



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1647f

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). A unit consists of five 2 mL ampoules, each containing approximately 1.3 mL of an acetonitrile solution of selected PAHs. The PAHs are identified by the U.S. Environmental Protection Agency (EPA) 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: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST. The measurand in each case is the total mass fraction and concentration of each analyte. Metrological traceability is to the SI unit indicated in Table 1.

Expiration of Certification: The certification of **SRM 1647f** is valid, within the measurement uncertainty specified, until **30 June 2024**, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements leading to certification was under the direction of L.C. Sander and S.A. Wise of the NIST Chemical Sciences Division.

Analytical determinations were performed by L.C. Sander and M. Nelson of the NIST Chemical Sciences Division.

Preparation and ampouling of SRM 1647f were carried out by L.C. Sander and M.P. Cronise and C.N. Fales of the NIST Office of Reference Materials.

Statistical evaluation of the data were provided by J. Yen of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

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Certificate Issue Date: 11 September 2014

Robert L. Watters, Jr., Director
Office of Reference Materials

WARNING TO USERS

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 (see Safety Data Sheet). Use proper methods for disposal of waste.

INSTRUCTIONS FOR 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 concentration values listed in Table 1 apply only to aliquots removed at 20 °C to 25 °C. Certified values are not valid for ampoules which have been stored after opening, even if resealed.

PREPARATION AND ANALYSIS⁽¹⁾

The acetonitrile solution of the selected PAHs was prepared gravimetrically from individual compounds. Four 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). Purities of the compounds obtained from J. Jacob and Fluka were determined at NIST by a combination of techniques including quantitative proton nuclear magnetic resonance spectroscopy using an internal standard approach ($q^1\text{H-NMR}_{\text{IS}}$), differential scanning calorimetry (DSC), and liquid chromatography with absorbance detection (LC/Abs). Purities of CRMs were certified by BCR and verified by LC/Abs measurements at NIST. 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 the selected PAHs by LC using an acetonitrile/water mobile phase. Concentrations for the selected PAHs were determined from a calibration based on linear regression response factors, which used gravimetric values and instrumental responses for two independently prepared calibration standards. Five previous issues of this SRM (1647a, 1647b, 1647c, 1647d, and 1647e) were used as control samples. An external standard calibration approach was used in the certification. A representative chromatogram and the separation conditions are shown in Figure 1.

Column Selection: Variations in C_{18} column selectivity for PAHs are known to result from different column manufacturing processes [2]. Columns prepared by reaction of monofunctional C_{18} silanes with silica (denoted monomeric 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” (nonsilica columns, often based on polystyrene particles). Better separations of PAH mixtures are often possible on polymeric C_{18} columns such as that used to produce the chromatogram shown in Figure 1, as 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 869b, *Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons)* [10]. Examples of chromatograms from various C_{18} columns as “monomeric” or “polymeric” are provided in the Certificate of Analysis for SRM 869b.

⁽¹⁾ Certain commercial equipment, instruments, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Certified Values: The certified values of selected PAHs are given in Table 1. Values are listed in units of milligram per kilogram (mass fraction) and for user convenience milligram per liter (concentration). The uncertainties are expanded uncertainties with a coverage factor (*k*) of 2 (95 % confidence), calculated in accordance with the International Committee for Weights and Measures CIPM method [11]. They include uncertainty due to the calibration of the chromatographic method, measurement of selected samples using the chromatographic method, purity of the reagents used to prepare the material, and allowances for differences between the concentrations determined by gravimetric preparation and chromatographic measurements [11–13]. Concentrations were obtained by multiplying the certified values in milligrams per kilogram by the density of acetonitrile at 23 °C (0.7789 g/mL), and an allowance for the change in this density over the range 20 °C to 25 °C is included in the uncertainty.

