National Institute of Advanced Industrial Science and Technology
National Metrology Institute of Japan

Reference Material Certificate
NMJ CRM 7502-a
No. +++

Trace Elements in White Rice Flour (Cd Level II)

This certified reference material (CRM) was produced in accordance with NMJ’s management system, and in compliance with ISO GUIDE 34:2009 and ISO/IEC 17025:2005. This CRM 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 18 trace elements, inorganic arsenic compounds (total amount of arsenite and arsenate), and dimethylarsinic acid in this CRM are given in the following table. The values are expressed in mass fractions based on 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%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified value, Mass fraction (mg/kg)</th>
<th>Expanded uncertainty, Mass fraction (mg/kg)</th>
<th>Analytical methods (see below)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.075</td>
<td>0.013</td>
<td>2, 3</td>
</tr>
<tr>
<td>Mn</td>
<td>11.2</td>
<td>0.4</td>
<td>3, 5, 6</td>
</tr>
<tr>
<td>Fe</td>
<td>4.48</td>
<td>0.20</td>
<td>1, 3, 5, 6</td>
</tr>
<tr>
<td>Ni</td>
<td>0.390</td>
<td>0.022</td>
<td>1, 3</td>
</tr>
<tr>
<td>Cu</td>
<td>3.02</td>
<td>0.11</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>Zn</td>
<td>26.0</td>
<td>0.9</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>As</td>
<td>0.109</td>
<td>0.005</td>
<td>3, 4, 6</td>
</tr>
<tr>
<td>Rb</td>
<td>1.77</td>
<td>0.07</td>
<td>1, 3</td>
</tr>
<tr>
<td>Sr</td>
<td>0.068</td>
<td>0.003</td>
<td>1, 3</td>
</tr>
<tr>
<td>Mo</td>
<td>0.79</td>
<td>0.03</td>
<td>1, 3</td>
</tr>
<tr>
<td>Cd</td>
<td>0.548</td>
<td>0.020</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>Ba</td>
<td>0.137</td>
<td>0.005</td>
<td>1, 3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0043</td>
<td>0.0006</td>
<td>2, 3</td>
</tr>
<tr>
<td>Na</td>
<td>5.8</td>
<td>0.8</td>
<td>5, 7, 8</td>
</tr>
<tr>
<td>Mg</td>
<td>560</td>
<td>21</td>
<td>3, 5, 7</td>
</tr>
<tr>
<td>P</td>
<td>1800</td>
<td>90</td>
<td>3, 4, 5</td>
</tr>
<tr>
<td>K</td>
<td>1430</td>
<td>50</td>
<td>5, 7, 8</td>
</tr>
<tr>
<td>Ca</td>
<td>60</td>
<td>3</td>
<td>3, 5, 8</td>
</tr>
</tbody>
</table>

Analytical methods:
1) Isotope dilution-inductively coupled plasma mass spectrometry (ID-ICP-MS)
2) ID-high-resolution ICP-MS
3) ICP-MS
4) High-resolution ICP-MS
5) ICP-optical emission spectrometry (ICP-OES)
6) Graphite furnace atomization atomic absorption spectrometry (GFAAS)
7) Flame-AAS
8) Flame photometry
(Microwave acid digestion or dry-ashing was performed for a sample pretreatment)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS No.</th>
<th>Certified value, Mass fraction (mg/kg)</th>
<th>Expanded uncertainty Mass fraction (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic arsenic compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(arsenite + arsenate)</td>
<td>1327-53-3 (arsenite)</td>
<td>0.098</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>7778-39-4 (arsenate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethylarsinic acid</td>
<td>75-60-5</td>
<td>0.0129</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

Analytical method: Heat extraction/high-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS)

