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 NMIJ’s management system and in compliance with JIS Q 0034 (ISO GUIDE 34). This CRM is intended for use in controlling the precision of analysis or confirming the validity of analytical methods or instruments during analysis 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 following table. The quoted uncertainty 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%.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>CAS No.</th>
<th>Certified value, Mass fraction (µg/kg)</th>
<th>Expanded uncertainty, Mass fraction (µg/kg)</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td>86-73-7</td>
<td>5.98</td>
<td>1.08</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>85-01-8</td>
<td>24.5</td>
<td>4.0</td>
<td>1, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Anthracene</td>
<td>120-12-7</td>
<td>3.59</td>
<td>1.14</td>
<td>3, 4, 5, 6</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>206-44-0</td>
<td>25.1</td>
<td>2.5</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Pyrene</td>
<td>129-00-0</td>
<td>22.2</td>
<td>3.5</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[c]phenanthrene</td>
<td>195-19-7</td>
<td>3.209</td>
<td>0.186</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>56-55-3</td>
<td>7.15</td>
<td>0.92</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Chryosene</td>
<td>218-01-9</td>
<td>8.39</td>
<td>0.74</td>
<td>2, 4, 6</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>205-99-2</td>
<td>24.9</td>
<td>7.7</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[j]fluoranthene</td>
<td>205-82-3</td>
<td>7.0</td>
<td>2.8</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>207-08-9</td>
<td>5.28</td>
<td>1.46</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[a]fluoranthene</td>
<td>203-33-8</td>
<td>1.56</td>
<td>0.70</td>
<td>1, 3, 5, 6</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>192-97-2</td>
<td>9.7</td>
<td>2.7</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Benzo[j]pyrene</td>
<td>50-32-8</td>
<td>4.57</td>
<td>0.53</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>Perylene</td>
<td>198-55-0</td>
<td>2.08 × 10^3</td>
<td>0.58 × 10^3</td>
<td>1, 4</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>193-39-5</td>
<td>5.6</td>
<td>2.1</td>
<td>1, 3, 5, 6</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>191-24-2</td>
<td>6.76</td>
<td>1.89</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
</tbody>
</table>

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 × 2 cycles
   - [Clean-up] Solid-phase extraction (silica-gel)
   - [GC/MS] Column: DB-17MS (J&W Scientific), electron impact 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 × 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

Each certified value was determined by isotope dilution-mass spectrometry as the primary method of measurement. Because the calibration solution for the measurements was prepared from a certified reference material (NIST SRM2260a), the certified values are traceable to the International System of Units (SI).

Information Values

Concentrations of Naphthalene and Triphenylene

Concentrations of naphthalene and triphenylene expressed as mass fractions (dry-mass basis) in this CRM are given in the following table. The expanded uncertainty was determined using a coverage factor (k) of 2, which gives an estimated level of confidence of approximately 95%.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>CAS No.</th>
<th>Information value, Mass fraction (µg/kg)</th>
<th>Expanded uncertainty, Mass fraction (µg/kg)</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylene</td>
<td>217-59-4</td>
<td>6.74</td>
<td>1.15</td>
<td>2, 4</td>
</tr>
</tbody>
</table>

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 ± standard deviation, n = 5). This concentration is available only when the same analytical method is performed.

The analytical results of dibenz[a,h]anthracene and naphthalene were 1 µg/kg and 35 µg/kg, respectively. The concentration of dibenz[a,h]anthracene increased and that of naphthalene decreased relative to respective certified values as of the revision of this certificate (Jan. 2010).

Expiration of Certification

This certificate is valid until March 31, 2018, provided that the material remains unopened and stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from natural lake sediment and is packaged in a glass bottle (60 g each).

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles selected by random sampling from 500 bottles. Five PAHs, phenanthrene, fluoranthene, benzo[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 not significant and is reflected in the uncertainty of the certified value.

Precautions for Storage
This CRM should be kept at 5 °C in the dark.

Instructions for Users
(1) Sample size
More than 5 g of the material should be used.

(2) Determination of water (dry mass)
The concentrations of constituents in this CRM are given on a dry-mass basis. The moisture content should be assessed by taking a portion of the material and drying it in an oven at 105–110 °C for 6 h. Analytical results must be calculated on a dry-mass basis. The samples 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 Method
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 60Co and stored at 4 °C until required.

Collaborator
The sampling for this CRM was carried out by Shimadzu Techno-Research Inc. The preparation of this CRM carried out by Environmental Technology Service Co., Ltd.

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.

Technical Information
Customer registration on the NMIJ Website (given below) will facilitate notification of any revision of the information given above. 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:
National Institute of Advanced Industrial Science and Technology,
National Metrology Institute of Japan,
Center for Quality Management of Metrology, Reference Materials Office,
Revision history

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

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