National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1647c

Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)

This Standard Reference Material (SRM) 1647c consists of five 2 mL ampoules, each containing approximately 1.2 mL of an acetonitrile solution of 16 polycyclic aromatic hydrocarbons (PAHs). The PAHs are the 16 identified by the U.S. Environmental Protection Agency as priority pollutants. SRM 1647c is intended primarily as a calibration solution for use in chromatographic methods for the determination of PAHs. It may also be useful in recovery studies for the addition of known amounts of these PAHs to a sample; and since the solution is miscible with water, it can be used to fortify aqueous samples with known concentrations of PAHs.

Certified Concentrations of PAHs

Certified concentrations of the 16 PAHs in μg/g and μg/mL at 23 ± 2 °C are given in Table 1. Values listed in units of μg/mL were calculated from the values in units of μg/g, using the density of acetonitrile[b] at 23 °C. The certified values in Table 1 are derived from the results obtained from liquid chromatography (LC) and gravimetry.

Table 1. Certified Values for SRM 1647c

Compound	Concentration (μg/g)[a]	Concentration (μg/mL)[b]
Naphthalene	25.62 ± 1.37	19.96 ± 1.07
Acenaphthylene	19.81 ± 0.39	15.43 ± 0.30
Acenaphthene	26.38 ± 0.70	20.55 ± 0.55
Fluorene	6.10 ± 0.07	4.75 ± 0.06
Phenanthrene	4.46 ± 0.04	3.47 ± 0.04
Anthracene	1.02 ± 0.04	0.79 ± 0.03
Fluoranthene	9.82 ± 0.11	7.65 ± 0.09
Pyrene	10.94 ± 0.08	8.52 ± 0.07
Benzo[*a*]anthracene	5.24 ± 0.14	4.08 ± 0.11
Chrysene	4.75 ± 0.09	3.70 ± 0.07
Benzo[*b*]fluoranthene	5.37 ± 0.05	4.19 ± 0.04
Benzo[*k*]fluoranthene	6.01 ± 0.07	4.68 ± 0.06
Benzo[*a*]pyrene	6.32 ± 0.15	4.92 ± 0.12
Dibenz[*a,h*]anthracene	4.62 ± 0.05	3.60 ± 0.04
Benzo[*ghi*]perylene	4.73 ± 0.05	3.69 ± 0.04
Indeno[1,2,3-*cd*]pyrene	5.53 ± 0.06	4.30 ± 0.05

[a]The certified values and associated uncertainties were calculated using an errors-in-variables statistical method [1]. The uncertainties represent a half-width approximate 95% confidence interval for the certified value.

[b]Concentration values in units μg/mL were calculated using the density of acetonitrile at 23 °C (0.7789 g/mL). An allowance for the change in this density over the range 23 ± 2 °C is included in the uncertainty.

Gaithersburg, MD 20899
April 25, 1994
(Revision of certificate dated 2-16-93)

Thomas E. Gills, Chief
Standard Reference Materials Program

(over)

Notice and Warnings to User

Expiration of Certification: This certification is valid, within the limits certified, for three (3) years from the date of shipment from NIST. In the event that the certification should become invalid before then, purchasers will be notified by NIST. Please return the attached registration card to facilitate notification.

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

Use: Samples of the SRM for analysis should be withdrawn from ampoules and used without delay. Certified values in Table 1 listed in units of μg/mL are valid within the stated uncertainty only for aliquots removed at 23 $\pm$ 2 °C. Certified values are not applicable to ampoules stored after opening, even if resealed.

Toxicity: This SRM contains small amounts of polycyclic aromatic hydrocarbons, some of which have been reported to have mutagenic and/or carcinogenic properties; therefore, care should be exercised during handling and use. Use proper methods for disposal of waste.

Consultation on the statistical design of the experimental work and evaluation of the data were performed by S.B. Schiller of the NIST Statistical Eningeering Division.

The coordination of the technical measurements leading to certification were performed in the NIST Organic Analytical Research Division under the direction of L.C. Sander, S.A. Wise, and W.E. May.

Analytical determinations were performed in the NIST Organic Analytical Research Division by L.C. Sander.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by T.E. Gills.

