

Certification of Standard Reference Material (SRM) 1941a, Organics in Marine Sediment

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Abstract. SRM 1941a, Organics in Marine Sediment, has been recently issued with certified concentrations for 23 polycyclic aromatic hydrocarbons, 21 polychlorinated biphenyl congeners, 6 chlorinated pesticides, and sulfur. Noncertified concentrations have been also reported for additional PAHs, PCB congeners, and chlorinated pesticides and for percent total organic carbon (TOC), aliphatic hydrocarbons, and trace elements. SRM 1941a is the most extensively characterized natural matrix SRM issued by the National Institute of Standards and Technology (NIST).

1 Introduction

SRM 1941, Organics in Marine Sediment, was issued in 1989 with certified concentrations for 11 PAHs and sulfur, and only noncertified or information concentration values were provided for polychlorinated biphenyl (PCB) congeners and chlorinated pesticides. Certified values for the PAHs were based on the agreement of results from two or more independent analytical procedures, whereas the noncertified values were based on results from only one technique. The supply of this material was exhausted in late 1993 and a new material, SRM 1941a, Organics in Marine Sediment, was prepared. To increase the usefulness of the new sediment SRM, three goals were established: (1) to prepare a larger quantity of the material to extend the availability, (2) to provide certified concentration values for a significantly larger number of PAHs and to reduce the uncertainties associated with the certified PAH concentrations compared to the original sediment SRM and (3) to provide certified concentration values for the PCB congeners and chlorinated pesticides rather than noncertified values as in the original material.

For the first goal sufficient material was collected and processed to provide approximately 1000 bottles of SRM 1941a, which is more than twice the quantity of SRM 1941 produced. To achieve the second goal of increasing the number of PAHs with certified concentrations, four different analytical approaches were implemented to provide measurements for a larger number of PAHs: (1) reversed-phase LC with fluorescence detection (LC-FL) 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) GC-MS analysis of the PAH fraction on a 5% phenyl-substituted methylpolysiloxane stationary phase (the typical GC stationary phase used for PAH analyses), and (4) GC-MS of the PAH fraction on a smectic liquid crystalline stationary phase which provides excellent shape selectivity for the separation of PAH isomers. These techniques have been reported previously for the measurement of PAHs in environmental SRMs [1–5]; however, only for the analysis of SRM 1941a have all four techniques been used together to achieve certified values. Based on the agreement of results from these four approaches, certified concentrations were determined for 23 PAHs and noncertified concentrations were reported for an additional 14 PAHs.

To provide certified concentrations for PCB congeners and chlorinated pesticides, the sediment was analyzed using gas chromatography with electron capture detection (GC-ECD) on two columns of different selectivity and using GC-MS. Using this approach certified concentrations were provided for 21 polychlorinated biphenyl (PCB) congeners and 6 chlorinated pesticides, and noncertified concentrations were determined for 10 additional PCB congeners/chlorinated pesticides. Noncertified concentrations were also determined for 17 aliphatic hydrocarbons, 27 inorganic constituents, and percent total organic carbon (TOC), thereby making this sediment material the

