National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7308-a
No. +++

Polycyclic Aromatic Hydrocarbons and Toxic Elements in Tunnel Dust

This certified reference material (CRM) is produced in accordance with the NMIJ's management system and is in compliance with ISO 17034 and ISO/IEC 17025. This CRM is intended for use in the evaluation or validation of analytical methods and instruments used for determination of polycyclic aromatic hydrocarbons (PAHs) and toxic elements in tunnel dust or similar matrices.

Certified Values

The certified values of this CRM, expressed as mass fractions, are given in the tables below. 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 (mg/kg)	Expanded uncertainty Mass fraction (mg/kg)	Analytical method
Fluorene	86-73-7	2.64	0.72	1, 2, 3
Anthracene	120-12-7	4.6	1.3	1, 2, 3
Fluoranthene	206-44-0	20.3	3.6	1, 2, 3
Pyrene	129-00-0	18.8	3.4	1, 2, 3
Benz[*a*]anthracene	56-55-3	2.62	0.23	1, 2, 3
Benzo[*b*]fluoranthene	205-99-2	1.96	0.17	1, 2, 3
Benzo[*k*]fluoranthene	207-08-9	0.899	0.080	1, 2, 3
Benzo[*a*]pyrene	50-32-8	1.39	0.18	1, 2, 3
Perylene	198-55-0	0.294	0.055	1, 2, 3
Indeno[1,2,3-*cd*]pyrene	193-39-5	1.41	0.36	1, 2, 3

Elements	CAS No.	Certified value Mass fraction (%)	Expanded uncertainty Mass fraction (%)	Analytical method
Cr	7440-47-3	1.071	0.025	4, 5
Ni	7440-02-0	0.285	0.007	4, 5, 6
Pb	7439-92-1	0.1078	0.0023	4, 5, 6

Elements	CAS No.	Certified value Mass fraction (mg/kg)	Expanded uncertainty Mass fraction (mg/kg)	Analytical method
Mn	7439-96-5	645	18	5, 6, 7
Cd	7440-43-9	43.4	1.4	4, 5

Analysis

The certified values of PAH were calculated from PAH concentrations determined by the following analytical methods.

Analytical methods:

1. Microwave-assisted solvent extraction and ID-GC/MS
   [Extraction] Solvent, toluene/methanol; temperature, 160 °C; extraction time, 40 min
   [Clean-up] Solid-phase extraction (silica gel)
   [GC/MS] Column: DB-17MS, EI, SIM
2. Soxhlet extraction and ID-GC/MS
   [Extraction] Solvent, toluene; 16 h
   [Clean-up] Solid-phase extraction (silica gel)
   [GC/MS] Column: LC-50, EI, SIM
3. Pressurized liquid extraction and ID-GC/MS
   [Extraction] Solvent, toluene; temperature, 190 °C (20 MPa); extraction time, 10 min x 2 cycles
   [Clean-up] Solid-phase extraction (silica gel)
   [GC/MS] Column: DB-17MS, EI, SIM

The certified values of element were calculated from element concentrations determined by the following analytical methods.

4. Microwave digestion (mixture of nitric acid, hydrofluoric acid, and perchloric acid) and isotope dilution inductivity coupled plasma mass spectrometry (ID-ICP-MS)
5. Microwave digestion (mixture of nitric acid, hydrofluoric acid, and hydrogen peroxide) and ICP-MS
6. Microwave digestion (mixture of nitric acid, hydrofluoric acid, and hydrogen peroxide) and inductivity coupled plasma optical emission spectrometry (ICP-OES)
7. Microwave digestion (mixture of nitric acid, hydrofluoric acid, and hydrogen peroxide) and graphite furnace atomic absorption spectrometry (GFAAS)

Metrological Traceability

The certified values of PAH were determined by isotope dilution mass spectrometry (IDMS) as the primary method of measurement and the calibration solutions for the measurements were prepared from a certified reference material (NIST SRM2260a). The certified values of element were determined by IDMS as a primary method of measurement and/or reliable methods validated by NMIJ. The calibration solutions for the measurements were prepared from JCSS (Japan Calibration Service System) standard solutions. Thus, the certified values are traceable to the International System of Units (SI).

