

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1647

Priority Pollutant Polynuclear Aromatic Hydrocarbons (in Acetonitrile)

This Standard Reference Material is intended for calibrating chromatographic instrumentation used in the determination of the polynuclear aromatic hydrocarbons (PAH's) certified in this SRM. It is also useful in recovery studies for adding known accurate amounts of these PAH's to a sample; and because of its miscibility with water, it can be used to fortify aqueous samples with known concentrations of PAH's.

Certified Concentrations of the PAH's:

The certified concentrations of the 16 organic constituents in acetonitrile are shown in Table 1. Because the density of acetonitrile changes with temperature, these concentrations are certified for the temperature range of 21 to 25 °C. Except for chrysene and dibenz[a,h]anthracene, each value is based on the concentration calculated from the mass of the PAH added to a known volume of the acetonitrile, on the analytical results obtained by high performance liquid chromatography (HPLC), and for six compounds, also by gas chromatography (GC). The concentrations of chrysene and dibenz[a,h]anthracene, which did not dissolve completely, were certified based on the concordant results of the two independent methods, HPLC and GC, only. The calculated concentrations of the other 14 PAH's were corrected for compound purity determined by GC. Thirteen of the 16 compounds added were at least 97.5% pure while the remaining three were at least 94% pure. Table 2 shows the calculated concentrations and the concentrations obtained by the analytical methods used in the certification.

NOTICE AND WARNINGS TO USER

Expiration of Certification: This certification is valid, within the limits certified, for one year from the date of purchase. In the event that the certification should become invalid before then, purchasers will be notified by NBS.

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

Use: Samples of the SRM for analysis should be withdrawn from ampoules held at 23 ± 2 °C immediately after opening and used without delay for any certified value in Table 1 to be valid within the stated uncertainty. Certified values are not applicable to ampoules stored after opening, even if resealed.

Analytical determinations were performed at the Center for Analytical Chemistry, Organic Analytical Research Division, by J.M. Brown-Thomas, F.R. Guenther, D.K. Hancock, and W.E. May.

Consultation on the statistical design of the experimental work was provided by K.R. Eberhardt of the Statistical Engineering Division.

The coordination of the technical measurements leading to certification were performed under the direction of W.E. May and H.S. Hertz.

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

PREPARATION AND ANALYSIS

The acetonitrile solution of the 16 PAH's was prepared at Serco, Inc., Roseville, Minn. and ampouled cold into 5-mL amber glass ampoules. The ampoules were purged with nitrogen just prior to filling and sealed under nitrogen. Samples representing early, middle, and final stages of ampouling were analyzed by HPLC. No significant differences in concentration of the 16 compounds were found.

Randomly selected ampoules were analyzed for all 16 PAH's by HPLC on a Vydac ODS (5 μ m) column using an acetonitrile-water mobile phase. Four external standard solutions were used to provide quantitative data.

GC on a fused silica SE-54 capillary column was used to determine 8 of the 16 compounds. Two standard solutions were used to obtain compound responses relative to 1-methylpyrene and m-tetraphenyl, the internal standards.

Ultraviolet absorption data between 205 and 600 nm are supplied as an aid in identifying each compound certified in this SRM. Table 3 gives the apparent specific molar absorbance for several prominent peaks in each spectrum. "Specific absorbance" is defined here as absorbance per unit pathlength and unit concentration. The term absorptivity was avoided because it is ambiguously defined (See Mielenz, K.D., Anal. Chem. 48, 1093-1094 (1976)). 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. Table 4 gives the apparent specific molar absorbances for each PAH at 254.0 nm. The apparent specific molar absorbance at 254.0 nm should be used with caution. Because the absorbances measured at 254 nm do not correspond to peak maxima, 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 Table 4 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 the calibration of his instrument at 254 nm.

Table 5 gives aqueous solubility values for 15 of the PAH's present in this SRM. These data, which are provided for information only, give an indication of how much of SRM 1647 can be added to a known volume of water without exceeding the aqueous solubilities of the PAH's.

