National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7405-b
No. +++

Arsenic Compounds and Trace Elements in Hijiki Seaweed

This certified reference material (CRM) was produced in accordance with the NMIJ's management system and in compliance with ISO GUIDE 34:2009 and ISO/IEC 17025:2005. This CRM is intended for use in the analytical accuracy control, and validation of analytical methods and instruments used for the quantification of arsenic compounds and trace elements in hijiki and other seaweeds.

Certified Values

The certified values for arsenic compounds, including arsenate and arsenosugar compounds, and five elements (As, Cd, Cu, Mn and Zn) in this CRM, are given in the table below. The values are expressed as a 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 %.

Compound	Certified value, Mass fraction (mg/kg, as As)	Expanded uncertainty, Mass fraction (mg/kg, as As)	Analytical methods (see below)
Arsenic acid [As(V)]	24.4	0.7	1), 2), 3), 4)
Arsenosugar-408* (Arsenosugar-SO_4, Molecular weight 408)	1.41	0.04	1), 5), 6), 7), 8)
Arsenosugar-328* (Arsenosugar-OH, Molecular weight 328)	0.44	0.02	1), 5), 6), 7), 9)

*IUPAC and common names and structural formulas of the arsenosugar compound are described in the Technical Information below.

Analytical methods: High-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS)
Measurement condition: [Extraction method] / [Extraction solvent] / [Extraction temperature] / [Column] / [Mobile phase] / [Calibrant]

1) Ultrasonication / Water / Room temperature / Reversed-phase C_{18} / 10 mmol L^{-1} sodium 1-butanesulfonate-4 mmol L^{-1} malonic acid-4 mmol L^{-1} tetramethylammonium hydroxide-0.05 % methanol (pH 3.0) / As(V)
2) Ultrasonication / Water / Room temperature / Reversed-phase C_{30} / 10 mmol L^{-1} sodium 1-butanesulfonate-4 mmol L^{-1} malonic acid-4 mmol L^{-1} tetramethylammonium hydroxide-2 mmol L^{-1} ammonium dihydrogen phosphate-0.05 % methanol / As(V)
3) Dry block bath / 0.07 mol L^{-1} HCl+ 0.1 g L^{-1} pepsin / 37 °C / Reversed-phase C_{28} / 10 mmol L^{-1} sodium 1-butanesulfonate-4 mmol L^{-1} malonic acid-4 mmol L^{-1} tetramethylammonium hydroxide-0.05 % methanol (pH 3.0) / As(V)
4) Ultrasonication / Water / Room temperature / Anion-exchange / 10 mmol L^{-1} ammonium dihydrogen phosphate-

-0.05 % methanol (pH 8.25) / As(V)

5) Dry block bath / 0.07 mol L^{-1} HCl+ 0.1 g L^{-1} pepsin / 37 °C / Reversed-phase C_{28} / 10 mmol L^{-1} sodium 1-butanesulfonate-4 mmol L^{-1} malonic acid-4 mmol L^{-1} tetramethylammonium hydroxide-2 mmol L^{-1} ammonium dihydrogen phosphate-0.05 % methanol (pH 2.7) / As(V)
6) Ultrasonication / Water / Room temperature / Reversed-phase C_{18} / 10 mmol L^{-1} ammonium dihydrogen phosphate -0.05 % methanol (pH 8.25) / As(V)
7) Dry block bath / 0.07 mol L^{-1} HCl+ 0.1 g L^{-1} pepsin / 37 °C / Reversed-phase C_{28} / 10 mmol L^{-1} sodium 1-butanesulfonate-4 mmol L^{-1} malonic acid-4 mmol L^{-1} tetramethylammonium hydroxide-2 mmol L^{-1} ammonium dihydrogen phosphate-0.05 % methanol (pH 2.7) / Arsenosugar-408 and -328
8) Rotating wheel / Water / Room temperature / Anion-exchange / 5 mmol L^{-1} formic acid (pH 4.0) / DMA
9) Rotating wheel / Water / Room temperature / Reversed-phase C_{18} / 5 mmol L^{-1} acetic acid (pH 5.0) / DMA

Element	Certified value, Mass fraction (mg/kg)	Expanded uncertainty, Mass fraction (mg/kg)	Analytical methods (see below)
As	49.5	1.0	1, 3, 4, 5
Cd	1.25	0.04	1, 2, 4, 5
Cu	4.48	0.12	1, 2, 4, 5
Mn	22.6	0.5	1, 3, 4, 5
Zn	13.6	0.5	1, 2, 4, 5

Analytical methods:
1 Inductively coupled plasma mass spectrometry (ICP-MS)
2 Isotope dilution-inductively coupled plasma mass spectrometry (ID-ICP-MS)
3 High resolution inductively coupled plasma mass spectrometry
4 Inductively coupled plasma optical emission spectrometry (ICP-OES)
5 Graphite furnace atomic absorption spectrometry
The sample digestion method for 2 was microwave digestion with nitric acid, hydrofluoric acid, and perchloric acid. The digestion method for all others was microwave digestion with nitric acid, hydrofluoric acid, and hydrogen peroxide.

