

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 7403-a
No. +++

Trace Elements, Arsenobetaine and Methylmercury in Swordfish 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 evaluating or validating analytical methods and instruments used for the determination of the elements listed below, arsenobetaine and methylmercury in fish tissue and similar matrices.

Certified Values

The certified values for 14 elements and two compounds in this CRM are given in the tables below. The values are expressed as mass fractions based on 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 %.

| Elements | Certified value, Mass fraction (mg/kg) | Expanded uncertainty, Mass fraction (mg/kg) | Analytical methods* (see below) |
|----------|---|--|------------------------------------|
| Mn | 0.201 | 0.010 | 2, 3, 5 |
| Fe | 13.1 | 0.5 | 1, 2, 4 |
| Cu | 1.31 | 0.04 | 1, 2, 5 |
| Zn | 33.6 | 1.0 | 1, 2 |
| As | 6.62 | 0.21 | 2, 3, 4, 5 |
| Se | 2.14 | 0.11 | 1, 2 |
| Sr | 1.13 | 0.03 | 1, 2, 5 |
| Cd | 0.159 | 0.006 | 1, 2, 3 |
| Hg | 5.34 | 0.14 | 1, 2, 8 |

| Elements | Certified value, Mass fraction (g/kg) | Expanded uncertainty Mass fraction (g/kg) | Analytical methods* (see below) |
|----------|--|--|------------------------------------|
| Na | 3.57 | 0.12 | 4, 6, 7 |
| Mg | 1.58 | 0.04 | 2, 4, 6 |
| P | 14.5 | 0.4 | 2, 3, 4 |
| K | 26.3 | 1.1 | 4, 6, 7 |
| Ca | 0.189 | 0.009 | 2, 4, 7 |

*Analytical methods:

- 1) Isotope dilution - inductively coupled plasma mass spectrometry (ID-ICP-MS)
- 2) ICP-MS
- 3) High resolution ICP-MS
- 4) Inductively coupled plasma atomic emission spectrometry (ICP-AES)
- 5) Graphite furnace atomic absorption spectrometry
- 6) Flame atomic absorption spectrometry
- 7) Flame photometry

- 8) Thermal decomposition Au-amalgam trap cold vapor atomic absorption spectroscopy
[1) - 7): with microwave acid digestion, 8): without digestion]

| Compound | Certified value, Mass fraction (mg/kg) | Expanded uncertainty Mass fraction (mg/kg) | Analytical methods* |
|-----------------------|---|---|---------------------|
| Arsenobetaine (as As) | 6.23 | 0.21 | 9, 10 |
| Methylmercury (as Hg) | 5.00 | 0.22 | 11, 12 |

*Analytical methods:

- 9) Ultrasonic extraction / high performance liquid chromatography - ICP-MS (HPLC-ICP-MS)
10) Ultrasonic extraction / isotope dilution - liquid chromatography - electro spray mass spectrometry (ID-LC-MS)
11) Ultrasonic alkali extraction / phenyl-derivatization / isotope dilution - gas chromatography - ICP-MS (ID-GC-ICP-MS)
12) Ultrasonic acid extraction / phenyl-derivatization / isotope dilution - GC-ICP-MS (ID-GC-ICP-MS)

Analysis

The certified values of this CRM are the weighted means of results from two or more analytical methods at NMIJ:

- (1) Single primary method and one or more reference methods
- (2) Three or more reference methods.

The expanded uncertainty in each certified value is equal to $U = k u_c$, where u_c is the combined standard uncertainty derived from the analytical results, the method-to-method variance, the standard solution, and the sample homogeneity. The expanded uncertainties were calculated using a coverage factor (k) of 2, which gives a level of confidence of approximately 95%

Metrological Traceability

For the trace elements, the certified values were determined by ID-ICP-MS with Japan Calibration Service System (JCSS) standard solutions and an NIST SRM 3149 Se standard solution and are traceable to the International System of Units (SI). For the arsenobetaine, the certified value was determined by ID-LC-MS with NMIJ CRM 7901-a and is traceable to SI. For the methylmercury, the certified value was determined by ID-GC-ICP-MS with a methylmercury standard solution, which was calibrated by using the JCSS standard solution and is traceable to SI. All sample preparation was carried out by the gravimetric method using a balance calibrated by JCSS.

