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Marine standards

Preparation and analysis of a marine sediment reference material for the determination of trace organic constituents

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Summary. A new marine sediment Standard Reference Material (SRM) has been prepared and analyzed for the determination of trace organic constituents. SRM 1941, Organics in Marine Sediment, has been certified for concentrations of 11 PAHs using results obtained from gas chromatography (GC) with flame ionization detection, gas chromatography-mass spectrometry, and liquid chromatography with fluorescence detection. Non-certified values for 24 additional PAHs are also reported. GC with electron capture detection was used to provide non-certified concentrations for 15 PCB congeners and 7 chlorinated pesticides. In addition to the organic contaminants, concentrations of 32 major and trace elements were determined using neutron activation analysis, and the sulfur content was also determined using isotope dilution thermal ionization mass spectrometry.

Introduction

A large number of laboratories are involved in analyzing marine sediments and tissues for the determination of organic and inorganic constituents as part of marine monitoring programs. Obtaining reliable data from the analysis of marine samples requires the use of analytical methods that have been validated as to their accuracy. In addition, these analytical methods must be continuously monitored to verify that they remain in control. One method for validating analytical procedures is the use of reference materials that have been well-characterized with respect to the analytes of interest. Several sediment reference materials, which are certified for trace element content, have been available from several organizations for a number of years [1 – 5]. However, only recently have marine sediment reference materials been developed for the determination of organic contaminants. The National Research Council of Canada (NRCC) provides a suite of four harbor sediments that have been characterized for polycyclic aromatic hydrocarbon (PAH) content and three additional sediments that have been characterized for polychlorinated biphenyl (PCB) content [6, 7]. The International Atomic Energy Agency (Vienna, Austria) also provides a marine sediment reference material characterized for the content of PCBs as Aroclor mixtures and selected chlorinated pesticides residues [5]. However, no single sediment reference material has been prepared and characterized for PAHs, PCBs, and chlorinated pesticides.

To meet the need for a single reference material that has been characterized for a variety of organic contaminants, the National Oceanic and Atmospheric Administration (NOAA) requested that the National Institute of Standards and Technology (NIST) prepare a marine sediment reference material, which would be characterized for PAHs, PCBs, and chlorinated pesticides, for use in marine pollution monitoring programs. Standard Reference Material (SRM) 1941, Organics in Marine Sediment, which was collected in the Baltimore harbor, has certified and information values for 35 PAHs, 15 PCB congeners, and 7 chlorinated pesticides. The PAHs were determined using three analytical techniques: gas chromatography with flame ionization detection (GC-FID), gas chromatography-mass spectrometry (GC-MS), and liquid chromatography with fluorescence detection (LC-FL). The PCB congeners and chlorinated pesticides were determined using GC with electron capture detection (GC-ECD). In addition to the organic contaminants, concentrations of 32 major and trace elements were measured using neutron activation analysis. The sulfur content of this material was also measured using isotope dilution thermal ionization mass spectrometry (ID-TIMS) to provide a certified concentration value. SRM 1941 represents the first marine sediment reference material available that has been characterized for such a wide range of organic and inorganic contaminants.

Experimental

Collection and preparation of SRM 1941

Sample collection. The sediment material for SRM 1941 was collected on February 4, 1987 in the Chesapeake Bay, at the mouth of the Baltimore (MD) harbor near the Francis Scott Key Bridge (Position 39°12.85′N and 76°31.70′W). The sample was collected using a Kynar-coated modified Van Veen type grab sampler, which has been used for the collection of sediments in the Mussel Watch Project of the NOAA National Status and Trends program [8]. The sampler is designed to sample sediment at a depth of approximately 10 cm. After draining the excess water, the wet sediment was dropped from the sampler into a Teflon bag inside a 5-gal metal can.

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Preparation of SRM 1941. The wet sediment was transported to the laboratory where it was spread out on shallow aluminum pans (150 × 90 × 3 cm) and air dried for 72 h using fans to circulate the air. The dried sediment had solidified into hard clods approximately 10 cm square. The sediment clods were pulverized using a "flailing hammer" coal pulverizer. This pulverizer consists of a number of pivoting hammers attached to a steel drum that rotates at high speed. A steel screen fits around the rotating drum such that the hammers strike the drum at high force. Any friable material fed into the space between the drum and the screen is pulverized by the hammers and forced through the screen. The pulverized material is entrained in a moving air stream and transferred to the point of collection. The pulverized sediment was sieved through a 100 mesh screen ($\leq$150 μm) to obtain approximately 40 kg of material. The sieved sediment was then homogenized in a large rotary cone blender, radiation sterilized (^{60}Co), and aliquoted into amber bottles (~75 g/bottles) as SRM 1941.

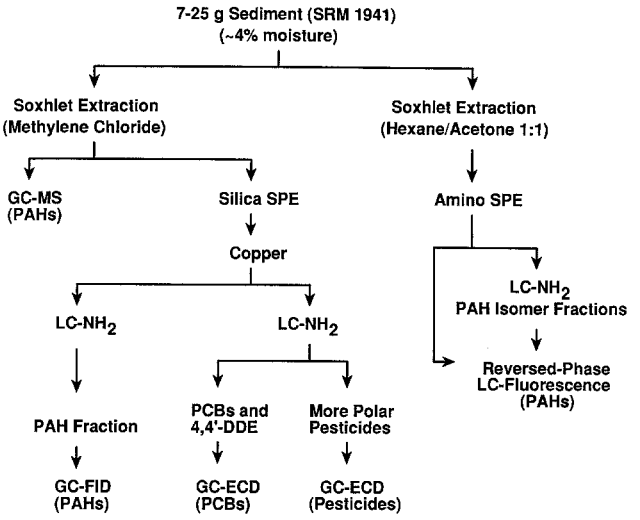

Fig. 1. Analytical scheme for the determination of organic constituents in SRM 1941

Materials

SRM 1491 (Aromatic Hydrocarbons in Hexane/Toluene), SRM 1647a (Priority Pollutant PAH in Acetonitrile), SRM 1645 (River Sediment), SRM 1646 (Estuarine Sediment), and SRM 2704 (Buffalo River Sediment) were obtained from the Office of Standard Reference Materials, National Institute of Standards and Technology (Gaithersburg, MD). CRM SD-N-1/2 was obtained from the International Atomic Energy Agency (Vienna, Austria). Pesticide standards were obtained from the U.S. Environmental Protection Agency Repository (Research Triangle Park, NC) and PCB congeners were obtained from Ultra Scientific (New Kingston, RI). All solvents were HPLC grade distilled in glass.

Determination of moisture content

The percent water in SRM 1941 was determined by both freeze-drying and oven drying. For the freeze drying studies, duplicate aliquots (~2–3 g) of the sediment were removed from 16 different bottles of SRM 1941 and dried in five batches at different times. The samples were weighed and then freeze-dried for 3–5 days at 1 Pa with a −10° C shelf temperature and a −50° C condenser temperature. The weight loss after drying was determined. For the oven drying studies, duplicate aliquots (~2 g) of the sediment were removed from eight of the same bottles used in the freeze drying study. The samples were dried in an oven at 90° C for 18 h and the weight loss determined.

Sample preparation for organic analysis

The analytical scheme for the organic analyses is shown in Fig. 1. Aliquots from twelve bottles (each from a different box of bottles) were extracted and fractionated for the determination of the PAHs by GC-FID, and aliquots from four bottles (each from a different box of bottles) were extracted and fractionated for the GC-ECD determination of PCBs and chlorinated pesticides. Aliquots from three and four bottles (each from a different box of bottles) were extracted for the determination of the PAHs by LC-fluorescence and GC-MS, respectively.

For extraction, an aliquot of 7 to 25 g of SRM 1941 was transferred from the bottle to a glass extraction thimble and weighed. Known weights of appropriate internal standards (see Table 1) were added to the top of the sediment in the extraction thimble. Response/recovery factor solutions were prepared by adding solutions (SRM 1491 for the GC-FID and GC-MS analyses and gravimetrically prepared solutions for the GC-ECD analyses) and appropriate internal standards to precleaned glass wool in glass extraction thimbles. Blanks were prepared by adding known weights of appropriate internal standards to precleaned glass wool in glass extraction thimbles. The samples analyzed by GC-FID, GC-ECD, and GC-MS were Soxhlet extracted for 16–20 h using 250 ml of methylene chloride while the samples analyzed by LC-fluorescence were Soxhlet extracted for 16–20 h using 250 ml of hexane/acetone (1:1 v/v). After Soxhlet extraction, the extracts were concentrated to ~30 ml using a rotary evaporator and then concentrated to a small volume (500 μl or 4 ml) by evaporation enhanced by passing a stream of filtered, dry nitrogen over the sample. The procedure followed from this point depended on the final analysis step (see Fig. 1 and discussion below).