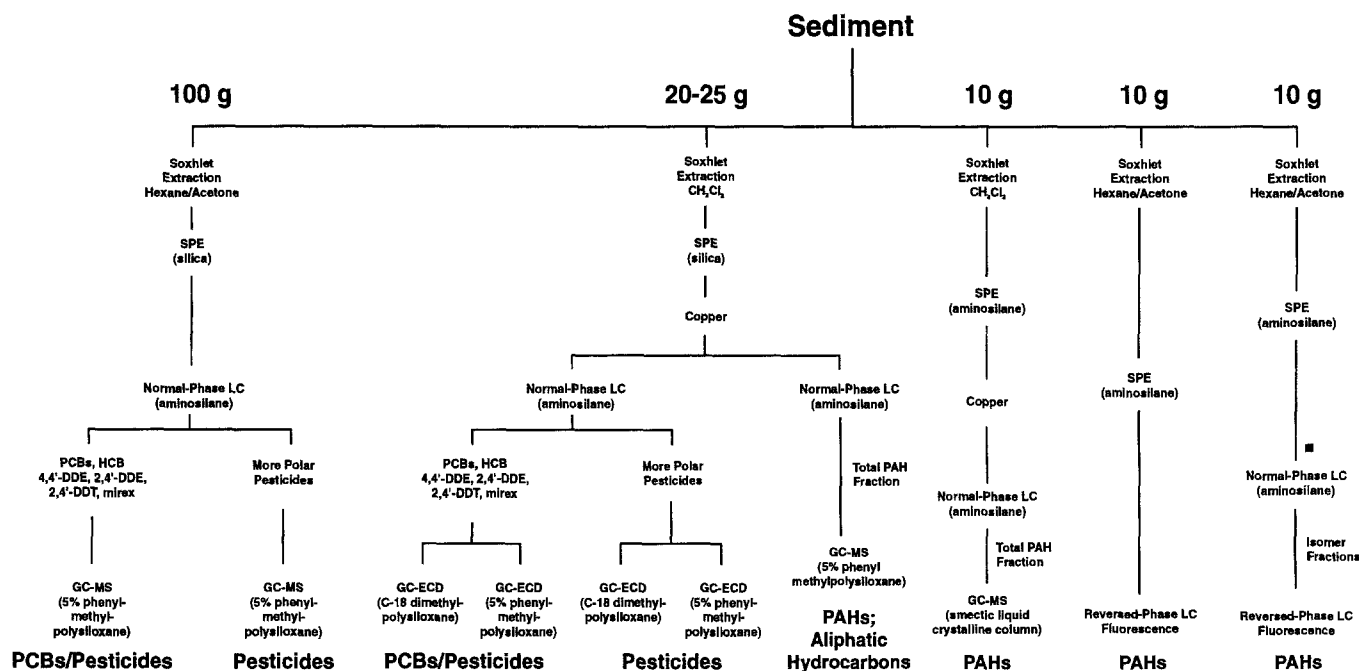


Fig. 1. Analytical scheme for the certification of organic contaminants in SRM 1941 a

most extensively characterized natural matrix SRM issued by NIST.

2 Experimental¹

SRM preparation

The marine sediment used to prepare this SRM was collected in the Chesapeake Bay at the mouth of the Baltimore (MD) Harbor near the Francis Scott Key Bridge (39°12.68'N and 76°31.33'W). The sediment was collected using a modified Van Veen type grab sampler designed to sample the sediment to a depth of 10 cm. The sediment was freeze dried, sieved (150–250 μm particles used for the SRM), homogenized in a cone blender, radiation (⁶⁰Co) sterilized, and then packaged in screw-capped amber glass bottles (~ 50 g/bottle).

Moisture determination

The results for both the organic and inorganic constituents in SRM 1941a are reported on a dry weight basis; however, the material “as received” contains residual moisture. The amount of moisture in SRM 1941a was determined by measuring the weight loss after oven drying at 90°C for 18 h for subsamples of 1–2 g. The moisture content in SRM 1941a at the time of the certification analyses was 2.2%.

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

Determination of polycyclic aromatic hydrocarbons

SRM 1941a was analyzed for selected PAHs using gas chromatography with mass spectrometric detection (GC-MS) and reversed-phase liquid chromatography with fluorescence detection (LC-FL). GC-MS analyses were performed on two columns with different selectivities for the separation of PAHs: a 5% phenyl-substituted methylpolysiloxane stationary phase and a smectic liquid crystalline stationary phase. Two different sample preparation/cleanup procedures were used prior to the analysis by GC-MS and LC-FL. A similar approach was used previously for the certification of PAHs in SRM 1941 [4].

For the GC-MS analyses, two sets of six samples (10–25 g each) from twelve randomly selected bottles were Soxhlet extracted for 18–20 h using methylene chloride. A silica or aminopropylsilane solid phase extraction column was eluted with 2% methylene chloride in n-hexane to remove the polar interferences from each sediment extract. Finely divided copper was then added to the extracts to remove elemental sulfur. The PAH fraction was isolated from each sediment extract by normal-phase liquid chromatography using a semi-preparative aminopropylsilane column [5]. The GC-MS analyses were performed on one set of six sample extracts using a 0.25-mm i.d. x 60-m fused silica capillary column with a 5% phenyl-substituted polysiloxane phase (0.25 μm film thickness) (DB-5 MS, J&W Scientific, Folsom, CA). The second set of six sample extracts was prepared as described above and then analyzed by GC-MS on a 0.2-mm i.d. x 25-m fused silica capillary column with a smectic liquid crystalline phase (0.15 μm film thickness) (SB-Smectic, Dionex, Inc., Salt Lake City, UT).

