

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 7307-a

No. +++



Polycyclic Aromatic Hydrocarbons in Fresh Water Lake Sediment

This certified reference material (CRM) was produced in accordance with the NMIJ's management system and in compliance with ISO GUIDE 34: 2000. This CRM is intended for use in accuracy control of analysis and validation of analytical techniques for the determination of polycyclic aromatic hydrocarbons (PAHs) in sediments or soil samples.

Certified Values

The certified values expressed as mass fractions (dry-mass basis) are given in the table below. The drying instruction is described in this certificate. The uncertainty of the certified value is the half-width of the expanded uncertainty interval calculated using a coverage factor (k) of 2, which gives a level of confidence of approximately 95 %.

PAHs	CAS No.	Certified value, Mass fraction ($\mu\text{g}/\text{kg}$)	Expanded uncertainty, Mass fraction ($\mu\text{g}/\text{kg}$)	Analytical method
Fluorene	86-73-7	6.0	1.7	2, 3, 4
Phenanthrene	85-01-8	24.5	4.0	1, 3, 4, 5, 6
Anthracene	120-12-7	3.6	1.5	3, 4, 5, 6
Fluoranthene	206-44-0	25.1	3.7	1, 2, 3, 4, 5, 6
Pyrene	129-00-0	22.2	4.2	1, 2, 3, 4, 5, 6
Benzo[<i>c</i>]phenanthrene	195-19-7	3.21	0.60	1, 2, 3, 4, 5, 6
Benzo[<i>a</i>]anthracene	56-55-3	7.1	1.3	1, 2, 3, 4, 5, 6
Chrysene	218-01-9	8.39	0.78	2, 4, 6
Benzo[<i>b</i>]fluoranthene	205-99-2	24.9	7.8	1, 2, 3, 4, 5
Benzo[<i>k</i>]fluoranthene	207-08-9	5.3	1.7	1, 2, 3, 4, 5, 6
Benzo[<i>j</i>]fluoranthene	205-82-3	7.0	3.1	1, 2, 3, 4, 5, 6
Benzo[<i>a</i>]fluoranthene	203-33-8	1.56	0.74	1, 3, 5, 6
Benzo[<i>e</i>]pyrene	192-97-2	9.7	3.2	1, 2, 3, 4, 5, 6
Benzo[<i>a</i>]pyrene	50-32-8	4.57	0.59	1, 2, 3, 4, 5, 6
Indeno[1,2,3- <i>cd</i>]pyrene	193-39-5	5.6	2.8	1, 3, 5, 6
Benzo[<i>ghi</i>]perylene	191-24-2	6.8	2.0	1, 2, 3, 4, 5, 6

Analysis

Each certified value was calculated from PAH concentrations determined by the following analytical methods:

Analytical methods:

1. Pressurized liquid extraction and isotope dilution-mass spectrometry (ID-GC/MS)

[Extraction] Solvent: toluene; temperature, 190 °C (20 MPa); extraction time, 10 min \times 2 cycles

[Clean-up] Solid-phase extraction (silica-gel)

[GC/MS] Column: DB-17MS (J&W Scientific), electron ionization (EI), selected ion monitoring (SIM)

2. Pressurized liquid extraction and ID-GC/MS

[Extraction] Solvent: toluene; temperature, 190 °C (20 MPa); extraction time, 10 min \times 2 cycles

[Clean-up] Solid-phase extraction (silica-gel)

[GC/MS] Column: LC-50 (J&K Scientific), EI, SIM

3. Pressurized liquid extraction and ID-GC/MS

[Extraction] Solvent: dichloromethane/ethyl acetate (1/1 by volume); temperature, 190 °C (20 MPa); extraction time, 10 min
× 2 cycles

[Clean-up] Solid-phase extraction (silica-gel)

[GC/MS] Column: DB-17MS (J&W Scientific), EI, SIM

4. Pressurized liquid extraction and ID-GC/MS

[Extraction] Solvent: dichloromethane/ethyl acetate (1/1 by volume); temperature, 190 °C (20 MPa); extraction time, 10 min
× 2 cycles

[Clean-up] Solid-phase extraction (silica-gel)

[GC/MS] Column: LC-50 (J&K Scientific), EI, SIM

5. Microwave-assisted solvent extraction and ID-GC/MS

[Extraction] Solvent: 1 M KOH/methanol; temperature, 190 °C; extraction time, 30 min

[Clean-up] Solid-phase extraction (reversed-phase polymer)

[GC/MS] Column: DB-17MS (J&W Scientific), EI, SIM

6. Microwave-assisted solvent extraction and ID-GC/MS

[Extraction] Solvent: 1 M KOH/methanol; temperature, 190 °C; extraction time, 30 min

[Clean-up] Solid-phase extraction (reversed-phase polymer)

[LC/MS] Column: Inertsil ODS-P (GL Sciences), dopant-assisted atmospheric-pressure photoionization (DA-APPI⁺), selected ion recording

Metrological Traceability

The certified values were determined by isotope dilution-mass spectrometry (IDMS) or internal standard technique with isotope-labeled structural isomers as internal standards. Because the calibration solution for the measurements was prepared from a certified reference material (NIST SRM 2260a), the certified values are traceable to the International System of Units (SI).

