National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1991

Mixed Coal Tar/Petroleum Extract in Methylene Chloride

This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), particularly in determining relative response factors for ASTM Method D7363-11 "Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode" [1]. All of the constituents for which certified, reference, and information values are provided are naturally present in the extract. A unit of SRM 1991 consists of five ampoules each containing 1.2 mL of a methylene chloride solution.

Certified Mass Fraction Values: Certified mass fraction values for PAHs are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of uncertainty have been investigated or taken into account [2]. The certified values are based on the agreement of results obtained at NIST and the Energy and Environmental Research Center (EERC) at the University of North Dakota (Grand Forks, ND) using multiple analytical techniques.

Reference Mass Fraction Values: Reference mass fraction values are provided in Table 2 for additional PAHs and in Table 3 for groups of alkylated PAHs. Reference values are noncertified values that are estimates of the true values. The values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [2].

Information Mass Fraction Values: Information mass fraction values are provided in Table 4 for additional PAHs. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess adequately the uncertainty associated with the value or only a limited number of analyses were performed [2].

Expiration of Certification: The certification of **SRM 1991** is valid, within the measurement uncertainty specified, until **01 May 2031** provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

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

Overall direction and coordination of technical measurements leading to certification were performed by M.M. Schantz and L.C. Sander formerly of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by J.A. Murray of the NIST Chemical Sciences Division, D.J. Miller and S.B. Hawthorne of the EERC, and M.M. Schantz.

Evaluation of the data was provided by N.A. Heckert and A.L. Pintar of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

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INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling: This material contains PAHs in methylene chloride, many of which have been reported to have mutagenic and/or carcinogenic properties and should be handled with care (see Safety Data Sheet). Use proper disposal methods.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C and 30 °C.

Use: Samples for analysis (minimum sample size of 400 mg) should be withdrawn at 20 °C to 25 °C immediately after opening ampoules and should be processed without delay for the certified values in Table 1 to be valid within the stated uncertainties. Certified values are not applicable to material stored in ampoules that have been opened longer than 4 minutes.

PREPARATION AND ANALYSIS[1]

Sample Preparation: The mixed coal tar/petroleum non-aqueous phase liquid (NAPL) used for this SRM was received from EERC. A known mass of the mixed coal tar/petroleum sample was diluted with a known mass of methylene chloride in a large glass carboy. The diluted mixture was stirred overnight and ampouled under an argon headspace the following day. Each 2 mL amber ampoule contains approximately 1.2 mL of the methylene chloride solution.

Polycyclic Aromatic Hydrocarbons: The general approach used for the value assignment of the PAHs in SRM 1991 consisted of combining results from analyses using various combinations of chromatographic separation and detection techniques [3].

Three sets of gas chromatography/mass spectrometry (GC/MS) results, designated as GC/MS (I) through GC/MS (III), were obtained at NIST. For GC/MS (I) analyses, duplicate test portions of 400 mg from 10 ampoules of SRM 1991 were transferred to individual vials, were spiked with a known amount of an internal standard solution (see below), and were analyzed on the GC/MS. They were then diluted approximately 1:10 (volume fraction) with methylene chloride and rerun on the GC/MS. Each sample was analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % (mole fraction) phenyl methylpolysiloxane phase (0.25 μm film thickness; DB-17MS, Agilent Technologies, Wilmington, DE). The results from the DB-17MS column are denoted as GC/MS (I).

For the GC/MS (II) and GC/MS (III) determination of the PAHs, one test portion (400 mg, exact mass known) from each of six ampoules was transferred to a vial and spiked with a known amount of internal standard solution (see below). The solutions were analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a relatively non-polar proprietary stationary phase (0.25 μm film thickness; DB-XLB, Agilent Technologies). The same samples were analyzed by GC/MS using a 0.25 mm i.d. × 15 m fused silica capillary column with a 50 % (mole fraction) liquid crystal polysiloxane phase (0.15 μm film thickness; LC-50, J&K Scientific, Milton, Ontario, Canada). The results from the DB-XLB column are denoted as GC/MS (II) and those from the LC-50 column as GC/MS (III).

For the methods described above, selected perdeuterated PAHs were added to the coal tar solution as described above for use as internal standards for quantification purposes.

In addition to the analyses performed at NIST, SRM 1991 was analyzed by EERC using a method similar to that described in Hawthorne et al. [4]. These data were used as the fourth data set, GC/MS (IV), in the determination of the values for PAHs in SRM 1991.

Homogeneity Assessment for PAHs: The homogeneity of SRM 1991 was assessed by analyzing duplicate test portions of 400 mg from 10 ampoules selected by stratified random sampling using GC/MS (I). No differences among ampoules were observed for the PAHs at the 400 mg test portion size.