For the LC-FL analyses, subsamples of 10 g of sediment from six randomly selected bottles were Soxhlet ex-

Table 1. Summary of analytical results and certified concentrations for PAHs in SRM 1941a

Compound	Concentration ($\mu\text{g}/\text{kg}$ dry weight) ^{a, b}						Certified values ^c		
	GC-MS (DB-5)		GC-MS (SB-smectic)		LC-FL (total)			LC-FL (fractions)	
Naphthalene	1095	(62)	1031	(34)	893	(66)	1010 \pm 140		
Fluorene	94.3	(7.3)	101.5	(9.5)			97.3 \pm 8.6		
Phenanthrene	492	(32)	476	(31)	491	(11)	489 \pm 23		
Anthracene	193	(12)	184	(11)	182.9	(6.1)	184 \pm 14		
Fluoranthene	1012	(57)	1009	(58)	929	(44)	981 \pm 78		
Pyrene	814	(33)	812	(51)	808	(38)	811 \pm 24		
Benz[<i>a</i>]anthracene	423	(19)	444	(26)			423	(12)	427 \pm 25
Chrysene	[592] ^d	(35)	396	(35)			379.3	(7.7)	380 \pm 24
Triphenylene			191	(10)			202.3	(3.0)	197 \pm 11
Benzo[<i>b</i>]fluoranthene	[979] ^e	(82)	739	(50)	800	(150)			740 \pm 110
Benzo[<i>j</i>]fluoranthene			341	(22)					
Benzo[<i>k</i>]fluoranthene	416	(45)	362	(26)	361	(21)			361 \pm 18
Benzo[<i>a</i>]fluoranthene	114	(13)	119.0	(7.8)					118 \pm 11
Benzo[<i>e</i>]pyrene	522	(46)	587	(45)					553 \pm 59
Benzo[<i>a</i>]pyrene	611	(44)	656	(93)	639	(34)			628 \pm 52
Perylene	495	(41)	434	(25)	434	(22)			452 \pm 58
Indeno[1,2,3- <i>cd</i>]pyrene	446	(23)	537	(38)			520	(25)	525 \pm 67
Benzo[<i>ghi</i>]perylene	480	(34)	576	(43)			522	(11)	501 \pm 72
Dibenz[<i>a,j</i>]anthracene	76.2	(4.8)	70.0	(7.7)			76.1	(4.7)	74.3 \pm 6.8
Dibenz[<i>a,c</i>]anthracene	[123] ^f	(10)	41.3	(4.3)			44.8	(3.0)	43.1 \pm 3.7
Dibenz[<i>a,h</i>]anthracene			76	(10)			73.6	(4.9)	73.9 \pm 9.7
Pentaphene	47.8	(2.7)	35.4	(2.6)			46.7	(8.4)	42 \pm 12
Benzo[<i>b</i>]chrysene	94.3	(5.8)	106	(13)			112	(17)	99 \pm 20
Picene	80.4	(8.2)	75.9	(9.4)			80.8	(6.6)	80.0 \pm 9.0

^a In all tables concentrations reported on dry weight basis; material as received contains approximately 2.2% moisture

^b Uncertainties (in parentheses) are reported as the standard deviation of a single measurement; subsamples from six bottles were extracted and analyzed in duplicate for each of the four techniques

^c The certified values are weighted means of results from two or more analytical techniques as described by Schiller and Eberhardt [1]. The uncertainty is based on a 95% confidence interval for the true concentration, and includes an allowance for differences among the analytical methods used

^d Concentration is the sum of the chrysene and triphenylene

^e Concentration is the sum of benzo[*b*]fluoranthene and benzo[*j*]fluoranthene

^f Concentration is the sum of dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene

tracted for 20 h using hexane:acetone (1:1 v/v). Each concentrated extract was placed on an aminopropylsilane solid phase extraction column and eluted with 2% methylene chloride in n-hexane to remove the polar constituents. The extract was then analyzed by reversed-phase LC using a polymeric octadecylsilane (C₁₈) column (4.6 mm i.d. x 25 cm, 5 μm particle size, Hypersil PAH, Keystone Scientific, Inc. Bellefonte, PA) with wavelength programmed fluorescence detection [6–8]; these results are designated as LC-FL (total) in Table 1. To quantify several PAHs that have low fluorescence sensitivity and/or selectivity, six additional subsamples were extracted and prepared as described above, and then the extract was fractionated on a semi-preparative aminopropylsilane column to isolate isomeric PAH fractions as described previously [6–8]. These isomeric PAH fractions were analyzed by reversed-phase LC-FL on a similar octadecylsilane column; these results are designated as LC-FL (fractions) in Table 1.

