

National Bureau of Standards Certificate

Standard Reference Material 1644

Generator Columns for Polynuclear Aromatic Hydrocarbons

SRM 1644 is intended to provide accurate concentrations of anthracene, benzo(a)anthracene (1,2-benzanthracene), and benzo(a)pyrene (3,4-benzopyrene) in water. The SRM consists of three 50 cm x 0.6 cm (coiled) stainless steel tubes, each packed with fine quintus quartz (sea sand) coated with approximately 0.5 percent by weight of the polynuclear aromatic hydrocarbon (PAH) of interest.

Principle of Operation: A saturated aqueous solution of the PAH of interest is generated by flowing high-purity water slowly through the column. Because the aqueous solubility of a compound is a well-defined thermodynamic quantity, a saturated solution has a fixed concentration (1, 2, 3).

Equilibration and Use of Generator Columns: To equilibrate a new column before initial use, purge with high-purity water, such as commercial HPLC grade water. The volume required for equilibration of each column is: 500 mL for anthracene, 1000 mL for benzo(a)anthracene, and 500 mL for benzo(a)pyrene. After equilibration, pump the high-purity water at a constant temperature (± 0.1 °C) through the column at a flow rate between 0.1 and 5 mL/min to produce a saturated solution. Record the temperature. The solution should be used immediately after generation to avoid sorption losses.

If either the temperature is changed by as much as 1 °C or the flow is interrupted for less than one hour, pump 25 mL water through the column under the new conditions to restore equilibrium prior to sample collection. However, if the flow is interrupted for more than one hour, pump 50 mL water prior to sample collection. During periods of frequent use, a column can be kept equilibrated by maintaining a steady, but low, flow rate of approximately 0.1 mL/min through the column. The flow rate can be increased to collect a large volume of sample and then decreased again. Columns should be purged with 10 liters of oil-free nitrogen prior to storage periods of more than one month.

Certified Concentrations: When used as directed, these columns generate saturated solutions. The concentrations of the compounds in these solutions at temperatures between 10 and 30 °C were determined by two independent analytical methods. The data obtained were combined by fitting an empirical expression of the form $\ln[\text{Conc}] = A + B(1/T) + C(1/T^2)$ by least squares. In this equation, $\ln[\text{Conc}]$ is the natural logarithm of the concentration, T is the absolute temperature, and A, B, and C are constants for each compound. The derived equations for anthracene, benzo(a)anthracene, and benzo(a)pyrene were used to calculate the certified concentrations at one degree intervals between 10 and 30 °C. These certified concentrations are given in Tables I-III.

Service Life of Columns: Generator columns for anthracene, benzo(a)anthracene, and benzo(a)pyrene are certified for either two years or for total aqueous purge volumes of 7.5×10^2 , 3×10^3 , and 1.5×10^4 liters, respectively, whichever comes first.

Consultation on the statistical design of the experimental work and statistical analysis of the data was provided by K. R. Eberhardt of the Statistical Engineering Division. Coordination of the technical measurements leading to certification was performed by W. E. May, R. A. Velapoldi, and H. S. Hertz. Technical measurements leading to the development and certification of SRM 1644 were performed by the following members of the Center for Analytical Chemistry: W. E. May, J. M. Brown-Thomas, W. J. Sonnefeld, R. A. Velapoldi, and P. A. White.

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

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George A. Uriano, Chief
Office of Standard Reference Materials

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The anthracene generator column, after equilibration, produces aqueous solutions that contain very small amounts of phenanthrene. Because of its relatively high solubility (1000 $\mu\text{g}/\text{kg}$), residual amounts of phenanthrene are depleted from the column at a rapid rate.

The benzo(a)anthracene generator column, after equilibration, produces aqueous solutions that contain as much as 0.3 $\mu\text{g}/\text{kg}$ anthracene in addition to the certified concentrations of benzo(a)anthracene. The concentration of anthracene in the generator column effluent varies with time (volume) and, therefore, is not certified.

