National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7304-a
No. +++

Polychlorinated Biphenyls and Organochlorine Pesticides in Marine Sediment (High Pollutant Concentrations)

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 controlling the precision of analyses and validating analytical methods and instruments used in the analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediment samples and similar materials.

Certified Values

The certified values of this CRM, expressed as mass fractions (dry-mass basis), 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 %.

Certified values of PCB congeners*

	CAS No.	Certified value, Mass fraction (μg/kg)	Expanded uncertainty, Mass fraction (μg/kg)	Analytical Method
CB3 (4-chlorobiphenyl)	2051-62-9	0.311	0.085	1, 3, 4, 5, 6, 8, 9
CB15 (4,4'-dichlorobiphenyl)	2050-68-2	2.26	0.24	1, 3, 4, 5, 6, 8, 9
CB28 (2,4,4'-trichlorobiphenyl)	7012-37-5	34.9	2.3	1, 3, 4, 5, 6, 8, 9
CB31 (2,4',5-trichlorobiphenyl)	16606-02-3	27.1	1.8	1, 3, 4, 5, 6, 8, 9
CB70 (2,3',4',5-tetrachlorobiphenyl)	32598-11-1	60.7	3.8	1, 3, 4, 5, 6, 8, 9
CB101 (2,2',4,5,5'-pentachlorobiphenyl)	37680-73-2	31.9	2.6	1, 3, 4, 5, 6, 8, 9
CB105 (2,3,3',4,4'-pentachlorobiphenyl)	32598-14-4	18.4	2.0	1, 3, 4, 5, 6, 8, 9
CB138 (2,2',3,4,4',5'-hexachlorobiphenyl)	35065-28-2	13.9	1.1	1, 3, 4, 5, 6, 8, 9
CB153 (2,2',4,4',5,5'-hexachlorobiphenyl)	35065-27-1	15.9	1.0	1, 3, 4, 5, 6, 8, 9
CB170 (2,2',3,3',4,4',5-heptachlorobiphenyl)	35065-30-6	3.62	0.22	1, 3, 4, 5, 6, 8, 9
CB180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)	35065-29-3	9.10	0.69	1, 3, 4, 5, 6, 8, 9

CB194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl)	35694-08-7	1.89	0.11	1, 3, 4, 5, 6, 8, 9
CB206 (2,2',3,3',4,4',5,5',6-nonachlorobiphenyl)	40186-72-9	0.476	0.050	1, 3, 4, 5, 6, 8, 9
CB209 (decachlorobiphenyl)	2051-24-3	1.28	0.20	1, 3, 4, 5, 6, 8, 9

*IUPAC number

Certified values of OCPs

	CAS No.	Certified value, Mass fraction (μg/kg)	Expanded uncertainty, Mass fraction (μg/kg)	Analytical Method
p,p'-DDT (1,1,1-trichloro-2,2-bis[chlorophenyl]ethane)	50-29-3	5.44	0.50	2, 3, 7, 10
p,p'-DDE (1,1-dichloro-2,2-bis[chlorophenyl]ethylene)	72-55-9	5.37	0.30	1, 3, 4, 5, 6, 10
p,p'-DDD (1,1-dichloro-2,2-bis[chlorophenyl]ethane)	72-54-8	12.4	1.9	1, 3, 4, 5, 6, 10
γ-HCH ((1α,2α,3β,4α,5α,6β)-hexachlorocyclohexane)	58-89-9	5.33	0.26	1, 3, 4, 5, 6

Analysis

The certified values of this CRM were calculated based on PCB congeners and OCPs concentrations which were determined by the following analytical methods.