For both the GC-MS and LC-FL analyses, selected perdeuterated PAHs were added to the sediment prior to

extraction for use as the internal standards for quantification purposes. Calibration response factors for the analytes relative to the internal standards were determined by analyzing aliquots of SRMs 1491 and 2260, "Aromatic Hydrocarbons in Hexane/Toluene," in the case of GC-MS analyses or SRM 1647b, "Polycyclic Aromatic Hydrocarbons in Acetonitrile," in the case of LC-FL analyses; gravimetrically prepared solutions of additional analytes not contained in SRMs 1491, 2260, or 1647b; and the internal standards.

Homogeneity assessment for PAHs

The homogeneity of SRM 1941a was assessed by analyzing duplicate samples of 10 g each from 10 randomly selected bottles. Samples were extracted, processed, and analyzed as described below for the GC-MS analyses (5% phenyl-substituted polysiloxane phase). No statistically significant differences between bottles were observed for the PAHs at the 10 g sample size.

Table 2. Noncertified concentrations of PAHs in SRM 1941a

PAH	Concentration ($\mu\text{g}/\text{kg}$ dry weight) ^{a,b}
Biphenyl ^{c,d}	175 \pm 18
Acenaphthene ^{c,d}	41 \pm 10
Acenaphthylene ^{c,d}	37 \pm 14
Dibenzothiophene ^{c,d}	70.0 \pm 9.4
3-Methylphenanthrene ^{c,d}	97 \pm 32
2-Methylphenanthrene ^{c,d}	158 \pm 32
1-Methylphenanthrene ^{c,d}	101 \pm 27
4H-Cyclopenta[def]phenanthrene ^{c,d}	92 \pm 15
Acephenanthrylene ^{c,d}	48.1 \pm 1.2
Benzo[ghi]fluoranthene ^d	97.9 \pm 3.1
Benzo[c]phenanthrene ^{c,d}	80 \pm 39
Benzo[j]fluoranthene ^d	341 \pm 22
Indeno[1,2,3-cd]fluoranthene ^c	20.0 \pm 2.3
Anthanthrene ^{c,e}	129 \pm 10

^a See Table 1

^b Concentrations are the mean determined by the technique indicated or the weighted mean from the results of two techniques. Uncertainties for the measurements are 95% confidence interval for the mean; six samples were extracted and analyzed in duplicate using the technique(s) indicated

^c Concentration determined by GC-MS on DB-5 column

^d Concentration determined by GC-MS on SB-Smectic column

^e Concentration determined by LC-FL

Determination of PCBs and chlorinated pesticides

SRM 1941a was analyzed for selected PCB congeners and chlorinated pesticides using GC-ECD and GC-MS using the general approach described previously [9]. For the GC-ECD analyses, a portion of the extract prepared for the PAH analyses by GC-MS (see above) was used. For the GC-MS analyses, additional samples of ~ 100 g each from six pairs of randomly selected bottles were Soxhlet extracted for 18 h using 1:1 n-hexane/acetone (v/v). In preparation for both the GC-ECD and GC-MS analyses, the extracts were fractionated on the 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 \times 60-m fused silica capillary column with a 5% phenyl-substituted methylpolysiloxane phase (0.25 μm film thickness) and 0.32 mm \times 100 m fused silica capillary column with a dimethylpolysiloxane phase containing 50% methyl C-18 (0.1 μm film thickness) (CPSil 5 C18 CB, Chrompack International, Middelburg, The Netherlands). The GC-MS analyses were performed on a 5% phenyl-substituted methylpolysiloxane phase as described above for the GC-ECD analyses.

Two PCB congeners, which are not present at significant concentrations in the sediment extract (PCB 103 and PCB 198 [2, 3]), and perdeuterated 4,4'-DDT were added to the sediment prior to extraction for use as internal standards for quantification purposes. Calibration response

factors for the analytes relative to the internal standards were determined by analyzing aliquots of SRMs 2261 (Concentrated Chlorinated Pesticides in Hexane), SRM 2262 (Concentrated PCB Congeners in Isooctane), gravimetrically prepared solutions of additional analytes not contained in SRMs 2261 and 2262, and the internal standards.

