



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1939

Polychlorinated Biphenyls (Congeners) in River Sediment A

This Standard Reference Material (SRM) is an air-dried river sediment. It is intended for use in validating analytical methods used in determining trace levels of selected PCB congeners in sediments and as a control material for laboratories measuring PCB congeners routinely in sediments and soils. A unit of SRM 1939 contains approximately 50 grams of sediment.

CERTIFIED CONCENTRATIONS OF SPECIFIC PCB CONGENERS

Certified concentrations of three PCB congeners present in SRM 1939 are provided in Table 1. These values are based on the results obtained from analyses of this material by two independent analytical methods: single column gas chromatography with electron capture detection (GC-ECD) and dual column (multidimensional) capillary gas chromatography (DCGC-MSD) with mass spectrometric detection. A different sample preparation procedure was used for each method. The certified values are the equally-weighted means of the results from the two analytical methods. The uncertainties include allowances for analytical error, material inhomogeneity, between-method bias, and uncertainty in the purity of the PCB congener. Each total uncertainty was calculated from a 95% prediction interval plus allowances for systematic error between the methods used and uncertainty in the congener purity. The allowance for systematic error is equal to the greatest difference between the 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 1.2 g (specifically, the statistical expected value of the coverage is 95%). The concentrations in Tables 1, 2, and 5 are based on analyses of the SRM "as received". SRM 1939 contains residual moisture of 2.7 ± 0.2 weight percent as determined from freeze-drying duplicate aliquots from four bottles.

Table 1. Certified Concentrations of PCB Congeners in SRM 1939.

PCB No. ^a	Compound Name	Concentration ($\mu\text{g/g}$)
26	2,3',5'-Trichlorobiphenyl	4.20 ± 0.29
28	2,4,4'-Trichlorobiphenyl	2.21 ± 0.10
44	2,2',3,5'-Tetrachlorobiphenyl	1.07 ± 0.12

^a The PCB congener numbers are taken from K. Ballschmiter and M. Zell, *Fresenius Z. Anal. Chem.*, **302**, 20-31 (1980).

METHOD DEPENDENT CONCENTRATIONS OF ADDITIONAL PCB CONGENERS

Concentrations of additional PCB congeners, determined by a method employing Soxhlet extraction and single column gas chromatography, are provided in Table 2. The listed uncertainties represent one standard deviation of a single measurement and reflect the precision of the measurement process only. These values, although method dependent, will be useful for the optimization and validation of PCB congener measurement procedures employing single-column gas chromatographic instrumentation.

Gaithersburg, MD 20899
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Table 2. Method-Dependent Concentrations^a of Additional PCB Congeners in SRM 1939.

PCB No. ^b	Compound Name	Mean Concentration ^c ($\mu\text{g/g}$)	Standard Deviation ^d
18	(2,2',5-Trichlorobiphenyl)	3.46	0.08
31	(2,4',5-Trichlorobiphenyl)	6.86	0.14
52	(2,2',5,5'-Tetrachlorobiphenyl)	4.48	0.06
49	(2,2',4,5'-Tetrachlorobiphenyl)	3.78	0.05
66	(2,3',4,4'-Tetrachlorobiphenyl)	0.93	0.01
101	(2,2',4,5,5'-Pentachlorobiphenyl)	0.82	0.01
118	(2,3',4,4',5-Pentachlorobiphenyl)	0.51	0.01
138	(2,2',3,4,4',5'-Hexachlorobiphenyl)	0.57	0.01
187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)	0.18	0.01
128	(2,2',3,3',4,4'-Hexachlorobiphenyl)	0.10	0.01
180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)	0.16	0.01
170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)	0.11	0.01

^aConcentrations determined by a method employing Soxhlet extraction and single column gas chromatography with electron capture detection described in the section "SRM Analyses".

^bThe PCB congener numbers are taken from K. Ballschmiter and M. Zell, *Fresenius Z. Anal. Chem.*, **302**, 20-31 (1980). The concentrations reported may include minor contributions from other coeluting PCB congeners.

^cThe mean value of the concentration, in $\mu\text{g/g}$, for 9 determinations.

^dThe standard deviation of a single measurement for 9 determinations.

