



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1647e

Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)

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

Certified Values and Uncertainties: The certified values of the 16 PAHs are given in Table 1. Values are listed in units of mg/kg (mass fraction) and for user convenience mg/L (concentration). The volume fraction values were calculated from the mass fraction values using the density of acetonitrile at 23 °C (0.7789 g/mL). An allowance for the change in this density over the range 23 °C ± 2 °C is included in the uncertainty. The uncertainties are expanded uncertainties with a coverage factor of 2 (95 % confidence), calculated in accordance with the International Committee for Weights and Measures CIPM method [1]. They include uncertainty due to the calibration of the chromatographic method, measurement of selected samples using the chromatographic method, and purity of the reagents used to prepare the material.

Expiration of Certification: This certification is valid until **31 December 2015**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Storage and Use"). However, the certification will be nullified if the SRM is damaged, contaminated, or modified. NIST will monitor this SRM over the period of its certification. If changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the technical measurements leading to certification was under the direction of L.C. Sander and S.A. Wise of the NIST Analytical Chemistry Division.

Analytical determinations were performed by L.C. Sander of the NIST Analytical Chemistry Division.

Preparation and ampouling of SRM 1647e were carried out by L.C. Sander of the NIST Analytical Chemistry Division, and M.P. Cronise and C.N. Fales of the NIST Measurement Services Division.

Statistical design of the experimental work and evaluation of the data were provided by S.D. Leigh of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 06 March 2006

Table 1. Certified Values for PAHs in SRM 1647e

Compound	CAS Registry No. ^(a)	Mass Fraction ^(b) (mg/kg)	Concentration ^(c) (mg/L) (at 23 °C ± 2 °C)
Naphthalene	91-20-3	25.48 ± 0.58	19.85 ± 0.45
Acenaphthylene	208-96-8	19.69 ± 0.47	15.34 ± 0.37
Acenaphthene	83-32-9	26.32 ± 0.60	20.50 ± 0.47
Fluorene	86-73-7	6.09 ± 0.14	4.74 ± 0.11
Phenanthrene	85-01-8	4.52 ± 0.11	3.52 ± 0.09
Anthracene	120-12-7	1.01 ± 0.02	0.79 ± 0.02
Fluoranthene	206-44-0	9.73 ± 0.21	7.58 ± 0.16
Pyrene	129-00-0	10.88 ± 0.22	8.47 ± 0.17
Benz[<i>a</i>]anthracene	56-55-3	5.25 ± 0.11	4.09 ± 0.09
Chrysene	218-01-9	4.62 ± 0.10	3.60 ± 0.08
Benzo[<i>b</i>]fluoranthene	205-99-2	5.38 ± 0.11	4.19 ± 0.09
Benzo[<i>k</i>]fluoranthene	207-08-9	6.02 ± 0.13	4.69 ± 0.10
Benzo[<i>a</i>]pyrene	50-32-8	6.25 ± 0.15	4.87 ± 0.12
Dibenz[<i>a,h</i>]anthracene	53-70-3	4.48 ± 0.26	3.49 ± 0.20
Benzo[<i>ghi</i>]perylene	191-24-2	4.71 ± 0.17	3.67 ± 0.13
Indeno[1,2,3- <i>cd</i>]pyrene	193-39-5	5.48 ± 0.17	4.27 ± 0.13

^(a) Chemical Abstracts, Fourteenth Collective Index Guide, American Chemical Society, Columbus, Ohio, 2001.

^(b) The results are expressed as the certified value ± the expanded uncertainty. The certified value is the mean of the concentrations determined by gravimetric and chromatographic measurements. The expanded uncertainty uses a coverage factor of 2 (95 % confidence) and includes both correction for estimated purity and allowance for differences between the concentration determined by gravimetric preparation and chromatographic measurements [1].

^(c) The concentrations listed in mg/L units were obtained by multiplying the certified values in mg/kg by the density of acetonitrile at 23 °C (0.7789 g/mL). These concentrations are for use in the temperature range of 21 °C to 25 °C and an allowance for the change in density over this temperature range is included in the uncertainties.

NOTICE AND WARNING TO USER

Toxicity: This SRM contains acetonitrile. Acute and chronic health hazards have been documented from exposure through inhalation, ingestion, and skin absorption. This SRM also contains small amounts of PAHs, 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.

INSTRUCTIONS FOR USE

Storage and Use: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C and 30 °C. Samples of the SRM for analysis should be withdrawn from ampoules and used without delay. The certified values listed in Table 1 apply only to aliquots removed at 23 °C ± 2 °C. Certified values are not valid for ampoules which have been stored after opening, even if resealed.