The benzo(a)pyrene generator column, after equilibration, produces aqueous solutions that contain as much as 0.1 $\mu\text{g}/\text{kg}$ benzo(a)anthracene and 1 $\mu\text{g}/\text{kg}$ chrysene in addition to the certified concentrations of benzo(a)pyrene. The concentration of these non-analyte components vary with time and, therefore, are not certified.

Analyses of the Saturated Aqueous Solutions: The concentrations of the saturated aqueous solutions of anthracene, benzo(a)anthracene, and benzo(a)pyrene in the effluent from the respective generator columns were determined by two independent analytical techniques. The first technique was high-performance liquid chromatography (HPLC). It involved quantitative extraction of the PAH of interest from the aqueous effluent by an "extractor column" packed with an octadecylsilane (C_{18}) bonded phase; use of an acetonitrile-water eluant to transfer components from the extractor column to an analytical C_{18} column for separation of the analyte from non-analyte components; and detection of the analyte by measuring its absorbance at 254 nm. The second technique involved the use of a "standard addition" spectrofluorimetric technique for "on stream" analysis. The aqueous effluent from the generator column was mixed with PAH standards dissolved in acetonitrile and the PAH concentration of the resultant mixture was determined by fluorescence at the following excitation (λ_{ex}) and emission (λ_{em}) wavelengths: anthracene, $\lambda_{\text{ex}} = 254 \text{ nm}$, $\lambda_{\text{em}} = 384$ and 404 nm ; benzo(a)anthracene, $\lambda_{\text{ex}} = 290 \text{ nm}$, $\lambda_{\text{em}} = 395 \text{ nm}$; benzo(a)pyrene, $\lambda_{\text{ex}} = 296 \text{ nm}$, $\lambda_{\text{em}} = 414 \text{ nm}$. The PAH effluent concentration was determined mathematically. Where necessary, corrections for inner filter effects or the emission-absorbance contributions by impurities were made to obtain the values for determining the certified PAH concentrations listed in Tables I-III.

References:

1. May, W. E., The Solubility Behavior of Polycyclic Aromatic Hydrocarbons in Aqueous Systems, American Chemical Society Advances in Chemistry Series 185 (7), 143-192 (1980).
2. May, W. E., Wasik, S. P., and Freeman, D. H., Determination of the Aqueous Solubility of Polynuclear Aromatic Hydrocarbons by a Coupled-Column Liquid Chromatographic Technique, Anal. Chem. 50, 1 (1978).
3. Schwarz, F. P. and Miller, J. M., Determination of the Aqueous Solubilities of Organic Liquids at 10°C, 20°C, and 30 °C by Elution Chromatography, Anal. Chem. 52, 2162-2164 (1980).

Table I. Certified Aqueous Concentrations of Anthracene and Their Uncertainties, in Micrograms/Kilogram and Nanomoles/Liter, as a Function of Temperature

Temperature °C	Concentration and Its Uncertainty ¹ ,	
	µg/kg	nmol/L
10	16.6 ± 0.7	93.1 ± 4.0
11	17.6 ± 0.6	98.7 ± 3.6
12	18.7 ± 0.6	105 ± 3.3
13	19.8 ± 0.5	111 ± 3.1
14	21.1 ± 0.5	118 ± 2.9
15	22.4 ± 0.5	126 ± 2.9
16	23.8 ± 0.5	134 ± 2.9
17	25.4 ± 0.5	142 ± 2.9
18	27.0 ± 0.5	151 ± 3.0
19	28.8 ± 0.5	161 ± 3.1
20	30.7 ± 0.6	172 ± 3.2
21	32.8 ± 0.6	184 ± 3.2
22	35.0 ± 0.6	196 ± 3.2
23	37.4 ± 0.6	210 ± 3.2
24	39.9 ± 0.6	224 ± 3.3
25	42.7 ± 0.6	239 ± 3.7
26	45.7 ± 0.8	256 ± 4.4
27	48.9 ± 1.0	273 ± 5.5
28	52.4 ± 1.3	293 ± 7.2
29	56.1 ± 1.7	313 ± 9.5
30	60.1 ± 2.2	336 ± 12

¹The uncertainties are 99 percent (Working-Hotelling) confidence bands for the entire regression curve. The difference between the true and certified concentrations should be less than the stated uncertainty at the 99 percent confidence level.