GC-FID and GC-ECD analysis

Sample preparation for GC analysis. The concentrated extract was placed on a silica solid phase extraction (SPE) column (Sep Pak, Waters Associates, Milford, MA), which had been precleaned with 15 ml of 10% methylene chloride in hexane, and was eluted with 15 ml of 10% methylene chloride in hexane to separate the more polar material from the fraction of interest. Copper was then added to the remaining extract to remove sulfur contamination. The remaining fraction was concentrated to ~400 μl for fractionation by normal-phase liquid chromatography on a semi-preparative aminosilane column (μBondapak NH_2, 9 mm i.d. × 30 cm, Waters Associates, Milford, MA). For the normal-phase LC fractionation, 2% methylene chloride in hexane was used as the mobile phase for the isolation of the PAH fraction; hexane was used as the mobile phase for the isolation of the PCB and 4,4′-DDE fraction; and 5%

Table 1. Internal standards used in the analysis of SRM 1941 for the determination of organic constituents

Technique[a]	Internal standard	Analytes determined
GC-FID	1-Butylpyrene	Phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, and benzofluoranthene isomers
	m-Tetraphenyl	Benzo[e]pyrene, benzo[a]pyrene, perylene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene
GC-ECD	PCB 103	PCB 18, 28, 52, 66, and 101
	PCB 198	PCB 118, 153, 105, 138, 187, 180, 170, 195, 206, 209, and 4,4′-DDE
	Endrin	Heptachlor epoxide, cis-chlordane, trans-nonachlor, dieldrin, 4,4′-DDD, and 4,4′-DDT
LC-FL (Total)	Phenanthrene-d_{10}	Phenanthrene and anthracene
	Fluoranthene-d_{10}	Fluoranthene, pyrene, benz[a]anthracene, and chrysene
	Perylene-d_{12}	Perylene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene
LC-FL (Fraction)	Triphenylene-d_{12}	Triphenylene, benz[a]anthracene, and chrysene
	Perylene-d_{12}	Perylene, benzo[k]fluoranthene, and benzo[a]pyrene
	Benzo[ghi]perylene-d_{12}	Benzo[ghi]perylene and indeno[1,2,3-cd]pyrene
GC-MS (Method A)	Naphthalene-d_8	Naphthalene, methyl/dimethylnaphthalenes, and biphenyl
	Acenaphthene-d_{10}	Acenaphthylene and acenaphthene
	Phenanthrene-d_{10}	Fluorene
GC-MS (Method B)	Phenanthrene-d_{10}	Phenanthrene, anthracene, and methyl/dimethylphenanthrenes
	Pyrene-d_{10}	Fluoranthene and pyrene
	Benz[a]anthracene-d_{12}	Benz[a]anthracene and chrysene/triphenylene
	Benzo[e]pyrene-d_{12}	Benzofluoranthene isomers, benzo[e]pyrene, benzo[a]pyrene, and perylene
	Benzo[ghi]perylene-d_{12}	Benzo[ghi]perylene and indeno[1,2,3-cd]pyrene

[a] See Experimental for description of the techniques used for the analyses

methylene chloride in hexane was used for the isolation of the pesticide fraction. The individual fractions were concentrated to ~500 µl for either GC-FID or GC-ECD analysis.

GC-FID and GC-ECD analysis. For the GC-FID analyses, a 0.25 mm × 60 m fused silica capillary column was used that contained an immobilized nonpolar stationary phase with a film thickness of 0.25 µm (DB-5, J & W Scientific, Folsom, CA). Automatic splitless injections of 2 µl were made with the splitter closed for 1 min and then opened at a split flow of 80 ml/min helium. The injector and FID temperatures were maintained at 300°C and 350°C, respectively. Helium was used as the carrier gas at an inlet pressure of 280 kPa (40 psi) and as the detector make-up gas at a flow rate of 30 ml/min. The column temperature was maintained initially at 50°C for 1 min, then programmed at a rate of 50°C per min to 150°C, where it was maintained for 5 min, and then programmed at a rate of 1.5°C per min to 280°C, where it was held for 30 min.

For the ECD analyses, a similar column and the same carrier gas conditions were used. Manual split injections of 2 µl were made with a split flow of 25 ml/min helium. The ECD temperature was 320°C, and nitrogen was used as the detector make-up gas at a flow rate of 30 ml/min. For the PCB and 4,4′-DDE analyses, the injector temperature was 280°C, and the column temperature was maintained at 200°C for 30 min, then programmed at 2°C per min to 270°C where it was held for 30 min. For the pesticide fraction, the injector temperature was 250°C, and the column temperature was initially held at 190°C for 50 min, programmed at 1.5°C per min to 215°C, and then programmed at 45°C per min to 270°C for 15 min.

GC-MS analysis

Sample preparation for GC-MS analysis. The concentrated extracts (~4 ml) were filtered through 0.45 µm fluoropolymer filters (13 mm dia., Gelman Sciences, Inc., LC-13, Ann Arbor, MI). The samples were concentrated under a stream of nitrogen to ~250 µl prior to analysis by GC-MS. The extracts contained a significant amount of precipitated elemental sulfur. The GC-MS analyses were performed without removing the precipitate from the extracts.

GC-MS analysis. Two different GC-MS procedures were used for the determination of PAHs in the sediment extracts. Eight of the more volatile PAHs (naphthalene, 1-methyl- and 2-methylnaphthalenes, 2,6-dimethylnaphthalene, biphenyl, acenaphthylene, acenaphthene and fluorene) were determined using Method A, whereas the other 25 species were measured using Method B. Both groups of PAHs were detected by MS in the single-ion monitoring (SIM) mode using a Mass Selective Detector (MSD). Approximately 0.3 µl of each extract was injected into the GC to determine the volatile PAH and a total of six measurements were performed. For the GC-MS analyses, a capillary column was used that was identical to the one described above for the GC-FID analyses. The injector and GC-MS interface temperatures were maintained at 300°C. Helium was used as the carrier gas with an inlet pressure of 175 kPa (25 psi) and a split flow of 6 and 30 ml/min for Methods A and B, respectively.

For Method A, the column temperature was maintained initially at 50°C for 1 min, then programmed to 100°C at

50° C/min where it was held for 2 min, then programmed to the final temperature of 268° C at a rate of 4° C/min. During the course of the GC analysis, the mass spectrometer monitored the following masses: 14–20 min, 128, 136, and 124 amu; 20–24 min, 152, 154, and 156 amu; 24–27.3 min, 155, 164, and 170 amu; and 27.3–34 min, 166, 178, and 188 amu. Injections of 1 to 2 µl were used in quantifying the nonvolatile PAHs.

For Method B, the column temperature was maintained initially at 150° C for 2 min, then programmed to 300° C at a rate of 4° C/min where it was held for 40 min. The single-ion monitoring program for Method B was as follows: 18–22 min, 178 and 188 amu; 22–26.5 min, 192 and 206; 26.5–35 min, 202 and 212; 35–41 min, 226, 228, and 240 amu; 41–46 min, 252 and 264; and 46–60 min, 276 and 288. After each GC run, the column was heated to 300° C and two large aliquots (5–10 µl) of dichloromethane were injected into the GC-MS to flush any contaminants from the instrument. One of the two response/recovery standards was run each day with the samples, and the resulting response/recovery factors were used in calculating the concentrations of PAHs in the extracts processed on that day.

Reversed-phase LC analyses

Sample preparation for LC analyses. The concentrated extract was placed on an amino (NH_2) solid phase extraction column (precleaned with 2% methylene chloride in hexane) and eluted with 20 ml of 2% methylene chloride in hexane. The eluant collected from the SPE column was defined as the "total PAH" fraction. This fraction was divided into two portions; one portion was used for normal-phase LC fractionation to isolate isomeric PAH fractions, based on the number of aromatic carbons, and the other portion was used for reversed-phase LC analyses after changing the solvent to acetonitrile (see below).

Normal-phase LC isolation of isomer fractions. The total PAH extract was fractionated on a semi-preparative aminosilane column (µBondapak NH_2, Waters Associates, Milford, MA) as described previously [9–12] using a mobile phase of 3% methylene chloride in n-hexane at 5 ml/min. Standards of benz[a]anthracene, triphenylene, benzo[a]pyrene, perylene, and benzo[ghi]perylene were run to determine the collection volumes for each of the three fractions of interest. The fractions were concentrated and the solvent changed to acetonitrile for the reversed-phase LC analyses.