9. [Extraction method] Dry block bath/[Extract] 0.15 mol L⁻¹ HNO₃/[Extraction temperature] 100 °C/[HPLC column]
   CAPCELL PAK C18MG/[Measurement] High-performance liquid chromatography-inductively coupled plasma mass spectrometry
10. [Extraction method] Dry block bath/[Extract] 0.15 mol L⁻¹ HNO₃/[Extraction temperature] 100 °C/[HPLC column]
    Shim-pack VP-C8/[Measurement] High-performance liquid chromatography-inductively coupled plasma mass spectrometry
11. [Extraction method] Dry block bath/[Extract] 0.0015 mol L⁻¹ HNO₃/[Extraction temperature] 100 °C/[HPLC column]
    CAPCELL PAK C18MG/[Measurement] High-performance liquid chromatography-inductively coupled plasma mass spectrometry

Analysis
The certified values of this CRM are the weighted means of the results from two or more analytical methods conducted at NMIJ. The quantitative analysis of elements was made by the aforementioned analytical methods (1)–8), 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 quantitative analysis of arsenic compounds was made after extraction with weak nitric acid (HNO₃) by HPLC-ICP-MS. Three different analytical methods were used with combinations of levels of HNO₃ concentrations and types of reverse-phase HPLC columns.

The expanded uncertainty of each certified value is equal to \( U = k u_c \), 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 JCSS (Japan Calibration Service System) standard solutions and NMIJ CRMs (NMIJ CRM 7912-a arsenate [As(V)] solution and NMIJ CRM 7913-a dimethylarsinic acid solution), and all are traceable to the International System of Units (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 (for Appendix C of the MRA see http://kcdb.bipm.org/AppendixC/default.asp).

Expiration of Certification
The certificate is valid from the data of shipment to March 31, 2023, provided that the material remains unopened and stored in
Sample Form
This CRM was prepared from rice that was powdered by freeze-pulverization after polishing. This CRM is white flour in an amber glass bottle (20 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 was determined by ICP-MS or ICP-OES after microwave acid digestion. Each arsenic compound was determined by HPLC-ICP-MS after extraction with weak nitric acid. 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 kept in a clean place at 5 °C to 35 °C and shielded from light.

Instructions for Use
1) Take care to prevent contamination of the CRM when opening the bottle and use up the CRM immediately.
2) Dry mass correction is required when the CRM is analyzed. The correction factor is obtained by the following procedure:
   (1) Weigh ca. 0.5 g of the CRM into a weighing glass vessel and then heat it at 95 °C for 12–16 h.
   (2) Weigh the CRM with the vessel after cooling in a desiccator.
   The difference in the mass before and after drying is assumed to be the moisture content. The dry mass correction factor at the time of the certification was ca. 10.5 %. Do not use the sample that was used for the correction for analysis.
3) Note the following points when the CRM is weighed:
   (1) Do not weigh in a high humidity conditions (over 60%).
   (2) Weighing must be done as quickly as possible.
   (3) Do not keep the bottle open.
   (4) Dry mass correction must be done for every analysis.
4) From the homogeneity, more than 0.5 g for the analysis of trace elements and arsenic compounds.

Precautions for Handling
This CRM is for laboratory use only. Care should be taken to prevent injuries when the bottle is opened. Use a protective mask and gloves for safety when this CRM is used. All relevant laws regarding waste handling and management must be obeyed when disposing of this CRM.

Preparation Method
This CRM was prepared from polished rice. The rice was powdered by freeze-pulverization. The powder was placed into amber glass bottles (20 g each) by using a split method and sterilized with γ-ray irradiation (60Co, 20 kGy). The bottles were sealed individually in polypropylene packages and stored at room temperature. 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 K. Chiba, the production manager is K. Inagaki, and the analysts are K. Inagaki, T. Narukawa, Y. Zhu, Y. Jinbo, and I. Narushima.

Technical Information
Customer registration on the NMIJ Website (given below) will facilitate notification of any revision of the information given above. 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.

Additional statement
This CRM was developed based upon completion of a project supported by the SME Intellectual Foundation Construction Project of Ministry of Economy 2006-2007, Trade and Industry, Japan.

April 1, 2015

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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Revision history
January 7, 2015: The certified values of inorganic arsenic compounds (arsenite + arsenate) and dimethylarsinic acid were added.
January 7, 2015: The description on Mutual Recognition Arrangement (CIPM MRA) was added.
April 1, 2015: "Metrology Management Center" was renamed to "Center for Quality Management of Metrology."