Analysis

These certified values are the weighted means of the results from two or more analytical methods conducted at NMIJ. Quantitative analysis of arsenic compounds was made after extraction by HPLC-ICP-MS. The different analytical methods were used, with combinations of different heating methods, extracts, and types of HPLC columns. The quantitative analysis of elements was made by the aforementioned analytical methods of 1 to 5, and combinations of these are based on: (1) a single primary method (ID-ICP-MS) with one or more reference methods or (2) three or more reference methods.
The expanded uncertainty in each certified value is equal to $U = ku_c$, where u_c is the combined standard uncertainty derived from: (a) the analytical results, (b) the method-to-method variance, (c) the dry mass correction, (d) the concentration of a standard solution, and (e) the sample homogeneity.

Metrological Traceability

The certified values were determined by isotope dilution mass spectrometry, or other accurate methods, with NMIJ CRM 7912-a Arsenate [As(V)] Solution and JCSS (Japan Calibration Service System) standard solutions. All sample preparation was carried out by a gravimetric method, using a balance calibrated by JCSS. Therefore, the certified values are traceable to the International System of Units (SI).

Mutual Recognition Arrangement under Meter Convention

The certified values of elements and As(V) among the certified values of this certificate are 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

This certificate is valid for one year from the date of shipment, provided that the material is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM was prepared from hijiki seaweed that was powdered by freeze-pulverization. The CRM is in the form of brown powder, which is placed into amber glass bottles (~ 20 g in each).

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles hierarchical-randomly sampled from 640 bottles. Each arsenic compound was determined by HPLC-ICP-MS after extraction procedure. Each trace element was determined by ICP-MS after microwave acid digestion with nitric acid, hydrofluoric acid, and perchloric acid. The inhomogeneity of the analytes, which was evaluated by ANOVA, is 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 and shielded from light.

Instructions for Use

(1) This CRM should be opened and used up as soon as possible after opening to prevent contamination. When the bottle is stored after opening, it should be sealed with tape and kept in a desiccator with silica gel to limit its absorption of moisture as much as possible.

(2) Dry mass correction is required when the CRM is analyzed, as each certified value is expressed as a mass fraction based on a dry mass. The correction factor should be obtained by the following procedure. Do not use the sample that is used for the correction for analysis.

1) Take 1.0 g of the CRM in a weighing glass vessel.
2) Dry the CRM in the vessel at 105 °C for 5 h in a drying oven.
3) Weigh the CRM with the vessel after cooling in a desiccator with silica gel for 30 min.
4) The difference in the masses before and after drying is assumed to be the moisture content.

At April 2019, the dry mass correction factor of the certified values was *ca*. 7.6 % (mass fraction).

(3) Care should be taken to address the following points when the CRM is weighed.

1) Do not weigh in conditions of high humidity (over 60 %).
2) Weighing needs to be performed as quickly as possible.
3) Do not leave the bottle open when not in use, in order to keep the time the CRM is weathered to a minimum.
4) Weighing for dry mass correction has to be done in parallel with weighing for analysis.

(4) From the viewpoint of homogeneity, more than 0.5 g of CRM should be used for each analysis.

Precautions for Handling

Wear a mask, gloves, and other protective equipment during handling. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

Approximately 22 kg of hijiki seaweed was obtained from the sea near Japan and used for preparation of the CRM after polishing. The hijiki seaweed was dried at 60 °C, and then freeze pulverized. The hijiki seaweed was again dried at 60 °C, and then placed into amber glass bottles (about 20 g in each) using a splitting method. The candidate CRM was the bottles were individually vacuum sealed into seal bags (Lamizip Aluminum), and was sterilized with ^{60}Co γ-ray irradiation (about 20 kGy). The preparation of the candidate material and γ-ray irradiation were performed by KANSO Technos and Radiation Application

Development Association, respectively.