Reversed-phase LC analysis of total PAH fraction. LC analyses were performed on a reversed-phase octadecylsilane column, 5 µm particle size, 4.6 mm i.d. × 25 cm (Vydac 201TP, The Separations Group, Hesperia, CA). Similar procedures have been reported previously for the determination of PAHs in an air particulate SRM [10] and more recently in a coal tar SRM [12]. The chromatographic conditions were as follows: linear gradient from 50% acetonitrile in water to 100% acetonitrile in 50 min at 1.5 ml/min; hold at 100% acetonitrile for 5 min. The fluorescence detector excitation bandpass was 10 nm and the emission bandpass was 2.5 nm. The fluorescence detector excitation and emission wavelengths were programmed as follows:

Wavelength change	Excitation (nm)	Emission (nm)	PAH determined
Initial	249	362	Phenanthrene-d_{10} Phenanthrene
1	250	400	Anthracene
2	285	450	Fluoranthene-d_{10} Fluoranthene
3	333	390	Pyrene
4	285	385	Benz[a]anthracene Chrysene
5	406	440	Perylene-d_{12} Perylene
6	296	405	Benzo[a]pyrene Benzo[k]fluoranthene Benzo[ghi]perylene
7	300	500	Indeno[1,2,3-cd]pyrene

Each of the three extracts was analyzed in triplicate. Response factors for each of the analytes were determined by running a calibration solution of SRM 1647a, perylene, and the internal standards.

Benzo[b]fluoranthene was determined in separate LC analyses under the same chromatographic conditions as above. The fluorescence detector was programmed as above with the exception that immediately after the elution of perylene-d_{12} wavelengths of excitation at 295 nm and emission at 425 nm were used to determine the benzo[b]fluoranthene.

Reversed-phase LC analysis of PAH isomer fractions. Triphenylene was determined in the four aromatic ring fraction which contains triphenylene, chrysene, and benz[a]anthracene. The same C_{18} column as above and the following conditions were used for the analysis: 60% acetonitrile in water for 15 min, then linear gradient to 100% acetonitrile in 5 min; flow rate of 1.5 ml/min. The fluorescence detection conditions were set to excitation/emission 252/352 nm (10/2.5 nm bandpass) to determine triphenylene-d_{12} and triphenylene; then after the elution of triphenylene, the fluorescence detection wavelengths were changed to excitation/emission 285/385 nm to determine benz[a]anthracene-d_{12}, benz[a]anthracene, and chrysene. Duplicate analyses were performed on each of the three samples.

Benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were determined in the six aromatic ring fraction using the same C_{18} column as above and the following conditions: 80% acetonitrile in water for 5 min, then linear gradient to 100% acetonitrile in 15 min at a flow rate of 1.5 ml/min. The fluorescence detection conditions were set to excitation/emission 380/405 nm (10/5 nm bandpass) to monitor benzo[ghi]perylene-d_{12} and benzo[ghi]perylene, then changed to 300/500 nm after the elution of benzo[ghi]perylene to monitor indeno[1,2,3-cd]pyrene. Duplicate analyses were performed on each of the three samples to measure benzo[ghi]perylene and indeno[1,2,3-cd]pyrene.

The five aromatic ring fraction was analyzed to obtain additional results for perylene, benzo[k]fluoranthene, benzo[b]fluoranthene, and benzo[a]pyrene. The same C_{18} column as above was used with an isocratic mobile phase of 75% acetonitrile in water at 1.5 ml/min. Fluorescence conditions were set at excitation/emission 406/440 nm (10/5 nm bandpass) to determine perylene-d_{12} and perylene, then changed to excitation/emission 296/405 nm to deter-

mine benzo[k]fluoranthene and benzo[a]pyrene. Triplicate analyses were performed on two samples.

Neutron activation analysis

The inorganic analysis procedure applied in this work followed the previously published principles for sequential multi-element determinations in marine biological materials [13]. The applied procedure is summarized briefly; however, a more detailed description of the methods has been described previously [14].

To determine as many elements as possible in each individual sample, three irradiations were performed at the research reactor at NIST. Three aliquots (~250 mg) of the sediment were removed from each of two bottles of SRM 1941 and pelletized. Aliquots of SRM 1645, SRM 1646, SRM 2704, and IAEA CRM SD-N-1/2 were also pelletized. The pellets were sealed in Teflon for irradiation at the Prompt Gamma Activation Analysis (PGAA) facility [15] at NIST for the determination of B, Na, Al, Si, S, Cl, K, Ti, Mn, Fe, Cd, Sm, and Gd. The samples were then transferred to linear polyethylene bags for instrumental neutron activation analysis (INAA). The first INAA step was an irradiation and counting cycle for the assay of elements that form short lived nuclides: Na, Al, Cl, Ti, V, and Mn. After decay, a second irradiation followed by three counts was conducted to determine the remaining elements reported in this work (i.e., Sc, Cr, Fe, Co, Zn, As, Se, Rb, Ag, Sb, Cs, La, Ce, Sm, Eu, Hf, Tb, Ta, Th, and U). In cases where an element was determined by both PGAA and INAA, (e.g., Na, Al, Cl, Ti, Mn, and Sm), the results with more precise counting statistics and/or less spectral interference are reported. The INAA irradiations were performed at the RT-4 pneumatic facility at NIST with a thermal fluence rate of $2 \cdot 10^{17}$ n $\cdot$ m$^{-2} \cdot$ s^{-1} [16]. The first irradiation was 30 s, counting time was 300 s after a 500 s decay; the second irradiation was 16 h followed by 4 h counts after 6–8 days and 20–22 day decay and by an 20–24 h count after 2 months decay. High resolution, high count rate techniques including loss-free counting [17] were applied with 1.8–1.9 keV full width at half maximum (FWHM), 25% relative efficiency spectrometers in the shorter counts; a 1.65 keV FWHM, 7% relative efficiency spectrometer was used in the long count. After these cycles, instrumental data evaluation provided quantitative results for 32 elements.

Isotope dilution thermal ionization mass spectrometry

The general procedure for the determination of sulfur by ID-TIMS has been described in detail previously [18, 19]. Sample aliquots of about 1 g were initially added to weighing bottles and allowed to equilibrate with laboratory air in a class 100 hood for 3.5 h. This allowed the samples to approach a constant weight and made weighing much easier and more accurate. The weight gain ranged from 0.689–0.795% relative. A single undried sample of approximately 100 mg was taken from each of the six different weighing bottles and added to Pyrex Carius tubes along with enriched ^{34}S tracer and NIST high purity nitric acid. The remaining sample was then dried at 90°C for 18 h to establish the dry weight. The range in weight loss for the six bottles was 5.06–5.24% relative. Immediately after the addition of the samples, the Carius tubes were sealed and heated at 240°C for 16 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. Samples were chemically processed in groups of three plus one blank. The sulfate in the samples was reduced to H_2S which was precipitated as As_2S_3. This compound is dissolved in aqueous ammonia and a small amount of this solution, equivalent to about 1.5 µg S, is mixed with silica gel on a rhenium filament and the sulfur is determined as the AsS^+ molecular ion. The reproducibility of this procedure is about 0.2% relative.

Results and discussion

Moisture determination

The results for both the organic and inorganic constituents in SRM 1941 are reported on a dry weight basis; however, the material "as received" contains residual moisture. The amount of moisture in SRM 1941 at the time of the certification analyses was determined by measuring the weight loss after freeze drying and oven drying. Seven batches of samples were dried; the mean of each batch was determined and the standard error from the seven batches was computed. The water content in SRM 1941 was determined to be $3.98 \pm 0.57\%$ (95% confidence limits). Analytical results were determined on an "as received" basis and then converted to a dry weight basis by using the correction factor for water loss of 1.04.

Determination of PAH

The results from at least two independent analytical procedures are used at NIST to determine the "certified" concentrations of the analytes in environmental SRM's. When only one analytical technique is used, then the concentrations are reported as "non-certified or information" values rather than "certified" values. The analytical approach for the measurement of the organic contaminants in SRM 1941 is shown in Fig. 1. Three analytical techniques were used for the determination of PAHs, i.e., gas chromatography with flame ionization detection (GC-FID), gas chromatography with mass spectrometric detection (GC-MS), and reversed-phase liquid chromatography with fluorescence detection (LC-FL). These three techniques have been used extensively at NIST for the measurement of PAHs in environmental samples [20]. Recently, the results of GC-MS and LC-FL analyses of several SRM's and reference samples were summarized and the comparability of the two techniques was discussed in detail [21].