Table II. Certified Aqueous Concentrations of Benzo(a)anthracene and Their Uncertainties, in Micrograms/Kilogram and Nanomoles/Liter, as a Function of Temperature

Temperature °C	Concentration and Its Uncertainty ¹ ,	
	µg/kg	nmol/L
10	3.38 ± 1.2	14.8 ± 5.3
11	3.60 ± 1.1	15.8 ± 4.6
12	3.83 ± 0.91	16.8 ± 4.0
13	4.09 ± 0.79	17.9 ± 3.4
14	4.36 ± 0.68	19.1 ± 3.0
15	4.65 ± 0.59	20.4 ± 2.6
16	4.96 ± 0.54	21.7 ± 2.4
17	5.29 ± 0.55	23.2 ± 2.4
18	5.65 ± 0.60	24.8 ± 2.6
19	6.04 ± 0.68	26.4 ± 3.0
20	6.45 ± 0.77	28.2 ± 3.4
21	6.90 ± 0.87	30.2 ± 3.8
22	7.38 ± 0.94	32.3 ± 4.1
23	7.90 ± 1.0	34.5 ± 4.4
24	8.45 ± 1.0	36.9 ± 4.5
25	9.05 ± 1.0	39.5 ± 4.6
26	9.69 ± 1.0	42.3 ± 4.6
27	10.4 ± 1.1	45.4 ± 4.7
28	11.1 ± 1.2	48.4 ± 5.0
29	11.9 ± 1.3	51.9 ± 5.9
30	12.8 ± 1.7	55.8 ± 7.3

¹The uncertainties are 99 percent (Working-Hotelling) confidence bands for the entire regression curve. The difference between the true and certified concentrations should be less than the stated uncertainty at the 99 percent confidence level.

Table III. Certified Aqueous Concentrations of Benzo(a)pyrene and Their Uncertainties, in Micrograms/Kilogram and Nanomoles/Liter, as a Function of Temperature

Temperature °C	Concentration and Its Uncertainty ¹ ,	
	µg/kg	nmol/L
10	0.59 ± 0.06	2.34 ± 0.23
11	0.63 ± 0.05	2.50 ± 0.20
12	0.67 ± 0.04	2.65 ± 0.17
13	0.71 ± 0.04	2.81 ± 0.15
14	0.76 ± 0.03	3.01 ± 0.12
15	0.81 ± 0.03	3.21 ± 0.11
16	0.87 ± 0.03	3.44 ± 0.10
17	0.93 ± 0.03	3.68 ± 0.10
18	0.99 ± 0.03	3.92 ± 0.11
19	1.06 ± 0.03	4.19 ± 0.12
20	1.13 ± 0.03	4.47 ± 0.13
21	1.21 ± 0.04	4.79 ± 0.15
22	1.30 ± 0.04	5.14 ± 0.16
23	1.39 ± 0.04	5.50 ± 0.16
24	1.49 ± 0.04	5.89 ± 0.17
25	1.59 ± 0.04	6.28 ± 0.17
26	1.71 ± 0.04	6.76 ± 0.18
27	1.83 ± 0.05	7.23 ± 0.19
28	1.96 ± 0.05	7.74 ± 0.22
29	2.11 ± 0.07	8.33 ± 0.27
30	2.26 ± 0.09	8.92 ± 0.35

¹The uncertainties are 99 percent (Working-Hotelling) confidence bands for the entire regression curve. The difference between the true and certified concentrations should be less than the stated uncertainty at the 99 percent confidence level.