

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1647a

Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)

Standard Reference Material (SRM) 1647a consists of five 2-mL vials, each containing approximately 1.2 mL of an acetonitrile solution of 16 polycyclic aromatic hydrocarbons (PAH's). The PAH's included in this SRM are the 16 identified by U. S. Environmental Protection Agency as priority pollutants. SRM 1647a is intended primarily as a calibration solution for use in liquid chromatographic methods for the determination of polycyclic aromatic hydrocarbons. Because the solution is miscible with water, it can be used to fortify aqueous samples with known concentrations of PAH's.

Certified Concentrations of PAH

Certified concentrations of the 16 PAH's are given in Table 1. The concentration values are certified in $\mu\text{g/g}$ units but are also reported in units of $\mu\text{g/mL}$ for user convenience ($\mu\text{g/mL}$ values were calculated using the density of acetonitrile at 23 °C). The certified values in Table 1 are derived from the concordant results obtained from liquid chromatography and gravimetry.

Notice and Warnings to User

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

Storage: Sealed ampoules, should be stored, as received, 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Use: Samples of the SRM for analysis should be withdrawn from ampoules held at 23 ± 2 °C and used without delay in order for certified concentrations in Table 1 to be valid within the stated uncertainty. 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 approved methods for disposal of waste.

Analytical determinations were performed at the Center for Analytical Chemistry, Organic Analytical Research Division, by L. C. Sander, R. E. Rebbert and D. Hancock.

Consultation on the statistical design of the experimental work was provided by M. A. Goes and R. C. Paule of the National Measurement Laboratory.

January 29, 1988
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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

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.

Table 1. Certified Concentrations of Polycyclic Aromatic Hydrocarbons in SRM 1647a.

Compound	Concentration ($\mu\text{g/g}$) ¹	Concentration ($\mu\text{g/mL}$) ²
naphthalene	25.6 \pm 0.5	19.9 \pm 0.4
acenaphthylene	20.4 \pm 0.2	15.9 \pm 0.2
acenaphthene	25.2 \pm 0.6	19.6 \pm 0.5
fluorene	6.11 \pm 0.08	4.76 \pm 0.06
phenanthrene	4.33 \pm 0.02	3.37 \pm 0.02
anthracene	0.990 \pm 0.005	0.771 \pm 0.004
fluoranthene	9.86 \pm 0.09	7.68 \pm 0.07
pyrene	10.59 \pm 0.02	8.25 \pm 0.02
benz[a]anthracene	4.90 \pm 0.02	3.82 \pm 0.02
chrysene	4.65 \pm 0.02	3.62 \pm 0.02
benzo[b]fluoranthene	5.24 \pm 0.06	4.08 \pm 0.05
benzo[k]fluoranthene	5.92 \pm 0.03	4.61 \pm 0.02
benzo[a]pyrene	6.19 \pm 0.04	4.82 \pm 0.03
dibenz[a,h]anthracene	4.77 \pm 0.07	3.72 \pm 0.05
benzo[ghi]perylene	4.82 \pm 0.03	3.75 \pm 0.02
indeno[1,2,3-cd]pyrene	5.54 \pm 0.10	4.32 \pm 0.08

¹The certified concentrations and associated uncertainties were derived from the weighted combination of LC and gravimetric data as described by Paule and Mandel in "Consensus Values and Weighting Factors," *Journal of Research of the National Bureau of Standards*, Vol. 87, No. 5, Sept-Oct (1982), pp 377-385. The listed uncertainties are \pm two standard deviations of the values and include both within and between analytical method differences.

²The concentration values and uncertainties, listed in $\mu\text{g/mL}$, are computed from the certified concentrations, in $\mu\text{g/g}$, multiplied by the density of acetonitrile at 23 °C (0.7789 g/mL).

Preparation and Analysis

The acetonitrile solution of the 16 PAH's was prepared gravimetrically (w/w) from individual compounds. Purities of the 16 PAH's are listed in Table 2. Compounds obtained from Community Bureau of Reference (BCR) are certified reference materials and therefore independent purity determinations were not carried out (Certificates of Analysis for these compounds list purities \geq 99%). The purity of compounds obtained from commercial sources was determined by liquid and gas chromatography. With the exception of acenaphthylene, PAH purities were \geq 99% and no corrections for impurities were made. Acenaphthylene was found to contain 4.01% acenaphthene (LC determination) and corrections were made to reflect the true concentrations. The SRM solution was aliquoted into 2-mL amber glass ampoules which were purged with argon prior to addition of the SRM solution. Samples representing early, middle, and final stages of ampouling were analyzed by LC. No evidence of sample inhomogeneity was observed.

