

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 7406-a
No. +++

Trace Elements in Squid Powder

This certified reference material (CRM) was 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 controlling the precision of analysis and validating analytical methods and instruments during the quantification of trace elements in squid and cephalopod matrix samples.

Certified Values

The certified values for 10 trace elements 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 %.

Element	Certified value, Mass fraction (mg/kg)	Expanded uncertainty Mass fraction (mg/kg)	Analytical methods (see below)
P	12500	300	1), 3), 5)
Mg	2500	60	1), 5), 7)
Ca	614	18	1), 5), 7), 8)
Zn	68.4	1.2	1), 2), 5)
Cu	11.3	0.2	1), 2), 5), 6)
Sr	8.64	0.12	1), 2), 5), 6)
As	8.34	0.19	1), 3), 5), 6)
Fe	6.0	0.2	1), 2), 5), 6)
Mn	0.757	0.015	1), 3), 6)
Cd	0.390	0.007	1), 2), 4), 5), 6)

Analytical Methods

- 1) Inductively coupled plasma mass spectrometry (ICP-MS)
- 2) Isotope dilution-inductively coupled plasma mass spectrometry (ID-ICP-MS)
- 3) High resolution ICP-MS (HR-ICP-MS)
- 4) Isotope dilution-HR-ICP-MS (ID-HR-ICP-MS)
- 5) ICP optical emission spectrometry (ICP-OES)
- 6) Graphite furnace atomic absorption spectrometry (GFAAS)
- 7) Flame atomic absorption spectrometry
- 8) Flame photometry

For 1), 3), and 5) to 8) microwave-assisted digestion with HNO₃-HF-H₂O₂ was performed as a sample pretreatment. For 2), and 4) microwave assisted digestion with HNO₃-HF-HClO₄ was performed for a sample pretreatment.

Analysis

The certified values of this CRM are the weighted means of the results from three or more analytical methods conducted at NMIJ. The quantitative analysis of elements was made using the aforementioned analytical methods, 1) to 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 expanded uncertainty in 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 between-pretreatment variance, (d) the dry mass correction, (e) the concentration of the standard solution, and (f) the sample homogeneity.

Metrological Traceability

The certified values were determined by the isotope dilution mass spectrometry, or other accurate methods, with JCSS (Japan Calibration Service System) standard solutions and all are traceable to the International System of Units (SI). All the working standards and sample solutions were prepared by a gravimetric method, using a balance calibrated by JCSS.

Expiration of Certification

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

Sample Form

This CRM is in the form of a squid powder produced by freeze-dry and freeze-pulverization. This CRM of *ca.* 30 g in net volume is kept in an amber glass bottle. The bottle is sealed in an aluminum-laminated plastic bag.

Homogeneity

The homogeneity of this CRM was determined by analyzing 10 bottles hierarchical-randomly sampled from 416 bottles. Each trace element was determined by ICP-MS or ICP-OES after microwave-assisted acid digestion. 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 uncertainty of the certified values.

Instructions for Storage

This CRM should be stored at a temperature between 5 °C and 35 °C in a clean place and shielded from light.

Instructions for Use

- (1) This CRM should be 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) A dry mass correction is required when the CRM is analyzed, as the certified values are expressed as mass fractions based on the dry mass. The correction factor should be obtained by the following procedure:
 - 1) *ca.* 1.0 g of the CRM is weighed into a glass weighing 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.
 - 5) Do not use the sample that is used for the correction for analysis.
The dry mass correction factor at the time of certification was *ca.* 6.7 % (mass fraction).
- (3) Care should be taken to address the following points when the 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 minimize the time the CRM is exposed to the atmosphere.
 - 4) Weighing for the dry mass correction has to be carried out in parallel with weighing for analysis.
- (4) From the viewpoint of homogeneity, more than 0.5 g of the CRM should be used for each analysis.

Precautions for Handling

This CRM is for laboratory use only. Take care to prevent injury when opening the bottle. When using CRM, wear protective masks and gloves for safety. All relevant laws regarding waste handling and management must be obeyed when the CRM is disposed of. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

This CRM was prepared from squids (*Heterololigo bleekeri*) with guts removed. The squid was freeze-dried and powdered by freeze-pulverization. The powder was placed in amber glass bottles (ca. 30 g each) using a split method and was sterilized with ^{60}Co γ -ray irradiation (about 20 kGy). The bottles were individually vacuum sealed into aluminum-laminated plastic bags. Preparation of the candidate material and γ -ray irradiation was performed by KANSO Technos and Radiation Application Development Association, respectively.

NMIJ Analysts

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

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

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