Preparation and Analysis

The acetonitrile solution of the 16 PAHs was prepared gravimetrically (w/w) from individual compounds. Sources and purities of the 16 PAHs are listed in Appendix A. Except for the PAHs obtained from the European Community Bureau of Reference (BCR), purities of the compounds were determined by a combination of techniques including differential scanning calorimetry (DSC), gas chromatography with flame ionization detection (GC-FID), and reversed-phase liquid chromatography with ultraviolet detection (LC-UV). Purities of BCR compounds were certified by BCR, and these values are included in Appendix A. With the exception of acenaphthylene, PAH purities were $\geq$ 99%. Corrections for impurities were made in calculation of gravimetric values for SRM 1647c and response factor solutions. Acenaphthylene was found to contain acenaphthene and corrections were made. The SRM solution was aliquoted into 2 mL amber glass ampoules, which were purged with argon prior to addition of the solution. Samples representing early, middle, and final stages of ampouling were analyzed by LC. No evidence of sample inhomogeneity was observed.

Twenty-four randomly selected ampoules were analyzed in duplicate for all 16 PAHs by LC using an acetonitrile-water mobile phase. Response factors for 14 of the 16 PAHs were determined from this and six separate standard solutions containing the 16 PAHs using errors-in-variables regression [1]. Napthalene and anthracene were determined using separately prepared response factor solutions. An external calibration approach was used in the certification. A representative chromatogram and the separation conditions are shown in Figure 1. Variations in C_{18} column selectivity for PAHs are known to result from different manufacturing processes [2]. Columns prepared by reaction of monofunctional C_{18} silanes with silica (denoted momomeric C_{18} phases) differ from columns prepared with silica substrates using trifunctional C_{18} silanes in the presence of water (denoted polymeric C_{18} phases). The designation "polymeric C_{18} column" should not be confused with "polymer substrate columns", (which are nonsilica columns, often based on polystyrene particles). Better separations of PAH mixtures are often possible on polymeric C_{18} columns (Figure 1) compared to monomeric C_{18} columns. A chromatogram illustrating the separation of the components in the SRM solution using a monomeric C_{18} column is provided for comparison (Figure 2). Baseline resolution of all components was not achieved with the monomeric C_{18} column. The classification of monomeric and polymeric C_{18} columns for the separation of PAHs has been described [2,9] and may be accomplished using SRM 869, "Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons)"[10].

Examples of various C_{18} columns as "monomeric" or "polymeric" are provided with SRM 869.

Ultraviolet absorption data between 205 and 600 nm are supplied as an aid in identifying each compound certified in this SRM. The values for apparent specific molar absorbance for several prominent peaks in each spectrum are provided in Appendix B. "Specific absorbance" is defined here as "absorbance per unit path length and unit concentration". The term absorptivity was avoided because it is ambiguously defined [11]. The term "apparent" is used because no corrections have been applied to the data for the effects of internal multiple reflections within the cuvette. The apparent molar specific absorbances were not corrected for PAH purity. In Appendix C the apparent specific molar absorbances for each PAH at 254.0 nm are listed. The apparent specific molar absorbance at 254.0 nm should be used with caution since the absorbances measured at 254.0 nm do not correspond to peak maxima and very small changes in wavelength may result in significant changes in the absorbance reading. The magnitude of this change is reflected in the last column of Appendix C which gives the percent change ϵ_a for a 1.0 nm shift away from 254.0 nm. It is important that the user check detector calibration at 254.0 nm.

Aqueous solubility values are summarized in Appendix D for 15 of the 16 PAHs present in this SRM.

REFERENCES

[1] Nelson, W., Measurement Error Models, John Wiley & Sons (1987).

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[9] Wise, S.A., Bonnett, W.J., Guenther, F.R., and May, W.E., A Relationship Between Reversed-Phase C_{18} Liquid Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons, J. Chromatogr., Sci., 19, 457-465 (1981).

[10] Certificate of Analysis, SRM 869 Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons), Standard Reference Materials Program, NIST, Gaithersburg, MD 20899.

[11] Mielenz, K.D., Comments on Spectrometry Nomenclature, Anal. Chem. 48, 1093-1094 (1976).

Appendices

The following supplementary information is supplied for the convenience of the user of this material. This information does not meet the requirements for certification by the National Institute of Standards and Technology.

Appendix A. Sources and Purities of PAHs Used to Formulate SRM 1647c

Compound	Source	Purity (weight %)[a] mean	uncertainty[d]
Naphthalene	commercial	99.70	0.4
Acenaphthylene	commercial	95.68[b]	0.24
Acenaphthene	commercial	99.78	0.25
Fluorene	commercial	99.00	0.3
Phenanthrene	commercial	99.60	0.3
Anthracene	commercial	99.73	0.21
Fluoranthene	BCR[c]	99.49	0.25
Pyrene	BCR	99.75	0.13
Benzo[*a*]fluoranthene	BCR	99.78	0.15
Chrysene	BCR	99.20	0.2
Benzo[*b*]fluoranthene	BCR	99.50	0.3
Benzo[*k*]fluoranthene	BCR	99.50	0.3
Benzo[*a*]pyrene	commercial	99.50	0.3
Dibenz[*a,h*]anthracene	BCR	99.00	0.6
Benzo[*ghi*]perylene	BCR	99.00	0.6
Indeno[1,2,3-*cd*]pyrene	BCR	99.00	0.5

[a]Purity values for compounds obtained from commercial sources are consensus estimations from DSC, GC-FID, and LC-UV measurements; purity values for BCR compounds are certified by BCR.