Notice and Warning to Users

Handling: PCB congeners are reported to be very toxic and/or carcinogenic and therefore this sample should be handled with care. Use proper disposal methods.

Expiration of Certification: This certification is valid within the specified uncertainty limits for one year from the date of purchase. In the event that the certification should change before then, purchasers will be notified by NIST. Please return the attached registration form to facilitate notification.

Storage: The sediment is in amber bottles and should be stored in the dark at a temperature of 25 °C or below.

Use: Subsamples for analysis of this SRM should be withdrawn from the bottle immediately after opening and used without delay for the certified values listed in Table 1 to be valid within the stated uncertainties. The bottle should be tightly closed immediately after removal of the subsamples and the remaining material stored for later analyses.

The sediment material from which this SRM was prepared was donated by the U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. The analytical measurements were performed in the NIST Center for Analytical Chemistry in the Organic Analytical Research Division by F. R. Guenther, R. E. Rebbert, B.J. Koster, and M.M. Schantz, and in the Gas and Particulate Science Division by J. A. Small.

Consultations on the statistical design of the experimental work and evaluation of the data were provided by K. R. Eberhardt and S. B. Schiller of the Statistical Engineering Division. The coordination of the technical measurements leading to certification was under the direction of S. N. Chesler and W.E. May.

The technical and support aspects involved in the preparation, certification and issuance of the Standard Reference Material were coordinated through the Standard Reference Materials Program by R. Alvarez and D. Friend.

PREPARATION AND ANALYSES

SRM Preparation. The sediment material was collected from the Hudson River in New York State. It was dried, passed through a 325 mesh (45 μm) size sieve, and homogenized in a V-blender. The material was then radiation sterilized (^{60}Co) at an estimated minimum dose of 3.2 megarads. Approximate 50-g quantities were then transferred to amber bottles fitted with Teflon-lined screw caps.

SRM Analyses. Selected PCB congeners were determined in this SRM using Soxhlet extraction (using different solvent blends) followed by single column gas chromatography with electron capture detection (GC-ECD) and dual column capillary gas chromatography with a mass spectrometric detection (DCGC-MSD).

For GC-ECD analyses, approximately 1.2-g portions of sediment from nine stratified, randomly selected samples were fortified with an internal standard and moistened with 1.0 mL of HPLC grade water. These samples were then Soxhlet extracted twice, for 16 hours each time, with about 200 mL of solvent, using first a methanol/hexane (1:1 by volume) solvent mixture and then using a acetone/hexane (1:1 by volume) solution. Prior to injection on the GC-ECD, the combined extracts were then reduced to approximately 12 mL in a rotary evaporator apparatus. The GC-ECD conditions used in these analyses are listed in Table 3. A representative chromatogram obtained from using these conditions is shown in Figure 1. The figure is provided as descriptive information only and should not be used as a reference for quantitative determination.

For DCGC-MSD analyses, approximately 5-gram portions of sediment were weighed from stratified randomly selected samples and fortified with a series of standard additions of six selected PCB congeners. These samples were then Soxhlet extracted for 16 hours using 200 mL of a 1:1 acetone/hexane solvent mixture. The extracts were evaporatively concentrated to 1 mL and then placed on a disposable silica solid-phase extraction column. Hexane was passed through the column to elute the PCB congeners while retaining polar interferences. The eluate was again evaporatively concentrated to < 1 mL before analysis by DCGC-MSD. A more detailed discussion of the analysis of SRM 1939 by DCGC-MSD has been reported [1].

SRM 1939 was examined by optical microscopy and found to be homogeneous with respect to the distribution of particle size both within and between SRM units.

Table 3. Experimental Conditions Used in the GC-ECD Analyses.

Column	Immobilized non-polar (60 m x 0.25 mm i.d. x 0.25 μm film)
Injection Mode	Split 30:1
Injector Temperature	280 $^{\circ}\text{C}$
ECD Temperature	310 $^{\circ}\text{C}$
Temperature Program	150 $^{\circ}\text{C}$ for 40 min; then 1 $^{\circ}\text{C}$ per min to 220 $^{\circ}\text{C}$; then 3 $^{\circ}\text{C}$ per min to 280 $^{\circ}\text{C}$
Helium Carrier Gas	290 kPa (42 psig)
Injection Volume	1.0 μL
Internal Standard	PCB Congener 121

The values given in Table 2 were all obtained using the GC-ECD analysis conditions. These values may be confounded by systematic errors caused by coelution of non-analyte PCB congeners. An example of this type of error is exhibited in Table 4 which shows the concentrations of six selected PCB congeners as determined both by DCGC-MSD and single column GC-ECD. The DCGC-MSD method, in which two columns are used for separation, is not significantly affected by coelution.

