200	4090	4.4%	2960 - 5220	2660 - 5520
selenium	166	147	3.5%	114 - 180	98.7 - 195
silver	40.1	35.2	7.0%	23.3 - 47.1	23.1 - 47.3
sodium	13500	538	7.1%	366 - 710	280 - 796
strontium	294	117	6.1%	94.8 - 139	82.3 - 151
thallium	197	173	3.2%	140 - 205	119 - 227
tin	189	164	5.3%	121 - 207	99.1 - 229
titanium	2920	381	2.8%	116 - 647	0.00 - 779
vanadium	155	93.9	4.4%	72.1 - 116	60.6 - 127
zinc	424	349	5.8%	280 - 418	252 - 446

Please see footnotes on back

APR - 8 2009

6000 West 54th Ave., Arvada, CO 80002 800-372-0122 fax: 303-421-0159 www.eraqc.com

International Atomic Energy Agency
Analytical Quality Control Services
Wagramer Strasse 5, P.O.Box 100, A-1400 Vienna, Austria

REFERENCE SHEET

REFERENCE MATERIAL

IAEA-405

TRACE ELEMENTS AND METHYLMERCURY IN ESTUARINE SEDIMENT

Date of issue: 1 August 2000

Recommended Values
(Based on dry weight)

Analyte	Recommended Value [mg/kg]	95% Confidence Interval [mg/kg]	N*
As	23.6	22.9 – 24.3	47
Cd	0.73	0.68 – 0.78	63
Co	13.7	13.0 – 14.4	50
Cr	84	80 – 88	63
Cu	47.7	46.5 – 48.9	80
Fe	37400	36700 – 38100	64
Hg	0.81	0.77 – 0.85	60
Li	72	65 – 79	25
Mg	12300	11400 – 13200	13
Mn	495	484 – 506	52
Ni	32.5	31.1 – 33.9	61
Pb	74.8	72.6 – 77.0	74
Sb	1.81	1.62 – 2.00	21
Se	0.44	0.32 – 0.56	12
Sn	7.6	6.3 – 8.9	17
V	95	90 – 100	29
Zn	279	272 – 286	87
MeHg§	0.00549	0.00496 – 0.00602	12

* *Number of accepted laboratory results which were used to calculate the recommended values and confidence intervals about the mean value*

§ *As inorganic Hg*

Information Values
(Based on dry weight)

Analyte	Information Value [mg/kg]	95% Confidence Interval [mg/kg]	N*
Al	77900	72700 – 83100	37
Br	85	60 – 110	4
Cs	12.5	10.4 – 14.6	4
Eu	1.25	0.89 – 1.61	5
Hf	5.80	4.93 – 6.67	3
K	24900	17700 – 32100	5
La	40.4	33.1 – 47.7	5
Lu	0.468	0.283 – 0.653	3
Sc	13.52	11.53 – 15.51	3
Sm	6.86	6.50 – 7.22	4
Sr	118	104 – 132	28
Tb	0.93	0.50 – 1.36	3
Th	14.3	12.2 – 16.4	5
U	3.01	1.86 – 4.16	5
Yb	3.04	2.19 – 3.89	4

* Number of accepted laboratory results which were used to calculate the information values and confidence intervals about the mean value

The values listed above were established on the basis of statistically and technically valid results submitted by laboratories which had participated in an international intercomparison exercise organized in 1998. The details concerning the criteria for qualification as a recommended or information value can be found in the report (IAEA/AL/127; IAEA/MEL/70), “Report on the World-wide Intercomparison Exercise for the Determination of Trace Elements and Methylmercury in Estuarine Sediment IAEA-405” [1]. This report is available free of charge upon request.

Intended Use

This material is intended to be used as a reference material for the measurement of trace elements and methylmercury (MeHg) in coastal sediments. It can also be used as a quality control material for the assessment of analytical procedures, in the elaboration and validation of analytical methods, and for educational purposes.

Origin and preparation of the material

A large quantity of sediment was collected in 1998 from the intertidal mudflats of the Tagus estuary (Portugal) for use as an intercomparison material. It was deep-frozen, freeze-dried, ground and sieved. The sediment fraction of particle size less than 150 µm was further homogenized by mixing in a stainless steel rotating drum for two weeks. After checking for the homogeneity of the sample material (see below), aliquots of about 35g were packed into cleaned brown borosilicate glass bottles with Teflon lined screw caps and sealed in plastic bags. A total of 530 bottles was produced.

Homogeneity

Extensive homogeneity tests were carried out on this material in order to ensure its suitability as an intercomparison sample. A preliminary test was performed before final bottling and sample dispatch and did not detect any inhomogeneity in the material. A final homogeneity test was conducted after completion of the bottling of sample material. The between-bottle homogeneity was tested by the determination of the concentration of some typical elements (Cu, Fe, Mn, Zn) on sample intakes of 100 mg and 200 mg taken from 15 bottles which were set aside at regular intervals during the whole period of bottling. The within-bottle homogeneity was assessed by 15 replicate determinations on the re-homogenized content of one bottle. A F-test at a significance level of 0.05 was performed for the different metals and did not reveal significant differences between the within- and between-bottle variances for 100 mg intakes. On the basis of these results, no inhomogeneities in the material were suspected. It was concluded that the material is homogeneous at an analytical portion of 100 mg and above for trace elements and, therefore, suitable for use as an intercomparison sample [1].

Dry weight determination

The average moisture content of the lyophilized sample after bottling, determined by drying to a constant weight at 105°C, was found to be 2.5 %. Since the moisture content can vary with the ambient humidity and temperature, it was recommended that the water content of this material be determined in a separate subsample (not used for analysis) by drying to a constant weight (~24 hours) at 105°C just prior to analysis. Final results should always be reported on a dry weight basis.

Stability of the material

The stability of several trace metals was tested to determine the suitability of this material as a candidate CRM. Five bottles of the IAEA-405 material were stored in the dark at +20 °C, –20 °C and +60 °C, respectively, over a period of 17 months (starting in September 1998) and the measurement of total Hg, Cu, Fe, Mn and Zn was performed at regular intervals during the storage period. On the basis of these results, it was concluded that no instability of the material could be demonstrated [1].

Instructions for use

The recommended minimum sample size for analysis is 100 mg. Analysts are reminded to take appropriate precautions in order to avoid contaminating the remaining material in the bottle. The bottle should be thoroughly mixed by shaking before use and tightly resealed immediately after use. The material should be stored in the dark and kept below 25 ºC.

Legal disclaimer

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

References

[1] Coquery M., Azemard S. and de Mora S. J., Report on the World-wide Intercomparison Exercise for the Determination of Trace Elements and Methylmercury in Estuarine Sediment IAEA-405, IAEA/AL/127 (IAEA/MEL/70), IAEA, Monaco, 2000.

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