Table 1. Certified Values for PAHs in SRM 1647f

Compound	CAS Registry No. ^(a)	Mass Fraction ^(c) (mg/kg)	Concentration ^(b) (mg/L)
Naphthalene	91-20-3	25.31 ± 0.35	19.71 ± 0.32
Acenaphthylene	208-96-8	19.09 ± 0.23	14.87 ± 0.22
Acenaphthene	83-32-9	26.44 ± 0.46	20.59 ± 0.40
Fluorene	86-73-7	5.93 ± 0.09	4.62 ± 0.08
Phenanthrene	85-01-8	4.57 ± 0.05	3.56 ± 0.05
Anthracene	120-12-7	1.13 ± 0.03	0.88 ± 0.03
Fluoranthene	206-44-0	9.71 ± 0.16	7.56 ± 0.14
Pyrene	129-00-0	10.83 ± 0.19	8.44 ± 0.16
Benz[<i>a</i>]anthracene	56-55-3	5.16 ± 0.07	4.02 ± 0.07
Chrysene	218-01-9	4.67 ± 0.08	3.64 ± 0.07
Benzo[<i>b</i>]fluoranthene	205-99-2	5.29 ± 0.06	4.12 ± 0.06
Benzo[<i>k</i>]fluoranthene	207-08-9	5.94 ± 0.09	4.63 ± 0.08
Benzo[<i>a</i>]pyrene	50-32-8	6.22 ± 0.11	4.84 ± 0.10
Dibenz[<i>a,h</i>]anthracene	53-70-3	4.55 ± 0.11	3.54 ± 0.09
Benzo[<i>ghi</i>]perylene	191-24-2	4.64 ± 0.12	3.61 ± 0.10
Indeno[1,2,3- <i>cd</i>]pyrene	193-39-5	5.40 ± 0.09	4.20 ± 0.08

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

^(b) These concentrations are for use in the temperature range of 20 °C to 25 °C.

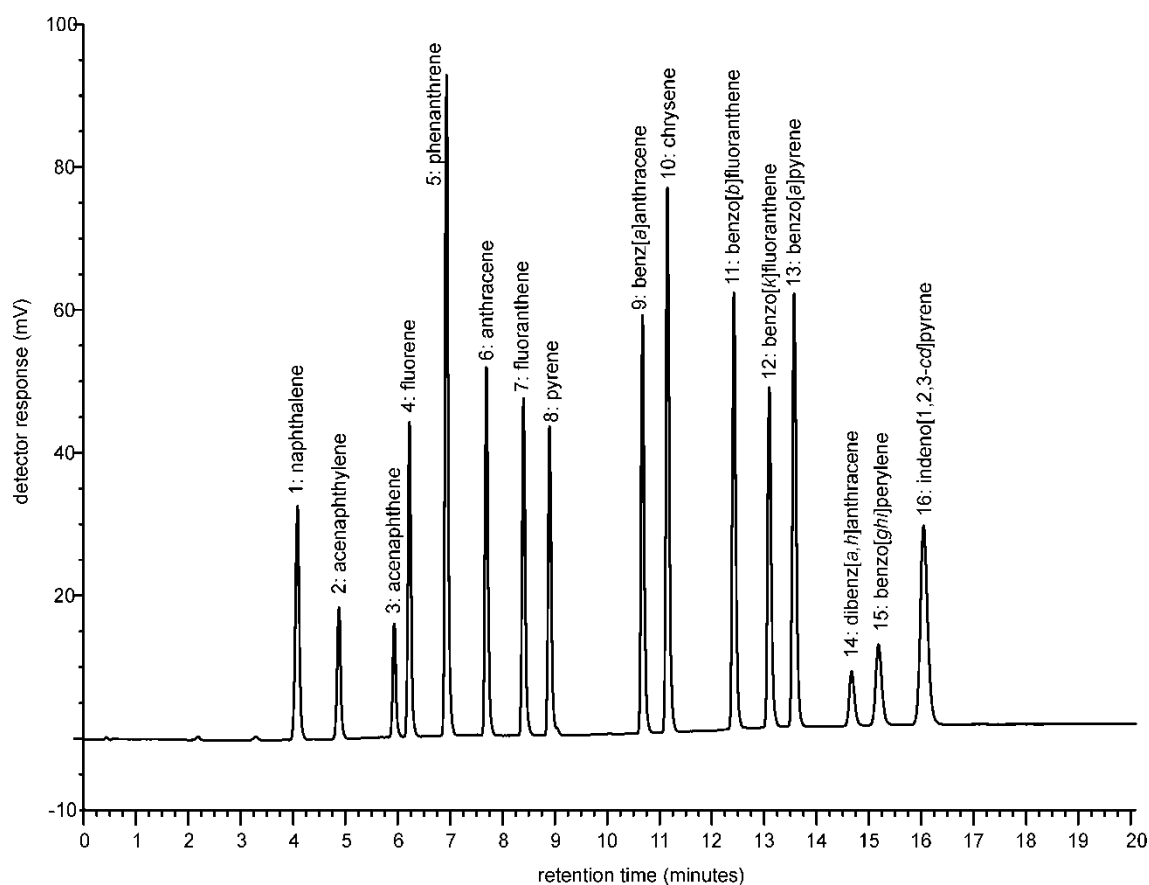


Figure 1. Reversed-phase LC separation of the 16 PAHs of SRM 1647f. A polymeric C_{18} column (Eclipse PAH column, $0.46\text{ cm} \times 10\text{ cm}$, $1.8\text{ }\mu\text{m}$ particle diameter; Agilent Technologies, Santa Clara, CA) was used with a gradient elution program: 2 minutes hold at 50 % water: 50 % acetonitrile; 10 minutes linear gradient to 100 % acetonitrile; and 8 minutes hold at 100 % acetonitrile, flow rate 1.5 mL/min . Detection was at 254 nm .