Table 4. Concentrations in $\mu\text{g/g}$ of Six Selected PCB Congeners by GC-ECD and DCGC-MSD.

	PCB18 ^a	PCB 26	PCB 28	PCB 52	PCB 44	PCB 101
GC-ECD ^b	3.46	4.24	2.22	4.48	1.09	0.82
DCGC-MSD ^c	2.32	4.16	2.20	3.86	1.04	0.46
Difference ^d	-32.9%	-1.9%	-0.9%	-13.8%	-4.6%	-43.9%
Mean		4.20	2.21		1.07	

^aThe PCB congener numbers are taken from K. Ballschmiter and M. Zell, *Fresenius Z. Anal. Chem.*, **302**, 20-31 (1980).

^bThe mean concentration from 9 determinations.

^cThe mean concentration from 6 determinations each consisting of a 5-point standard addition set.

^dThe large negative difference between DCGC-MSD and GC-ECD for PCB 18, PCB 52 and PCB 101 indicates the possible presence of a coeluting non-analyte congener in the GC-ECD determination.

APPENDIX

Noncertified concentrations of five polycyclic aromatic hydrocarbons (PAHs), two additional PCB congeners and five chlorinated pesticides in this SRM sediment are summarized in Table 5. Although noncertified, these concentrations should be useful for SRM users interested in analyses of a sediment type matrix for the determination of PAHs and chlorinated pesticides. The concentrations of the PAHs were determined by GC-MSD while the concentrations of the PCB congeners and chlorinated pesticides were determined by GC-ECD. The sediment was first Soxhlet extracted with methylene chloride. The PAH fraction was isolated from a portion of the sediment extract by normal-phase liquid chromatography (LC) using a semi-preparative aminosilane column. The PCBs and chlorinated pesticide fractions were isolated from a second portion of the extract using a similar normal-phase LC procedure. A detailed description of the analytical procedure used for these measurements has been published [2,3]. This SRM also complements SRM 1941, *Organics in Marine Sediment* [3], since the PAH concentrations in SRM 1939 are five to ten times lower than those in SRM 1941, and the PCB and pesticide concentrations in SRM 1939 are one to two orders of magnitude higher than those in SRM 1941.

Table 5. Noncertified Concentrations of Selected PAHs, PCBs and Chlorinated Pesticides in SRM 1939

	<u>Concentration ($\mu\text{g/g}$)</u>	<u>Standard Deviation^a</u>
Polycyclic Aromatic Hydrocarbons		
Phenanthrene	0.13	0.01
Fluoranthene	0.19	0.01
Pyrene	0.17	0.02
Benz[a]anthracene	0.046	0.001
Chrysene/Triphenylene	0.051	0.001
Polychlorinated Biphenyls		
PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl)	0.40	0.01
PCB 105 (2,3,3',4,4'-Pentachlorobiphenyl)	0.25	0.01
Chlorinated Pesticides		
Heptachlor Epoxide/Oxychlorane	0.51	0.02
<i>cis</i> -Chlordane (alpha-Chlordane)	0.22	0.01
<i>trans</i> -Nonachlor	0.27	0.01
4,4'-DDE	0.54	0.01
4,4'-DDD	0.06	0.01

^a The standard deviation of a single measurement for 6 determinations (duplicate samples from three bottles).

References

- [1] F.R. Guenther, S.N. Chesler and R.E. Rebert, *The Analysis of Polychlorinated Biphenyls by Multidimensional Gas Chromatography*, *J. High Resolution Chromatography* **12**, 821-824 (1989).
- [2] M. M. Schantz, B. A. Benner, Jr., S. N. Chesler, B. J. Koster, K. E. Hehn, S. F. Stone, W. R. Kelly, R. Zeisler and S. A. Wise, *Preparation and Analysis of a Marine Sediment Reference Material for the Determination of Trace Organic Constituents*, *Fresenius J. Anal. Chem.*, **338**, 501-514 (1990).
- [3] *Certificate of Analysis, SRM 1941 "Organics in Marine Sediment*, National Institute of Standards and Technology, Gaithersburg, MD, June, 1990.