[b]Acenaphthylene contains 3.83% acenaphthene.

[c]BCR = Community Bureau of Reference, Directorate General XII, Commission of the European Communities, 200 rue de la Loi, B-1049 Brussels.

[d]Uncertainties for non-BCR components are expressed as the standard deviation of a single measurement. Uncertainties for BCR components are expressed as a 95% confidence interval.

Appendix B. Apparent Specific Molar Absorbances at λ max

Compound	λmax,nm	Apparent Specific Molar Absorbance ϵ_a,L · mol^{-1} · cm^{-1}	Relative ϵ_a
Naphthalene	220.4	98,000	100.%
	285.7		4.0
	283.4		3.9
	275.8		5.9
	266.2		5.3
	258.2*		4.0
Acenaphthene	227.0	84,100	100.%
	320.7		2.4
	312.4		1.3
	306.4		3.8
	300.6		4.8
	289.2		7.6
	280.7		6.6
Acenaphthylene	229.0	51,800	100.%
	338.8		7.7
	321.6		19.5
	310.6		15.4
	274.6		4.5
	264.6		5.0
Fluorene	260.7	18,810	100.%
	299.6		46.7
	292.0*		27.8
	288.4		32.3
	270.8		71.1
	263.4		99.6
	219.9		88.0
Anthracene	251.5	186,000	100.%
	375.9		4.0
	356.9		4.2
	339.8		2.8
	324.1		1.5
	221.2		5.8
	218.2		5.6
Phenanthrene	250.7	63,500	100.%
	292.7		21.3
	281.2		16.1
	273.9		20.2
	244.1		76.8
	219.8		31.7
	211.3		51.4
Fluoranthene	235.6	50,800	100.%
	358.3		16.3
	342.0		15.9
	322.0		12.1
	308.6		7.0
	286.2		81.2
	281.1		35.1
	275.5		45.4
	271.4		23.5
	260.5		23.6
	209.6		77.6
Pyrene	240.1	83,100	100.%
	334.4		56.2
	318.9		33.1
	305.4		13.1
	294.1		5.3
	272.2		60.1
	261.8		29.0
	251.7		13.3
	231.0		51.5
	207.0*		15.2
Benz[*a*]anthracene	287.0	93,000	100.%
	384.3		1.1
	374.8		0.8
	357.8		5.2
	341.0		7.4
	327.8		6.5
	314.2		5.0
	299.7		8.4
	276.5		79.6
	266.7		42.9
	256.1		40.8
	227.7		36.2
	221.7		39.4
Chrysene	267.1	133,600	100.%
	360.7		0.5
	319.8		9.2
	306.4		9.2
	294.3		8.6
	281.0		8.9
	257.6		55.4
	241.2		16.1
	220.6		24.1

* Shoulder

Appendix B. Apparent Specific Molar Absorbances at λmax (cont.)

Compound	λmax,nm	Apparent Specific Molar Absorbance ϵ^a, L · mol^{-1} · cm^{-1}	Relative, ϵ_a
Benzo[*b*]fluoranthene	255.6	44,400	100.%
	367.5		16.3
	349.2		25.5
	341.1		24.7
	300.4		82.8
	291.7		61.9
	289.7		61.5
	275.7		62.5
	244.8		84.3
	239.2		84.2
	221.3		91.9
Benzo[*k*]fluoranthene	306.7	58,200	100.%
	400.0		20.5
	378.4		19.1
	359.4		9.8
	336.0*		8.7
	321.4*		12.3
	295.2		72.3
	282.9		38.3
	270.3*		29.7
	267.0		34.0
	244.3		91.4
	236.9		94.6
	214.6		61.0
Benzo[*a*]pyrene	295.8	57,930	100.%
	403.3		6.0
	384.4		45.2
	378.1		41.1
	364.5		40.5
	347.0		20.9
	331.5		8.6
	283.8		76.9
	271.6		51.9
	264.8		87.1
	254.6		72.2
	226.6		46.2
	220.0		42.9
Benzo[*ghi*]perylene	299.0	56,200	100.%
	383.0		35.3
	380.8		35.1
	361.8		31.6
	344.7		16.1
	338.9		14.8
	329.3		11.2
	323.9		8.6
	313.4		10.7
	288.6		71.1
	276.5		42.1
	253.7		27.0
	222.2		82.4
Dibenz[*a,h*]anthracene	296.5	158,400	100.%
	393.8		0.8
	372.8		0.7
	348.4		8.6
	332.6		9.9
	319.7		12.1
	287.9		59.1
	285.6*		56.9
	277.4		30.3
	274.8*		27.8
	229.9		17.1
	221.3		36.7
	215.8		25.4
Ideno[1,2,3-*cd*]pyrene	249.6	71,300	100.%
	405.6		9.2
	382.8*		16.7
	376.9		18.0
	359.2		20.6
	314.7		38.0
	302.4		46.6
	291.4		35.8
	275.2		32.9
	209.8		58.1