Determination of aliphatic hydrocarbons

Ten sediment extracts prepared for the homogeneity study of PAHs by GC-MS and six extracts prepared for the measurement of PAHs by GC-MS were analyzed on the same 5% phenyl-substituted methylpolysiloxane column for the determination of aliphatic hydrocarbons. Perdeuterated dodecane, eicosane, and triacontane were added prior to extraction as internal standards for quantification purposes. Calibration response factors for the analytes relative to the internal standards were determined by analyzing SRM 1494 (Aliphatic Hydrocarbons in 2,2,4-Trimethylpentane).

Determination of sulfur

by isotope dilution thermal ionization mass spectrometry (ID-TIMS)

The procedure for the determination of sulfur by ID-TIMS in a variety of matrices has been described in detail previously [10–12] including the previous marine sediment in this series, SRM 1941 [4]. Single samples of about 100 mg from six different bottles of SRM 1941a were transferred to Pyrex Carius tubes. Enriched ³⁴S tracer was added to the tubes followed by 8 g of NIST high purity nitric acid. The tubes were sealed and heated in a laboratory oven at 240°C for 12 h. This procedure oxidizes all sulfur to sulfate and completely mixes the spike, which is in the sulfate form, with the sulfur in the sample. The sulfate in the samples was reduced to H₂S which was precipitated as As₂S₃. This compound was dissolved in aqueous ammonia and a small amount of this solution, equivalent to about 1.5 μg S, was mixed with silica gel on a rhenium filament and the sulfur determined as the AsS⁺ molecular ion in a single sector thermal ionization mass spectrometer. The reproducibility of this procedure was about 0.2% relative. The percent sulfur of the previous marine sediment, SRM 1941, was also determined in this study as a control and found to be 1.714 \pm 0.011 (1s) which is in good agreement with the certified value of 1.717 \pm 0.027.

Determination of inorganic constituents

SRM 1941a was analyzed for 27 inorganic constituents using instrumental neutron activation analysis (INAA). The INAA was performed using previously developed procedures for sequential instrumental multi-element determinations in biological materials [13, 14]. Two subsamples (~ 300 mg) from each of six bottles of the sediment were pelletized and analyzed using the sequential INAA procedure.

Table 3. Summary of analytical results and certified/noncertified values for PCB congeners in SRM 1941 a