Indicative values

Concentrations of 5 PAHs and zinc in this CRM are given as indicative values in the table below. They are expressed as mass fractions. 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 (mg/kg)	Expanded uncertainty Mass fraction (mg/kg)	Analytical method
Naphthalene	91-20-3	11.6	1.9	1, 3
Benzo[*c*]phenanthrene	195-19-7	0.72	0.21	1*, 2*, 3*
Chrysene	218-01-9	2.83	0.20	2
Benzo[*e*]pyrene	192-97-2	2.4	1.2	1*, 2*, 3*

Elements	CAS No.	Indicative value Mass fraction (%)	Expanded uncertainty Mass fraction (%)	Analytical method
Zn	7440-66-6	8.85	0.22	5

Analytical methods are represented in the clause "**Analysis**"; however internal standard techniques using deuterium-labeled

structural isomers were applied for the method marked with an asterisk instead of IDMS.
The IDMS cannot be applied for benzo[*c*]phenthrene and benzo[*e*]pyrene, and different columns cannot be applied for naphthalene and chrysene. Zinc was determined by only ICP-MS. The sample pretreatment and uncertainty evaluation were carried out in the same way as those for certified values.

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 is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from dust sample in a road tunnel in Japan. This CRM is packaged in a glass bottle (1 g each).

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles selected by random sampling from 500 bottles. All PAHs were determined by microwave-assisted extraction and ID-GC/MS method (Analytical method: 1) and toxic elements were determined by microwave digestion and ICP-MS method (Analytical method: 5), and the inhomogeneity was evaluated by ANOVA. The inhomogeneity of analytes is not significant and 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 0.2 g of the material should be used for PAHs and 0.05 g for elements.
(2) The CRM should be placed at room temperature for more than 1 h before use.
(3) Wear a mask, gloves and other protective gears during handling.

Precautions for Handling

A mask, gloves and other protective equipment must be worn during handling. The handling, storage and disposal of this CRM must be performed in accordance with all applicable laws. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

Dried dust was collected from a settlement tank used for regular maintenance of an electric dust collector in a road tunnel in Japan. The dust was dried further and pulverized. Then, the portion of sample passing 106-μm sieve was homogenized, and subsampled into 1-g portions. Bottled samples were stored at 4 °C until required.

Collaborator

The preparation of this CRM was carried out by KANSO.

Technical Information

Mass fraction of phenanthrene in this CRM at the time of certification was 46 mg/kg (by the methods 1, 2, and 3), however it is gradually decreasing. Mass fraction of benzo[*ghi*]perylene in this CRM at the time of certification was 2.54 mg/kg (by the methods 1, 2, and 3), however it is gradually increasing. Mass fraction of benzo[*a*]pyrene obtained by a Japanese official method

(The toxic pollutant measuring method manual, Mercury benzo[*a*]pyrene, Environment Agency Air Quality Bureau, Environment Agency of Japan, 1999) was 1.65 mg/kg. Particle diameter obtained by the liquid suspension method using a laser diffraction instrument was 4.7 μm (10 % diameter), 19 μm (50 % diameter), and 54 μm (90 % diameter). Specific surface area determined by nitrogen adsorption to samples Brunauer–Emmet–Teller (BET) method (single-point) was 51 m^2/g.

NMIJ Analysts

The technical manager and production manager for this CRM is NUMATA M. and ITOH N., respectively. Analytical measurements for the certification of this CRM were performed at NMIJ by ITOH N., INAGAKI K., NARUKAWA T., AOYAGI Y., NARUSHIMA I., and KOGUCHI M.

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, 2020

ISHIMURA Kazuhiko
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
November 12, 2014: The description in "Expiration of Certification" was changed to "one year from the date of shipment."
"Mutual Recognition Arrangement under Meter Convention" was added.
April 1, 2015: "Metrology Management Center" was renamed to "Center for Quality Management of Metrology."
January 15, 2019: The certified value of benzo[*ghi*]perylene was eliminated based on stability monitoring.