Analytical methods:

1. Soxhlet extraction and isotope dilution – gas chromatography / mass spectrometry (ID-GC/MS)
   ［Extraction］Solvent: hexane/acetone mixture (1:1, vol.); Extraction time: 24 hours
   ［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）
   ［GC/MS］Column: DB-XLB (Agilent), Mass resolution: 10 000 (SIM)
2. Soxhlet extraction and ID-GC/MS
   ［Extraction］Solvent: hexane/acetone mixture (1:1, vol.); Extraction time: 24 hours
   ［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）
   ［GC/MS］Column: DB-5 (J&W), Mass resolution: 10 000 (SIM)
3. Soxhlet extraction and ID-GC/MS
   ［Extraction］Solvent: dichloromethane; Extraction time: 24 hours
   ［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）
   ［GC/MS］Column: HT-8 (SGE), Mass resolution: 10 000 (SIM)
4. Pressurized fluid extraction and ID-GC/MS
   ［Extraction］Solvent: hexane/acetone mixture (1:1, vol.); Temperature: 150 °C(15 MPa); Extraction time: 30 min x 2 cycles
   ［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）
   ［GC/MS］Column: HT-8 (SGE), Mass resolution: 10 000 (SIM)
5. Pressurized fluid extraction and ID-GC/MS
   ［Extraction］Solvent: dichloromethane; Temperature: 150 °C (15 MPa); Extraction time: 30 min x 2 cycles

［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）

［GC/MS］Column: DB-XLB (Agilent), Mass resolution: 10 000 (SIM)

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

［Extraction］Solvent: hexane/acetone mixture (1:1, vol.); Temperature: 145 °C; Extraction time: 20 min

［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）

［GC/MS］Column: DB-XLB (Agilent), Mass resolution: 10 000 (SIM)

7. Microwave-assisted extraction and ID-GC/MS

［Extraction］Solvent: hexane/acetone mixture (1:1, vol.); Temperature: 145 °C; Extraction time: 20 min

［Cleanup］Activated copper treatment, Solid phase extraction (silica gel) and normal phase high performance liquid chromatography（NH_2-silica gel column）

［GC/MS］Column: DB-5 (J&W), Mass resolution: 10 000 (SIM)

8. Supercritical fluid extraction and ID-GC/MS

［Extraction］CO_2; temperature: 140 °C (30 MPa); Extraction time: static mode: 15 min + dynamic mode: 30 min

［Cleanup］None

［GC/MS］Column: HT-8 (SGE), Mass resolution: 10 000 (SIM)

9. Saponification-liquid/liquid extraction and ID-GC/MS

［Saponification-Extraction］Sequential extraction with 1 M KOH/ethanol (50 mL) + 10 ml water (Shake at room temperature, 60 min → reflux at 80 °C, 60 min) Extract both supernatants with hexane

［Cleanup］Sulfuric acid treatment, Solid phase extraction (silica gel)

［GC/MS］Column: HT-8 (SGE), Mass resolution: 10 000 (SIM)

10. Sonication and ID-GC/MS

［Extraction］Solvent: acetone, (Shaking: 10 min + Sonication: 10 min, Supernatant recovery by centrifuge) x 3 cycles Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)

［Cleanup］Silica gel-open column chromatography and normal phase high performance liquid chromatography（NH_2-silica gel column）

［GC/MS］Column: HT-8 (SGE), Mass resolution: 10 000 (SIM)

Metrological Traceability

The certified values of this CRM are determined by the IDMS which is the primary method of measurement. Because the calibration solution for the measurements is prepared from the high purity reagents (CB3, CB15, CB31, CB70, CB194, *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD) evaluated by NMIJ and the certified reference materials (NIST SRM1492 and SRM1493) , the certified values are traceable to the International System of Units (SI).

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

The certification of this CRM is valid until March 31, 2024, provided that the material remains unopened and is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from a marine sediment sample. This CRM of 60 g in net volume is kept in an amber glass bottle.

Homogeneity

The homogeneity of this CRM was determined by analyzing 10 bottles which were randomly sampled from 1000 bottles. PCB congeners (CB28, CB105, CB180) and *p,p'*-DDE were determined by the pressurized liquid extraction and ID-GC/MS method. The inhomogeneity of the analytes evaluated by the ANOVA is not significant and it has been incorporated into the uncertainties of the certified values.

Instructions for Storage

This CRM should be stored at a temperature around 5 °C and shielded from light.

Instruction for Use

(1) Sample size

More than 2.5 g of the material should be used.

