National Institute of Advanced Industrial Science and Technology

# National Metrology Institute of Japan

## Reference Material Certificate

NMIJ CRM 7532-a
No. +++

National Institute of Advanced Industrial Science and Technology
AIST

## Arsenic Compounds and Trace Elements in Brown Rice Flour

This certified reference material (CRM) was produced in accordance with NMIJ's management system, and in compliance with ISO GUIDE 34:2009 and ISO/IEC 17025:2005. It is intended for use in controlling the precision of analysis, or confirming the validity of analytical methods or 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 following tables. The values are expressed as a mass fraction, based on a dry mass (the drying procedure is given in this certificate). The quoted uncertainty 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) | 0.298 | 0.008 |
| Dimethylarsinic acid | 75-60-5 | 0.0186 | 0.0008 |

| Element | Certified value, Mass fraction (mg/kg) | Expanded uncertainty, Mass fraction (mg/kg) | Analytical methods (see below) |
|---|---|---|---|
| Mg | 1310 | 29 | 2, 3, 4 |
| Ca | 113.6 | 3.4 | 2, 3, 4 |
| Mn | 27.6 | 0.5 | 2, 3, 4, 5 |
| Fe | 12.4 | 0.4 | 1, 2, 4 |
| Cu | 4.07 | 0.10 | 1, 2, 4 |
| Zn | 29.2 | 1.2 | 1, 2, 4 |
| As | 0.320 | 0.010 | 2, 3, 5 |
| Cd | 0.429 | 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) 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 conducted at NMIJ. Quantitative analysis of arsenic compounds was made after extraction with weak nitric acid ($HNO_3$) by high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Five 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 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 CRMs (7912-a Arsenate [As(V)] Solution and 7913-a Dimethylarsinic Acid Solution) and JCSS (Japan Calibration Service System) standard solutions, and all 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) 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 (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 remains unopened and stored in accordance with the instructions given in this certificate.

**Sample Form**

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

**Homogeneity**

The homogeneity of the CRM was determined by analyzing 10 bottles from a hierarchically random sampling of 640 bottles. Each arsenic compound was determined by HPLC-ICP-MS after extraction with weak nitric acid. Each trace 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, 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.

**Precautions for Storage**

This CRM should be kept in a clean place at 5 °C to 30 °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:
   1) Take ~ 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.
5) Do not use the sample that is used for the correction for analysis.

The dry mass correction factor at the time of the certification was ~ 7.1 % (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.

**Instructions for Handling**

This CRM is for laboratory use only, and is not edible. Care should be taken to prevent injuries when the bottle is opened, and a protective mask and gloves should be worn for safety when the CRM is used. All relevant laws regarding waste handling and management must be obeyed when the CRM is disposed of.

**Preparation Method**

Approximately 30 kg of fresh brown rice, for which the average Cd concentration and coefficient of variation (homogeneity) were confirmed to be in a range of 0.3 mg/kg to 0.4 mg/kg and ≤ 15 % ($n$ = 6), respectively, was obtained from a domestic market and used for preparation of the 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 (~ 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 (~ 20 kGy).

**NMIJ Analysts**

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

**Technical Information**

Customer registration on the NMIJ WEB site shown below will facilitate notification of any revision of the information contained above. Technical reports regarding this CRM can be also obtained from the contact details shown below.

**Reproduction of Certificate**

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

January 8, 2014

Ryoji Chubachi
President
National Institute of Advanced Industrial Science and Technology

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