Table 1. Certified Concentrations of Polynuclear Aromatic Hydrocarbons
in SRM 1647 at 23 ± 2 °C

<u>Compound</u>	<u>Concentration, $\mu\text{g/mL}$*</u>
Naphthalene	22.5 ± 0.2
Acenaphthylene	$19.1 \pm .2$
Acenaphthene	$21.0 \pm .4$
Fluorene	$4.92 \pm .10$
Phenanthrene	$5.06 \pm .10$
Anthracene	$3.29 \pm .10$
Fluoranthene	$10.1 \pm .2$
Pyrene	$9.84 \pm .10$
Benz[a]anthracene	$5.03 \pm .10$
Chrysene	$4.68 \pm .10$
Benzo[b]fluoranthene	$5.11 \pm .10$
Benzo[k]fluoranthene	$5.02 \pm .10$
Benzo[a]pyrene	$5.30 \pm .10$
Benzo[ghi]perylene	$4.01 \pm .10$
Dibenz[a,h]anthracene	$3.68 \pm .10$
Indeno[1,2,3-cd]pyrene	$4.06 \pm .10$

*The estimated uncertainty given for each compound is based on judgment, and represents an evaluation of the combined effects of method imprecision, and possible systematic errors among methods.

Table 2. Summary of Results by the Analytical Methods Used in Certification

	<u>Concentration, $\mu\text{g/mL}$</u>		
	<u>Calculated</u>	<u>HPLC</u>	<u>GC</u>
Naphthalene	22.5	22.4 ± 0.5^a	
Acenaphthylene	19.0	$19.2 \pm .5$	
Acenaphthene	20.8	$21.2 \pm .4$	
Fluorene	4.89	$4.96 \pm .18$	
Phenanthrene	5.00	$5.12 \pm .18$	
Anthracene	3.25	$3.33 \pm .10$	
Fluoranthene	9.99	$10.3 \pm .5$	
Pyrene	9.82	$9.85 \pm .58$	
Benz[a]anthracene	4.99	$5.12 \pm .14$	4.97 ± 0.06^a
Chrysene ^b		$4.69 \pm .15$	$4.68 \pm .06$
Benzo[b]fluoranthene	5.11	$5.13 \pm .21$	$5.09 \pm .06$
Benzo[k]fluoranthene	5.00	$5.06 \pm .15$	$4.99 \pm .10$
Benzo[a]pyrene	5.28	$5.32 \pm .13$	$5.31 \pm .19$
Benzo[ghi]perylene	4.00	$4.09 \pm .30$	$3.99 \pm .14$
Dibenz[a,h]anthracene ^b		$3.73 \pm .12$	$3.63 \pm .07$
Indeno[1,2,3-cd]pyrene	4.07	$4.11 \pm .15$	$4.02 \pm .06$

^aUncertainty is given as 95% confidence limits for the mean.

^bIncomplete dissolution of compound.

Table 3. Apparent Specific Molar Absorbances at λ_{\max} .

Compound	λ_{\max} , nm	Apparent specific molar absorbance		Compound	λ_{\max} , nm	Apparent specific molar absorbance	
		ϵ_a , L·mol ⁻¹ ·cm ⁻¹	Relative ϵ_a			ϵ_a , L·mol ⁻¹ ·cm ⁻¹	Relative ϵ_a
Naphthalene	220.4	98,000 ⁱⁱ	100%	Fluoranthene	235.6	50,800	100%
	285.7		4.0		358.3		16
	283.4		3.9		342.0		16
	275.8		5.9		322.0		12
	266.2		5.3		308.6		7.0
	258.2*		4.0		286.2		81
Acenaphthene	227.0	84,100	100%	281.1		35	
	320.7		2.4	275.5		45	
	312.4		1.3	271.4		24	
	306.4		3.8	260.5		24	
	300.6		4.8	209.6		78	
	289.2		7.6	Pyrene	240.1	83,100	100%
	280.7		6.6		334.4		56
			318.9			33	
Acenaphthylene	229.0	51,800	100%	305.4		13	
	338.8		7.7	294.1		5.3	
	321.6		19	272.2		60	
	310.6		15	261.8		29	
	274.6		4.5	251.7		13	
	264.6		5.0	231.0		52	
Fluorene	260.7	18,800	100%	207.0*		15	
	299.6		47	Benz[a]anthracene	287.0	93,000	100%
	292.0*		28		384.3		1.1
	288.4		32		374.8		0.8
	270.8*		71		357.8		5.2
	263.4		100		341.0		7.4
	219.9		88		327.8		6.5
			314.2			5.0	
Anthracene	251.5	186,000	100%	299.7		8.4	
	375.9		4.0	276.5		80	
	356.9		4.2	266.7		43	
	339.8		2.8	256.1		41	
	324.1		1.5	227.7		36	
	221.2		5.8	221.7		39	
	218.2		5.6				
				Chrysene	267.1	134,000	100%
Phenanthrene	250.7	63,500	100%		360.7		0.5
	292.7		21		319.8		9.2
	281.2		16		306.4		9.2
	273.9		20		294.3		8.6
	244.1		77		281.0		8.9
	219.8		32		257.6		55
	211.3		51		241.2		16
				220.6		24	

