National Research Council Canada | Conseil national de recherches Canada

Certificate of Analysis

Certified Reference Material

ROCA-1

Cacao Powder Certified Reference Material for Trace Metals and Carbon Isotope Delta

ROCA-1 is a cacao powder Certified Reference Material (CRM) produced by the National Research Council of Canada (NRC) with values on toxic elements and carbon isotope delta. Each unit of ROCA-1 consists of approximately fifteen (15) grams of homogenized cacao powder packaged in an amber glass vial and sealed within a trilaminate foil pouch. This material is primarily intended for use in method development, validation, and quality control for the determination of toxic elements (arsenic, cadmium, lead and mercury) and carbon isotope delta in cacao powder and similar matrices.

Table 1 shows the certified and reference values established for the mass fraction of toxic elements expressed on a dry mass basis and the certified carbon isotope delta value on the Vienna Peedee Belemnite (VPDB) and VPDB-LSVEC (lithium carbonate prepared by H. J. Svec) carbon isotope delta scales [1]. The expanded uncertainties associated with those values were calculated according to the JCGM Guide [2] and correspond to approx. 95 % confidence (k = 2).

Table 1: **Quantity values and expanded uncertainties (k = 2) for ROCA-1**

Analyte	Quantity	Value	Type of value
arsenic (b)*	mass fraction	0.022 ± 0.004 mg/kg	certified
cadmium (a,b)*	mass fraction	0.137 ± 0.014 mg/kg	certified
lead (a,b)*	mass fraction	0.084 ± 0.010 mg/kg	certified
mercury (c)*	mass fraction	0.0039 ± 0.0006 mg/kg	reference
$^{13}C/^{12}C$ (d)	isotope delta vs VPDB-LSVEC	−30.50 ± 0.06 ‰	certified
$^{13}C/^{12}C$ (d)	isotope delta vs VPDB	−30.37 ± 0.06 ‰	certified

Refer to the sections below for additional explanations
*expressed on a dry mass basis

Period of validity: until February 2030
Storage conditions: at approximately −20°C or below under typical freezer conditions

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Intended use

ROCA-1 is primarily intended for use in method development, validation, and quality control for the determination of arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and carbon isotope delta values in cacao powder and similar matrices.

Preparation of material

This certified reference material was produced from commercially available cacao powder. The material was sieved through an 850 µm nylon screen, thoroughly blended and bottled into amber glass vials. Following bottling, the material was sterilized by subjecting it to a minimum gamma irradiation dose of 25 kGy.

Characterization of material

The explanatory list of letters next to each compound (Table 1) refers to the instrumental method used for measurements:

a) Isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS) [3]
b) Standard addition inductively-coupled plasma mass spectrometry (SA-ICP-MS)
c) Thermal decomposition atomic absorption spectrometry (TD-AAS)
d) Elemental analysis - isotope ratio mass spectrometry (EA-IRMS)

ROCA-1 was also used in the SIM supplementary comparison, SIM.QM-S18, *Natural toxic elements (Cd, Pb) in cacao powder* [4]. The certified values presented here are in good agreement with the results reported by the fourteen National Metrology Institutes that participated in the comparison.

Metrological traceability

The mass fractions of toxic elements presented in this certificate are traceable to the International System of Units (SI) through gravimetrically prepared standards of established purity and international measurement intercomparisons.

The *Comité international des poids et mesures* (CIPM) has noted that isotope delta measurements that cannot be traceable to the SI should be made traceable to materials recognized as international standards by the IUPAC Commission on Isotopic Abundances and Atomic Weights [5,6]. The carbon isotope delta value in ROCA-1 is traceable to the internationally recognized reference materials listed in Table 1 of Chartrand *et. al.* [7] (with the exception of NBS 19, which was not employed).

As such, ROCA-1 serves as suitable reference material for use in laboratory quality assurance programs, as outlined in ISO/IEC 17025.

Homogeneity

The material was tested for homogeneity at the NRC using ICP-MS for As, Cd and Pb, TD-AAS for Hg, and IRMS for carbon isotope delta measurements. Results from sub-samples of randomly selected bottles, representing the entire production batch, were evaluated using Bayesian analysis of variance (BANOVA) [8]. The uncertainty due to homogeneity was evaluated using Bayesian random effects model and is included in the uncertainty budget.

Stability

ROCA-1 stability was assessed and deemed to be both physically and chemically stable during transport and long-term storage for all measurands.