Twenty randomly selected ampoules were analyzed in duplicate for all 16 PAH's by reversed-phase LC on a polymeric C₁₈ column (Vydac 201TP column,* 5 μm , 4.6 mm x 25 cm) using an acetonitrile-water mobile phase. Other columns (e.g., Chromspher PAH, Bakerbond C₁₈) provide similar separations (Ref 1). The following gradient conditions were used for the separation: step (1) 4 minutes equilibration at 50% water: 50% acetonitrile, step (2) injection, step (3) 3 minutes hold at 50% water:50% acetonitrile, step (4) 15 minutes linear gradient to 100% acetonitrile, step (5) 6 minutes hold at 100% acetonitrile, and step (6) 1 minute linear gradient to 50% water: 50% acetonitrile. A representative chromatogram is shown in Figure 1. Response factors were determined from two

* Certain commercial equipment, instruments, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 3. Apparent Specific Molar Absorances at λ_{max}
 The values in this table are for information only and are not certified

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

*Shoulder

separate standard solutions containing the 16 PAH's. Triphenylene was added to both the SRM and response factor solutions for use as an internal standard. A chromatogram illustrating separation of the compounds in the SRM solution using a monomeric C₁₈ column (Zorbax C₁₈ column, 5 μ m, 4.6 mm x 25 cm) is provided for comparison (Figure 2). Other monomeric C₁₈ columns (e.g. Hypersil ODS, Microsorb C₁₈, Partisil ODS-3, Ultrasphere ODS, μ Bondapak C₁₈) provide a similar separation of the PAH's in SRM 1647a.

Ultraviolet absorption data between 205 and 600 nm are supplied as an aid in identifying each compound certified in this SRM. The apparent specific molar absorbances for several prominent peaks in each spectrum are provided in Table 3. "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. In Table 4, 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 because the absorbances measured at 254 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 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 detector calibration at 254 nm.

Aqueous solubility values are summarized in Table 5 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 1647a can be added to a known volume of water without exceeding the aqueous solubilities of the individual PAH's.

Table 2. Sources and Purities of PAH's used to prepare SRM 1647a.

Component	Source	Purity, weight percent		BCR ^a
		GC	LC	
naphthalene	Commercial	99.5	98.8	
acenaphthylene	Commercial	95.8	96.0	
acenaphthene	Commercial	99.8	100	
fluorene	Commercial	98.5	99.0	
phenanthrene	Commercial	99.6	99.3	
anthracene	Commercial	99.8	99.5	
fluoranthene	BCR			99.4
chrysene	Commercial	99.8	99.7	
benzo[b]fluoranthene	BCR			99.5
benzo[k]fluoranthene	BCR			99.5
benzo[a]pyrene	Commercial	99.5	99.3	
benzo[ghi]perylene	BCR			99.0
dibenz[a,h]anthracene	BCR			99.0
indeno[1,2,3-cd]pyrene	BCR			99.0
benz[a]anthracene	BCR			99.7
pyrene	BCR			99.7

^aBCR = Bureau Community Reference, Directorate General XII, Commission of the European Communities, 200 rue de la Loi, B-1049 Brussels. The listed values of purity are certified.

References

1. Sander, L.C., and Wise, S.A., "Determination of Column Selectivity Toward Polycyclic Aromatic Hydrocarbons", J. High Resol. Chromatogr. Chromatogr. Commun., in press.

Table 4. Apparent Specific Molar Absorbances at 254.0 nm for PAH's in SRM 1647a

Compound	Apparent Specific Molar Absorbance $\epsilon_a, \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \times 10^{-3}$	$\% \text{ Relative } \epsilon_a = \frac{\epsilon_a, 254.0 \text{ nm}}{\epsilon_a, \lambda_{\text{max}}} \times 100$	$\% \text{ error in } \epsilon_a \text{ for } 1 \text{ nm error}$
Naphthalene	3.1	3.2%	11.0%
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 1647a

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).