For each of the three approaches used for the determination of PAHs (see Fig. 1), different sample extraction and preparation steps were employed, as well as several different internal standards (see Table 1). Sample preparation for both the GC-FID and LC-FL analyses involved the isolation of the PAH fraction using normal-phase LC. However, the degree of cleanup of the PAH fraction was dependent on the selectivity of the final detection step. Since the flame ionization detector is a universal detector, the PAH fraction was isolated from the aliphatic hydrocarbons and the more polar compounds by using normal-phase LC on an aminosilane column. However, since fluorescence detection in LC provides excellent selectivity for the determination of PAHs, a relatively simple cleanup on a solid phase extraction column (aminosilane) could be used to remove only the more polar compounds. Mass spectrometry offers the most

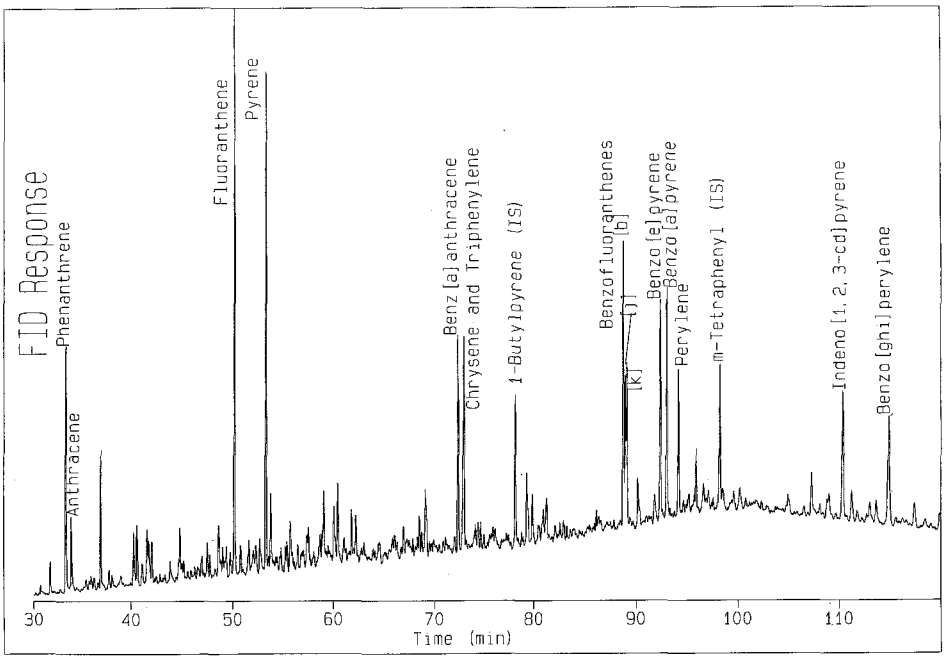

Fig. 2
Chromatogram from the GC-FID analysis of the PAH fraction of SRM 1941

Table 2. Summary of analytical results for the determination of PAHs in SRM 1941

Compound	Concentration (ng/g dry weight)[a]			
	GC-FID	GC-MS	LC-FL (Direct)	LC-FL (Fraction)
Phenanthrene	597 ± 4[b]	603 ± 10	531 ± 12	
Anthracene	202 ± 6	228 ± 12	174 ± 8	
Fluoranthene	1116 ± 20	1401 ± 41	1135 ± 10	
Pyrene	1008 ± 16	1238 ± 18	989 ± 34	
Benz[a]anthracene	538 ± 12	599 ± 14	516 ± 7	521 ± 1[d]
Chrysene	577 ± 12[c]	702 ± 16[b]	425 ± 42	473 ± 5[d]
Triphenylene				192 ± 3[d]
Benzo[b]fluoranthene	635 ± 17	864 ± 28	839 ± 14	843
Benzo[j]fluoranthene	351 ± 14			
Benzo[k]fluoranthene	439 ± 19	857 ± 25[f]	456 ± 6[e]	443 ± 16
			441 ± 8[e]	
Benzo[e]pyrene	472 ± 25	672 ± 24		
Benzo[a]pyrene	566 ± 12	754 ± 49	674 ± 12	690 ± 25
Perylene	415 ± 8	437 ± 27	411 ± 6	426 ± 5
Benzo[ghi]perylene	478 ± 14	566 ± 26		504 ± 7
Indeno[1,2,3-cd]pyrene	572 ± 28	559 ± 19	573 ± 20	575 ± 8

[a] Concentrations reported on dry weight basis; material as received contains residual moisture
[b] Uncertainties for GC-FID, LC-FL, and GC-MS measurements are ± one standard deviation of a single measurement; for GC-FID measurements, 12 samples analyzed in triplicate; for LC measurements, three samples analyzed in triplicate; for GC-MS measurements, four samples analyzed in duplicate
[c] Value is for chrysene and triphenylene
[d] Determined using triphenylene-d_{12} as internal standard
[e] Benzo[k]fluoranthene was determined at different times, i.e., during initial analyses of total PAH fraction and during benzo[b]fluoranthene analyses
[f] Value is for benzo[k]fluoranthene and benzo[j]fluoranthene

selective detection approach, provided that the PAH isomers are separated from each other by GC. Because of the selectivity of MS detection, the extracts were analyzed directly by GC-MS with no cleanup or PAH isolation step, thereby providing an approach completely independent of the LC cleanup steps used by both the GC-FID and LC-FL approaches. It should be noted that due to the high sulfur content of this sediment material (1.7%, see discussion below), sulfur precipitates out of solution when the extracts are concentrated to small volumes if no cleanup step is taken to remove the sulfur. The GC-MS analyses were performed without removing the precipitate from the extracts. The chromatogram from the GC-FID analyses of the PAH fraction isolated from the sediment extract is shown in Fig. 2.

The results for the determination of 15 major PAHs using GC-FID, LC-FL, and GC-MS are summarized and

Table 3. Certified concentrations of polycyclic aromatic hydrocarbons in SRM 1941

Compound	Concentration (μg/g dry weight)[a,b]
Phenanthrene	0.577 ± 0.059
Anthracene	0.202 ± 0.042
Fluoranthene	1.22 ± 0.24
Pyrene	1.08 ± 0.20
Benz[a]anthracene	0.550 ± 0.078
Benzo[b]fluoranthene	0.78 ± 0.19
Benzo[k]fluoranthene	0.444 ± 0.049
Benzo[a]pyrene	0.67 ± 0.13
Perylene	0.422 ± 0.033
Benzo[ghi]perylene	0.516 ± 0.083
Indeno[1,2,3-cd]pyrene	0.569 ± 0.040

[a] Concentrations reported on dry weight basis; material as received contains residual moisture

[b] The certified values are weighted means of results from two or more analytical techniques. The weights for the weighted means were computed according to the iterative procedure of Paule and Mandel [22]. Each uncertainty is obtained from a 95% prediction interval plus an allowance for systematic error among the methods used. The allowance for systematic error is equal to the greatest difference between the weighted mean (certified value) and the component means for the analytical methods used. In the absence of systematic error, the resulting uncertainty limits will cover the concentration of approximately 95% of samples of this SRM having a minimum sample size of approximately 5 g

Table 4. Non-certified concentrations of additional PAHs in SRM 1941

Compound[a]	Concentration (ng/g dry weight)[b]
Naphthalene	1322 ± 14
2-Methylnaphthalene	406 ± 36
1-Methylnaphthalene	229 ± 19
Biphenyl	115 ± 15
2,6-Dimethylnaphthalene	198 ± 23
Acenapthylene	115 ± 10
Acenaphthene	52 ± 2
Fluorene	104 ± 5
3-Methylphenanthrene	150 ± 5
2-Methylphenanthrene	190 ± 6
2-Methylanthracene	66 ± 7
9-Methyl and 4-methylphenanthrene[c]	145 ± 8
1-Methylphenanthrene	109 ± 6
2,6-Dimethylphenanthrene	68 ± 4
2,7-Dimethylphenanthrene	52 ± 4
1,3-, 2,10-, 3,9-, and 3,10-Dimethylphenanthrene[c]	161 ± 11
1,6- and 2,9-Dimethylphenanthrene[c]	93 ± 6
1,7-Dimethylphenanthrene	62 ± 4
2,3-Dimethylphenanthrene	36 ± 3
Benzo[a]fluoranthene	146 ± 4
Triphenylene[d]	192 ± 3
Chrysene[d]	(449)
Benzo[j]fluoranthene[e]	351 ± 14
Benzo[e]pyrene[e]	(573)

[a] Naphthalene through fluorene determined using GC-MS Method A; remaining PAHs determined using GC-MS Method B