The transportation stability was carried out using an isochronous approach under elevated temperature conditions (+40°C) for at least 6 weeks, accounting for possible shipping delays, while long-term stability was evaluated for over one year.

In addition, NRC food-related CRMs with similar or higher fat content level have been periodically analyzed for more than fifteen years at NRC and have demonstrated both physically and chemical stability over this period with respect to trace metals concentrations. We expect similar results for ROCA-1. Uncertainty components for transport and long-term stability were considered negligible and are set to zero.

Uncertainty

The expanded uncertainty (U) for all values is equal to $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the Joint Committee for Guides in Metrology (JCGM) [2] and k is the coverage factor. A coverage factor of $k = 2$ was applied which corresponds to a level of confidence of approximately 95 %.

All reasonable sources of uncertainty related to the certified and reference values in Table 1 were considered. Included in the combined uncertainty estimate are uncertainties in the batch characterization, uncertainties related to possible between-unit variation and uncertainties related to inconsistency between the various measurement methods [9].

Storage

The material should be stored in its original vial at approximately −20 °C or below under typical freezer conditions.

Instructions for handling and use

Prior to use, the vial shall be thawed and allowed to equilibrate to room temperature. Before opening, the vial contents shall be thoroughly mixed to ensure homogeneity. It is recommended that the vial be opened only in a clean environment. Following sampling, the vial shall be immediately tightly closed, then sealed in a trilaminate foil pouch to minimize the risk of contamination or moisture uptake. The material shall subsequently be stored under the conditions specified in the storage instruction.

Repeated sub-sampling is permitted, provided that appropriate precautions are taken to prevent contamination and preserve the integrity of the material. The certified values are based on a minimum sub-sample mass of 250 mg for arsenic (As), cadmium (Cd) and lead (Pb), 75 mg for mercury (Hg) and 0.9 mg for carbon isotope delta. Users are responsible for ensuring that sub-sampling below the recommended sample masses and the use of alternative storage procedures do not impact the integrity or validity of the certified values.

Instructions for drying

Determination of dry mass should be performed on a separate sample to avoid contamination. For this purpose, a representative sample aliquot shall be dried to a constant mass in a desiccator over anhydrous calcium sulphate or magnesium perchlorate. The sample should remain in the desiccator for a minimum of 10 days or until constant mass is achieved. The estimated moisture content of ROCA-1 is approximately 4.0 %.

Health and safety information

Only qualified personnel should handle the material and appropriate disposal methods should be used. A Safety Data Sheet (SDS) is available at doi.org/10.4224/crm.2026.roca-1. For laboratory use only; not for human consumption, therapeutic, drug, household, or any other uses.

Period of validity

The certified and reference values are valid until February 2030, provided the storage and instructions for handling and use specified in this certificate are followed.

Quality Management System

The NRC is Canada's National Metrology Institute (NMI) and is a signatory of the International Committee for Weights and Measures Mutual Recognition Arrangement (CIPM MRA). The CIPM MRA was developed in a response to a growing need for an open, transparent, and comprehensive scheme to give users reliable quantitative information on the comparability of national metrology services and to provide the technical basis for wider agreements negotiated for international trade, commerce, and regulatory affairs. Our Quality Management System for measurement services and certified reference materials conforms to the requirements of ISO/IEC 17025 and ISO 17034.

The Calibration and Measurement Capabilities (CMC) supporting the results in Table 1 are listed in the International Bureau of Weights and Measures (BIPM) Key Comparison Database (https://www.bipm.org/kcdb/) which recognizes the validity of the measurements performed by NMIs participating in the CIPM MRA. The NRC has the following CMCs relevant for this material: measurements applied for determining certified values of As (SIM-QM-CA-000001E8-1), Cd (SIM-QM-CA-000001EA-1), and Pb (SIM-QM-CA-000001EG-1) in food matrices, and for carbon isotope delta (SIM-QM-CA-00000O95-1) in organic compounds.

Description of terms

Certified values are those for which the NRC has the highest confidence and that all known and suspected sources of bias have been considered by the NRC and are reflected in the stated expanded uncertainties.

Reference values are those for which not all uncertainty contributions may have been fully investigated or metrological traceability has not been fully established by the NRC.

Supplemental information

Bibliographic information and any additional technical supplemental information are available at doi.org/10.4224/crm.2026.roca-1 .

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This certificate is only valid if the corresponding material was obtained directly from the NRC or an authorized reseller. Users should ensure that the certificate they have is current. For updates, please refer to doi.org/10.4224/crm.2026.roca-1.

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