

Certificate of Analysis

CERTIFIED REFERENCE MATERIAL HRM – 2003A

Arsenic, Cadmium, Calcium and Lead in Mushroom Powder

Batch Number

STY-0011-001

Description

The certified reference material (CRM) was prepared from a batch of mushroom powder purchased in Singapore. The powdery material was found to contain appropriate levels of As, Cd, Ca and Pb. The material was first sifted through a 200 μm sieve and homogenised using a mixer for a period of about 10 days. The material (25 g) was then packed in a pre-cleaned amber glass bottle and flushed with nitrogen before capping. The bottled samples were disinfected with γ -irradiation at about 5 kGy¹.

The reference material was produced with reference to the requirements set out in ISO/IEC 17025:2017 [1], ISO 17034:2016 [2] and ISO Guide 35:2017 [3].

Certified Mass Fraction Values

A certified value is a value for which a laboratory has the highest confidence in its accuracy, in that all known or suspected sources of biases have been investigated and accounted for. The certified mass fraction values for the four elements in the CRM are listed below. The certified mass fraction values for Cd and Pb were determined by inductively coupled plasma high resolution mass spectrometer using isotope dilution mass spectrometry (ICP-HR-IDMS) [4]. The certified mass fraction value for As was determined by inductively coupled plasma high resolution mass spectrometer (ICP-HR-MS) using standard addition method. The certified mass fraction value for Ca was determined by inductively coupled plasma optical emission spectrometer (ICP-OES) using standard addition method.

	Mass fraction	Unit
Arsenic	5.61 $\pm$ 0.59	mg/kg
Cadmium	1.191 $\pm$ 0.079	mg/kg
Calcium	1.444 $\pm$ 0.099	mg/g
Lead	5.23 $\pm$ 0.94	mg/kg

The mass fraction value is expressed as the certified value $\pm$ the expanded uncertainty.

The uncertainty listed with the certified value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95% confidence). The certified value has an associated

¹ The irradiation work was performed by a subcontractor.

measurement uncertainty attributed to uncertainty contribution from characterisation of the material (u_{char}) and uncertainty in the homogeneity of the material (u_{bb}). The u_{char} was evaluated by combining uncertainties from method precision, the concentration of calibration solution, weighing, moisture content, and different ion pairs used (for Cd and Pb), in accordance with ISO/IEC Guide 98-3:2008 [5].

Homogeneity

Homogeneity testing on the analytes in the material was performed on one sub-sample taken from ten bottles and five sub-samples taken from one bottle using external calibration method by ICP-MS. The sample size taken for homogeneity testing was about 0.2 g. The material was found to be sufficiently homogeneous. The u_{bb} was evaluated from the uncertainty due to between-bottle inhomogeneity.

Stability

Short-term stability testing on the analytes in the material at 40 °C (maximum allowable transportation temperature) showed that they were stable over up to 14 days.

The long-term stability of the analytes at storage temperature (18 °C to 25 °C) was evaluated on three occasions over a period of up to 2 months after preparation. The results showed that the analytes were stable over the study period. The uncertainty contribution from long-term stability (u_{stab}) was covered by the method precision component of u_{char} and no additional factor was included in the overall uncertainty.

Validity of Certified Mass Fraction Values

The certified mass fraction values are valid within its measurement uncertainty until **30 Nov 2027**, provided that the CRM is subjected to the same handling and storage conditions as stated in this Certificate of Analysis (COA).

The CRM will be continuously monitored during the validity period to determine if any substantive change to the certified values has occurred. If necessary, its user will be advised if the CRM can continue to be used or an updated COA may be issued.

Analytical Methods

The certified mass fractions of Cd and Pb in the material were determined by exact-matching ICP-HR-IDMS. Standard reference materials from NIST (Product No. SRM3108 for Cd and SRM3128 for Pb) were used as calibration standards for IDMS measurements. Enriched isotopes ^{111}Cd and ^{208}Pb from Oak Ridge National Laboratory were used as the internal standards. The calibration blends were prepared gravimetrically by mixing appropriate amount of calibration standard solutions and internal standard solutions. The sample blends were prepared by spiking appropriate amount of internal standard into the material. Quality control blends were also prepared and analysed concurrently. Both sample and quality control blends were subjected to microwave acid digestion using 5 mL HNO_3 , 0.4 mL HF and 2 mL H_2O_2 to give a clear digest.

The certified mass fraction of As was determined by ICP-HR-MS using standard addition method. Ga standard reference material from NIST (Product No. SRM3119a) was added to the sample digest as internal standard. Different amounts of As standard reference material from NIST (Product No. SRM3103a) were then spiked into the sample digest to produce sample blends. Quality control blends were also prepared and analysed concurrently.

The certified mass fraction of Ca was determined by ICP-OES using standard addition method. Different amounts of standard working solution prepared from NIST's Ca standard reference material (Product No. SRM3109a) were spiked into the material to produce sample blends. Quality control blends were also prepared and analysed concurrently.

Metrological Traceability

The certified mass fraction values are traceable to the International System of Units (SI) through the use of standard reference materials from NIST.

Intended Use

For the validation of methods or as quality controls used to determine the mass fraction of As, Cd, Ca and Pb in botanical materials, and materials of similar matrix.

Instruction for Use

Prior to use, the material should be thoroughly mixed by shaking the bottle prior to opening. After use, the bottle should be re-capped, sealed with Parafilm and stored at storage temperature. If results differ from certified value in subsequent sampling, customers are advised to purchase a new CRM. To reduce moisture absorption, weighing needs to be performed as quickly as possible and the amber glass bottle should not be left open after sampling. The minimum sample size for each use should be about 0.2 g. A correction for dry mass should be made by taking 1.0 g of sample and drying over anhydrous calcium sulphate (e.g. DRIERITE®) in a desiccator at room temperature for a minimum of 10 days until constant mass. Dry mass correction and sample analysis should be carried out at the same time. The moisture content at the time of certification was ca. 7.7 %.

Storage

The material should be stored at 18 °C to 25 °C in its original bottle. Exposure to direct intense light and ultraviolet radiation should be avoided.

Safety Precautions for Users

Treat the material as hazardous substance. Use appropriate work practices when handling the material, in order to avoid skin or eye contact or ingestion.

Further Information

Please direct all enquiries regarding this CRM to the contact provided in this COA.

References

1. ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories.
2. ISO 17034:2016 General requirements for the competence of reference material producers.
3. ISO Guide 35:2017 Reference materials – Guidance for characterisation and assessment for homogeneity and stability.
4. Sargent, M.; Harrington, C.; Harte, R.; *Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry*, RSC Publishing, 2002.
5. ISO/IEC Guide 98-3:2008 Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM:1995).

Certificate Revision Records

Certificate Ref. No.	Date of issue	Reason for issuance
CML-HRM2003A/01	1 Dec 2012	Issuance of first certificate
CML-HRM2003A/02	1 Jul 2014	Extension of expiry date
CML-HRM2003A/03	12 Nov 2015	Extension of expiry date
CML-HRM2003A/04	1 Nov 2017	Extension of expiry date
CML-HRM2003A/05	22 Oct 2019	Extension of expiry date
CML-HRM2003A/06	14 Oct 2021	Extension of expiry date
CML-HRM-2003A/07	6 Nov 2024	Extension of expiry date

Note

HSA does not assume any liability with respect to any loss caused by improper use and/or storage of the CRM by the customer.

A handwritten signature in black ink, appearing to read 'Dr Teo Tang Lin', written over a horizontal line.

Dr Teo Tang Lin
Division Director
Chemical Metrology Laboratory
Chemical Metrology Division