

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 7404-a
No. +++

Organic Pollutants in Japanese Seabass Tissue

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 fish tissue 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 values are expressed as mass fraction based on a dry mass (the drying procedure is given 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 %.

Certified values of PCB congeners*

	CAS No.	Certified value, Mass fraction ($\mu\text{g}/\text{kg}$)	Expanded uncertainty, Mass fraction ($\mu\text{g}/\text{kg}$)	Analytical Method
CB28 (2,4,4'-trichlorobiphenyl)	7012-37-5	4.73	0.58	1,2,3
CB70 (2,3,4',5-tetrachlorobiphenyl)	32598-11-1	5.7	0.6	
CB105 (2,3,3',4,4'-pentachlorobiphenyl)	32598-14-4	2.62	0.27	
CB153 (2,2',4,4',5,5'-hexachlorobiphenyl)	35065-27-1	14.0	0.5	
CB170 (2,2',3,3',4,4',5-heptachlorobiphenyl)	35065-30-6	1.05	0.06	

*IUPAC number

Certified values of OCPs

	CAS No.	Certified value Mass fraction (µg/kg)	Expanded uncertainty Mass fraction (µg/kg)	Analytical Method
<i>p,p'</i> -DDT (1,1,1-trichloro-2,2-bis[chlorophenyl]ethane)	50-29-3	1.76	0.12	1,2,4
<i>p,p'</i> -DDE (1,1-dichloro-2,2-bis[chlorophenyl]ethylene)	72-55-9	18.0	1.8	
<i>p,p'</i> -DDD (1,1-dichloro-2,2-bis[chlorophenyl] ethane)	72-54-8	4.30	0.25	
Dieldrin ((1 α ,2 β ,2 α ,3 β ,6 β ,6 α ,7 β ,7 α)-3,4,5,6,9,9 -hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro- 2,7:3,6-dimethanonaphth[2,3-b]oxirene)	60-57-1	1.57	0.06	
<i>trans</i> -Nonachlor ((1 α ,2 β ,3 α ,3 α ,4 β ,7 β ,7 α)-1,2,3,4,5,6,7,8,8 -nonachloro-2,3,3a,4,7,7a-hexahydro-4,7- methano-1H-indene)	39765-80-5	6.15	0.25	

Analysis

The certified values of this CRM were determined based on the analytical results of PCB congeners and OCPs which were obtained by the following methods;

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

[Extraction] Solvent, hexane/acetone (1/1, v/v); Temperature: 120 °C (15 MPa); Extraction time: 10 min × 2 cycles

[Clean-up] Gel permeation chromatography (GPC, divinylbenzene-polystyrene column), Solid-phase extraction (SPE, silica gel), normal phase liquid chromatography (nHPLC, NH₂ column)

[GC/MS] Column: HT8-PCB (for PCB congeners and *p,p'*-DDE, Kanto Chemical) or DB-35MS (for OCPs except *p,p'*-DDE, Agilent Technologies); Mass resolution: ≥10000; Electron impact ionization (EI); Selected ion monitoring (SIM)

2. Soxhlet extraction and ID-GC/MS

[Extraction] Solvent, hexane/acetone (1/1, v/v); 16 h

[Clean-up] GPC (divinylbenzene-polystyrene column), SPE (silica gel), nHPLC (NH₂ column)

[GC/MS] Column: DB-5MS (for CB105 and OCPs, Agilent Technologies) or DB-XLB (for CB28, CB70, CB153, and CB170, Agilent Technologies); Mass resolution: ≥10000; EI; SIM

3. Saponification-solvent extraction and ID-GC/MS

[Saponification] 50 mL 1 M ethanolic potassium hydroxide at 80 °C with reflux

[Extraction] Solvent: hexane

[Clean-up] Shaking (with sulfuric acid), SPE (silica gel)

[GC/MS] Column: HT8-PCB (for PCB congeners, Kanto Chemical); Mass resolution: ≥10000; EI; SIM

4. Homogenization extraction and ID-GC/MS

[Extraction] Solvent: hexane/acetone (2/1, v/v); Extraction time: 2 min × 2 cycles

[Clean-up] Shaking (with acetonitrile saturated with hexane, and then, with hexane), Column chromatography (silica gel containing 5% water)

[GC/MS] Column: HT8-PCB (for *p,p'*-DDE, Kanto Chemical) or DB-5MS (for OCPs except *p,p'*-DDE, Agilent Technologies); Mass resolution: ≥10000; EI; SIM

Metrological Traceability

The certified values of this CRM were determined by the IDMS, the primary method of measurement. Because the calibration solution for the measurements was prepared from the certified reference materials (NMIJ CRM 4206-a1, 4207-a1, 4208-a1,

4210-a1, 4211-a1, and NIST SRM2261), 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 November 30, 2019, 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 the Japanese seabass. The fish tissue was powdered by the freeze-pulverization. This CRM is in the form of a brown powder and it of ca. 10 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 400 bottles. PCB congeners (CB28, CB105, CB153, CB170) and *p,p'*-DDE were determined by the pressurized liquid extraction and ID-GC/MS method. The inhomogeneity of the analytes determined by the ANOVA, is not significant and it has been incorporated into the uncertainty of the certified value. This material is homogeneous within the range of 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.

Instruction for Use

(1) Sample size

More than 2 g of the material should be used.

(2) Determination of water content (dry mass)

The concentrations of the constituents in this CRM are given on a dry-mass basis. The water content should be evaluated by taking a portion (about 1 g) of the material and drying it in an oven at 105 °C for 15 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 5 %.

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

Precautions for Handling

This CRM is for laboratory use only. This CRM is not edible. Care must be taken to avoid injuries when a bottle is opened. Use a protective mask and gloves for safety when using the CRM. Dispose of this CRM in accordance with the Waste Management and Public Cleansing Act. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

The Japanese seabass was collected from Tokyo Bay, and the edible part was used for analysis. The sample was freeze-dried, pulverized, sieved (mesh size of < 250 μm), homogenized, and subdivided into 10-g bottles. The bottled material was sterilized by the γ-ray irradiation with ⁶⁰Co and stored at 5 °C. The preparation of this CRM was carried out by the Funtai-giken Co., Ltd., Japan Chemical Analysis Center, and Radiation Application Development Association.

Technical Information

The concentration of perfluorosulfonate as free acid (in dry-mass fraction) is $(11.4 \pm 1.4) \mu\text{g}/\text{kg}$ (average \pm expanded uncertainty). The concentration of perfluorosulfonate was determined by the IDMS combined with the LC/MS/MS by using NMIJ CRM 4220-a (PFOS-K in methanol) as the SI traceable calibrant. Specifically, two different extraction solvents (acetonitrile and methanol), two different solid-phase extraction cartridges (ion exchange and reversed-phase), and two different LC columns (C_{18} and ion-exchange) were used. The homogeneity was separately evaluated. The uncertainty of the reference value includes the uncertainties derived from the measurements and the homogeneity.

NMIJ Analysts

The technical manager for this CRM is NUMATA M. and the production manager is OTAKE T. The analysts are OTAKE T., AOYAGI Y., YARITA T., and NUMATA 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

February 10, 2014: The description of “Technical Information” and “Mutual Recognition Arrangement under Meter Convention” were added.

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