National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7533-a
No. +++

Arsenic Compounds and Trace Elements in Brown 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 in controlling the precision of analysis, and validating analytical methods and instruments, during the analysis of arsenic compounds and trace elements in rice and other grains.

Certified Values

The certified values for inorganic arsenic compounds, including arsenite and arsenate, dimethylarsinic acid, and eight elements (Mg, Ca, Mn, Fe, Cu, Zn, As, and Cd) in this CRM, are given in the tables 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	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)	0.530	0.016
Dimethylarsinic acid	75-60-5	0.092	0.004

Element	Certified value Mass fraction (mg/kg)	Expanded uncertainty Mass fraction (mg/kg)	Analytical methods (see below)
Mg	1375	19	2, 3, 4, 5
Ca	104.2	1.8	2, 3, 4, 5
Mn	23.7	0.4	2, 3, 4, 6
Fe	13.6	0.3	1, 2, 4
Cu	4.29	0.07	1, 2, 4
Zn	29.2	0.8	1, 2, 4
As	0.63	0.02	2, 3, 6
Cd	0.273	0.007	1, 2, 4

Analytical methods:

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

The sample digestion method for 1) and 3) was microwave acid digestion with nitric acid, hydrofluoric acid, and perchloric acid. The digestion method for all others was microwave acid digestion with nitric acid, hydrofluoric acid, and hydrogen peroxide.

Analysis

The certified value of this CRM was the weighed mean of the results from two or more analytical methods conducted at NMIJ. The 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 with weak nitric acid by high-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Four different analytical methods were used, with combinations of different heating methods, levels of nitric acid concentrations, and types of reverse-phase HPLC columns. The quantitative analysis of elements was made using the aforementioned analytical methods, 1) to 6), 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 the standard solution, and (e) the sample homogeneity.

Metrological Traceability

Each certified value was determined by the primary method (ID-ICP-MS), or other accurate reference methods, with NMIJ CRMs (7912-a Arsenate [As(V)] Solution and 7913-a Dimethylarsinic Acid Solution) and JCSS (Japan Calibration Service System) standard solutions. The certified values, therefore, are traceable to the International System of Units (SI). All sample preparation was carried out by a 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 https://kcdb.bipm.org/AppendixC/default.asp).

Expiration of Certification

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

Sample Form

This CRM was prepared from brown rice that has been powdered by freeze-pulverization. The CRM is in the form of light brown flour, which is placed into amber glass bottles (about 20 g in each). The glass bottle is sealed in a plastic bag.

Homogeneity

The homogeneity of this CRM was determined by analyzing 10 bottles from a hierarchically random sampling of 1000 bottles. Each arsenic compound was determined by HPLC-ICP-MS after extraction with weak nitric acid. Each element was determined by ICP-MS after microwave acid digestion with nitric acid, hydrofluoric acid, and hydrogen peroxide. The inhomogeneity of the analytes, 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 in a clean place at temperatures of 5 °C to 35 °C and protected 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 this 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 procedure shown below. Do not use the

sample that is used for the correction for analysis.

(1) Take *ca.* 0.5 g of the CRM in a weighing glass vessel.
(2) Dry the CRM in the vessel 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.* 9.0 % (mass fraction).

3) Care should be taken to address the following points when this CRM is weighed.
(1) Do not weigh it 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 it is not in use, in order to keep to a minimum the time the CRM is weathered.
(4) Weighing for dry mass correction must 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, and is not edible. Wear a protective mask and gloves when handling. Obey relevant law regarding waste disposal. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

Approximately 30 kg of fresh brown rice, for which the average Cd concentration was confirmed to be in a range of 0.2 mg/kg to 0.4 mg/kg, was obtained from a domestic market and used for preparation of this CRM. The fresh brown rice was dried at 60 °C for 8 h, and then freeze pulverized. The brown 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 bottles were individually vacuum sealed into seal bags (Lamizip Aluminum). Finally, the candidate CRM was sterilized with ^{60}Co γ-ray irradiation (about 20 kGy).

NMIJ Analysts

The technical manager for this CRM is INAGAKI K., the production manager is MIYASHITA S., and the analysts are MIYASHITA S., NARUKAWA T., E. VALLE-MOYA,* ZHU Y., KOGUCHI M., and KUDO I.

* Centro Nacional de Metrologia (CENAM)

Information

If substantive technical changes occur that affect the certification before the expiration of this certificate, NMIJ will notify the registered customers. 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

This CRM was developed within "Specific program: Toxic metals in unpolished rice: version 13 Dec. 2011" under the MoU signed with Centro Nacional de Metrologia (CENAM) on metrology and measurement standards for 2011 to 2015. The participants from CENAM for the program were Ms. Maria del Rocio Arvizu Torres and Ms. Edith Valle-Moya. Ms. Edith Valle-Moya participated in developing this CRM as one of the analysts.

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
December 18, 2019: The description in "Expiration of Certification" was changed to "one year from the date of shipment."