Technical Information

The CRM provides information, mass fractions for 3 kinds of arsenic compounds and 13 kinds of elements obtained in the certification process (June 2019). Dimethylarsinic acid (DMA), arsenosugar-482 and -392 were determined by HPLC-ICP-MS based on NMIJ CRM 7912-a As (V). The element concentrations were determined by calibration curve method using JCSS standard solution. Ba, Co, Cr, Ni, P, Pb and Sr were quantified by ICP-MS, and Al, Ca, Fe, K, Mg and Na were quantified by ICP-OES.

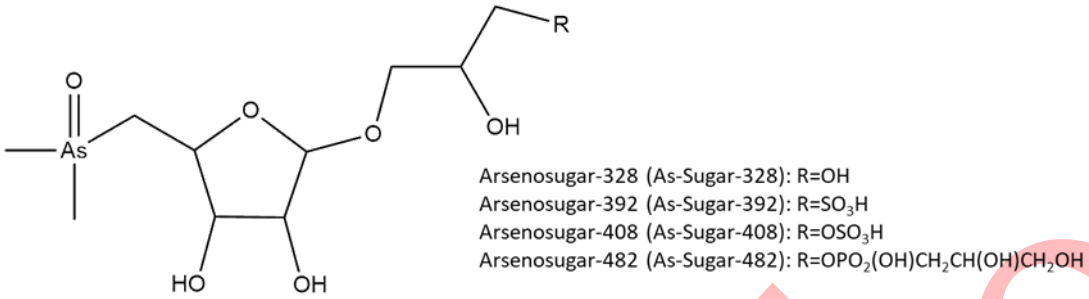
Compound	Mass fraction (mg/kg) (as As)
DMA	0.24
Arsenosugar-482 (Arsenosugar-PO_4, Molecular weight 482)	0.20
Arsenosugar-392 (Arsenosugar-SO_3, Molecular weight 392)	0.16

Element	Mass fraction (mg/kg)	Element	Mass fraction (mg/kg)
Al	310	Mg	4000
Ba	17	Na	9000
Ca	18000	Ni	3
Co	1.9	P	780
Cr	5.5	Pb	0.2
Fe	210	Sr	1600
K	36000		

The name, chemical structure and the molecular weight of arsenosugar compounds determined in the CRM are as follows.

Names of Arsenosugars in NMIJ 7405-b

Abbreviation			Name
Arsenosugar-328	Arsenosugar-OH	IUPAC	2-(2,3-dihydroxypropoxy)-5-(dimethylarsorylmethyl)oxolane-3,4-diol
		Common	3-[5'-deoxy-5'-(dimethylarsinoyl)-β-ribofuranosyloxy]propylene glyco
Arsenosugar-392	Arsenosugar-SO_3	IUPAC	3-[5-(dimethylarsorylmethyl)-3,4-dihdroxyoxolan-2-yl]oxy-2-hydroxypropane-1-sulfonic acid
		Common	3-[5'-deoxy-5'-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropanesulfonic acid
Arsenosugar-408	Arsenosugar-SO_4	IUPAC	[3-[5-(dimethylarsorylmethyl)-3,4-dihydroxyoxolan-2-yl]oxy-2-hydroxypropyl] hydrogen sulfate
		Common	3-[5'-deoxy-5'-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropyl hydrogen sulfate
Arsenosugar-482	Arsenosugar-PO_4	IUPAC	2,3-dihydroxypropyl [3-[5-(dimethylarsorylmethyl)-3,4-dihydroxyoxolan-2-yl]oxy-2-hydroxypropyl]hydrogen phosphate
		Common	3-[5'-deoxy-5'-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropyl 2,3-dihydroxypropyl hydrogen phosphate



Structural formula of arsenosugars in NMIJ 7405-b

NMIJ Analysts

The technical manager is K. Inagaki, the production manager is T. Narukawa, and the analysts are Y. Zhu, S. Miyashita, T. Ariga, M. Koguchi and I. Kudoh.

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.

Note

For the value assignment of the mass fractions of arsenosugar compounds in this CRM, the inter-laboratory study based on NMIJ-University of Graz Joint Research, “Analysis of arsenosugar compounds in Hijiki seaweed powder (2017-2018)”, was performed together with the analysis by NMIJ. The certification of arsenosugar-328 and -408 were calculated from the analytical results performed by Dr. Georg Raber of Graz University and NMIJ.

July 18, 2019

Ryoji Chubachi
President
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If you have any questions about this CRM, please contact:
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