[b] Concentrations reported on dry weight basis; material as received contains residual moisture; four sediment extracts were analyzed in duplicate; uncertainties are ± one standard deviation of a single measurement

[c] Represents co-elution of two or more compounds

[d] Triphenylene and chrysene were determined by LC-fluorescence; value for chrysene is the mean value of results obtained by the two LC-fluorescence procedures

[e] Benzo[j]fluoranthene and benzo[e]pyrene were determined by GC-FID; value for benzo[e]pyrene is the mean value of the results obtained by GC-FID and GC-MS

compared in Table 2. Eleven of the PAHs determined by LC-FL were measured by analysis of the total PAH fraction from the extract [LC-FL (Direct) in Table 2]. However, it was not possible to measure accurately several PAHs in the total PAH fraction (i.e., triphenylene and benzo[ghi]-perylene) due to their low fluorescence sensitivity and/or interferences. To provide results for triphenylene and benzo-[ghi]perylene, a normal-phase LC procedure was used to isolate isomeric PAH fractions which were then analyzed by LC-FL [LC-FL (Fraction) in Table 2]. This sequential normal-phase/reversed-phase LC procedure has been reported previously [9–11] and was described most recently for the determination of these same two compounds in a coal tar SRM [12]. In the analysis of the total PAH fraction, the peaks for chrysene and benz[a]anthracene were not completely resolved from other peaks. Thus, chrysene and benz[a]anthracene were measured along with triphenylene during the analysis of the four ring aromatic fraction. The five aromatic ring fraction was analyzed to determine additional results for perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene. The six aromatic ring fraction was analyzed to obtain results for benzo[ghi]-perylene and additional data for indeno[1,2,3-cd]pyrene.

As shown in Table 2, the differences among the results from the three techniques generally ranged between 20–30% for most of the PAHs. Much better agreement for the results from the three techniques was obtained for phenanthrene, perylene, and indeno[1,2,3-cd]pyrene, which differed by only 14, 6, and 3%, respectively. In general, the agreement between the LC-FL and the GC-FID results was good with differences of only 1–5% for most of the analytes. The largest difference between the LC-FL and GC-FID results was 18% for benzo[a]pyrene.

The determination of chrysene and triphenylene is of particular interest since these two PAH are generally not separated by GC. Concentrations for chrysene and triphenylene as determined by GC are generally reported as a combined value. Reversed-phase LC is capable of separating these two compounds; however, quantification of triphenylene in natural mixtures is difficult because of low sensitivity and selectivity for this PAH with fluorescence detection. To overcome this problem, the four aromatic ring fraction was isolated from the total PAH fraction using normal-phase LC and then analyzed by reversed-phase LC as described previously [10, 12]. The two LC results for chrysene (Direct and Fraction) are in good agreement (425 ± 42 and 473 ± 5 ng/g). The GC-FID and GC-MS results for chrysene/triphenylene are 577 ± 12 and 702 ± 16, respectively, (mean of 639 ng/g) compared to the sum of LC results for triphenylene (192 ng/g) and chrysene (mean of 449 ng/g) which is 641 ng/g.

Six PAHs with five aromatic rings were measured using various combinations of the three analytical techniques.

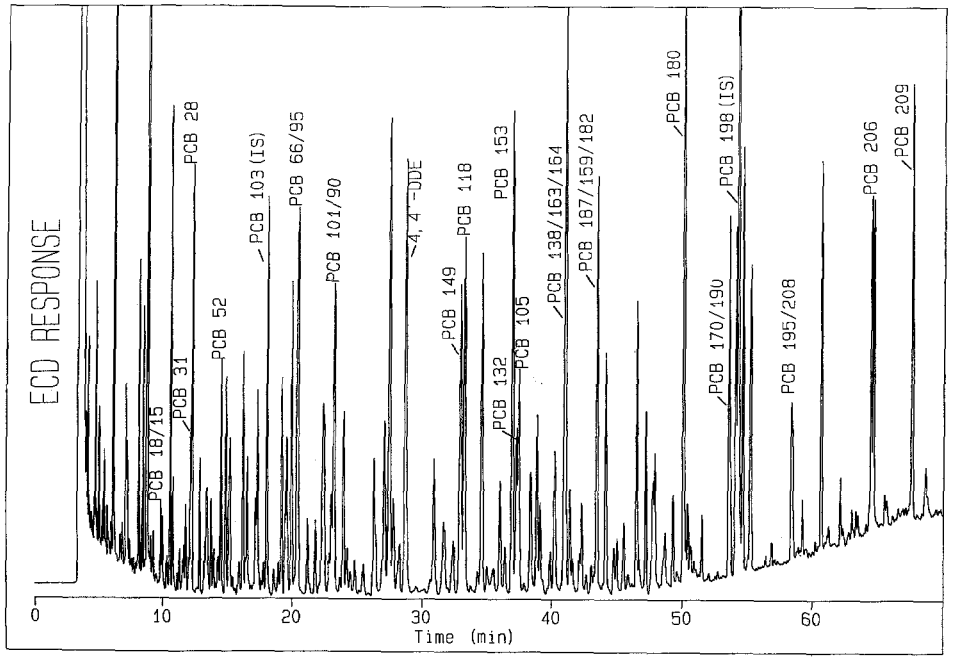

Fig. 3
Chromatogram from the GC-ECD analysis of the PCB and 4,4′-DDE fraction from SRM 1941

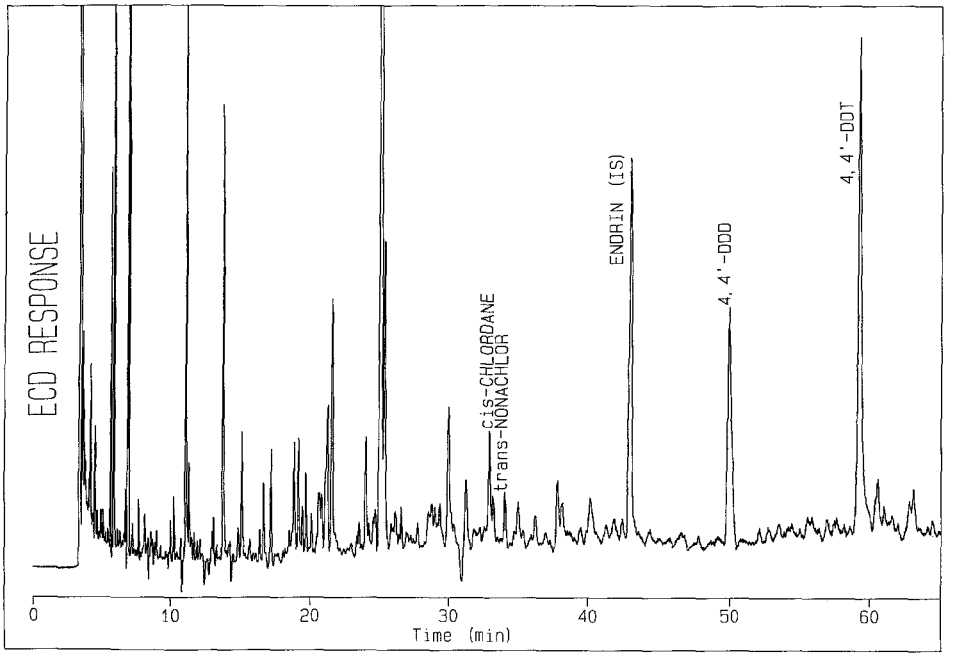

Fig. 4
Chromatogram from the GC-ECD analysis of the more polar pesticide fraction from SRM 1941

Three benzofluoranthene isomers (b, j, and k) are difficult to separate using conventional non-polar GC stationary phases. Sufficient resolution was obtained in the GC-FID analyses on the 60 m column to provide results for each isomer. However, in the GC-MS analyses using a similar column, the benzo[k]fluoranthene and the benzo[j]fluoranthene were not resolved. The agreement among the LC and GC-FID results for benzo[k]fluoranthene was excellent, and if the GC-FID results for benzo[j]fluoranthene and benzo[k]fluoranthene are combined (790 ng/g), the result compares favourably with the GC-MS result for these two PAHs (857 ± 25). For benzo[b]fluoranthene, the GC-FID results were about 25% lower than those obtained from the other techniques. Among the three techniques, the results for benzo[a]pyrene differed by the largest amount (33%), whereas the results for perylene differed by only 6%.