PCB congener ^c		Concentration ($\mu\text{g}/\text{kg}$ dry weight) ^{a,b}				
		GC-ECD ^d		GC-MS		Certified/ Noncertified values ^e
PCB 8	(2,4'-Dichlorobiphenyl)	1.39	(0.15)			
PCB 18	(2,2',5-Trichlorobiphenyl)	1.15	(0.13)			1.15 \pm 0.16 ^f
PCB 28	(2,4,4'-Trichlorobiphenyl)	9.8	(1.3)	[13.9] ^g	(1.0)	9.8 \pm 3.7 ^f
PCB 31	(2,4',5-Trichlorobiphenyl)	6.20	(0.85)			6.2 \pm 2.4 ^f
PCB 44	(2,2',3,5'-Tetrachlorobiphenyl)	4.99	(0.46)	4.60	(0.60)	4.80 \pm 0.62
PCB 49	(2,2',4,5'-Tetrachlorobiphenyl)	10.89	(0.48)	8.04	(0.62)	9.5 \pm 2.1
PCB 52	(2,2',5,5'-Tetrachlorobiphenyl)	6.89	(0.36)	6.89	(0.50)	6.89 \pm 0.56
PCB 66	(2,3',4,4'-Tetrachlorobiphenyl)	7.45	(0.59)	6.08	(0.48)	6.8 \pm 1.4
PCB 87	(2,2',3,4,5'-Pentachlorobiphenyl)	6.71	(0.43)	6.70	(0.80)	6.70 \pm 0.37
PCB 95	(2,2',3,5',6-Pentachlorobiphenyl)	8.17	(0.38)	6.78	(0.53)	7.5 \pm 1.1
PCB 99	(2,2',4,4',5-Pentachlorobiphenyl)	4.03	(0.33)	4.30	(0.32)	4.17 \pm 0.51
PCB 101	(2,2',4,5,5'-Pentachlorobiphenyl)	11.87	(0.86)	10.1	(0.63)	11.0 \pm 1.6
PCB 105	(2,3,3',4,4'-Pentachlorobiphenyl)	3.69	(0.18)	3.61	(0.41)	3.65 \pm 0.27
PCB 110	(2,3,3',4',6-Pentachlorobiphenyl)	9.88	(0.46)	9.07	(0.60)	9.47 \pm 0.85
PCB 118	(2,3',4,4',5-Pentachlorobiphenyl)	10.69	(0.51)	9.38	(0.79)	10.0 \pm 1.1
PCB 128	(2,2',3,3',4,4'-Hexachlorobiphenyl)	2.09	(0.13)	1.64	(0.24)	1.87 \pm 0.32
PCB 138	(2,2',3,4,4',5'-Hexachlorobiphenyl)	13.70	(0.47)	13.07	(0.61)	13.38 \pm 0.97
163	(2,3,3',4',5,6-Hexachlorobiphenyl)					
164	(2,3,3',4',5',6-Hexachlorobiphenyl)					
PCB 149	(2,2',3,4',5',6-Hexachlorobiphenyl)	9.71	(0.55)	8.66	(0.60)	9.2 \pm 1.1
PCB 151	(2,2',3,5,5',6-Hexachlorobiphenyl)			2.62	(0.17)	2.62 \pm 0.22 ^f
PCB 153	(2,2',4,4',5,5'-Hexachlorobiphenyl)	17.9	(1.2)	17.31	(0.83)	17.6 \pm 1.9
PCB 156	(2,3,3',4,4',5-Hexachlorobiphenyl)	0.835	(0.068)	1.028	(0.069)	0.93 \pm 0.14
PCB 170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)	3.20	(0.20)	2.79	(0.29)	3.00 \pm 0.46
190	(2,3,3',4,4',5,6-Heptachlorobiphenyl)					
PCB 180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)	5.60	(0.25)	6.06	(0.49)	5.83 \pm 0.058
PCB 183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)			1.63	(0.16)	1.63 \pm 0.15 ^f
PCB 187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)	9.30	(0.42)	4.64	(0.50)	7.0 \pm 2.6 ^f
182	(2,2',3,4,4',5,6'-Heptachlorobiphenyl)					
PCB 194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl)	1.89	(0.19)	1.66	(0.23)	1.78 \pm 0.23
PCB 206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl)	4.28	(0.23)	3.07	(0.26)	3.67 \pm 0.87
PCB 209	(Decachlorobiphenyl)	8.57	(0.31)	8.11	(0.49)	8.34 \pm 0.49

^a See Table 1

^b Uncertainties (in parentheses) for the results from each analytical technique (GC-ECD and GC-MS) are reported as the standard deviation of a single measurement; subsamples from six bottles were extracted and analyzed in duplicate for both techniques

^c PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell [2] and later revised by Schulte and Malisch [3] to conform with IUPAC rules; for the specific congeners mentioned in this SRM, the Ballschmiter-Zell [2] numbers correspond to those of Schulte and Malisch [3]. When two or more congeners are known to coelute, the PCB congener listed first is the major component and the additional congeners may be present as minor components. The quantitative results are based on the response of the congener listed first

^d Results for GC-ECD are a combination of the results from analyses of the same sample extracts on both the C-18 and DB-5 columns

^e The certified values (bold) are weighted means of results from two analytical techniques as described by Schiller and Eberhardt [1]. The uncertainty is based on a 95% confidence interval for the true concentration, and includes an allowance for differences between the analytical methods used

^f Noncertified concentrations are the mean values determined by the technique indicated; uncertainties for the measurements are a 95% confidence interval for the mean

^g PCB 28 and PCB 31 coelute in the GC-MS analyses

Percent total organic carbon determination

Three laboratories provided results for the percent Total Organic Carbon (TOC) measurements using similar procedures. Briefly, subsamples of ~ 200 mg were reacted

with 6 mol/L 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.

Table 4. Summary of analytical results and certified concentrations for chlorinated pesticides in SRM 1941a

Chlorinated pesticides	Concentration ($\mu\text{g}/\text{kg}$ dry weight) ^{a, b}				Certified values ^d
	GC-ECD ^c		GC-MS		
Hexachlorobenzene	82.0	(6.3)	58.6	(8.6)	70 \pm 25
<i>cis</i> -Chlordane (α -Chlordane)	2.69	(0.27)	1.97	(0.21)	2.33 \pm 0.56
<i>trans</i> -Nonachlor	1.30	(0.11)	1.21	(0.12)	1.26 \pm 0.13
Oxychlordane	2.59	(0.22)			2.59 \pm 0.19 ^e
Dieldrin	1.26	(0.55)			1.26 \pm 0.37 ^e
2,4'-DDE	0.798	(0.040)	0.653	(0.058)	0.73 \pm 0.11
4,4'-DDE	6.85	(0.32)	6.33	(0.35)	6.59 \pm 0.56
4,4'-DDD	4.96	(0.23)	5.16	(0.47)	5.06 \pm 0.58
4,4'-DDT	1.25	(0.12)			1.25 \pm 0.10 ^e

