National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2270

Perdeuterated PAH-II 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. The approach to the quantitation of PAHs using perdeuterated PAHs as internal standards has been discussed in detail in reference 1. A unit of SRM 2270 consists of five 2 mL ampoules, each containing approximately 1.2 mL of a solution of six perdeuterated polycyclic aromatic hydrocarbons (PAHs) in hexane/toluene (96:4 volume fraction).

Certified Concentrations of Constituent Perdeuterated PAHs: The certified concentration values for six 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 [2]. 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.

Information Values: 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 [3-6]. A summary of the gravimetric and gas chromatographic measurements for SRM 2270 is also provided in Table 2. This information is **NOT** to be used as a substitute for NIST certified values. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification **SRM 2270** is valid, within the measurement uncertainty specified, until **15 November 2029**, 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 or register online) will facilitate notification.

Coordination of the technical measurements leading to the certification of this SRM was under the direction of S.A. Wise of the NIST Chemical Sciences Division, and M.M. Schantz formerly of NIST.

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

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Analytical measurements were performed R.M. Parris, and D.L. Poster of NIST, and L.K. Walton formerly of NIST.

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

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Certificate Revision History on Last Page

Steven J. Choquette, Director
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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 2270 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 2270 added to the unknown sample and the external standard solution are accurately known, the absolute concentration of the perdeuterated compounds are not relevant to the quantitation. This approach has been discussed in detail elsewhere in references 1 and 6.

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, 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 Values of the Perdeuterated PAHs in SRM 2270

Compound	Mass Fraction mg /kg[a]	Concentration µg/mL[b]
Naphthalene-d_8	77.0 ± 2.2	51.2 ± 1.5
Acenaphthene-d_{10}	7.61 ± 0.22	5.06 ± 0.15
Pyrene-d_{10}	74.5 ± 1.6	49.5 ± 1.1
Benzo[*a*]pyrene-d_{12}	37.3 ± 1.1	24.80 ± 0.73
Perylene-d_{12}	29.88 ± 0.75	19.86 ± 0.50
Benzo[*ghi*]perylene-d_{12}	35.34 ± 0.93	23.49 ± 0.62

[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/JCGM Guide [7] 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. The certified values are metrologically traceable to the SI derived unit of mass fraction (expressed as milligrams per kilograms).

[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. Information Values for Perdeuterated PAHs in SRM 2270[a]

Compound	Mass Fraction Gravimetric[b] mg/kg	GC/MS[c] mg/kg	% D[d]
Naphthalene-d_8	76.4	77.6 (± 0.7)	99
Acenaphthene-d_{10}	7.54	7.68 (± 0.10)	99
Pyrene-d_{10}	74.4	74.7 (± 1.0)	98
Benzo[*a*]pyrene-d_{12}	36.9	37.6 (± 0.2)	98
Perylene-d_{12}	29.8	30.0 (± 0.1)	98
Benzo[*ghi*]perylene-d_{12}	35.1	35.6 (± 0.3)	98

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

[2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (2000); available at https://www.nist.gov/system/files/documents/srm/SP260-136.PDF (accessed Dec 2019).

[3] 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).

[4] 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.

[5] 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.

[6] 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).

[7] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Dec 2019); 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 https://www.nist.gov/pml/nist-technical-note-1297 (accessed Dec 2019).

Certificate Revision History: 06 December 2019 (Change of expiration date; editorial changes); 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 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 https://www.nist.gov/srm.