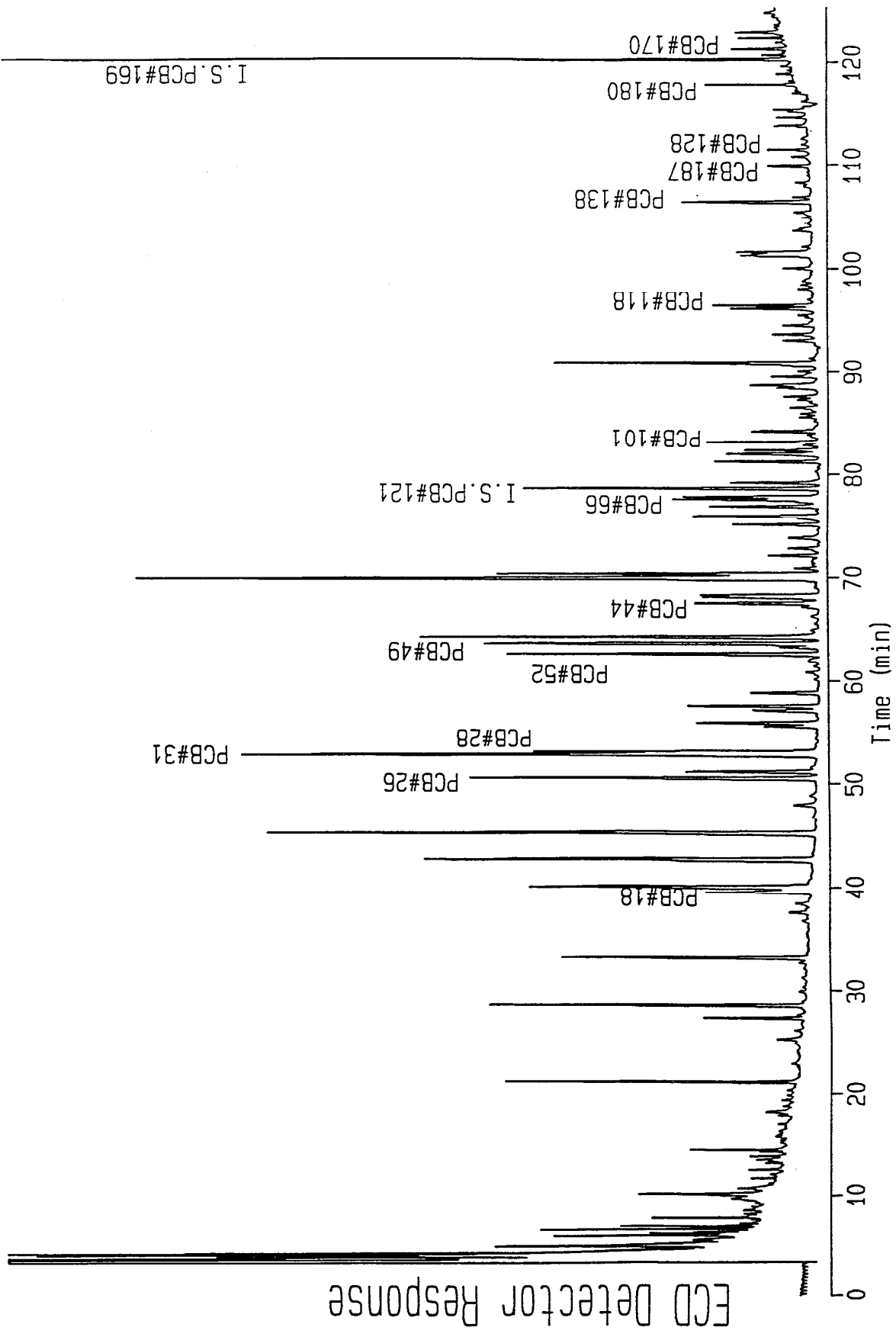


Figure 1. Capillary Gas Chromatogram of SRM 1939 with Internal Standards.