^a See Table 1

^b Uncertainties (in parentheses) for the results from each analytical technique (GC-ECD and GC-MS) are reported as the standard deviation of a single measurement; subsamples from six bottles were extracted and analyzed in duplicate for both techniques

^c Results for GC-ECD are a combination of the results from analyses of the same sample extracts on both the C-18 and DB-5 columns

^d The certified values (bold) are weighted means of results from two analytical techniques as described by Schiller and Eberhardt [1]. The uncertainty is based on a 95% confidence interval for the true concentration, and includes an allowance for differences between the analytical methods used

^e Noncertified concentrations are the mean values determined by the technique indicated; uncertainties for the measurements are a 95% confidence interval for the mean

Table 5. Noncertified concentrations of aliphatic hydrocarbons in SRM 1941a

Aliphatic hydrocarbon	Concentration ($\mu\text{g}/\text{kg}$ dry weight) ^{a, b}
<i>n</i> -Decane (<i>n</i> -C ₁₀)	230 \pm 15
<i>n</i> -Dodecane (<i>n</i> -C ₁₂)	164 \pm 10
<i>n</i> -Tridecane (<i>n</i> -C ₁₃)	207 \pm 25
<i>n</i> -Tetradecane (<i>n</i> -C ₁₄)	264 \pm 35
<i>n</i> -Pentadecane (<i>n</i> -C ₁₅)	470 \pm 120
<i>n</i> -Hexadecane (<i>n</i> -C ₁₆)	147 \pm 19
<i>n</i> -Heptadecane (<i>n</i> -C ₁₇)	269 \pm 38
Pristane (2,6,10,14-Tetramethylpentadecane)	61 \pm 25
<i>n</i> -Octadecane (<i>n</i> -C ₁₈)	151 \pm 15
Phytane (2,6,10,14-Tetramethylhexadecane)	74 \pm 22
<i>n</i> -Nonadecane (<i>n</i> -C ₁₉)	129 \pm 14
<i>n</i> -Eicosane (<i>n</i> -C ₂₀)	167 \pm 17
<i>n</i> -Docosane (<i>n</i> -C ₂₂)	128 \pm 11
<i>n</i> -Tetracosane (<i>n</i> -C ₂₄)	168 \pm 16
<i>n</i> -Hexacosane (<i>n</i> -C ₂₆)	186 \pm 48
<i>n</i> -Octacosane (<i>n</i> -C ₂₈)	138 \pm 24
<i>n</i> -Triacosane (<i>n</i> -C ₃₀)	108 \pm 11

^a See Table 1

^b Concentrations are the mean values determined by GC-MS; uncertainties for the measurements are a 95% confidence interval for the mean. Subsamples from 16 bottles were extracted and analyzed in duplicate

3 Results and discussion

The analytical scheme for the analysis of SRM 1941a for certification of PAHs, PCB congeners, and chlorinated pesticides is illustrated in Fig. 1. The PAHs were deter-

Table 6. Noncertified value for total organic carbon and certified sulfur concentration in SRM 1941a

Noncertified total organic carbon	4.8 \pm 1.2% by weight ^{a, b}
Certified sulfur	0.9589 \pm 0.0058% by weight ^{a, c}

^a See Table 1

^b The TOC value is an equally weighted mean value from routine measurements made by three laboratories;

^c The uncertainty was calculated according to *ISO Guide to the Expression of Uncertainty in Measurement* [17] and has an approximate level of confidence of 95%

mined using four analytical approaches. A more detailed discussion of the certification of the PAHs in this material is published elsewhere [15]. The results from each of the four analytical techniques for the determination of 24 PAHs are summarized in Table 1. The results were in good agreement and were combined to provide certified values for 23 PAHs (see Table 1), which represents the largest number of PAHs certified in a NIST natural matrix SRM. One of the goals for the reissue of the sediment SRM was to reduce the uncertainties associated with the certified values, i.e., reduce the differences among the results from the different analytical methods. Eleven PAHs were certified in the original SRM 1941 with uncertainties ranging from 7–24%. The uncertainties associated with the certified values for SRM 1941a for the 11 PAHs previously certified in SRM 1941 ranged from 3–15% and were reduced compared to SRM 1941 for all but two of the PAHs certified previously. Noncertified concentrations were determined for 14 additional PAHs and are listed in Table 2. Most of these additional compounds were determined by GC-MS analysis on both stationary