The largest molecular weight PAHs determined by two or more techniques were benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. Benzo[ghi]perylene is difficult to measure by LC-FL in a total PAH fraction due to coeluting peaks and low sensitivity and selectivity [21]. Thus, the benzo[ghi]perylene fraction (six aromatic ring fraction) was isolated by normal-phase LC to enrich the concentration of the analytes of interest and to reduce the number of potential interfering compounds in the analysis [22]. Using this approach, the LC results for benzo[ghi]perylene (504 ± 7) were in good agreement with the GC-FID results (478 ± 14 ng/g) and within about 12% of the GC-MS measurements (567

Table 5. Non-certified concentrations of selected PCB congeners and chlorinated pesticides in SRM 1941 as determined by GC-ECD

Polychlorinated biphenyls[a]		Concentration (ng/g dry weight)[b]
PCB 18	(2,2′,5-Trichlorobiphenyl)	9.90 ± 0.25
15	(4,4′-Dichlorobiphenyl)	
PCB 28	(2,3,3′-Trichlorobiphenyl	16.1 ± 0.4
PCB 52	(2,2′,5,5′-Tetrachlorobiphenyl)	10.4 ± 0.4
PCB 66	(2,3′,4,4′-Tetrachlorbiphenyl)	22.4 ± 0.7
95	(2,2′,3,5′,6-Pentachlorobiphenyl)	
PCB 101	(2,2′,4,5,5′-Pentachlorobiphenyl)	22.0 ± 0.7
90	(2,2′,3,4′,5-Pentachlorobiphenyl)	
PCB 105	(2,3,3′,4,4′-Pentachlorobiphenyl)	5.76 ± 0.23
PCB 118	(2,3′,4,4′,5-Pentachlorobiphenyl)	15.2 ± 0.7
PCB 138	(2,2′,3,4,4′,5′-Hexachlorobiphenyl)	24.9 ± 1.8
163	(2,3,3′,4′,5,6-Hexachlorobiphenyl)	
164	(2,3,3′,4′,5′,6-Hexachlorobiphenyl)	
PCB 153	(2,2′,4,4′,5,5′-Hexachlorobiphenyl)	22.0 ± 1.4
PCB 170	(2,2′,3,3′,4,4′,5-Heptachlorobiphenyl)	7.29 ± 0.26
190	(2,3,3′,4,4′,5,6-Heptachlorobiphenyl)	
PCB 180	(2,2′,3,4,4′,5,5′-Heptachlorobiphenyl)	14.3 ± 0.3
PCB 187	(2,2′,3,4′,5,5′6-Heptachlorobiphenyl)	12.5 ± 0.6
159	(2,3,3′,4,5,5′-Hexachlorobiphenyl)	
182	(2,2′3′,4,4′,5,6′-Heptachlorobiphenyl)	
PCB 195	(2,2′,3,3′,4,4′5,6′-Octachlorobiphenyl)	1.51 ± 0.10
208	(2,2′3,3′,4,5,5′,6,6′-Nonachlorobiphenyl)	
PCB 206	(2,2′,3,3′,4,4′,5,5′,6-Nonachlorobiphenyl)	4.81 ± 0.15
PCB 209	(Decachlorobiphenyl)	8.35 ± 0.21
Chlorinated pesticides		
Heptachlor epoxide		0.23 ± 0.02
cis-Chlordane (alpha-Chlordane)		2.06 ± 0.05
trans-Nonachlor		0.97 ± 0.03
Dieldrin		0.63 ± 0.03
4,4′-DDE		9.71 ± 0.17
4,4′-DDD		10.3 ± 0.1
4,4′-DDT		1.11 ± 0.05

[a] PCBs are numbered according to reference [32]; PCB congener listed first is the major component; additional PCB congeners listed may be present as minor components

[b] Concentrations reported on dry weight basis; material as received contains approximately 4% moisture. Four extracts were analyzed in triplicate; uncertainties are ± one standard deviation of a single measurement

Table 6. Comparison of concentrations of PAHs in SRM 1941 and NRCC reference material HS-4

Compound	Concentration (ng/g)[a]	
	SRM 1941	HS-4[b]
Naphthalene	(1322)[c]	150[d]
Acenaphthylene	(115)[c]	150[d]
Acenaphthene	(52)[c]	150[d]
Fluorene	(104)[c]	150[d]
Phenanthrene	577 ± 59	680 ± 80
Anthracene	202 ± 42	140 ± 70
Fluoranthene	1220 ± 240	1250 ± 100
Pyrene	1080 ± 200	940 ± 120
Benz[a]anthracene	550 ± 78	530 ± 50
Chrysene	(472)[c]	650 ± 80
Benzo[b]fluoranthene	778 ± 187	700 ± 150
Benzo[k]fluoranthene	444 ± 49	360 ± 50
Benzo[a]pyrene	670 ± 130	650 ± 80
Benzo[ghi]perylene	516 ± 83	580 ± 220
Indeno[1,2,3-cd]pyrene	569 ± 40	510 ± 150

[a] Concentrations for SRM 1941 are reported on dry weight basis whereas HS-1 and HS-2 are reported on an "as received" basis

[b] Results for HS-4 are from NRCC [36]

[c] Non-certified concentration

[d] Represent upper limit for concentration

± 26 ng/g). For indeno[1,2,3-cd]pyrene all four results agreed within 3% i.e., 572 ± 28 ng/g (GC-FID), 573 ± 20 ng/g (LC Direct), 575 ± 8 ng/g (LC Fraction), and 559 ± 19 ng/g (GC-MS).

Based on the results from the three different techniques, certified concentrations of 11 PAHs were determined and these values are summarized in Table 3. In addition to the 15 PAHs listed in Table 2, a number of lower molecular weight PAHs and methyl- and dimethylphenanthrene/anthracene isomers were determined by the GC-MS procedure to provide information values (see Table 4). The first eight PAHs in Table 4 were determined in response to the needs of the NOAA National Status and Trends marine monitoring program [23].

The methylphenanthrene isomer distribution has been used as an indicator of the maturity of ancient organic matter and could also be used to differentiate a pyrolytic or petrogenic source [24–28]. Two methylphenanthrene indices have been used to differentiate sources: MPI (ratio of the sum of 2-methyl and 3-methylphenanthrene to the sum of the other three methylphenanthrene isomers) and ΣMP/P (ratio of the sum of all methylphenanthrene isomers to the phenanthrene concentration) [24, 25]. Using the results from Table 4, the MPI and ΣMP/P values for SRM 1941 are about 1.3 and 1.0, respectively, indicating pyrolytic inputs as major sources when compared to values obtained on a variety of environmental samples (e.g., air particulate matter, crude oils, and recent and ancient marine sediments) [24–28]. The indice ΣMP/P exhibits values greater than 2 if the input is petrogenic. The ratio of phenanthrene/anthracene also confirms these observations, i.e., the low values observed in this sediment (Phen/Anth = 2.85) are typically found in high temperature processes while values greater than 10 are found in fossil fuel material [26–28]. The GC fingerprint of the dimethylphenanthrene isomers in this sediment is similar to those observed in extracts of air particulate matter [29], mobile source emissions [30], and oil shale [31] indicating the presence of most of the isomers previously identified in other matrices [31].

Determination of PCB congeners and chlorinated pesticides

The PCBs were separated from the majority of the chlorinated pesticides (except 4,4′-DDE) prior to GC-ECD analysis (see Fig. 1). The chromatograms from the GC-ECD analyses of these two fractions are shown in Figs. 3 and 4. The results for the determination of 15 PCB congeners and 7 chlorinated pesticides in SRM 1941 are given in Table 5. The concentrations for the PCB congeners range from 1.51 ng/g for PCB 195 to 24.9 ng/g for PCB 138 while the concentrations for the pesticides are lower, ranging from 0.23 ng/g for heptachlor epoxide to 10.3 ng/g for 4,4′-DDD. These concentrations were determined using only one analytical method (i.e., GC-ECD), as shown in Fig. 1, and are

Table 7. Comparison of concentrations of PCB congeners in SRM 1941 and NRCC reference materials HS-1 and HS-2

Compound	Concentration (ng/g)[a]		
	SRM 1941	HS-1[b]	HS-2[b]
PCB 101	22.0 ± 0.7	1.62 ± 0.21	5.42 ± 0.34
PCB 138	24.9 ± 1.8	1.98 ± 0.28	6.92 ± 0.58
PCB 153	22.0 ± 1.4	2.27 ± 0.28	6.15 ± 0.67
PCB 170	7.29 ± 0.26	0.27 ± 0.05	1.07 ± 0.15
PCB 180	14.3 ± 0.3	1.17 ± 0.15	3.70 ± 0.33
PCB 209	8.35 ± 0.21	0.33 ± 0.10	0.90 ± 0.14

