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Certification of Trace Element Mass Fractions in Marine Sediment IAEA-475

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CERTIFICATION OF TRACE ELEMENT MASS FRACTIONS IN MARINE SEDIMENT IAEA-475

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FOREWORD

Monitoring contaminants in the marine environment is a prerequisite for the development of accurate environmental assessments and for evaluating the effectiveness of pollution control. Such assessments and evaluations can only be valid if the monitoring results, obtained in different places and at different times, are comparable. Comparability of the environmental data is only achievable when results are traceable to a common system of reference.

Because of the need to base scientific conclusions on valid and internationally comparable measurement results, and to provide policy makers with correct information on the state of the environment, it is indispensable to ensure the quality of measurement results produced by laboratories involved in marine monitoring studies.

Since the 1960s, the IAEA has been providing help to its Member States in the field of data quality and quality assurance. To support Member States in their monitoring activities, the IAEA Environment Laboratories produce certified reference materials (CRMs) characterized for trace elements and methylmercury using samples of marine origin — biota and sediments.

This publication describes the production of a new CRM for trace element mass fractions in a sediment matrix in accordance with the requirements of international guidelines for the production and characterization of CRMs. Eight laboratories with demonstrated measurement capabilities participated in the characterization of the sediment sample.

The IAEA-475 sediment sample was produced in the frame of a Peaceful Uses Initiative project for the production of a CRM for trace elements and organic contaminants in marine sediment from the Pacific. The sediment matrix used for the IAEA-475 sample is from the Australian marine coastal zone and is an appropriate matrix CRM for monitoring studies along the Australian coast.

The IAEA is grateful to the Government of Monaco for the support provided to the IAEA Environment Laboratories and to the Australian Government for funding this project through the Peaceful Uses Initiative. The IAEA would also like to thank J. Daniel of James Cook University and M. Johansen of the Australian Nuclear Science and Technology Organisation for organizing the sampling campaign and for the delivery of sediment samples to the IAEA Environment Laboratories. The IAEA is grateful to all participants and laboratories taking part in the characterization study and production process of the IAEA-475 sediment sample. The IAEA officers responsible for this publication were E. Vasileva and S. Azemard of the IAEA Environment Laboratories.

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1. INTRODUCTION

Despite the ongoing reduction of emissions of contaminants into the environment, the ocean still represents the most anthropogenically impacted ecosystems worldwide. Sound strategies for marine chemical monitoring call for measurement systems capable of producing comparable analytical results with demonstrated quality. Comparability of monitoring data is mandatory for evaluating spatial and temporal contamination trends and is achievable only if reliable measurement results are considered. The use of suitable certified reference materials (CRM) is mandatory for the quality assurance of any measurement result produced by monitoring laboratories. They are also used for the validation of analytical methods and for traceability of obtained results to the common system of references –SI system. They are valuable tools for the straightforward assessment of the trueness of the method applied. To ensure the reliability of analytical results, quality assurance through the use of CRMs are regarded as the crucial prerequisites in ISO 17025 [1].

Selection and use of marine matrix CRMs that match the matrix of the analysed sample and the concentration range of analytes of interest in the "real" samples is essential for obtaining high quality measurement results. While there are many CRMs certified for trace elements, there is still a noticeable lack of matrix CRMs for environmental monitoring studies.

Certified reference material IAEA-475 will assist laboratories in validating their analytical methods and controlling the quality of produced analytical results for the determination of trace elements in marine sediment samples [1]. It will meet particularly the needs of laboratories involved in monitoring studies in the Pacific coast of Australia, as the sediment used for the IAEA-475, was sampled at the Pacific coast of Australia.

2. METHODOLOGY

2.1. PREPARATION OF THE MATERIAL

The base material for IAEA-475 coastal sediment was collected around Townsville, Australia during the sampling campaign organised by the Marine Environment Studies Laboratory (MESL), James Cook University and Australia's Nuclear Science Technology Organization Australia. Approximately 50 kg sediment sample were collected at 2.2-2.5 m depth into polyester buckets and transferred at 4ºC to MESL, Monaco.

After freeze drying, the sample was grinded by micronisation. The obtained sample showed 100% of particulates in the sample below 20 µm (Figure 1). The bulk material was then sterilised by gamma irradiation (30 kGy).

