[This document is just explanation translated from the original Japanese certificate and some information is omitted from it.]

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7305-a
No. +++

National Institute of Advanced Industrial Science and Technology
AIST

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

This certified reference material (CRM) was produced based on NMIJ's quality system in compliance with JIS Q 0034 (ISO GUIDE 34), for use in controlling the precision of analysis or confirming the validity of analytical methods or instruments during analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediment samples and similar materials.

Certified Values

The certified values, expressed as mass fractions (dry-mass basis), are given in the following table. The expanded uncertainty was determined using coverage factor ($k = 2$), corresponding to an estimated confidence interval 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	0.15	0.07	1, 4, 6, 8, 11, 16
CB15 (4,4'-dichlorobiphenyl)	2050-68-2	0.31	0.05	1, 4, 6, 8, 11, 14, 16
CB28 (2,4,4'-trichlorobiphenyl)	7012-37-5	2.9	0.2	1, 4, 6, 8, 11, 14, 16
CB31 (2,4',5-trichlorobiphenyl)	16606-02-3	2.26	0.18	1, 4, 6, 8, 11, 14, 16
CB70 (2,3',4',5-tetrachlorobiphenyl)	32598-11-1	4.0	0.3	1, 4, 6, 8, 11, 14, 16
CB101 (2,2',4,5,5'-pentachlorobiphenyl)	37680-73-2	2.6	0.3	2, 4, 6, 9, 12, 15, 16
CB105 (2,3,3',4,4'-pentachlorobiphenyl)	32598-14-4	1.27	0.14	1, 4, 6, 8, 11, 14, 16
CB138 (2,2',3,4,4',5'-hexachlorobiphenyl)	35065-28-2	1.92	0.15	1, 4, 6, 8, 11, 14, 16
CB153 (2,2',4,4',5,5'-hexachlorobiphenyl)	35065-27-1	3.2	0.3	1, 4, 6, 8, 11, 14, 16
CB170 (2,2',3,3',4,4',5-heptachlorobiphenyl)	35065-30-6	0.92	0.16	1, 4, 6, 8, 11, 14, 16
CB180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)	35065-29-3	2.4	0.5	1, 4, 6, 8, 11, 14, 16
CB194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl)	35694-08-7	0.62	0.13	1, 4, 6, 8, 11, 14, 16

CB206 (2,2',3,3',4,4',5,5',6-nonachlorobiphenyl)	40186-72-9	0.15	0.03	1, 4, 6, 8, 11, 14, 16
CB209 (decachlorobiphenyl)	2051-24-3	0.16	0.03	1, 4, 6, 8, 11, 14, 16

*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	2.2	0.5	3, 5, 7, 10, 13, 18
p,p'-DDE (1,1-dichloro-2,2-bis[chlorophenyl]ethylene)	72-55-9	1.79	0.11	1, 4, 6, 8, 11, 17
p,p'-DDD (1,1-dichloro-2,2-bis[chlorophenyl]ethane)	72-54-8	3.3	0.3	3, 5, 7, 10, 13, 18
γ-HCH ((1α,2α,3β,4α,5α,6β)-hexachlorocyclohexane)	58-89-9	0.89	0.12	3, 5, 7, 10, 13

Determination of Certified Values

The certified values were calculated from PCB congeners and OCPs concentrations 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-5MS (J&W), Mass resolution: 10 000 (SIM)
3. 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)
4. 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: HT8-PCB (Kanto Chemical), Mass resolution: 10 000 (SIM)
5. 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: DB-35MS (J&W), Mass resolution: 10 000 (SIM)
6. Pressurized fluid extraction and ID-GC/MS
   [Extraction] Solvent: hexane/acetone mixture (1:1, vol.); temperature: 150 ºC(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: HT8-PCB (Kanto Chemical), Mass resolution: 10 000 (SIM)
7. Pressurized fluid extraction and ID-GC/MS
   [Extraction] Solvent: hexane/acetone mixture (1:1, vol.); temperature: 150 ºC(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-35MS (J&W), Mass resolution: 10 000 (SIM)
8. Pressurized fluid extraction and ID-GC/MS
   [Extraction] Solvent: dichloromethane; temperature: 150 ºC (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)