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, 2019, provided that the material is unopened and is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from fish tissue, which was powdered by freeze-pulverization after freeze-drying. This CRM is in the form of a pale yellow powder in an amber glass bottle (10 g each).

Homogeneity

The homogeneity of this CRM was determined by analyzing 10 bottles from a hierarchically random sampling of 650 bottles. Each trace element except Hg was determined by ICP-MS or ICP-AES after microwave acid digestion. Hg was determined by thermal decomposition Au-amalgam trap cold vapor atomic absorption spectroscopy without pretreatment. The arsenobetaine was determined by HPLC-ICP-MS after ultrasonic extraction. The methylmercury was determined by ID-GC-ICP-MS after

ultrasonic alkali extraction/phenyl-derivatization. The inhomogeneity of each analyte, which was evaluated by ANOVA, was not significant and is reflected in 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 5 °C and 35 °C in a clean place and shielded from light.

Instructions for Use

- 1) Be careful of contamination when opening. The bottle must be tightly sealed for storage after opening.
- 2) After opening, be careful of contamination. It is desirable to use this CRM promptly once the bottle is opened.
- 3) Dry mass correction is required when the CRM is analyzed. The correction factor is obtained by the following procedure:
 - ① Weigh approximately 0.3 g of the CRM in a weighing glass vessel and then heat it at 102 °C ± 5 °C for 6 h in a drying oven.
 - ② Weigh the CRM with the vessel after cooling in a desiccator with silica gel.
 - ③ The difference in the mass before and after drying is assumed to be the moisture content.
 - ④ Weighing for dry mass correction has to be done simultaneously with weighing for analysis.The dry mass correction factor at the time of the certification was ca. 5% (mass fraction).
- 4) From the viewpoint of homogeneity for the determination of each element except for Hg and methylmercury, more than 300 mg of this CRM should be used. More than 20 mg of this CRM should be used for the determination of Hg, and more than 500 mg of the CRM should be used for the determination of arsenobetaine.

Precautions for Handling

This CRM is for laboratory use only and is not edible. A protective mask and gloves should be worn for safety when this CRM is used. All relevant laws regarding waste handling and management must be obeyed when disposing of this CRM. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

The swordfish for this CRM was caught at the Pacific close to Japan. The fish was filleted and only muscle tissue was collected. The fillets were freeze-dried, freeze-pulverized, sieved (250 µm) and mixed for homogenization. The homogenized sample was packaged into amber glass bottles (10 g each) and sterilized by ⁶⁰Co γ radiation (20 kGy). The bottles were sealed individually in aluminum-coated nylon packages. These preparation procedures were carried out by Japan Chemical Analysis Center (Japan), Funtai Giken Co., Ltd. (Japan), Radiation Application Development Association, Takasaki Establishment (Japan), and Asahi-rika seisakusho Co., Ltd. (Japan).

NMIJ Analysts

The technical manager for this CRM is CHIBA K., the production manager is KUROIWA T., and the analysts are KUROIWA T., INAGAKI K., NARUKAWA T., ZHU Y., NARUSHIMAI. and JIMBO Y.

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.

Note

This CRM was used for an international Key comparison CCQM-K43.1; As, Hg, Se and methylmercury in swordfish (coordinated by NMIJ) in Consultative Committee for Amount of Substance (CCQM) of the International Committee of Weights and Measures (CIPM). The certified values of these elements and compound were validated by the results of the Key comparison.

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:
National Institute of Advanced Industrial Science and Technology,
National Metrology Institute of Japan,
Center for Quality Management of Metrology, Reference Materials Office,
1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan
Phone: +81-29-861-4059; Fax: +81-29-861-4009; <https://unit.aist.go.jp/nmij/english/refmate/>

Revision history

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