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[1] Certain commercial equipment, instruments, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Certified Mass Fraction Values: The certified values are weighted means of average mass fractions, with one average from each of two or more analytical methods [5,6]. The expanded uncertainty is the half width of a symmetric approximately 95 % parametric bootstrap confidence interval [7], which is consistent with the ISO/JCGM Guide [8,9]. The effective coverage factor, k, is included in the table for each PAH.

Table 1. Certified Mass Fraction Values for Selected PAHs in SRM 1991

	Mass Fraction[a] (mg/kg)			k
Naphthalene[a,b,c]	26.0	±	1.1	2.02
1-Methylnaphthalene[a,b,c]	8.02	±	0.32	1.97
2-Methylnaphthalene[a,b,c]	11.7	±	0.5	1.98
Biphenyl[a,b]	2.03	±	0.06	1.97
Dibenzothiophene[a,b,d]	1.20	±	0.06	1.97
Phenanthrene[a,b,c,d]	12.1	±	0.6	1.96
Anthracene[a,b,c,d]	3.33	±	0.43	1.97
1-Methylphenanthrene[a,b]	1.54	±	0.12	1.97
3-Methylphenanthrene[a,b,d]	2.40	±	0.10	1.97
9-Methylphenanthrene[a,b]	1.17	±	0.05	1.97
2-Methylanthracene[a,b,d]	1.35	±	0.04	1.96
4H-Cyclopenta[*def*]phenanthrene[a,b,d]	1.80	±	0.15	1.97
Fluoranthene[a,b,c,d]	3.54	±	0.39	1.97
Pyrene[a,b,c,d]	5.91	±	0.16	1.97
Benzo[*ghi*]fluoranthene[a,b,d]	0.292	±	0.019	1.96
Benzo[*c*]phenanthrene[a,b,d]	0.440	±	0.025	1.97
Benz[*a*]anthracene[a,b,c,d]	1.79	±	0.21	1.97
Chrysene[a,b,d]	1.32	±	0.15	1.97
Benzo[*a*]fluoranthene[a,b,d]	0.342	±	0.020	1.97
Benzo[*b*]fluoranthene[a,d]	0.565	±	0.050	1.97
Benzo[*j*]fluoranthene[a,d]	0.479	±	0.041	1.97
Benzo[*k*]fluoranthene[a,b,d]	0.336	±	0.012	1.97
Benzo[*e*]pyrene[a,b,c,d]	0.652	±	0.028	1.97
Benzo[*a*]pyrene[a,b,c,d]	1.33	±	0.12	1.97
Perylene[a,b,c,d]	0.203	±	0.017	1.96
Benzo[*ghi*]perylene[a,b,c,d]	0.549	±	0.028	1.97
Indeno[1,2,3-*cd*]pyrene[a,b,c,d]	0.382	±	0.030	1.97
Dibenz[*a,c*]anthracene[a,d]	0.071	±	0.003	1.96
Dibenz[*a,h*]anthracene[a,d]	0.128	±	0.025	1.96
Benzo[*b*]chyrsene[a,b,d]	0.183	±	0.015	1.97
Picene[a,b,d]	0.121	±	0.017	1.97

[a] GC/MS (I) – analysis on a DB-17MS column
[b] GC/MS (II) – analysis on a DB-XLB column
[c] GC/MS (IV) – analysis at EERC
[d] GC/MS (III) – analysis on an LC-50 column

Reference Mass Fraction Values for PAHs: The reference values are weighted means of average mass fractions, with one average from each of two or more analytical methods [5,6], when available. The expanded uncertainty is the half width of a symmetric approximately 95 % parametric bootstrap confidence interval [7], which is consistent with the ISO/JCGM Guide [8,9]. For PAHs analyzed by only one method, the reference mass fraction value is the mean of results obtained using that analytical technique. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is one standard deviation of the analyte mean, and the coverage factor, k, is determined from the Student's t-distribution corresponding to the associated degrees of freedom and a 95 % confidence level for each analyte. The effective coverage factor k is included in the table for each PAH.

Table 2. Reference Mass Fraction Values for Selected PAHs in SRM 1991

	Mass Fraction (mg/kg)			k
Acenaphthene[a,b,c]	6.83	±	0.89	1.97
Fluorene[a,b,c]	3.8	±	1.0	1.97
1-Methylfluoranthene[b]	0.098	±	0.009	2.57
3-Methylfluoranthene[b]	0.257	±	0.025	2.57
1-Methylpyrene[a,b,d]	0.638	±	0.043	1.97
4-Methylpyrene[a,b,d]	0.65	±	0.12	1.98
Cyclopenta[cd]pyrene[b,d]	0.216	±	0.011	1.97
Triphenylene[b,d]	0.255	±	0.016	1.97
3-Methylchrysene[a,b,d]	0.226	±	0.005	1.99
Anthanthrene[a,b, f]	0.204	±	0.009	1.96
Dibenz[a,j]anthracene[a,b,d]	0.124	±	0.024	1.97
Coronene[b]	0.114	±	0.017	2.57
Dibenzo[b,k]fluoranthene[b]	0.122	±	0.006	2.57
Dibenzo[a,e]pyrene[b]	0.105	±	0.007	2.57
Dibenzo[a,h]pyrene[b]	0.027	±	0.005	2.57