[a] Concentrations for SRM 1941 are reported on dry weight basis whereas HS-1 and HS-2 are reported on an "as received" basis
[b] Results for HS-1 and HS-2 are from NRCC [36]

Table 8. Non-certified concentrations of inorganic constituents in SRM 1941

Element	Concentration (μg/g dry weight)[a,b]	Element	Concentration (μg/g dry weight)[a,b]
B[c]	75.5 ± 1.7	Rb	92.1 ± 1.3
Na (%)	1.29 ± 0.03	Ag	1.24 ± 0.5
Al (%)	6.48 ± 0.24	Sb	15.2 ± 0.4
Si[c] (%)	22.2 ± 0.80	Cd[c]	2.32 ± 0.4
Cl (%)	1.64 ± 0.04	Cs	4.78 ± 0.13
K[c] (%)	1.58 ± 0.01	La	359 ± 12
Sc	34.4 ± 0.4	Ce	272 ± 4
Ti[c] (%)	1.72 ± 0.03	Sm[c]	25.7 ± 0.4
V	812 ± 31	Eu	2.19 ± 0.06
Cr	635 ± 10	Tb	2.15 ± 0.6
Mn	788 ± 10	Gd[c]	15.2 ± 0.4
Fe (%)	10.6 ± 0.1	Hf	22.4 ± 0.3
Co	27.5 ± 0.1	Ta	16.4 ± 0.5
Zn	1010 ± 40	Th	25.6 ± 0.3
As	75.4 ± 4.0	U[d]	22 ± 2
Se	10.1 ± 0.5		

[a] Results are reported in μg/g, except where noted in percent; concentrations reported on dry weight basis; results based on a sample size of 250 mg
[b] Uncertainties represent $ts/\sqrt{n}$ at the 95% confidence level
[c] Results determined by PGAA
[d] Uranium concentration was obtained using fission product decay to ^{140}La daughter

therefore provided as non-certified values. The Soxhlet extraction, solid phase extraction column, and sulfur removal steps are the same as for the GC-FID analysis; however, the normal-phase LC step is different. The aminosilane column, which separates on the basis of polarity, is used to separate the PCB congeners and lower polarity pesticides, in this case 4,4′-DDE, from the more polar pesticides [33]. The use of such a polarity separation minimizes possible interferences between the pesticides and PCBs during the GC analysis.

It should be noted that the PCB concentrations reported in Table 5 are based on the assumption that the chromatographic peak represents only one PCB congener. Several of the PCB congeners, however, coelute with each other in the GC-ECD analysis step [34]. For the 15 PCB congeners listed in Table 6, seven congeners probably have some contribution from coeluting congeners, e.g., PCB 15 with PCB 18, PCB 95 with PCB 66, PCB 90 with PCB 101, PCB 164 and PCB 163 with PCB 138, PCB 159 and PCB 182 with PCB 187, and PCB 208 with PCB 195. The extent of the contribution of the coeluting congeners has been shown to vary in marine samples [35]. For example, PCB 163 and 164 generally contribute approximately 10% to the concentration of PCB 138 [35]. Despite these coelution problems, PCB 28, 52, 101, 138, 153, and 180 (i.e., the peaks eluting at the retention of these standard compounds including any coeluting congeners) are widely used as representative congeners for quantitation of complex PCB mixtures [34].

Another potential problem with the PCB analysis is the high sulfur content of this sediment. The cleanup step using copper, which is described in the Experimental Section, is sufficient to remove the sulfur; however, if this step is not performed properly, the sulfur contamination peak obscures a large portion in the center of the GC-ECD chromatogram for the analysis of the PCB fraction.

Comparison with other marine sediment reference materials for the determination of organic constituents

As mentioned in the Introduction, several marine sediment reference materials are available from the National Research Council of Canada (NRCC) for the determination of organic contaminants [6, 7, 36]. Four sediment samples are available for the determination of PAHs (HS-3, HS-4, HS-5, and HS-6). These sediment reference materials are from four harbors in Nova Scotia, Canada, and range in concentration levels from 680 to 85000 ng/g for phenanthrene, 1250 to 60000 ng/g for fluoranthene, and 650 to 7400 ng/g for benzo[a]pyrene. The PAH concentrations in SRM 1941 are very similar to the lowest concentration level NRCC marine sediment reference material (i.e., HS-4) as shown in Table 6. The reference values for the PAH concentrations (16 compounds) in the NRCC sediments were determined by combining results obtained from several laboratories (including NIST [21]) using GC-FID, GC-MS, and reversed-phase LC with fluorescence, UV and MS detection [6, 36]. An additional sediment reference material, Spiked Estuarine Sediment (SES-1), is also available from NRCC with fortified levels of 15 common PAHs ranging from 1200 to 7200 ng/g.

Three different sediment reference materials are available from the NRCC for PCB determinations and they are designated as CS-1, HS-1, HS-2 [36]. CS-1 is a coastal sediment collected midway between Nova Scotia and Newfoundland, and HS-1 and HS-2 were collected from Nova Scotian harbors. Concentrations for 10 individual PCB congeners are reported for HS-1 and HS-2 by NRCC [36]; concentrations for the six PCB congeners that were reported in both the NRCC materials and SRM 1941 are compared in Table 7. As shown in Table 7, SRM 1941 has concentrations of PCB congeners that are generally a factor of about 4 higher than HS-2 and a factor of 10 or more higher than HS-1. The concentration of Aroclor 1254 as a mixture is also reported by NRCC for CS-1, HS-1, and HS-2 based on packed column gas chromatography [36].

Determination of inorganic constituents by neutron activation analysis

Even though the main purpose of this SRM is for use in the determination of organic contaminants, the sediment was analyzed by NAA to determine major and minor elemental

Table 9. Sulfur concentrations in SRM sediments

SRM	Mean concentration %	Relative uncertainty %	Range relative[a] %	Certified value %
Isotope dilution – thermal ionization mass spectrometry				
2704 Buffalo River sediment[b]	0.3970 ± 0.0031[c]	0.78	1.5	
1941 Organics in marine sediment[d]	1.7168 ± 0.0221[c]	0.65	1.5	1.717 ± 0.027[e]
Prompt gamma activation analysis				
1941 Organics in marine sediment[b]	1.64 ± 0.08[f]	5.1	9.9	

[a] The range was computed from largest and smallest values relative to the smallest value
[b] Three aliquots were analyzed from each of two different bottles
[c] The uncertainties are 95% confidence intervals for the mean plus estimated bias due to blank
[d] One aliquot was analyzed from each of six different bottles
[e] The stated uncertainty is a 95% prediction interval for the concentration in a randomly chosen bottle of SRM 1941, plus an allowance for systematic error in the chemical analysis method. Neglecting systematic error, the uncertainty limits will cover the concentration of approximately 95% of samples of this SRM having a minimum sample size of 100 mg
[f] Uncertainty represents $ts/\sqrt{n}$ at the 95% confidence level

constituents, thereby providing the analyst with an SRM that was characterized extensively for both organic and inorganic constituents. The non-certified element concentrations for SRM 1941 are summarized in Table 8. Appropriate selection of reference energies and applicable interference corrections have been considered, and several different sediment reference materials have been used to assess the accuracy of this procedure. Included in the analytical method development for SRM 1941 was consideration of recent work on the extent of nuclear and spectral interference in marine sediments [37]. Some of the interferences resulted in additional uncertainty in the peak evaluation, which was included in the uncertainties of the recommended values. Variances of less than 1% have been found for a large suite of elements including major constituents and the rare earths. The low variances for the measurement of these elements is an indication that a sample size of 250 mg is representative of the bulk material for the elements determined. Analytical uncertainties for some elements were larger than predicted by counting statistics.

Determination of sulfur by isotope dilution thermal ionization mass spectrometry

During the solvent extraction of organic constituents from SRM 1941, a relatively large quantity of elemental sulfur was observed. Since elemental sulfur can interfere with the determination of some organic contaminants, the determination of sulfur was made by ID-TIMS to obtain a certified sulfur concentration. This procedure is highly precise and accurate and is considered to be a definitive method for sulfur for the certification of SRM's. The sulfur concentration of this sediment and SRM 2704 (Buffalo River Sediment) as determined by ID-TIMS are given in Table 9. The concentration of sulfur in SRM 1941 was determined by ID-TIMS to be $1.717 \pm 0.011\%$. The sulfur concentration in the Buffalo River Sediment was determined to be $0.3970 \pm 0.0031\%$. The range in sulfur values for both sediments is 1.5% relative which is probably dominated by inhomogeneity of the samples at the 100 mg level. The sulfur content of SRM 1941 was also determined by prompt gamma neutron activation and was found to be $1.64 \pm 0.08\%$ which is in good agreement with the ID-TIMS value. A certified concentration of sulfur of $1.717 \pm 0.027\%$ was determined based on the ID-TIMS results (i.e., a definitive method). For the determination of sulfur in sediments, SRM's 2704 and 1941 represent materials with relatively low and high sulfur content, respectively.