*Shoulder

Appendix C. Apparent Specific Molar Absorbances at 254.0 nm for PAHs in SRM 1647c

Compound	Apparent Specific Molar Absorbance ϵ_a L · mol^{-1} · cm^{-1}x10^{-3}	% Relative ϵ_a = ϵ_α · 100,254.0 nm / ϵ_a, λ max	% error in ϵ_a for 1 nm error
Naphthalene	3.1	3.2%	11%
Acenaphthene	1.2	1.4	18
Acenaphthylene	2.2	4.1	2
Fluorene	17	88	1
Anthracene	96	52	52
Phenanthrene	43	68	16
Fluoranthene	13	25	6
Pyrene	10	12	5
Benz[*a*]anthracene	33	36	3
Chrysene	52	39	15
Benzo[*b*]fluoranthene	43	96	4
Benzo[*k*]fluoranthene	28	48	15
Benzo[*a*]pyrene	42	72	2
Benzo[*ghi*]perylene	16	27	0.7
Dibenz[*a,h*]anthracene	11	7	6
Ideno[1,2,3-*cd*]pyrene	38	53	22

Appendix D. Aqueous Solubility Data for the Individual PAHs Present in SRM 1647c

Compound	Aqueous Solubility at 25 °C[a] (ng/mL)
Naphthalene	31700
Acenaphthylene	-----
Acenaphthene	3930[b]
Fluorene	1685
Phenanthrene	1000
Anthracene	45
Fluoranthene	206
Pyrene	132
Benz[*a*]anthracene	9.4
Chrysene	1.8
Benzo[*b*]fluoranthene	1.5
Benzo[*k*]fluoranthene	0.8
Benzo[*a*]pyrene	1.6
Benzo[*ghi*]perylene	0.7
Dibenz[*a,h*]anthracene	0.5[c]
Indeno[1,2,3-*cd*]pyrene	0.2

[a]Unless noted otherwise, solubility values were determined at NIST using Dynamic Coupled Column Liquid Chromatographic Technique [W.E. May, S.P. Wasik, and D.H. Freeman, Anal. Chem. 50, 175-179 (1978) and Anal. Chem. 50, 997-1000 (1978)].

[b]D. MacKay and W. Shiu, J. Chem. Eng. Data. 22, 4 (1977).

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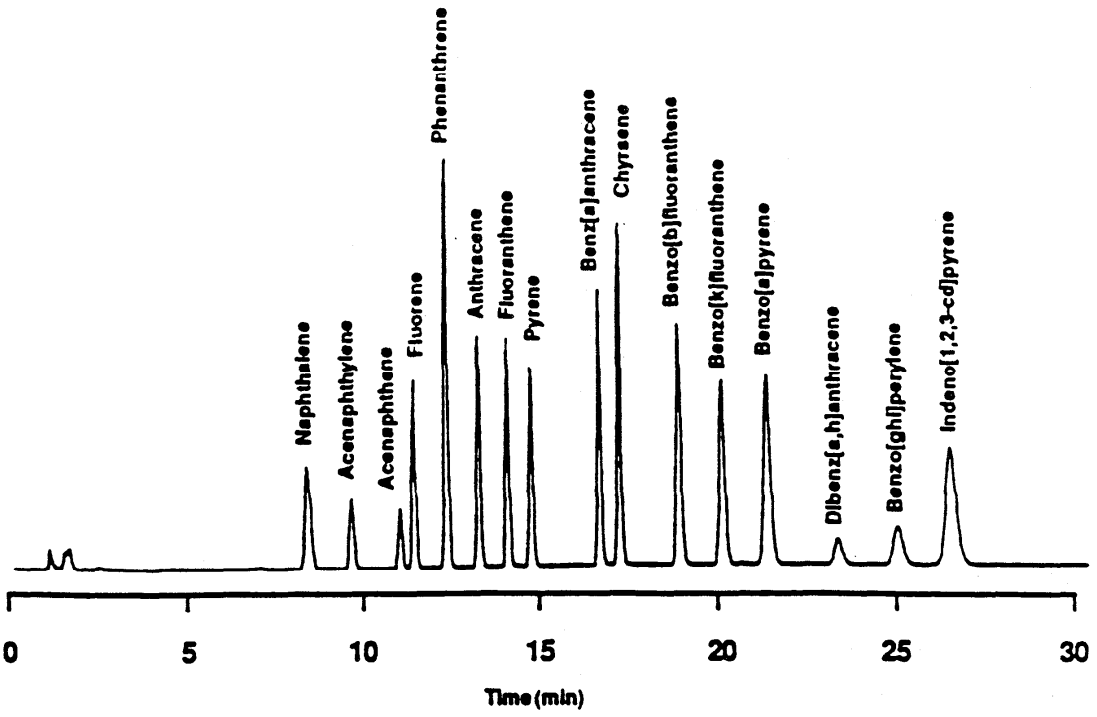