[a] GC/MS (I) – analysis on a DB-17MS column
[b] GC/MS (II) – analysis on a DB-XLB column
[c] GC/MS (IV) – analysis at EERC
[d] GC/MS (III) – analysis on an LC-50 column

Reference Mass Fraction Values for Alkylated PAH Groups: The reference values are weighted means of average mass fractions, with one average from each of two or more analytical methods [5,6], when available. The expanded uncertainty is the half width of a symmetric approximately 95 % parametric bootstrap confidence interval [7], which is consistent with the ISO/JCGM Guide [8,9]. For C3-fluorenes, the reference mass fraction value is the mean of results obtained using one analytical technique. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is one standard deviation of the analyte mean, and the coverage factor, k, is determined from the Student's t-distribution corresponding to the associated degrees of freedom and a 95 % confidence level for each analyte. The effective coverage factor k is included in the table for each PAH.

Table 3. Reference Mass Fraction Values for Selected Alkylated PAH Groups[a] in SRM 1991

	Mass Fraction (mg/kg)		k
C2-naphthalenes[b,c]	21.3	± 2.8	1.97
C3-naphthalenes[b,c]	29.5	± 1.5	1.97
C4-naphthalenes[b,c]	33.8	± 4.7	1.97
C1-fluorenes[b,c]	5.62	± 0.27	1.98
C2-fluorenes[b,c]	7.20	± 0.39	2.40
C3-fluorenes[b]	5.16	± 0.50	2.57
C1-dibenzothiophenes[b,d]	1.53	± 0.04	1.98
C2-dibenzothiophenes[b,d]	1.06	± 0.09	1.98
C3-dibenzothiophenes[b,d]	0.415	± 0.036	1.97
C1-phenanthrenes/anthracenes[b,c,d]	10.7	± 3.2	1.97
C2-phenanthrenes/anthracenes[b,c,d]	15.5	± 1.9	1.97
C3-phenanthrenes/anthracenes[b,c,d]	15.1	± 0.2	1.96
C4-phenanthrenes/anthracenes[b,c]	10.2	± 1.1	2.43
C1-fluoranthenes/pyrenes[b,c,d]	6.86	± 0.54	1.98
C2-fluoranthenes/pyrenes[b,d]	1.67	± 0.44	1.96
C1-benzanthracenes/chrysenes/triphenylenes[b,c,d]	1.54	± 0.46	1.97
C2-benzanthracenes/chrysenes/triphenylenes[b,d]	0.44	± 0.12	1.96

[a] For GC/MS (II) and GC/MS (III), the compounds used for quantification were:
   C2-naphthalenes – an average response from 1,2-, 1,6-, and 2,6-dimethylnapthalene;
   C3-napthalenes – 2,3,5-trimethylnaphthalene;
   C1- to C3-fluorenes – fluorene;
   C1- to C3-dibenzothiophenes – dibenzothiophene;
   C1-phenathrenes/anthracenes – an average response from 1-, 2-, 3-, and 9-methylphenantherene;
   C2-, C3-, and C4-phenanthrenes/anthracenes – 1,7-dimethylphenanthrene;
   C1- and C2-fluoranthenes/pyrenes – an average response from 3- and 6-methylfluoranthene and 1- and 4-methylpyrene;
   C1- and C2-benzanthracenes/chrysenes/triphenylenes – an average response from 3- and 6-methylchrysene.
   For GC/MS (IV), the compounds used for quantification are described in reference [4].
[b] GC/MS (II) – analysis on a DB-XLB column
[c] GC/MS (IV) – analysis at EERC
[d] GC/MS (III) – analysis on an LC-50 column

Table 4. Information Mass Fraction Values for Selected PAHs in SRM 1991

	Mass Fraction (mg/kg)
1,6-Dimethylnaphthalene[a,b]	3.9
Acenaphthylene[a,b,c]	0.5
2-Methylphenanthrene[a,b,d]	2.0
1,7-Dimethylphenanthrene[a,b,d]	0.5

[a] GC/MS (I) – analysis on a DB-17MS column
[b] GC/MS (II) – analysis on a DB-XLB column
[c] Acenaphthylene may be unstable in the solution. The value from EERC was 4.6 mg/kg.
[d] GC/MS (III) – analysis on an LC-50 column

REFERENCES

[1] ASTM Method D7363-11; *Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode*; ASTM Committee D19, Subcommittee D19.06 (2011).

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[8] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/en/publications/guides (accessed May 2021); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed May 2021).

[9] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the Guide to the Expression of Uncertainty in Measurement – Propagation of Distributions Using a Monte Carlo Method*; Joint Committee for Guides in Metrology (JCGM) (2008); available at https://www.bipm.org/en/publications/guides (accessed May 2021).

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