The homogenization of the sediment sample was performed by dividing the total mass of material to 7 lots, each of them with the weight of 800 g. The material of each lot was transferred into a clean plastic bottle and mixed with a shaker (Turbula, Switzerland) for 2 hours.

Immediately after finalizing the mixing operation, aliquots of about 20 g were packed into pre - cleaned polyethylene bottles with secured screw caps. The process was repeated 7 times and bottles were labeled with the respective bottle numbers.

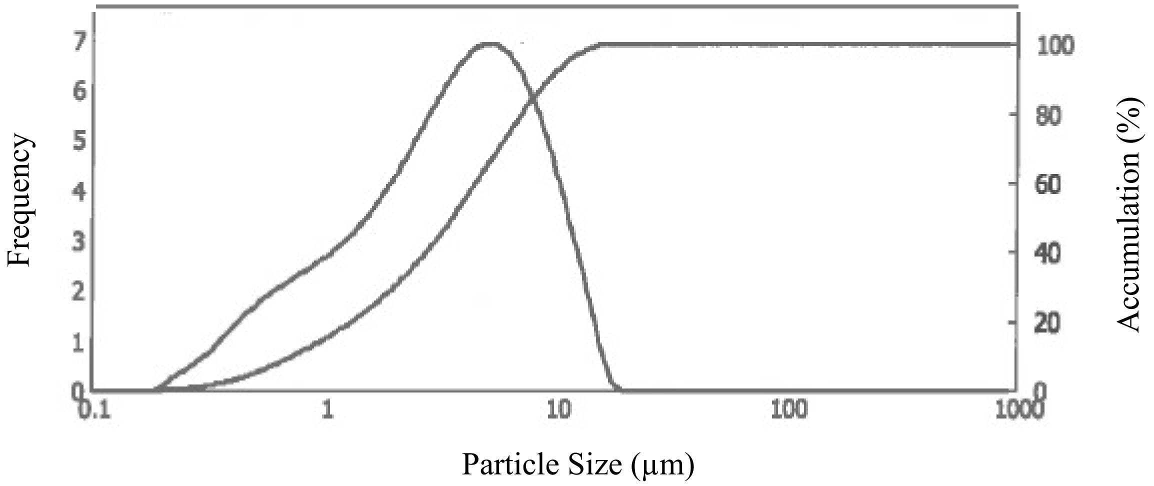

FIG. 1. Grain size distribution of final sample.

2.2. SELECTION OF LABORATORIES

The selection of participants for the characterization study was based on the measurement performances demonstrated by laboratories in the previous three ILCs, organized by the IAEA in the past years. Only results of laboratories having a quality system in place, using validated methods, applying uncertainty and traceability concepts were used for the calculation of the assigned values and their uncertainties [2].

The list of laboratories participating in the IAEA-475 characterization study is presented on page 41.

2.3. HOMOGENEITY ASSESSMENT

A key requirement for any certified reference material is the equivalence between the various CRM units. In this respect, the important issue is whether the variation between units is significant when compared with the uncertainty of the certified value. Consequently, ISO Guide 17034 [2] requires reference material producers to quantify the between unit variation.

The between unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all produced units, within the stated uncertainty. In total, 14 bottles from the whole batch were selected, using random stratified sampling. Duplicate subsamples from each bottle were analysed for their total element and methyl mercury mass fractions in International Atomic Energy Agency (IAEA), MESL, inorganic chemistry laboratories.

The within unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an sample aliquot that is representative for the whole unit. Quantification of within unit (in this case: within bottles) inhomogeneity is, therefore, necessary to determine the minimum sample intake.

The ISO 35 [3] recommends this assessment when the minimum sample intake is significantly less than the unit size. In total 6 subsamples from the same unit were prepared and each subsample was analysed in triplicates.