*Shoulder

ⁱⁱThese values are for information only and are not certified.

Table 3. Apparent Specific Molar Absorbances at λ_{\max} (Cont.)

Compound	λ_{\max} , nm	Apparent specific molar absorbance		Compound	λ_{\max} , nm	Apparent specific molar absorbance			
		ϵ_a , L·mol ⁻¹ ·cm ⁻¹	Relative ϵ_a			ϵ_a , L·mol ⁻¹ ·cm ⁻¹	Relative ϵ_a		
Benzo[b]fluoranthene	255.6	44,400 ^a	100%	Benzo[ghi]perylene	299.0	56,200	100%		
	367.5		16		383.0		35		
	349.2		26		380.8		35		
	341.1		25		361.8		32		
	300.4		83		344.7		16		
	291.7		62 ^a		338.9		15		
	289.7		62		329.3		11		
	275.7		63		323.9		8.6		
	244.8		84		313.4		11		
	239.2		84		288.6		71		
	221.3		92		276.5		42		
Benzo[k]fluoranthene	306.7	58,200	100%	Dibenz[a,h]anthracene	253.7		27		
	400.0		21		222.2		82		
	378.4		19		296.5	158,000	100%		
	359.4		9.8					393.8	0.8
	336.0*		8.7					372.8	0.7
	321.4*		12					348.4	8.6
	295.2		72					332.6	9.9
	282.9		38					319.7	12
	270.3*		30					287.9	59
	267.0		34					285.6*	57
	244.3		91					277.4	30
236.9		95	274.8*	28					
214.6		61	229.9	17					
Benzo[a]pyrene	295.8	57,900	100%	221.3		37			
	403.3		6.0	215.8		25			
	384.4		45	249.6	71,300	100%			
	378.1		41				405.6	9.2	
	364.5		41				382.8*	17	
	347.0		21				376.9	18	
	331.5		8.6				359.2	21	
	283.8		77				314.7	38	
	271.6		52				302.4	47	
	264.8		87				291.4	36	
	254.6		72				275.2	33	
	226.6		46				209.8	58	
	220.0		43						

*Shoulder

^aThese values are for information only and are not certified.

Table 4. Apparent Specific Molar Absorbances at 254.0 nm

Compound	Apparent specific molar absorbance $\epsilon_a, \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \times 10^{-3}$	% Relative $\epsilon_a = \frac{\epsilon_a, 254.0 \text{ nm}}{\epsilon_a, \lambda_{\text{max}}} \times 100$	% 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
Indeno[1,2,3-cd]pyrene	38	53	22

The values in this table are for information only and are not certified.

Table 5. Aqueous Solubility Data for the Individual PAH Compounds Present in SRM 1647

Compound	Aqueous Solubility at 25 °C, (ng/mL)
Naphthalene	(31700) ^a
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 These values are supplied for information and are not certified. They are provided for users who wish to add this acetonitrile solution to water for recovery studies. Note that the solubilities are for individual PAH's and may change in an aqueous solution of the 16 PAH's.

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

^c W. Davis, M. Krahl and G. Clowes, J. Am. Chem. Soc. 64, 108-14 (1942).

All other solubility values were determined at NBS using Dynamic Coupled Column Liquid