Preparation and Analysis: The acetonitrile solution of the 16 PAHs was prepared gravimetrically from individual compounds. Four of the compounds (acenaphthylene, acenaphthene, phenanthrene, anthracene), were obtained from J. Jacob (Ahrensburg, Germany), naphthalene and fluorene were from Fluka (Milwaukee, WI), and the other ten compounds were Certified Reference Materials (CRMs) produced by the Community Bureau of Reference (BCR) Brussels, Belgium and obtained from the Institute for Reference Materials and Measurements (IRMM) Geel, Belgium. The purities of all PAHs used to make this SRM were ≥ 99 %. Purities of the compounds obtained from J. Jacob and Fluka were determined at NIST by a combination of techniques including differential scanning calorimetry (DSC), gas chromatography with flame ionization detection (GC-FID), and liquid chromatography with absorbance detection. Purities of CRMs were certified by BCR. 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 liquid chromatography (LC). No evidence of sample inhomogeneity was observed.

Randomly selected ampoules were analyzed for all 16 PAHs by LC using an acetonitrile-water mobile phase. Concentrations for the 16 PAHs were determined from a calibration based on averaged response factors, which used gravimetric values and instrumental responses for four independently prepared calibration standards. Four previous issues of this SRM (1647a, b, c, and d) were used as control samples. An internal standard calibration approach was used in the certification, with triphenylene as the internal standard. A representative chromatogram and the separation conditions are shown in Figure 1.

Comments on Column Selection: Variations in C₁₈ column selectivity for PAHs are known to result from different column manufacturing processes [2]. Columns prepared by reaction of monofunctional C₁₈ silanes with silica (denoted monomeric C₁₈ phases) differ from columns prepared with silica substrates using trifunctional C₁₈ silanes in the presence of water (denoted polymeric C₁₈ phases). The designation “polymeric C₁₈ column” should not be confused with “polymer substrate columns” (nonsilica columns, often based on polystyrene particles). Better separations of PAH mixtures are often possible on polymeric C₁₈ columns such as that used to produce the chromatogram shown in Figure 1, as compared to monomeric C₁₈ columns. A chromatogram illustrating the separation of the components in the SRM solution using a monomeric C₁₈ column is provided for comparison (Figure 2). Baseline resolution of all components was not achieved with the monomeric C₁₈ column. The classification of monomeric and polymeric C₁₈ columns for the separation of PAHs has been described [2-9] and may be accomplished using SRM 869a, *Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons)* [10]. Examples of various C₁₈ columns as “monomeric” or “polymeric” are provided with SRM 869a.

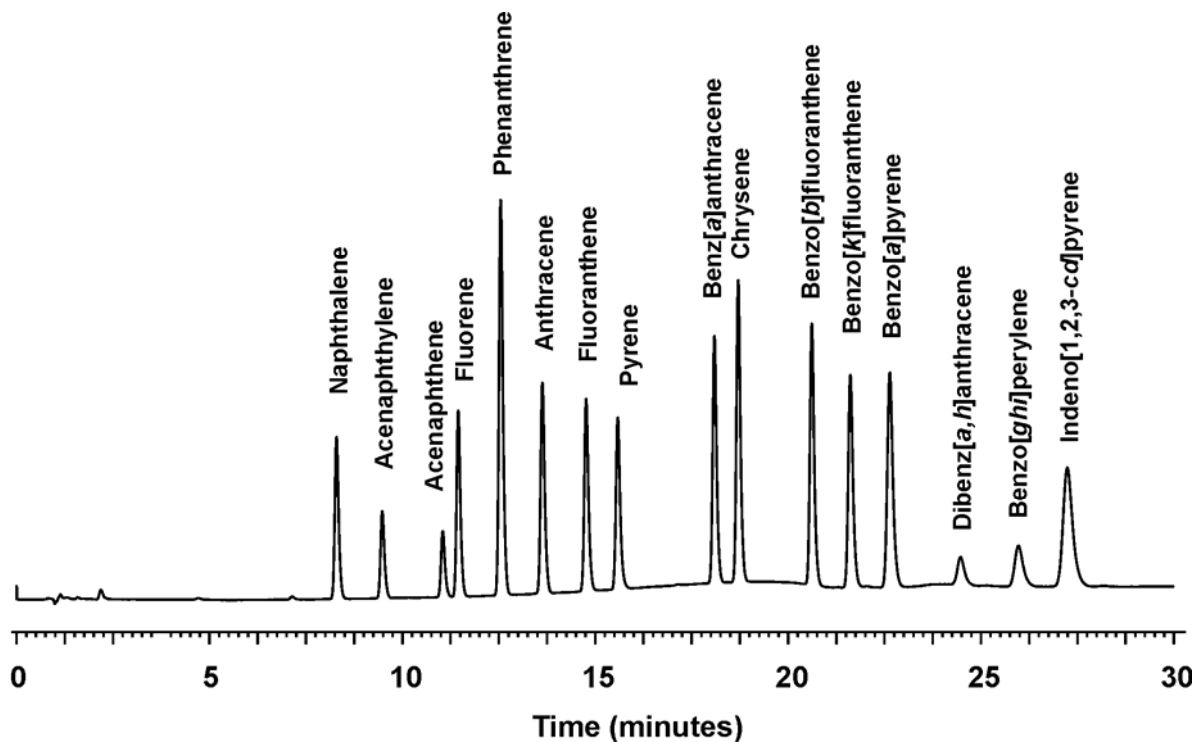


Figure 1. Reversed-phase LC separation of the 16 components of SRM 1647e. A polymeric C₁₈ column (Pinnacle II PAH column, 5 μm, 0.46 cm × 25 cm; Restek, Bellefonte, PA) was used with a gradient elution program: 3 minutes hold at 50 % water: 50 % acetonitrile; 15 minutes linear gradient to 100 % acetonitrile; and 15 minutes hold at 100 % acetonitrile.

