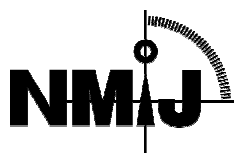


National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 7903-a

No. +++



Polychlorinated Biphenyls in Insulation Oil (Low 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) in mineral oil 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 ($\mu\text{g}/\text{kg}$)	Expanded uncertainty Mass fraction ($\mu\text{g}/\text{kg}$)	Analytical Method
CB52 (2,2',5,5'-tetrachlorobiphenyl)	35693-99-3	0.33	0.12	1,3,6
CB101 (2,2',4,5,5'-pentachlorobiphenyl)	37680-73-2	0.38	0.24	1,2,3,4,5,6
CB118 (2,3',4,4',5- pentachlorobiphenyl)	31508-00-6	0.42	0.15	1,3,5,6
CB138 (2,2',3,4,4',5'- hexachlorobiphenyl)	35065-28-2	0.27	0.23	1,3,5,6
CB153 (2,2',4,4',5,5'- hexachlorobiphenyl)	35065-27-1	0.21	0.14	1,2,3,4,5,6

*IUPAC number

Concentrations of 6 PCB congeners in this CRM given in the following table are undetectable by the analytical methods used for the characterization. Their signal-noise ratios (S/N) of the GC/MS signals were lower than 3 or were not higher than the signals obtained from procedural blank tests significantly. The ranges of concentrations equivalent to the respective detection limits (S/N=3) are shown in the table below.

Certified values of PCB congeners*(estimated from the respective lowest limits of detection)

	CAS No.	Certified value Mass fraction ($\mu\text{g}/\text{kg}$)	Analytical Method
CB3 (4-chlorobiphenyl)	2051-62-9	<0.22	1
CB8 (2,4'-dichlorobiphenyl)	34883-43-7	<0.19	1
CB28 (2,4,4'-trichlorobiphenyl)	7012-37-5	<0.12	1
CB180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)	35065-29-3	<0.12	1
CB194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl)	35694-08-7	<0.13	1
CB206 (2,2',3,3',4,4',5,5',6-nonachlorobiphenyl)	40186-72-9	<0.09	1

*IUPAC number

Determination of Certified Values

Each certified value was determined by the following analytical method:

1. Dimethylsulfoxide extraction and isotope dilution – gas chromatography / mass spectrometry (ID-GC/MS)
[Cleanup] Dimethylsulfoxide extraction, Sulfuric acid treatment, and Silica gel-open column chromatography

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- [GC/MS] Column: HT8-PCB (Kanto Chemical), Mass resolution: 10 000 (EI, SIM)
2. Dimethylsulfoxide extraction and isotope dilution – gas chromatography / mass spectrometry (ID-GC/MS)
- [Cleanup] Dimethylsulfoxide extraction, Sulfuric acid treatment, and Silica gel-open column chromatography
- [GC/MS] Column: DB-1701 (Agilent Technologies), Mass resolution: 10 000 (EI, SIM)
3. Gel permeation chromatography, Reverse phase chromatography, and ID-GC/MS
- [Cleanup] Solid phase extraction (aminopropylsilica), Gel permeation chromatography and Reverse phase chromatography (C18-silica gel column)
- [GC/MS] Column: DB-XLB (Agilent Technologies), Mass resolution: 10 000 (EI, SIM)
4. Gel permeation chromatography, Reverse phase chromatography, and ID-GC/MS
- [Cleanup] Solid phase extraction (aminopropylsilica), Gel permeation chromatography and Reverse phase chromatography (C18-silica gel column)
- [GC/MS] Column: DB-1MS (Agilent Technologies), Mass resolution: 10 000 (EI, SIM)
5. Sulfoxide modified silica chromatography and ID-GC/MS
- [Cleanup] Solid phase extraction (silica) and Sulfoxide modified silica chromatography
- [GC/MS] Column: HT8-PCB (Kanto Chemicals), Mass resolution: 10 000 (EI, SIM)
6. Normal phase chromatography and ID-GC/MS
- [Cleanup] Solid phase extraction (benzene sulfonic acid/silica) and normal phase high performance liquid chromatography (NH₂-silica gel column and DIOL-silica gel column)
- [GC/MS] Column: DB-XLB (Agilent Technologies), Mass resolution: 10 000 (EI, 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 NMIJ standard solutions of CB28 (CRM 4206-a1), CB153 (CRM 4207-a1) and CB194 (CRM 4209-a1); and high purity other PCB congeners of which purities were evaluated in NMIJ, the certified values are traceable to the International System of Units (SI).