Figure 1. Reversed-phase LC separation of the 16 components of SRM 1647c. A polymeric C_{18} column (Hypersil Green PAH column, 5 μm, 4.6 mm x 25 cm) was used with a gradient elution program: 3 min. hold at 50% water: 50% acetonitrile; 15 min. linear gradient to 100% acetonitrile; and 15 min. hold at 100% acetonitrile.

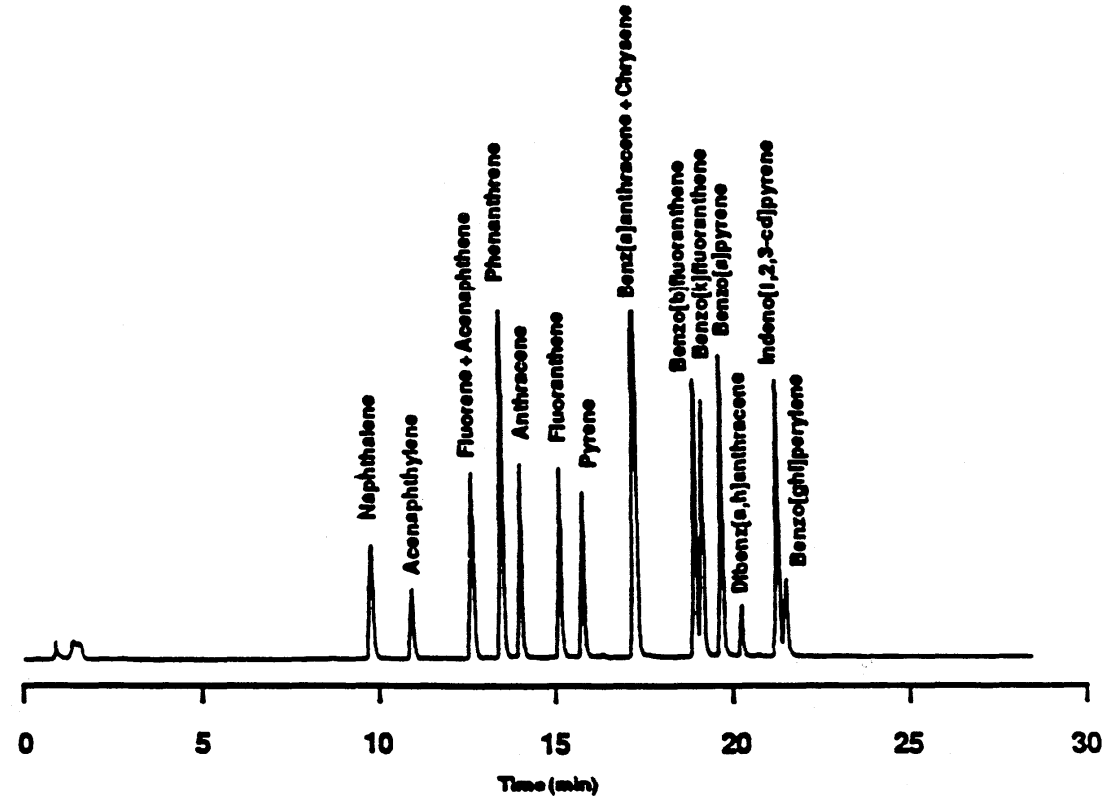

Figure 2. Reversed-phase LC separation of the 16 components of SRM 1647c using a monomeric C_{18} column (Zorbax ODS column, 5 μm, 4.6 mm x 25 cm) and the same gradient elution program as in Figure 1.