The between and within unit homogeneities were tested by the determination of the mass fractions of Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Li, Mn, Ni, Pb, Sr, and Zn in the subsamples, selected for the respective study. For all analytes except Hg and MeHg, subsamples of 0.2 g were mineralized with 5 ml of nitric acid and 2ml of hydrofluoric acid in a microwave oven. Digested solutions were then treated with boric acid to remove excess of hydrofluoric acid and fluorine precipitates. The final measurements were performed by inductively coupled plasma mass spectrometry (ICP-MS) or Flame Atomic Absorption Spectrometry (AAS) under repeatability conditions, and in a randomized way. The determination of the total Hg was done in solid subsamples (50 mg) with an advanced mercury analyser. Methylmercury determination are performed by gas chromatography coupled to atomic fluorescence spectroscopy (GC-AFS) after solvent extraction.

The results were corrected for the moisture content determined in each unit by using the procedure describe in Section 2.6.

All methods used for homogeneity studies were previously validated in IAEA, MESL, inorganic chemistry laboratories.

2.4. STABILITY STUDY

Stability testing is necessary to establish conditions for storage (long term stability) as well as conditions for dispatch to the customers (short term stability).

Time, temperature and radiation were regarded as the most important influences on the stability of the materials. The influence of light was minimized by choice of the container and packaging which eliminates most of the incoming light. In addition, materials are stored in the dark, thus practically eliminating the possibility of degradation by radiation. Additionally, the material was sterilized by γ-irradiation treatment to eliminate microbial growth. Therefore, only the influences of time and temperature needed to be investigated.

Stability studies were carried out using an isochronous design [5]. In this approach, samples are stored for a given time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the samples were analysed under repeatability conditions.

Analysis of the material (after various exposure times and temperatures) under repeatability conditions significantly improves the sensitivity of the stability tests.

For the evaluation of the influence of long term storage conditions, 10 bottles have been stored under so called "reference" conditions at (-20 ± 2) °C in the dark since the time of bottling (February 2018). All other produced unit were stored under "normal" conditions at (+20 ± 3) C° in the dark.

In order to evaluate potential degradation of the material during transport, some bottles were stored at (60 ± 3) °C. After 1, 2, 3 and 4 weeks, respectively, two bottles each were selected and placed under "reference" condition. Duplicates subsamples from each bottle were analysed by IAEA, MESL, inorganic chemistry laboratories for their total element and methyl mercury mass fractions as describe in the Section 2.3.

The measurements were performed under repeatability conditions and in randomized way in order to separate a potential analytical drift from a trend related to the storage time. The results were corrected for the moisture content, determined in each unit, applying the protocol described in the Section 2.6.

2.5. CHARACTERIZATION

The sediment sample was initially analysed in the MESL in Monaco. The final characterization was based on the results delivered by selected laboratories with demonstrated measurement capabilities (2.2).

Each laboratory received one bottle of sediment sample, accompanied by an information sheet and one reporting form. Participants were requested to analyse Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Li, Mn, Ni, Pb, Sr, and Zn using validated analytical methods. They were asked to report measurement results (three replicates and average value), expanded uncertainty, information on the applied quality control procedures as well as the information on the standard calibration solutions used in the measurement step.

In addition, each participant also received 1 bottle of IAEA-458 (CRM with similar matrix composition) as a blind quality control sample. The reported results for the quality control sample were evaluated against the certified values and associated uncertainties of the CRM IAEA-458 [6]. Except for Ag and MeHg mass fraction as no certified values were available.

Laboratories were requested to provide results corrected for moisture, as the result for the moisture content in the sample is operationally dependent parameter, the method for moisture determination was prescribed to all participating laboratories.

The results of laboratories not fulfilling the above described requirements were excluded from the further evaluation. Datasets with noncompliance to the preliminary defined criteria or considered as not technically valid are listed in Table 1.

TABLE 1. DATASET EXCLUDED FROM THE FURTHER EVALUATION AFTER TECHNICAL REVIEW

Element	Lab code	Description
As	7	high uncertainty (>20%) when compared to other expert laboratories
As	15	QC result does not agree within uncertainties
Fe	2	high uncertainty (>20%) when compared to other expert laboratories
Hg	2	high uncertainty (>20%) when compared to other expert laboratories
MeHg	13	high uncertainty (>50%) when compared to other expert laboratories
Mn	13 and 15	QC result does not agree within uncertainties
Ni	13	QC result does not agree within uncertainties
Sr	13	QC result does not agree within uncertainties

The characterization of the trace elements mass fractions in the sample was based on the application of several analytical techniques. They are summarized in Figure 2. The abbreviations of the analytical techniques applied in this characterization study are given in Table 2.