Table 7. Noncertified concentrations of inorganic constituents in SRM 1941a

Element	Concentration (mg/kg dry weight) ^{a, b}	Element	Concentration (mg/kg dry weight) ^{a, b}
Na (%)	1.16 ± 0.03	Rb	86 ± 6
Al (%)	7.4 ± 0.3	Sb	11.4 ± 0.4
Cl (%)	1.36 ± 0.08	Cs	5.7 ± 0.2
K (%)	1.63 ± 0.08	La	147 ± 6
Sc	29.4 ± 0.8	Ce	117 ± 3
Ti (%)	1.8 ± 0.2	Sm	12 ± 3
V	830 ± 30	Eu	1.95 ± 0.07
Cr	600 ± 20	Tb	1.2 ± 0.2
Mn	870 ± 20	Hf	33 ± 1
Fe (%)	8.1 ± 0.2	Ta	26.9 ± 0.7
Co	24.8 ± 0.8	Hg	0.5 ± 0.2
Zn	610 ± 20	Au	0.017 ± 0.006
As	55 ± 9	Th	26.3 ± 0.9
Se	3.9 ± 0.6		

^a Results are reported in mg/kg, except where noted in percent. Two subsamples (~ 300 mg each) were analyzed from each of six bottles

^b Overall estimated analytical uncertainty at the 95% confidence level

phases; however, the results are listed as noncertified values generally because of the larger disagreement between the results from the two methods and/or because of the lack of extensive experience in measuring these particular PAHs on the liquid crystalline phase.

The PCB congeners and chlorinated pesticides were determined by GC-ECD and GC-MS (see Fig. 1) using the general approach reported recently by Schantz et al. [16]. The results from these analyses are summarized in Tables 3 and 4. Certified concentrations were determined for 21 PCB congeners and 6 pesticides with the remaining 10 compounds reported as noncertified concentrations based on results obtained from only one technique (GC-ECD). Aliphatic hydrocarbons were determined by GC-MS and the results are reported in Table 5 as noncertified concentrations. A noncertified value for percent total organic carbon (TOC) is reported in Table 6 based on results obtained from three laboratories outside NIST using the same procedure.

Even though SRM 1941a is intended primarily for the determination of organic contaminants, a certified value for sulfur and noncertified concentrations for 27 trace elements are reported. Since elemental sulfur is often present in marine sediments in relatively large quantities (several percent) and it can interfere with the determination of some organic constituents, the determination of sulfur was made by ID-TIMS to obtain a certified sulfur concentration. The ID-TIMS procedure is highly accurate and precise and is considered a definitive method for sulfur at NIST. The certified concentration for sulfur in SRM 1941a is given in Table 6. Instrumental neutron activation analysis (INAA) was used to provide the results for the major and minor elements in Table 7.

Comparison of SRM 1941a with SRM 1941

The sediment material used for SRM 1941a was collected at the same location as the previous material SRM 1941. However, a larger particle size fraction (150–250 μm) was

used compared with the original material (< 250 μm). The concentrations of the PAHs in SRM 1941a are 10–25% lower than in SRM 1941 for phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene, whereas the concentrations of benzo[*a*]pyrene, perylene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene are nearly the same in both materials. For the PCB congeners and the chlorinated pesticides, the concentrations in SRM 1941a are 30–50% lower than in SRM 1941.

The concentration of sulfur in SRM 1941a is approximately one-half the concentration in SRM 1941 (0.9589% vs. 1.717%). For the major elements (Na, Al, Cl, K, Ti, and Fe) and the majority of the trace elements (i.e., V, Cr, Mn, Co, Rb, and Sb), the concentrations in both sediment SRMs are within 10–20%. For Zn, Se, and As the concentrations in SRM 1941a are approximately one half those in SRM 1941. These differences in concentrations of both the organic and inorganic contaminants may be due to the use of the larger particle size material for the new SRM or it may be due to real differences in the levels of contamination at the sampling site after a period of four years.

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