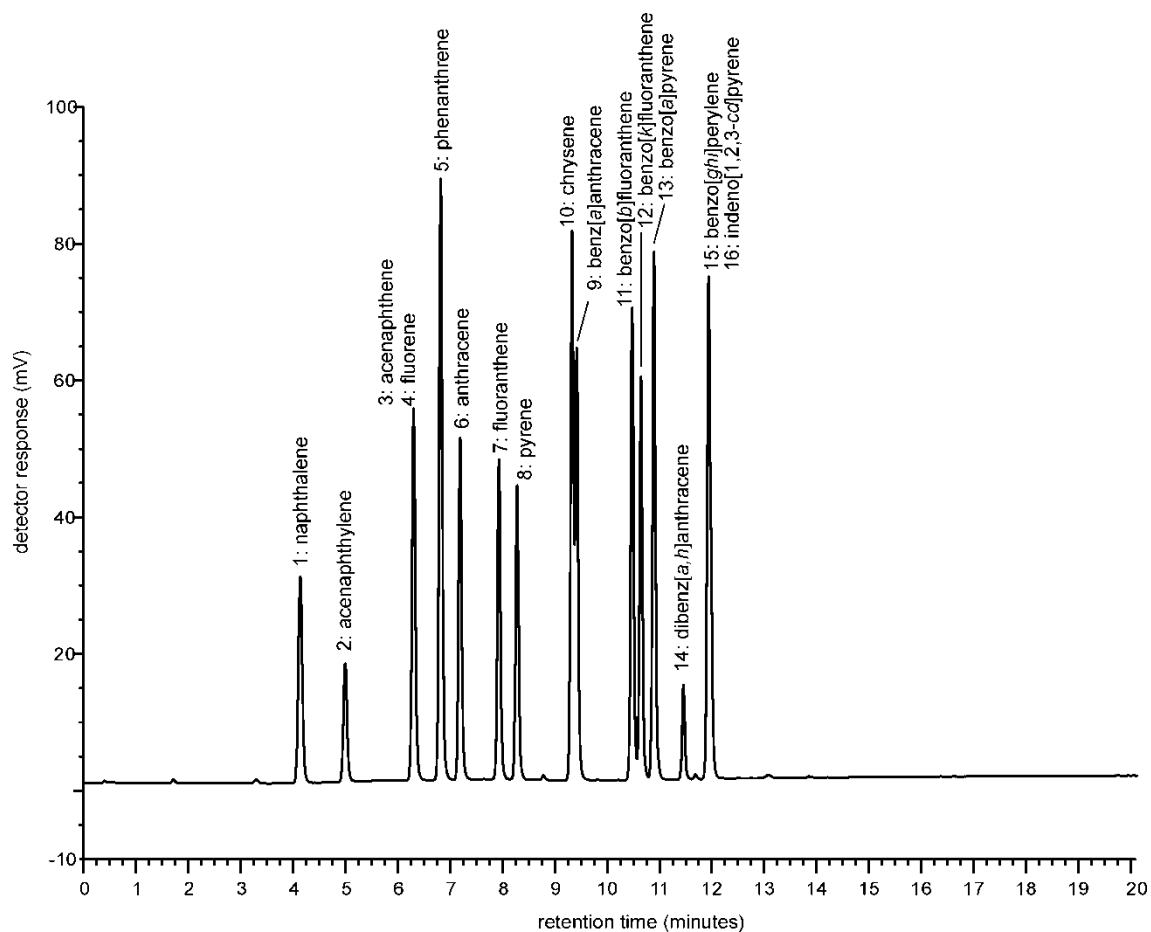


Figure 2. Reversed-phase LC separation of the 16 PAHs of SRM 1647f using a monomeric C₁₈ column (Ascentis Express C₁₈ column, 5 µm core shell particle diameter, 0.3 cm × 10 cm; Sigma-Aldrich, Milwaukee, WI). The same gradient elution program was used as in Figure 1, with reduced flow rate of 0.75 mL/min to adjust for the column configuration.

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Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.