National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2269

Perdeuterated PAH-I Solution in Hexane/Toluene

This Standard Reference Material (SRM) is intended primarily for use as an internal standard, or surrogate internal standard, solution that is used to spike both the unknown sample and the calibration or external standard solution of non-labeled PAHs. A unit of SRM 2269 consists of five 2 mL ampoules, each containing approximately 1.2 mL of a solution of five perdeuterated polycyclic aromatic hydrocarbons (PAHs) in hexane/toluene (96:4 volume fraction).

A similar solution containing six additional perdeuterated PAHs is available as SRM 2270 Perdeuterated PAH-II Solution in Hexane/Toluene. Examples of calibration or external standard solutions for the determination of PAHs are SRM 1491 Aromatic Hydrocarbons in Hexane/Toluene [1] or SRM 2260 Aromatic Hydrocarbons in Toluene (Nominal Concentration 60 µg/mL) [2]. This approach to the quantitation of PAHs using perdeuterated PAHs as internal standards has been discussed in detail in reference 3.

Certified Concentrations of Constituent Perdeuterated PAHs: The certified concentration values for five perdeuterated PAHs are given in Table 1. These values are based on results obtained from the gravimetric preparation of this solution and from the analytical results determined by using gas chromatography. 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 accounted for by NIST. Please note however, the extent of deuteration is always less than 100 % for perdeuterated compounds. The certified concentrations in Table 1 represent the sums of all isotopomers for each compound.

Supplemental Information: The expected deuterium enrichments, as reported by the supplier and confirmed at NIST, are listed in Table 2. During mass spectrometric analysis, however, the extent of hydrogen-deuterium exchange can be affected by the source conditions in both electron ionization and chemical ionization mass spectrometer sources [4–7]. A summary of the gravimetric and gas chromatographic measurements for SRM 2269 is also provided in Table 2. This information is **NOT** to be used as a substitute for NIST certified values.

Expiration of Certification: The certification **SRM 2269** is valid, within the measurement uncertainty specified, until **31 January 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for 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 technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of the technical measurements leading to the certification of this SRM was under the direction of S.A. Wise and M.M. Schantz of the NIST Analytical Chemistry Division.

Consultation on the statistical design of the experimental work and evaluation of the data were provided by S.B. Schiller and S.D. Leigh of the NIST Statistical Engineering Division.

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

Stephen A Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 06 November 2009
See Certificate Revision History on Last Page

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

Partial support for the preparation and certification of this SRM was provided by the National Oceanic and Atmospheric Administration, National Ocean Service, Center for Coastal Monitoring and Assessment, Silver Spring, MD.

Preparation and analytical measurements of the SRM were performed by M.P. Cronise of the NIST Standard Reference Materials Program and R.M. Parris, D.L. Poster, and L.K. Walton of the NIST Analytical Chemistry Division.

INSTRUCTIONS FOR USE

Handling: This material contains polycyclic aromatic hydrocarbons, many of which have been reported to have toxic, mutagenic, and/or carcinogenic properties, and should be handled with care. Use proper disposal methods.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures lower than 30 °C.

Opening of Ampoule: Open ampoules carefully to prevent contamination and injury. The ampoules are prescored and should **NOT** be opened using a file. Sample aliquots for analysis should be withdrawn at 20 °C to 25 °C **immediately** after opening the ampoules and should be processed without delay for the certified values in Table 1 to be valid within the stated uncertainties. Because of the volatility of hexane and toluene, certified values are not applicable to material stored in ampoules that have been opened for more than 2 minutes, even if they are resealed.

Use of SRM 2269 as an Internal Standard: To minimize the problem of not knowing the extent of deuteration and the effect of hydrogen-deuterium exchange, this solution is to be used to spike the unknown sample and the external standard solution. If the relative quantities of SRM 2269 added to the unknown sample and the external standard solution are accurately known, the absolute concentrations of the perdeuterated compounds are not relevant to the quantitation. This approach has been discussed in detail elsewhere in references 3 and 7.

PREPARATION AND ANALYSIS

SRM Preparation: The perdeuterated PAHs used in the preparation of this SRM were obtained from Cambridge Isotope Laboratories, Andover, MA. The solution was prepared at NIST by weighing and mixing the individual perdeuterated PAHs first with toluene and then adding the hexane. The weighed components were added to the toluene and mixed until completely dissolved. The hexane was then added, and the solution was homogenized. The total mass of this solution was measured and the concentrations calculated from this gravimetric procedure are given in Table 2 for the components. These gravimetric concentrations were adjusted for the consensus purity estimation of each component which was determined by using capillary gas chromatography with flame ionization detection and differential scanning calorimetry. This bulk solution was then chilled to approximately –5 °C and 1.2 mL aliquots were dispensed into 2 mL amber glass ampoules which were then flame sealed.