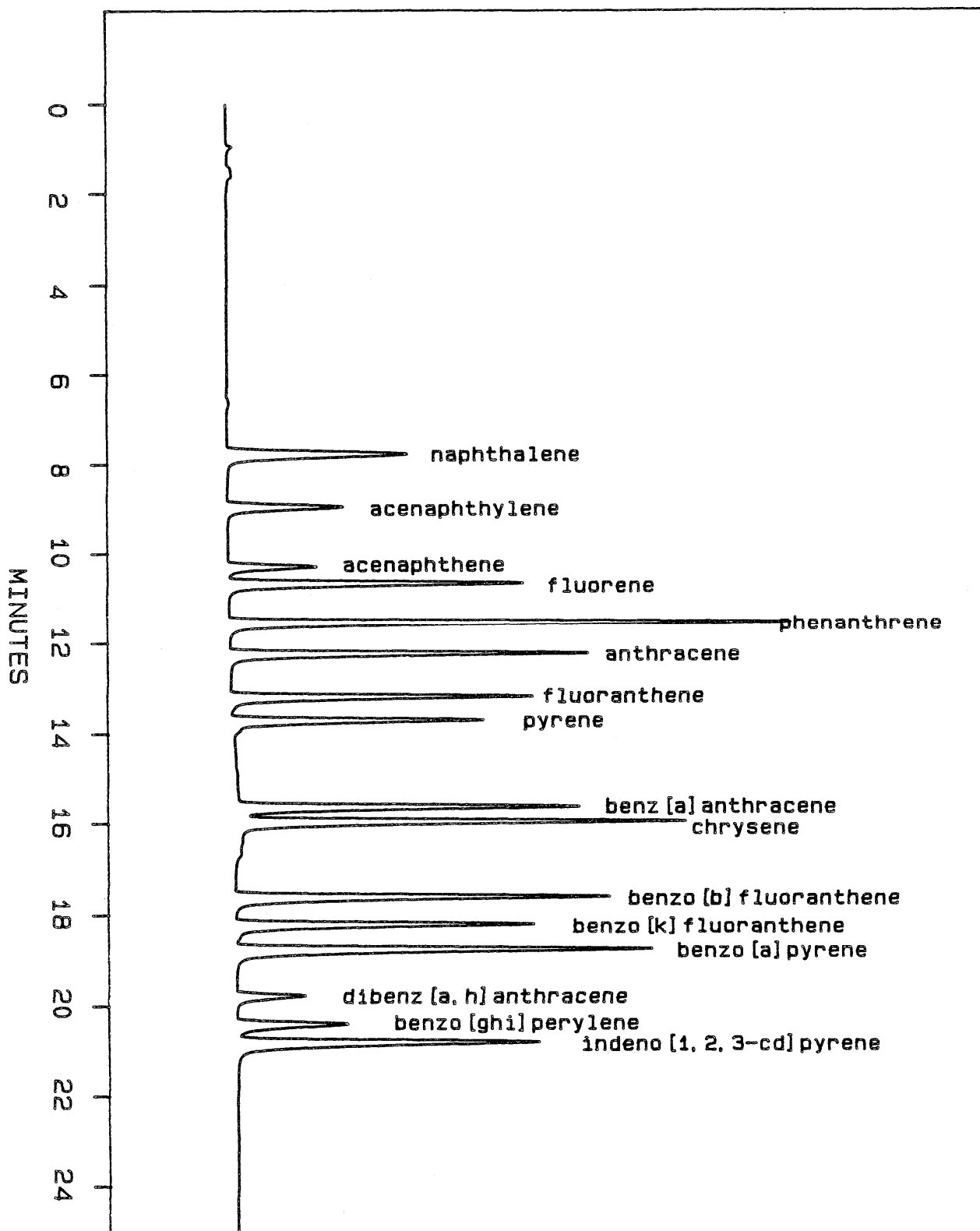
All other solubility values were determined at NBS using Dynamic Coupled Column Liquid Chromatographic Technique [W.E. May, S.P. Wasik, and D.H. Freeman, *Anal. Chem.* 50, 175-179 (1978) and *Anal. Chem.* 50, 997-1000 (1978)].

Table 3. Apparent Specific Molar Absorbances at λ_{max} (cont.)
The values in this table are for information only and are not certified

Compound	λ_{max} , nm	Apparent Specific Molar Absorbance ϵ_{λ} , L mole ⁻¹ cm ⁻¹	Relative ϵ_{λ}	Compound	λ_{max} , nm	Apparent Specific Molar Absorbance ϵ_{λ} , L mole ⁻¹ cm ⁻¹	Relative ϵ_{λ}
Benzol[b]fluoranthene	255.6	44,400	100.0%	Benzol[g,h]iperylene	299.0	56,200	100.0%
	367.5		16.3		383.0		35.3
	349.2		25.5		380.8		35.1
	341.1		24.7		361.8		31.6
	300.4		82.8		344.7		16.1
	291.7		61.9		338.9		14.8
	289.7		61.5		329.3		11.2
	275.7		62.5		323.9		8.6
	244.8		84.3		313.4		10.7
	239.2		84.2		288.6		71.1
	221.3		91.9		276.5		42.1
				253.7	27.0		
				222.2	82.4		
Benzol[k]fluoranthene	306.7	58,200	100.0%	Dibenz[a,h]anthracene	296.5	158,400	100.0%
	400.0		20.5		393.8		0.8
	378.4		19.1		372.8		0.7
	359.4		9.8		348.4		8.6
	336.0*		8.7		332.6		9.9
	321.4*		12.3		319.7		12.1
	295.2		72.3		287.9		59.1
	282.9		38.3		285.6*		56.9
	270.3*		29.7		277.4		30.3
	267.0		34.0		274.8*		27.8
	244.3		91.4		229.9		17.1
236.9	94.6	221.3	36.7				
214.6	61.0	215.8	25.4				
Benzol[a]pyrene	295.8	57,930	100.0%	Indenol[1,2,3,c,d]pyrene	249.6	71,300	100.0%
	403.3		6.0		405.6		9.2
	384.4		45.2		382.8*		16.7
	378.1		41.1		376.9		18.0
	364.5		40.5		359.2		20.6
	347.0		20.9		314.7		38.0
	331.5		8.6		302.4		46.6
	283.8		76.9		291.4		35.8
	271.6		51.9		275.2		32.9
	264.8		87.1		209.8		58.1
	254.6		72.2				
226.6	46.2						
220.0	42.9						