Comparison with other marine sediment reference materials for the determination of trace elements

A number of sediment reference materials are available for the determination of trace elements. SRM 1646 "Estuarine Sediment" and SRM 2704 "Buffalo River Sediment" (a replacement for SRM 1645 "River Sediment") are available from NIST. The NRCC has a suite of three sediment materials representing estuarine (BCSS-1 and MESS-1) and harbor sediments (PACS-1) [41]. The Community Bureau of Reference (BCR) has prepared three sediment reference materials: Lake Sediment (CRM 280) Estuarine Sediment (CRM 277) and River Sediment (CRM 320) [4]. The National Institute for Environmental Studies (NIES) in Japan has certified a pond sediment (NIES No. 2) [5]. Several sediment materials for trace element determinations are also available from the IAEA [2]. The concentrations of selected elements in a number of marine sediment reference materials are listed in Table 10, and are compared to the concentrations found for SRM 1941. Some differences are readily apparent. The concentrations of many elements in SRM 1941 are higher than in most of the other sediment reference materials (except the As in the PACS-1 sediment, and the Cd in the IAEA CRM SD-N-1/2 sediment). It is probable that the concentrations in SRM 1941 represent upper limits for the elemental concentrations encountered in the analyses of most unknown marine sediment samples. It is interesting to note that the concentrations of many of the rare earth elements are elevated compared to the other reference materials where information on concentrations for these elements is available.

To investigate whether the measured concentrations in SRM 1941 actually indicate enrichments of certain elements, especially the rare earths, the elemental concentrations for SRM 1941 were normalized to Al and compared to similarly

Table 10. Comparison of selected elements in marine sediment reference materials (μg/g, unless otherwise noted)

Element	NIST SRM 1941 non-certified values	NIST SRM 1646 estuarine sediment[a]	NIST SRM 2704 Buffalo River sediment[b]	IAEA CRM SD-N-1/2 sediment[c]	NRCC MESS-1 estuarine sediment[d]	NRCC PACS-1 harbor sediment[d]	BCR CRM 277 estuarine sediment[e]
B	76	[80][f]	[[92]][g]	[[90]][g]			
Na (%)	1.3	(2.0)[h]	0.547	(1.04)[h]	1.85	3.26	(1.20)[e]
Al (%)	6.5	6.25	6.11	(3.75)	5.83	6.46	(4.78)
Si (%)	22.2	(31)	29.08	(28.05)	31.5	26.0	(23)
S (%)	1.72[i]	(0.96)	(0.4)[h]	[[0.3]]	0.72	1.32	
Cl (%)	1.64	[1.4]	(≤0.01)	(0.9040)	0.82	2.39	
K (%)	1.58	(1.4)	2.00	(1.54)	1.86	1.24	(1.64)
Sc	34.4	(10.8)	(12)	7.10			9.00
Ti (%)	1.72	(0.51)	0.457	(0.27)	0.542	0.421	(0.33)
V	810	94	95	77.7	72.4	127	(102)
Cr	640	76	135	149	71	113	192
Mn	790	375	555	777	513	470	(1580)
Fe (%)	10.6	3.35	4.11	(3.64)	3.05	4.87	(4.55)
Co	27.5	10.5	14.0	12.1	10.8	17.5	(17.0)
Zn	1010	138	438	439	191	824	547
As	75	11.6	23.4	50.0	10.6	211	473
Se	10.1	(0.6)	(1.1)	(2.90)	0.34	1.09	2.04
Rb	92	(87)	(100)	74.2			(95)
Ag	1.2	[0.088]	[[0.12]]	2.3			(3.3)
Sb	15.2	(0.4)	3.79	3.62	0.73	171	(3.9)
Cd	2.3	0.36	3.45	11.0	0.59	2.38	11.9
Cs	4.8	(3.7)	(6)	4.9			(6.3)
La	360	[37]	(29)	31.9			(47)
Ce	272	(80)	(72)	60.3			(81)
Sm	25.7	[6.4]	(6.7)	5.58			
Eu	2.19	(1.5)	(1.3)	1.16			(1.6)
Gd	15.2	[4.5]	[[5.8]]	[[5.4]]			
Tb	2.2	[0.95]	[[0.8]]	0.86			
Hf	22.4	[11.2]	(8)	(8.40)			
Ta	16.4	[1.00]	[[1.0]]	(1.10)			
Th	25.6	(10)	(9.2)	7.04			(8.8)
U	22	[2.99]	3.13	2.41	4.2		(3.2)

[a] Reference [39]
[b] Reference [40]
[c] Reference [2]
[d] References [41, 42]
[e] Reference [4]; values in parentheses are "indicative values" determined by the participants in the course of the certification and should not be used as certified values
[f] Values in brackets are from Reference [43]
[g] Values in double brackets were determined at NIST by INAA or PGAA during the analysis of SRM 1941 as control materials
[h] Values in parentheses are non-certified concentrations
[i] Certified value determined by ID-TIMS

normalized values for sedimentary rock, as taken from Vinogradov [38]. The comparison of these normalized concentrations is illustrated in Fig. 5 as enrichment factors, where a factor of 1 indicates no enrichment, factors greater than 1 indicate enrichment, and factors less than 1 indicate depletion of that element. Enrichment of elements such as V, Zn, As, Se, Sb, and Cd appear to be confirmed by this comparison. The enrichment of these elements is a normal indication of biological or anthropogenic inputs. These elements also show higher variances in the analytical results than in the rare earth elements and major constituents as mentioned above [14]. As would be expected in a marine sample, Na and Cl are enriched versus sedimentary rock. A more unusual finding was that most of the rare earth elements and some major constituents (i.e., Fe and Cr) had considerable enrichment compared to sedimentary rock. The one exception to this general finding was Cs, which shows depletion. One possible explanation of these results is that a source (or sources) in the Baltimore harbor, as yet not known, is "enriching" the harbor environment with rare earths, and perhaps at the same time, depleting it of Cs. A similar comparison of SRM 1941 and sedimentary rock was performed using Si as the normalizing element, and the resulting enrichment factors, not shown here, were essentially the same as the factors normalized to Al.

For the suite of marine sediment reference materials available (see Table 10), SRM 1941 represents the highest concentration of sulfur, and SRM 2704 represents a low level concentration. With many of the crustal elements (i.e., Fe, Ti, Cr, and the rare earths) and sulfur at high levels, SRM

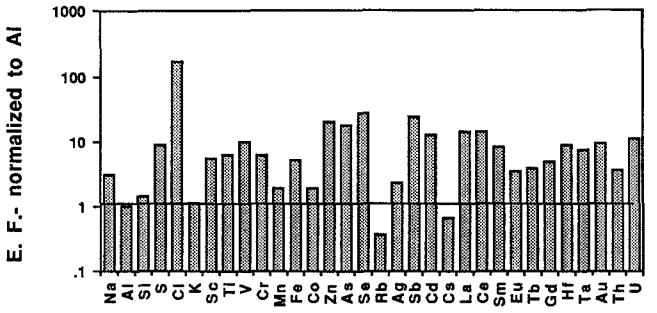

Fig. 5. Plot of enrichment factors for elemental concentrations in SRM 1941 compared to sedimentary rock, both normalized to aluminum

1941 presents a challenge for many inorganic analytical techniques. "Upper limit" reference materials are needed to test the validity of the response function of procedures routinely used. Indeed, great care was required in the INAA and PGAA analyses to ensure accurate results [14].

Conclusions

SRM 1941 is the most extensively characterized environmental matrix SRM available, with certified concentrations of 11 PAHs and sulfur and with non-certified concentrations of 24 additional PAHs, 15 PCB congeners, 7 chlorinated pesticides, and 31 additional inorganic constituents. The concentrations of the organic and inorganic contaminants are typical of an urban harbor environment. Even though the primary focus of this SRM is for organic contaminants, the characterization of SRM 1941 for major and minor trace elements provides an additional marine sediment, which has relatively high levels of contaminants of interest, to the suite of reference materials available to inorganic analysts. A frozen mussel tissue homogenate, SRM 1974 "Organics in Mussel Tissue (*Mytilus edulis*)", is currently under development to provide a marine tissue matrix as an SRM for the determination of organic contaminants.

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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.

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