National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7503-b
No. +++

Arsenic Compounds and Trace Elements in White Rice Flour

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 the calibration of instruments, and validation of analytical methods and instruments used for the quantification of arsenic compounds and trace elements in rice and other grains.

Certified Values

The certified values of this CRM are given in the table below. The values are expressed as a mass fraction, based on a dry mass. 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	CAS No.	Certified value, Mass fraction (mg/kg, as As)	Expanded uncertainty, Mass fraction (mg/kg, as As)
Inorganic arsenic compounds (arsenite + arsenate)	1327-53-3 (arsenite) 7778-39-4 (arsenate)	0.153	0.010
Dimethylarsinic acid	75-60-5	0.0111	0.0005

Analytical methods:

1) [Extraction method] Dry block bath / [Extract] 0.15 mol L^{-1} HNO_3 / [Extraction temperature] 100 °C / [HPLC column] CAPCELL PAK C18MG / [Measurement] HPLC-inductively coupled plasma mass spectrometry (quadruple system) (HPLC-ICP-MS)
2) [Extraction method] Dry block bath / [Extract] 0.15 mol L^{-1} HNO_3 / [Extraction temperature] 100 °C / [HPLC column] Develosil C30-UG-5 / [Measurement] HPLC-ICP-MS
3) [Extraction method] Dry block bath / [Extract] 0.05 mol L^{-1} HNO_3 / [Extraction temperature] 105 °C / [HPLC column] CAPCELL PAK C18MG / [Measurement] HPLC-ICP-MS

Element	Certified value, Mass fraction (mg/kg)	Expanded uncertainty, Mass fraction (mg/kg)	Analytical methods (see below)
Zn	25.2	0.8	1, 2, 4
Mn	8.6	0.3	2, 4, 5
Cu	4.15	0.13	1, 2, 4
Fe	3.82	0.17	1, 2, 4
Mo	1.97	0.06	1, 2, 4
Cd	0.448	0.016	1, 2, 4, 5
As	0.164	0.005	2, 3, 5

Analytical methods:

1) Isotope dilution-ICP-MS with quadruple system (ID-ICP-MS with quadruple system)
2) ICP-MS with quadruple system
3) ICP-MS with double focusing system

Sample

4) Inductively coupled plasma optical emission spectrometry
5) Graphite furnace atomic absorption spectrometry

The sample digestion method for 1) and 3) 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. Quantitative analysis of arsenic compounds was made after extraction with weak nitric acid (HNO_3) by HPLC-ICP-MS. Three different analytical methods were used, with combinations of different heating methods, levels of HNO_3 concentrations, and types of reverse-phase HPLC columns. The quantitative analysis of elements was made by the above 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 CRMs (7912-a Arsenate [As(V)] Solution and 7913-a Dimethylarsinic Acid 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

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 https://www.bipm.org/kcdb/).

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 white rice that was powdered by freeze-pulverization. The CRM is in the form of white flour, ca. 20 g in net volume is kept in an amber glass bottle.

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 bottles hierarchical-randomly sampled from 417 bottles. Each arsenic compound was determined by HPLC-ICP-MS after extraction with diluted nitric acid. Each trace element was determined by ICP-MS with quadruple system after microwave acid digestion with nitric acid, hydrofluoric acid, and hydrogen peroxide. 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) Be careful of contamination when opening the bottle, then this CRM should be used up as soon as possible. When the

Sample

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 *ca*. 1.0 g of the CRM is weighted into a weighting glass vessel.
② The CRM in the vessel is heated at 135 °C for 1.5 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.

The dry mass correction factor at the time of the certification was ca. 8.2 % (mass fraction).

(3) Care should be taken to address the following points when the CRM is weighed, since this CRM is highly hygroscopic.

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

This CRM is for laboratory use only. Take care to prevent injuries when the bottle is opened, and wear a mask, gloves, and other protective equipment during handling. Entrust disposal of this reference material to a professional waste disposal company licensed by prefectural governor. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

Approximately 30 kg of fresh brown rice was obtained from a domestic market and used for preparation of the CRM after polishing. The fresh white rice was dried at 60 °C for 8 h, and then freeze pulverized. The white rice flour was again dried at 60 °C for 8 h, 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.

NMIJ Analysts

The technical manager is INAGAKI K., the production manager is NARUKAWA T., and the analysts are ZHU Y., MIYASHITA S., ARIGA T., KOGUCHI M. and KUDO I.

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

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