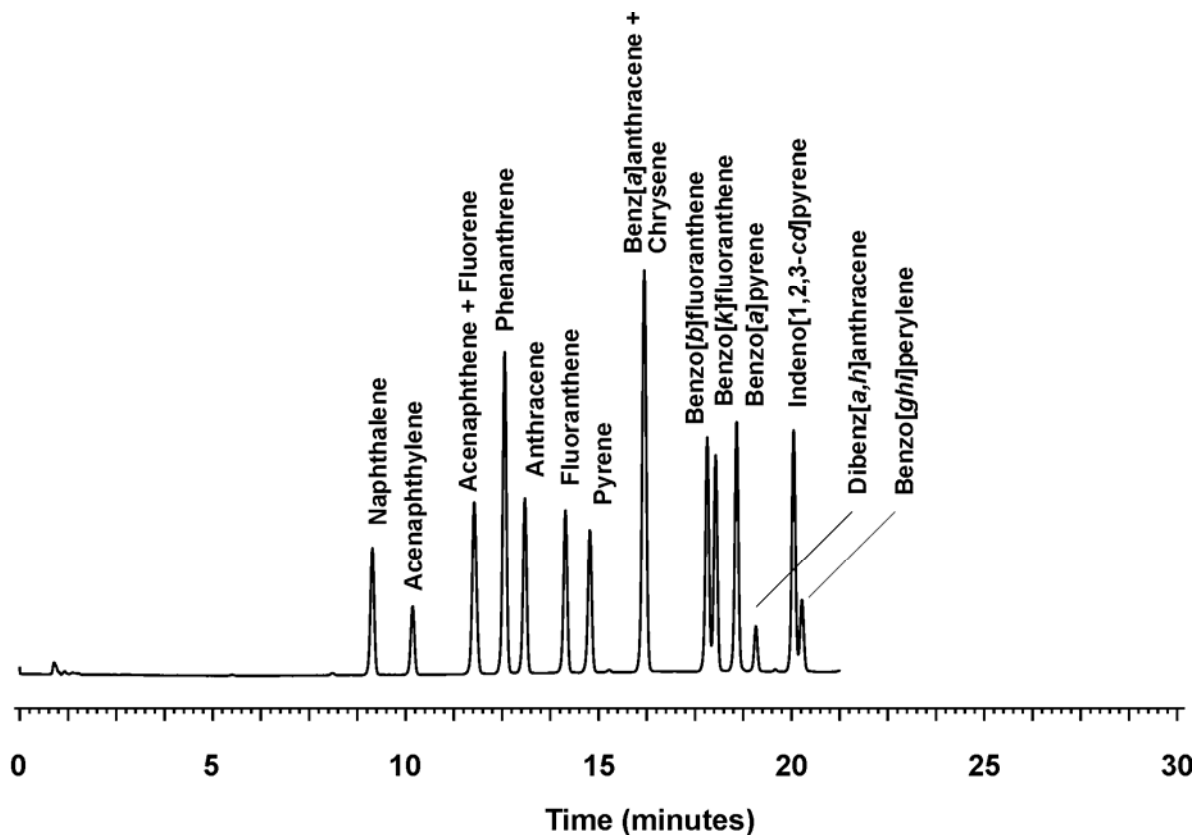


Figure 2. Reversed-phase LC separation of the 16 components of SRM 1647e using a monomeric C₁₈ column (Zorbax ODS column, 5 μm, 0.46 cm × 25 cm; Mac-Mod Analytical Inc., Chadds Ford, PA) and the same gradient elution program as in Figure 1.

REFERENCES

- [1] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); 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 <http://physics.nist.gov/Pubs/>.
- [2] Sander, L.C.; Wise, S.A.; *Evaluation of Shape Selectivity in Liquid Chromatography*; LC-GC, Vol. 8, pp. 378–390 (1990).
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- [7] Sander, L.C.; Wise, S.A.; *Influence of Substrate Parameters on Column Selectivity with Alkyl Bonded-Phase Sorbents*; *J. Chromatogr.*, Vol. 316, pp. 163-181 (1984).
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- [9] Wise, S.A.; Bonnett, W.J.; Guenther, F.R.; May, W.E.; *A Relationship Between Reversed-Phase C₁₈ Liquid Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons*; *J. Chromatogr. Sci.*, Vol. 19, pp. 457-465 (1981).
- [10] *Column Selectivity Test Mixture for Liquid Chromatography; (Polycyclic Aromatic Hydrocarbons), Certificate*; SRM 869a; NIST, U.S. Department of Commerce: Gaithersburg, MD (1998).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>