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Certificate of Analysis

CERTIFIED REFERENCE MATERIAL
HRM – 2008B

Cadmium, Lead, Arsenic and Arsenic Species in Apple Juice

Batch Number
STY-0059-002

Description
The certified reference material (CRM) was produced from apple juice spiked with standard solutions of cadmium (Cd), lead (Pb), arsenic (As) and As species, which include dimethylarsinic acid (DMAA), arsenite [As(III)] and arsenate [As(V)]. The material (100 mL) is bottled in a high-density polyethylene (HDPE) bottle and contains benzoic acid and methyl paraben as a preservative.

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 elements and As species in the CRM are listed below. The certified mass fraction values for Cd and Pb were determined by inductively coupled plasma mass spectrometer using isotope dilution mass spectrometry (ICP-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 values for As species were determined by high performance liquid chromatography inductively coupled plasma mass spectrometer (HPLC-ICP-MS) using standard addition method.

	Certified Mass Fraction	Unit	*k*
Cadmium	0.259 ± 0.012	mg/kg	2.00
Lead	0.306 ± 0.018	mg/kg	2.00
Arsenic	0.2976 ± 0.0098	mg/kg	2.00

	Certified Mass Fraction as As	Unit	*k*
Dimethylarsinic acid	0.143 ± 0.018	mg/kg	2.45
Inorganic arsenic compounds (arsenite + arsenate)	0.159 ± 0.017	mg/kg	2.00

The mass fraction value is expressed as the certified value ± the expanded uncertainty.

The uncertainty listed with the certified value is an expanded uncertainty about the mean, with coverage factor, *k*, corresponding to approximately 95% confidence. The certified value has an associated measurement uncertainty attributed to uncertainty contribution from characterisation of the material (u_{char}), uncertainty in the homogeneity of the material (u_{bb}) and uncertainty in the stability of the material (u_{stab}). The u_{char} was evaluated by combining uncertainties from method precision, the concentration of calibration solution and weighing, different ion pairs used, isotope ratios (for Cd and Pb), the relative atomic mass (for Pb only) and linear regression (As species), in accordance with ISO/IEC Guide 98-3:2008 [5].

Homogeneity

Homogeneity testing on the analytes in the apple juice was performed on at least 11 bottles with two sub-samples taken from each bottle. ICP-MS was employed for the determination of Cd, Pb and As, while HPLC-ICP-MS was employed for the determination of As species. The sample size taken for homogeneity testing was about 1.0 g for Cd, Pb and As, and about 0.5 g for As species. No significant differences in the between- and within-bottle variances were found for Cd, Pb, As and inorganic As compounds using one-way ANOVA at 95 % confidence level [3]. The between-bottle standard deviation for DMAA was sufficiently small compared to the standard uncertainty of the certified mass fraction value [3]. Thus, the material was regarded 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 4 °C (maximum allowable transportation temperature) showed that they were stable for up to 21 days.

The long-term stability of the analytes at storage temperature (-20 °C) was evaluated on three occasions over a period up to 3.5 months after preparation. The results showed that the analytes were stable over the study period. The u_{stab} was estimated from the standard error of the slope.

Validity of Certified Mass Fraction Values

The certified mass fraction values are valid within their respective measurement uncertainties until **30 Mar 2026**, 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 or an updated COA will be issued when the property value of the CRM is found to have changed.

Analytical Methods

The certified mass fraction values of Cd and Pb in the material were determined by exact-matching ICP-IDMS. Standard reference materials from the National Institute of Standards and Technology (NIST, USA) (Product No. SRM3108 for Cd and SRM3128 for Pb) were used as calibration standards. Enriched isotopes ^{111}Cd and ^{206}Pb from Oak Ridge National Laboratory (USA) 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 with appropriate amount of internal standard into the material and digesting the material with concentrated HNO_3. Quality control blends were also prepared and analysed concurrently.

The certified mass fraction value of As was determined by ICP-HR-MS using standard addition method. The sample was digested overnight using concentrated HNO_3 at ambient temperature. 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 values of As species were determined by HPLC-ICP-MS using standard addition method. Different amounts of As species certified reference material from NIST [Product No. SRM3037 for As(III), SRM3036 for As(V) and SRM3031 for DMAA] were then spiked into the diluted sample 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 in the determination of the mass fraction of Cd, Pb, As and As species in aqueous based beverages.

Instruction for Use

Prior to use, the material should be equilibrated to ambient temperature (20 °C ± 5°C) and thoroughly mixed by inverting the bottle. After use, the bottle should be re-capped, sealed with Parafilm and stored at -20 °C. The minimum sample size for each use should be about 1.0 g for Cd, Pb and As, and about 0.5 g for As species.

Storage

The material should be stored at -20 °C ± 5°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).

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.

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