SRM Analysis: Aliquots from nine randomly selected ampoules were analyzed in duplicate by using capillary gas chromatography/mass spectrometry employing an immobilized non-polar stationary phase column. An internal standard solution, prepared from SRM 2260 [2], was added to each sample for quantification purposes. Calibration solutions consisting of weighed amounts of the perdeuterated PAHs (adjusted for the consensus purity estimation) and internal standard compounds in hexane/toluene (96:4 volume fraction) were chromatographically analyzed to determine analyte response factors. The analytical values determined for the compounds also are given in Table 2.

Table 1. Certified Concentrations of the Perdeuterated PAHs in SRM 2269

Compound	Concentrations mg/kg[a]			μg/mL[b]		
Biphenyl-d_{10}	7.84	±	0.19	5.21	±	0.13
Phenanthrene-d_{10}	37.25	±	0.97	24.76	±	0.64
Fluoranthene-d_{10}	62.6	±	1.7	41.6	±	1.1
Benz[*a*]anthracene-d_{12}	37.93	±	0.88	25.22	±	0.58
Dibenz[*a*,*h*]anthracene-d_{14}	7.47	±	0.17	4.97	±	0.11

[a] Each result is expressed as the certified value ± the expanded uncertainty. The certified value is the unweighted average of the concentrations determined by gravimetric and chromatographic measurements. The expanded uncertainty, at the 95 % level of confidence, is calculated as $U = ku_c$, where u_c is a combined standard uncertainty calculated according to the ISO Guide [8] and $k = 2$ is the coverage factor. The value of u_c includes both a correction for estimated purity and an allowance for differences between the concentration determined by gravimetric preparation and chromatographic measurements.

[b] The certified concentrations, in μg/mL units, were obtained by multiplying the certified mass values by the measured density of the SRM solution at 20 °C (0.6648 g/mL). These concentrations are for use over the temperature range of 20 °C to 25 °C, and an allowance for the change in density over this temperature range is included in the uncertainties.

Table 2. Supplemental Information for Perdeuterated PAHs in SRM 2269[a]

Compound	Concentrations Gravimetric[b] mg/kg	GC/MS[c] mg/kg		% D[d]
Biphenyl-d_{10}	7.81	7.87	(± 0.05)	99
Phenanthrene-d_{10}	36.7	37.7	(± 0.2)	98
Fluoranthene-d_{10}	62.2	63.1	(± 0.9)	98
Benz[*a*]anthracene-d_{12}	37.8	38.1	(± 0.2)	98
Dibenz[*a*,*h*]anthracene-d_{14}	7.47	7.46	(± 0.12)	97

[a] The summary of results given above is presented for use **only** as background information.

[b] Calculated concentration based on the mass of the perdeuterated PAH added to the total mass of the solution corrected for the chemical purity.

[c] Measured concentrations determined by gas chromatography/mass spectrometry (GC/MS) corrected for the purity of the components. The listed uncertainties in parentheses represent one standard deviation of a single measurement for these results and recognize only the within-method variability.

[d] Expected deuterium enrichment as reported by the supplier and confirmed by NIST.

REFERENCES

[1] SRM 1491; *Aromatic Hydrocarbons in Hexane/Toluene*, National Institute of Standards and Technology, U.S. Department of Commrce, Gaithersburg, MD, (August 1989).

[2] SRM 2260, *Aromatic Hydrocarbons in Toluene* (*Nominal Concentration* 60 *µg/mL*), National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD (June 1991).

[3] Boyd, R.K.; *Quantitative Trace Analysis by Combined Chromatography and Mass Spectrometry Using External and Internal Standards*; Rapid Commun. Mass Spectrom. **7**, pp. 257–271 (1993).

[4] Joachims, H.W.; Rasekh, H.; Rühl, E.; Baumgärtel, H.; Leach, S.; *Deuterium Isotope Effects in the Photofragmentation of Naphthalene Monocations*; J. Phys. Chem., Vol. 97, pp. 1312–1317 (1993).

[5] MACSP Reference Material Documentation: DPAC-1: *Solution of 21 Deuterated Polycyclic Aromatic Compounds in Toluene*; National Research Council of Canada, Halifax, Nova Scotia, Canada, v941101.

[6] MACSP Reference Material Documentation: DPAC-2: *Solution of 6 Deuterated Polycyclic Aromatic Compounds in Toluene*; National Research Council of Canada, Halifax, Nova Scotia, Canada, v941101.

[7] Quilliam, M.A.; Hardstaff, W.R.; Anacleto, J.F.; LeBlanc, M.D.; Stergiopoulos, V.; Dick, K.L.; Bowser, M.T.; Curtis, J.M.; Embree, D.J.; Sim, P.G.; Boyd, R.K.; *Preparation and Certification of Solutions of Perdeuterated Polycyclic Aromatic Compounds Intended for Use as Surrogate Internal Standards*; Fresenius J. Anal. Chem., Vol. 350, pp. 109–118 (1994).

[8] 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/.

Certificate Revision History: 06 November 2009 (This revision reflects an extension of the certification period and editorial changes); 02 July 2001 (Original certificate date).

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) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.