9. Pressurized fluid extraction and ID-GC/MS
［Extraction］ Solvent: dichloromethane; temperature: 150 ºC (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-5MS (J&W), Mass resolution: 10 000 (SIM)
10. Pressurized fluid extraction and ID-GC/MS
［Extraction］ Solvent: dichloromethane; temperature: 150 ºC (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-5 (J&W), Mass resolution: 10 000 (SIM)
11. Microwave-assisted extraction and ID-GC/MS
［Extraction］ Solvent: hexane/acetone mixture (1:1, vol.); temperature: 145 ºC; 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)
12. Microwave-assisted extraction and ID-GC/MS
［Extraction］ Solvent: hexane/acetone mixture (1:1, vol.); temperature: 145 ºC; 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-5MS (J&W), Mass resolution: 10 000 (SIM)
13. Microwave-assisted extraction and ID-GC/MS
［Extraction］ Solvent: hexane/acetone mixture (1:1, vol.); temperature: 145 ºC; 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)
14. Supercritical fluid extraction and ID-GC/MS
［Extraction］ CO_2; temperature: 140 ºC (30 MPa); extraction time: static mode: 15 min + dynamic mode: 30 min
［Cleanup］ None
［GC/MS］ Column: DB-XLB (Agilent), Mass resolution: 10 000 (SIM)
15. Supercritical fluid extraction and ID-GC/MS
［Extraction］ CO_2; temperature: 140 ºC (30 MPa); extraction time: static mode: 15 min + dynamic mode: 30 min
［Cleanup］ None
［GC/MS］ Column: DB-5MS (J&W), Mass resolution: 10 000 (SIM)
16. 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 ºC, 60 min) Extract both supernatants with hexane
［Cleanup］ Sulfuric acid treatment, Solid phase extraction (silica gel)
［GC/MS］ Column: HT8-PCB (Kanto Chemical), Mass resolution: 10 000 (SIM)
17. 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: HT8-PCB (Kanto Chemical), Mass resolution: 10 000 (SIM)
18. 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: DB-35MS (J&W), Mass resolution: 10 000 (SIM)

Traceability

The certified values were determined by IDMS as a primary method of measurement. Because the calibration solution for the measurements was prepared from high purity reagents (CB3, CB15, CB31, CB70, CB194, and *p,p'*-DDD) which were evaluated by NMIJ and certified reference materials (NMIJ CRM 4201-a1, CRM 4202-a1, CRM 4203-a1, and SRM1493) , the certified values are traceable to the International System of Units (SI).

Expiration of Certification

The certification of this CRM is valid until November 30, 2014, provided that the material is unopened and stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from a marine sediment sample. This CRM is packaged in a glass bottle (60 g each).

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles randomly sampled from 1000 bottles. PCB congeners (CB28, CB101, CB180) and *p,p'*-DDE were determined by pressurized liquid extraction and ID-GC/MS method. The inhomogeneity of the analytes, which was evaluated by ANOVA, is not significant and is reflected in the uncertainty of the certified value.

Precautions for Storage

This CRM should be kept at 5 °C under dark condition.

Notice and Warning to Users

(1) Sample size

More than 3 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 assessed by taking a portion (about 1 g) of the material and drying it in an oven at 105 °C-110 °C for 6 h. The weighing should be done after cooling 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 was found to be 3 %.

(3) The CRM should be equilibrated to room temperature before use.

(4) Analysis by saponification

To reduce dechlorination of highly chlorinated biphenyls, water of approximately five times of sample weight should be added to the saponifying solution (1 M ethanolic potassium hydroxide solution) in the case of PCB analysis by Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)

Precautions for Handling

Wear a mask, gloves and other protective gears during handling. Handle, store and dispose this CRM in accordance with laws.

Preparation Method

This CRM is a marine sediment sample collected near urban area in Japan. The sediment was air-dried, pulverized, sieved (<106 μm particles used), homogenized and subsampled into 60-g portions in screw-capped amber glass bottles. The bottled samples were sterilized by 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.

Information value

The mass fraction ranges of PCB homologues (dry-mass basis) at the 95% level of confidence were the results of a collaborative analysis among 12 laboratories by a 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 fractions (μg kg^{-1})
(mono)chlorobiphenyls	0.28 — 0.45
dichlorobiphenyls	1.7 — 3.2
trichlorobiphenyls	8.3 — 16
tetrachlorobiphenyls	23 — 37
pentachlorobiphenyls	13 — 22
hexachlorobiphenyls	8.4 — 16

heptachlorobiphenyls	5.7 — 12
octachlorobiphenyls	0.99 — 4.1
nonachlorobiphenyls	0.15 — 0.32
decachlorobiphenyls	0.11 — 0.25

Analytical measurements for the PCB homologues were the results of a collaborative analysis among 12 laboratories (see below) coordinated by the 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 18: Endocrine Disrupting Chemicals Interim Investigation Manual (water, sediments, aquatic organisms) (Environment Agency of Japan, 1998)) was shown in 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 CRM7305-a by the Japanese official method

	Mass fractions (μg kg^{-1})
γ-HCH	0.55

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

Concentration of elements in CRM 7304-a

	Mass fractions (%)		Mass fractions (%)		Maas fractions (%)		Mass fractions (%)
Al	7.0	Fe	5.3	K	1.6	Ti	0.4
Ca	4.1	Mg	1.2	Na	1.9		

NMIJ Analysts
The technical manager and production manager for this CRM is A. Takatsu and T. Yarita, respectively. Analytical measurements for the certification of this CRM were performed at NMIJ by M. Numata, T. Yarita, Y. Aoyagi and Y. Yamamoto.

Technical Information
Customers will be notified of any revision to this CRM including a change in certified value. Technical information on this CRM can be obtained from the home page and other contact routes (see below).

[This document is just explanation translated from the original Japanese certificate and some information is omitted from it.]

Reproduction of Certificate

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

November 2004
Hiroyuki Yoshikawa
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,
Metrology Management Centre, Reference Materials Office,
1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, Japan
Phone: +81-29-861-4059; Fax: +81-29-861-4009, http://www.nmij.jp/

Note: This certificate is a translation of the original Japanese certificate and is not an official document.