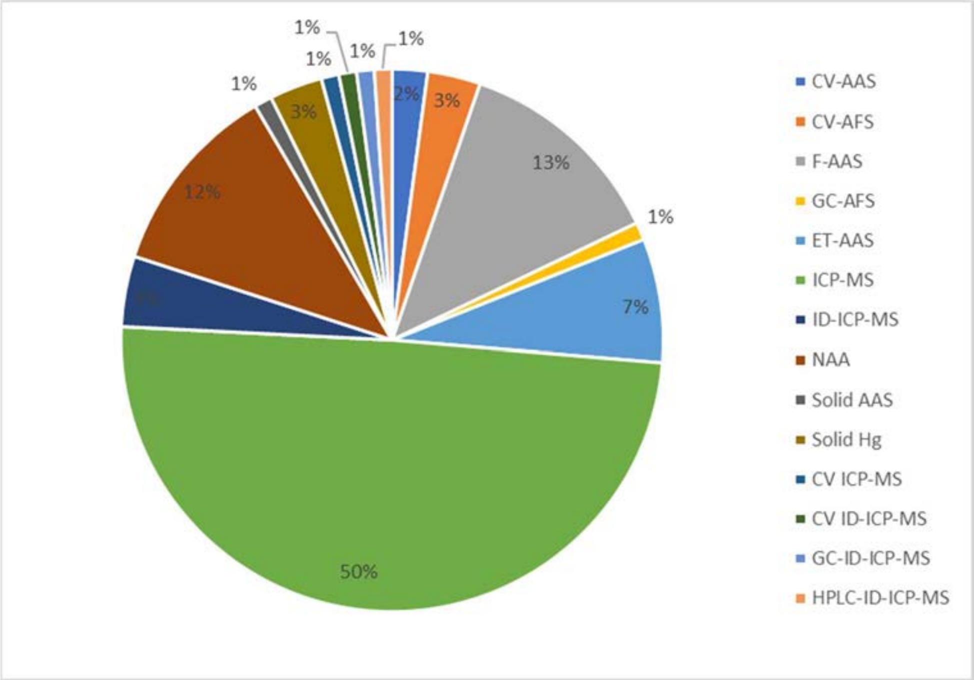

FIG. 2. Analytical methods used for the characterization of trace elements in the IAEA-475.

TABLE 2. ABBREVIATION USED FOR ANALYTICAL TECHNIQUES

Abbreviation	
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
CV	Cold Vapor
ET	Electro Thermal
F	Flame
GC	Gaz chromatography
HPLC	High performance liquid chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ID	Isotope Dilution
NAA	Neutron Activation Analysis (or instrumental neutron activation)

2.6. MOISTURE DETERMINATION

The determination of the moisture content in the samples is to some extent an ‘operationally defined’ parameter. In view of the comparability of results, the protocol for the correction for moisture content was developed at the IAEA and prescribed to other participants. Correction for dry mass should be obtained by drying of minimum 0.5 g of the material at (105 ± 3) °C until the constant sample mass is attained (usually 24 hours).

Moisture, determined at MESL (10 subsamples from 5 bottles) was found to be 2.3 (± 0.4) % for bottles kept at 20°C.

3. RESULTS AND DISCUSSION

3.1. RESULTS OF HOMOGENEITY STUDY

3.1.1. Between unit homogeneity

For the between bottle homogeneity study, 14 units of sample were selected by using a random stratified sample selecting scheme and analyzed for their trace elements contents in duplicate.

Regression analyses were performed to evaluate potential trends in the analytical and processing sequences. Grubbs and Dixon tests at 95% and 99% confidence levels were performed to identify potentially outlying individual results or bottle means. As a prerequisite for the application of analysis of variance (ANOVA), as a statistical tool for the estimation of uncertainty arising from homogeneity, it was verified whether the individual results and unit means follow an approximatively normal distribution and are unimodally distributed.

No processing trends were observed and all datasets (means and individuals) were found to be normally distributed.

Individual outliers were detected for Mn and Hg, but since no technical reasons were found for observed single outliers, and distributions were normal, all reported results were retained for further evaluation. No outlying unit mean were detected.