(2) Determination of water (dry mass)

The concentrations of the constituents in this CRM are given on a dry-mass basis. The moisture content should be evaluated by taking a portion (about 1 g) of the material and drying it in an oven at a temperature between105 °C to 110 °C for 6 hours. The sample portion should be weighed after it is cooled down to room temperature in a desiccator. Analytical results must be calculated on a dry-mass basis. The samples used for the determination of water should not be used for determination of the pesticides. The approximate moisture content is found to be 4 %.

(3) The bottles of this CRM should be allowed to warm to room temperature before use.

(4) Analysis by saponification

To suppress dechlorination of highly chlorinated biphenyls, water of approximately five times heavier than a sample should be added to the saponifying solution (1 M ethanolic potassium hydroxide solution) in case that the PCB analysis is performed in accordance with Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)

Precautions for Handling

Use a mask, gloves and other protective gears when during handling this CRM. Handle, store and dispose this CRM in accordance with relevant laws. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

This CRM is a marine sediment sample collected near urban area in Japan. The sediment was air-dried, pulverized, sieved (with mesh size of <106 μm), homogenized, and subdivided into 60-g screw-capped amber glass bottles. The bottled material was sterilized by the γ-ray irradiation of ^{60}Co (20 kGy). The preparation of this CRM was carried out by the Environmental Technology Service Co., Ltd. and Radiation Application Development Association.

Technical Information

The mass fraction ranges of PCB homologues (dry-mass basis) at the 95% level of confidence were obtained in the collaborative analysis of 12 laboratories by using the Japanese official method for the determination of PCBs (saponification: Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)).

PCB homologue concentrations in CRM 7304-a based on the Japanese official method

	Mass fraction (μg kg^{-1})				Mass fraction (μg kg^{-1})		
(mono)chlorobiphenyls	0.66	—	1.2	hexachlorobiphenyls	41	—	92
dichlorobiphenyls	5.3	—	20	heptachlorobiphenyls	22	—	36
trichlorobiphenyls	90	—	200	octachlorobiphenyls	4.0	—	10
tetrachlorobiphenyls	310	—	570	nonachlorobiphenyls	0.39	—	0.92
pentachlorobiphenyls	160	—	280	decachlorobiphenyl	0.85	—	1.5

The analytical measurements for the PCB homologues were performed in the collaborative analysis of 12 laboratories (see below) coordinated by NMIJ.

Participants of collaborative analysis for the determination of PCB homologues:
Chemical Evaluation and Research Institute (CERI)
Environmental Control Center Co., Ltd.
Metocean Environment Inc.
Shimazdu Techno-Research, Inc.
Kaneka Techno Research Co., Ltd.
Nittech Research Co., Ltd.
Sumika Chemical Analysis Service, Ltd.
Unitika Environmental Technical Center Ltd.
Kokan Keisoku K.K.
Kawaju Techno Service Co.
Chugai Technos Co., Ltd.
National Metrology Institute of Japan (NMIJ)

Concentration (mass fraction) of γ-HCH in this CRM determined by a Japanese official method (Method 10: Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)) is given in the table below.
Concentrations of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD determined by this method were in the ranges of certified values.

Concentration of γ-HCH in CRM7304-a by the Japanese official method

	Mass fraction (μg kg^{-1})
γ-HCH	3.9

Information concentrations (dry-mass basis) for selected inorganic constituents are given in the table below. The results were obtained by ICP-AES.

Concentration of elements in CRM 7304-a

	Mass fraction (%)		Mass fraction (%)		Maas fraction (%)		Mass fraction (%)
Al	7.9	Fe	5.3	K	1.6	Ti	0.4
Ca	3.6	Mg	1.4	Na	2.1		

NMIJ Analysts
The technical manager for this CRM is TAKATSU A. and the production manager is YARITA T. The analysts are NUMATA M., YARITA T., AOYAGI Y. and YAMAZAKI 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	
August 10, 2012:	The expiration of this certificate was extended from "November 30, 2013" to "March 31, 2024." The description of "Metrological Traceability" and "Mutual Recognition Arrangement under Meter Convention" were added.
April 1, 2015:	"Metrology Management Center" was renamed to "Center for Quality Management of Metrology."