*Shoulder

Figure 1. Separation of the 16 components of SRM 1647a. A Vydac 201TP column (5 μ m, 4.6 mm x 25 cm) was used



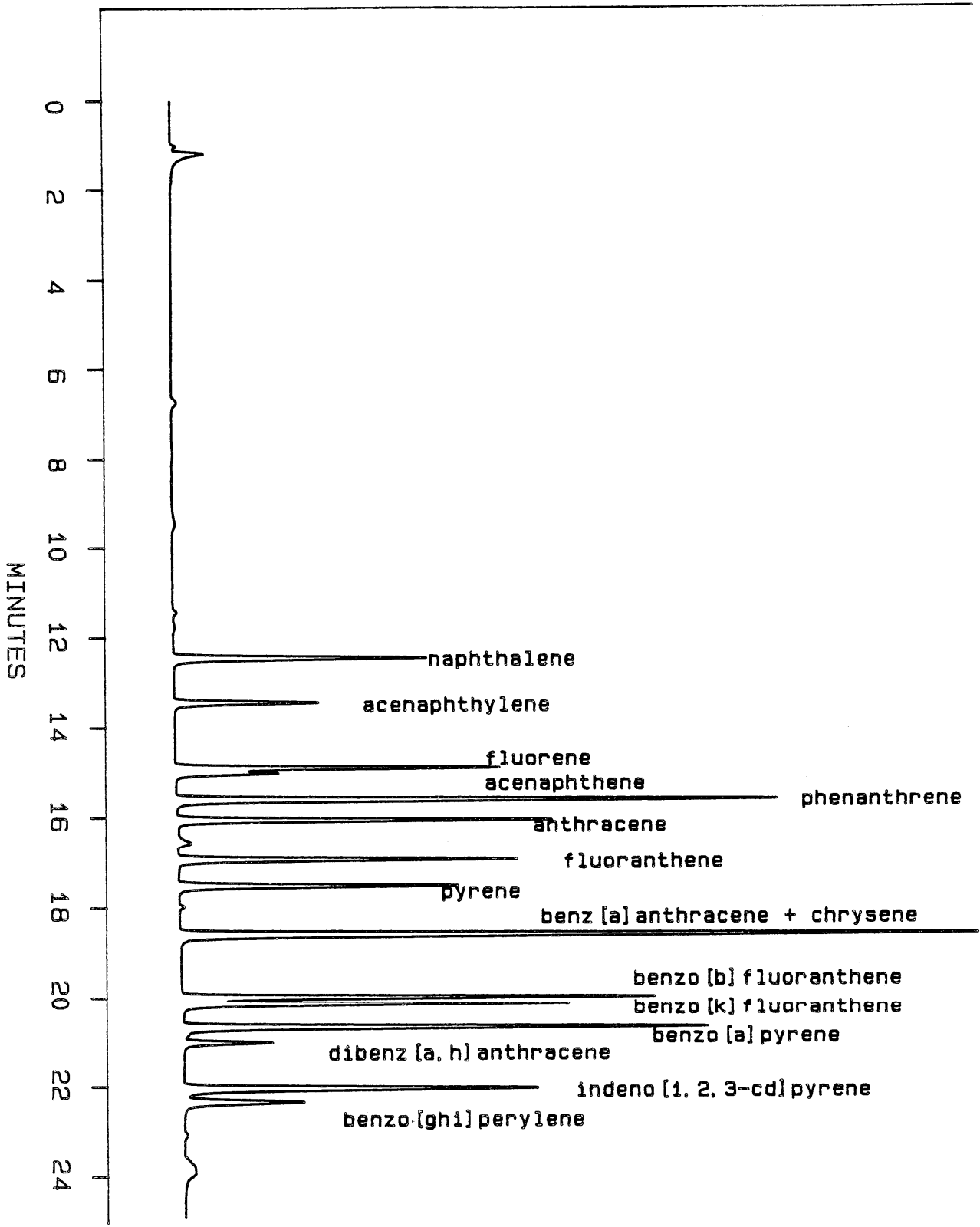


Figure 2. Separation of the SRM solution using a Zorbax C18 column (5µm, 4.6 mm x 25 cm) and the same gradient elution program as in Figure 1.