Indicative Value

Concentration of triphenylene expressed as mass fractions (dry-mass basis) in this CRM are given in the table below. The uncertainty of the indicative value is the half-width of the expanded uncertainty interval calculated using a coverage factor (k) of 2, which gives a level of confidence of approximately 95 %.

PAHs	CAS No.	Indicative value, Mass fraction (µg/kg)	Expanded uncertainty, Mass fraction (µg/kg)	Analytical method
Triphenylene	217-59-4	6.7	1.2	2, 4

Mutual Recognition Arrangement under Meter Convention

This certificate is consistent with the calibration and measurement capabilities (CMCs) that are included in Appendix C of the Mutual Recognition Arrangement (MRA) drawn up by the International Committee for Weights and Measures (CIPM). Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (as for Appendix C of MRA, see <http://kcdb.bipm.org/AppendixC/default.asp>).

Expiration of Certification

This certificate is valid for one year from the date of shipment, provided that the material remains unopened and is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM is in the form of a brown powder. This CRM of 60 g in net volume is kept in a glass bottle.

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles selected by random sampling from 500 bottles. Five PAHs, phenanthrene, fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]perylene, were determined by pressurized liquid extraction and ID-GC/MS (Analytical method 1), and the inhomogeneity was evaluated by ANOVA. The inhomogeneity of the analytes is reflected in the uncertainty of the certified value.

Instructions for Storage

This CRM should be stored at a temperature between 2 °C and 10 °C and shielded from light.

Instructions for Use

(1) Sample size

More than 5 g of the material should be used.

(2) Determination of water (dry mass)

The certified values of this CRM are given on a dry-mass basis. The moisture content (loss on drying) should be assessed by taking a portion of the material and drying it in an oven at 105 °C to 110 °C for 6 h. Analytical results must be calculated on a dry-mass basis. The samples that were used for determination of water should not be used for determination of PAHs. The approximate moisture content was found to be 2.6 %.

(3) The CRM should stand at room temperature for more than one hour before use.

Precautions for Handling

Wear a mask, gloves, and other protective gear during handling. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

The sediment sample was collected from the southern basin of Lake Biwa in Japan. The sediment sample was air-dried, pulverized, sieved (particles less than 106 µm in size were used as the sample), homogenized, and bottled in 60-g portions. The bottled samples were sterilized by γ -ray irradiation with ^{60}Co and stored at 4 °C until required.

Technical Information

The concentration of benzo[*a*]pyrene (dry-mass basis) obtained by a Japanese official method [Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediment, and aquatic organisms), Environment Agency of Japan, 1998] was (3.05 ± 0.09) µg/kg (average \pm standard deviation, $n = 5$; Dec. 2007). This concentration is available only when the same analytical method is performed.

The analytical results of dibenz[*a,h*]anthracene, naphthalene and perylene were 1 µg/kg, 35 µg/kg and 2.08×10^3 µg/kg respectively (Dec. 2007).

NMIJ Analysts

The technical manager is T. Yarita and the production manager is N. Itoh. Analytical measurements for the certification of this CRM were performed at NMIJ by N. Itoh, Y. Aoyagi, and A. Takatsu.

Information

If substantive technical changes occur that affect the certification before the expiration of this certificate, NMIJ will notify the registered customer. Customer registration on the NMIJ Website (given below) will facilitate notification. Technical reports regarding this CRM can be obtained from the contact details given below.

Reproduction of Certificate

In reproducing this certificate, it should be clearly indicated that the document is a copy.

April 1, 2015

Ryoji Chubachi
President

National Institute of Advanced Industrial Science and Technology

If you have any questions about this CRM, please contact:
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Revision history

January 26, 2010: Certified value of dibenz[*a,h*]anthracene and reference value of naphthalene were eliminated based on long-term stability monitoring.

April 1, 2015: "Metrology Management Center" was renamed to "Center for Quality Management of Metrology."

July 19, 2016: Expanded uncertainty was changed and the description on Mutual Recognition Arrangement under Meter Convention was added.

The description in "Expiration of Certification" was changed to "one year after the date of shipment"

February 13, 2018: Certified value of perylene was eliminated based on long-term stability monitoring. The analytical result of perylene at the time of the certification was added in "Information."