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Certificate of Analysis

CERTIFIED REFERENCE MATERIAL
HRM – 2015A

Trace Elements in Water

Batch Number
STY-0130-001

Description
A unit of the certified reference material (CRM) HRM-2015A consists of a low-density polyethylene (LDPE) bottle containing 200 mL of acidified purified water (approximately 5 % v/v of nitric acid) spiked with standard solutions of aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni) and selenium (Se).

The CRM 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 13 elements in the CRM are listed below. The certified mass fraction values for Al and As were determined by inductively coupled plasma high resolution mass spectrometer (ICP-HR-MS) using standard addition method. The certified mass fraction value for Mn was determined by inductively coupled plasma tandem mass spectrometer (ICP-MS/MS) using standard addition method [4]. The certified mass fraction values for Sb, Ba, Cd, Ca, Cr, Cu, Pb, Mo, Ni and Se were determined by inductively coupled plasma mass spectrometer using isotope dilution mass spectrometry (ICP-IDMS) [5].

	Certified Mass Fraction	Unit	Coverage Factor, *k*
Aluminium	0.278 ± 0.026	mg/kg	2.00
Barium	0.95 ± 0.11	mg/kg	2.00
Calcium	28.5 ± 1.4	mg/kg	2.57
Copper	3.01 ± 0.24	mg/kg	2.00
Manganese	0.569 ± 0.014	mg/kg	2.00

	Certified Mass Fraction	Unit	Coverage Factor, *k*
Antimony	37.6 ± 1.0	µg/kg	2.00
Arsenic	14.53 ± 0.56	µg/kg	2.00
Cadmium	7.64 ± 0.92	µg/kg	2.00
Chromium	61.4 ± 1.5	µg/kg	2.00
Lead	16.9 ± 1.2	µg/kg	2.00
Molybdenum	79.1 ± 2.0	µg/kg	2.00
Nickel	78.0 ± 3.3	µg/kg	2.00
Selenium	40.4 ± 4.9	µg/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, weighing, different ion pairs used (for Ba, Cd, Ca, Cr, Pb, Mo, Ni and Se), isotope ratios (for Sb, Ba, Cd, Ca, Cr, Cu, Pb, Mo, Ni and Se) and the relative atomic mass (for Pb only), in accordance with ISO/IEC Guide 98-3:2008 Uncertainty of Measurement – Part 3: Guide to the Expression of Uncertainty in Measurement (GUM:1995) [6].

Homogeneity

Homogeneity testing on the analytes in the water was performed on eleven bottles with two sub-samples taken from each bottle. ICP-MS was employed for the determination of all the analytes. The sample size taken for homogeneity testing was about 0.5 g for Ba, Ca, Cu and Mn, about 0.75 g for other analytes. No significant differences in the between and within-bottle variances were found using one-way ANOVA at 95 % confidence level [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 50 °C (maximum allowable transportation temperature) showed that they were stable for 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 up to 6 months after preparation. The results showed that the analytes were stable over the study period. The u_{stab} was evaluated 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 **23 April 2028**, 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 may be issued when the property value of the CRM is found to have changed.

Analytical Methods

The certified mass fractions of Al and As were determined by ICP-HR-MS using standard addition method. Gallium (Ga) standard reference materials (SRM) from the National Institute of Standards and Technology (NIST, USA) (SRM 3119a) was added to the sample as internal standard. Different amounts of Al or As standard reference material from NIST (SRM 3101a for Al and SRM 3103a for

As) were then spiked into the sample to produce sample blends.

The certified mass fraction of Mn was determined by ICP-MS/MS using standard addition method. Indium (In) SRM from NIST (SRM 3124a) was added to the sample as internal standard. Different amounts of Mn standard reference material from NIST (SRM 3132) were spiked into the material to produce sample blends.

The certified mass fractions of Sb, Ba, Cd, Ca, Cr, Cu, Pb, Mo, Ni and Se in the material were determined by exact-matching ICP-IDMS. SRMs from NIST (SRM 3102a for Sb, SRM 3104a for Ba, SRM 3108 for Cd, SRM 3109a for Ca, SRM 3112a for Cr, SRM 3114 for Cu, SRM 3128 for Pb, SRM 3134 for Mo, SRM 3136 for Ni and SRM 3149 for Se) were used as calibration standards. Enriched isotopes ^{123}Sb from Isoflex (USA) and ^{135}Ba, ^{111}Cd, ^{42}Ca, ^{53}Cr, ^{65}Cu, ^{206}Pb, ^{100}Mo, ^{61}Ni and ^{77}Se 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 appropriate amount of internal standard into the material. 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 Al, Sb, As, Ba, Cd, Ca, Cr, Cu, Pb, Mn, Mo, Ni and Se in water.

Instruction for Use

Prior to use, the material should be thoroughly mixed by inverting the bottle. After use, the bottle should be re-capped, sealed with Parafilm and stored at 18 °C to 25 °C. The minimum sample size for each use should be about 0.5 g for Ba, Ca, Cu and Mn and about 0.75 g for other analytes.

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. Abbyad, P.; Tromp, J.; Lam, J.; Salin, E.; *Optimization of the technique of standard additions for inductively coupled plasma mass spectrometry*, J. Anal. At. Spectrom. (2001) 16: 464 – 469.
5. Sargent, M.; Harrington, C.; Harte, R.; *Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry*, RSC Publishing, 2002.
6. 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-HRM-2015A/01	23 April 2021	Issuance of first certificate
CML-HRM-2015A/02	12 April 2022	Extension of expiry date
CML-HRM-2015A/03	04 April 2023	Extension of expiry date
CML-HRM-2015A/04	21 April 2025	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 reference material by the customer.

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