Expiration of Certification

The certification of this CRM is valid until March 31, 2017, provided that the material is unopened and stored in accordance with the instructions given in this certificate.

Sample Form

This CRM is electric insulation oil mainly composed with paraffin oil. The form of CRM is 10 mL of yellow viscous oil sealed in an amber ampoule with argon gas.

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 ampoules selected by random sampling of 600 ampoules. The PCB congeners were determined by the normal phase liquid chromatography and ID-GC/MS method, and the inhomogeneity was evaluated by ANOVA. The inhomogeneity of analytes is not significant and is reflected in the uncertainty of the certified value.

Precautions for Storage

This CRM should be kept at room temperature (below 30 °C) under dark condition.

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 commercial insulating oil (JIS C2320 class 1-2) that had been used as transformer oil for 26 years was collected from a transformer (three phases, 300 kVA). The collected oil was filtered with a glass fiber filtration paper (retention particle diameter: 0.5 µm), then ca. 10 mL of the oil was sealed in an amber ampoule with argon gas. The collection of the oil was carried out by the General Environmental Technos Co., Ltd.

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Information value

a. Concentrations of PCB homologues obtained by a Japanese official method

Concentrations of PCB homologues were the results by a Japanese official method for the determination of PCBs in waste (the method (1) and (2)): Notification No. 192 of the Ministry of Welfare (1992)). To estimate concentrations of homologues, the GC/MS response factors of PCB isomers are assumed to be same.

If signal-noise ratio (S/N) of the GC/MS signal of a certain congener was lower than 3 or were not higher than the signals obtained from procedural blank tests significantly, concentration of the congener is regarded as zero (nd: all isomers are not detectable). The concentrations of each congener estimated from respective lowest detection limits are also shown in the table below.

The expanded uncertainty was determined using coverage factor $k = 2$, corresponding to an estimated confidence interval of approximately 95%. However, uncertainties of PCB concentrations in the calibration solutions, difference of the response factors between isomers are not considered.

Because detection limit of decachlorobiphenyl by the analytical method 7 (see below) was lower than the official method, the data obtained by the method 7 was used.

PCB homologue concentrations (mass fractions) in CRM 7903-a based on the Japanese official method

	Concentration ($\mu\text{g}/\text{kg}$)	Expanded uncertainty ($\mu\text{g}/\text{kg}$)	Detection limit ** ($\mu\text{g}/\text{kg}$)
(Mono)Chlorobiphenyls	nd	—	0.22
Dichlorobiphenyls	0.33	0.81	0.19
Trichlorobiphenyls	0.38	0.60	0.12
Tetrachlorobiphenyls	1.13	0.59	0.09
Pentachlorobiphenyls	2.80	0.42	0.13
Hexachlorobiphenyls	1.24	0.41	0.30
Heptachlorobiphenyls	0.21	0.05	0.12
Octachlorobiphenyls	nd	—	0.13
Nonachlorobiphenyls	nd	—	0.09
Decachlorobiphenyl***	nd	—	0.06

** Concentration of each isomer estimated from respective lowest detection limit

Analytical method***

7. Normal phase chromatography and ID-GC/MS (NCI)

[Cleanup] Solid phase extraction (benzene sulfonic acid/silica) and normal phase high performance liquid chromatography (NH₂-silica gel column and Diol-silica gel column)

[GC/MS] Column: DB-XLB (Agilent Technologies), Mass resolution: 3 000 (NCI, SIM)

b. Density

Density of this CRM at room temperature is 0.87751 g/mL (20 °C), 0.87417 g/mL (25 °C) or 0.87081 g/mL (30 °C). The measurement was performed with an oscillational density meter.

NMIJ Analysts

The technical manager and production manager for this CRM is T. Yarita and M. Numata, respectively. Analytical measurements for the certification of this CRM were performed at NMIJ by M. Numata, N. Hanari, K. Ishikawa, Y. Aoyagi, M. Matsuo and S. Otsuka.

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).

Reproduction of Certificate

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

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March 2007
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/>

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