Regression analyses to evaluate potential trends in each analytical sequence was performed at a 95 % confidence level and significant analytical sequence trend was found for As, Li, Mn, Ni, Sr and Zn.

Correction of trends was therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between bottles heterogeneities. A linear model was chosen as a reasonable approximation. Before applying any statistical analysis, trends significant at, at least at 95 % confidence level, were corrected following Equation 1:

$$\text{Corrected result} = \text{Measured Result} - (b \times i) \tag{1}$$

Where b is the slope of the linear model and i is the position of the analysed subsample in the run.

Quantification of between unit homogeneity was done by one-way ANOVA which can separate the between unit variation from the within unit variation (s_{wb}). The latter is equivalent to the method repeatability, if the individual aliquots are representative for the whole unit.

Using ANOVA the between unit standard deviation (s_{bb}) can be computed from the between group mean square (MS_{bb}), the within group mean square (MS_{wb}), and the number of replicate per unit (n) using the equation described below:

$$s_{wb} = \sqrt{MS_{wb}} \tag{2}$$

$$s_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{n}} \tag{3}$$

where s_{bb} and s_{wb} are the estimates of the standard deviations and are therefore subject to random fluctuations. The mean square between groups can be smaller than the mean square within groups, resulting in negative value under the square root. The value under the squire root is used for the estimation of the between unit variation, whereas the true variation cannot be lower than zero. In this case, the maximum heterogeneity u^*_{bb}, that could be hidden by the method repeatability, was calculated as described by Linsinger et al. [7]. u^*_{bb} is comparable to the limit of detection of the analytical method, yielding the maximum heterogeneity that might be undetected by the applied experimental setup.

$$u_{bb}^{*} = \sqrt{\frac{MS_{wb}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MS_{wb}}}} \tag{4}$$

where n is the number of replicate sub-samples per bottle; and ν_{MSwb} is the degrees of freedom of MS_{wb}.

The uncertainty contributions due to the between unit homogeneity were estimated according to the ISO Guide 35 [3] as the maximum values obtained with Eq. 3 or Eq. 4 and presented in Table 3. As can be seen in Table 3 the between unit variations for all analytes were sufficiently small to demonstrate the homogeneity of the material for the specified sample masses.

TABLE 3. ESTIMATED CONTRIBUTIONS OF INHOMOGENEITY TO THE COMBINED UNCERTAINTY OF THE CERTIFIED VALUES FOR EACH TRACE ELEMENTS

	s_{bb}	u^{*}_{bb}	u_{bb}
Ag	0.5%	1.0%	1.0%
Al	1)	1.3%	1.3%
As	1.3%	0.7%	1.3%
Cd	2.0%	2.5%	2.5%
Co	1.2%	0.6%	1.2%
Cr	1)	1.5%	1.5%
Cu	1.5%	1.3%	1.5%
Fe	1)	1.1%	1.1%
Hg	1)	1.9%	1.9%
MeHg	1)	4.9%	4.9%
Li	0.2%	1.7%	1.7%
Mn	2.7%	1.3%	2.7%
Ni	1.4%	1.1%	1.4%
Pb	1)	1.4%	1.4%
Sr	0.2%	1.0%	1.0%
Zn	1.1%	1.3%	1.3%

1) Not defined due to negative argument under the square root

3.1.2. Within unit homogeneity

For the within bottle study 6 sub samples from 1 unit were digested as already described in (2.3) and each of the obtained solutions measured 3 times, using a randomize scheme. Regression analyses were performed to evaluate potential trends in the analytical run. Grubbs and Dixon tests at 95% and 99% confidence levels were performed to identify potentially outlying individual results. As a prerequisite for the application of ANOVA for the estimation of uncertainty arising from within unit homogeneity, it was verified whether the individual results follow an approximately normal distribution and are unimodally distributed.

When applying ANOVA the within unit standard deviation (s_{wb}) can be computed from the between group mean square (MS_{wb}), the within group mean square (MS_{method}) and the number of replicates per subsample (n) using the equations described below. For Total Hg, as only one measurement can be performed per subsample, s_{method} is obtained from validation and is estimated as 2.3%:

$$s_{method} = \sqrt{MS_{method}} \tag{5}$$

$$s_{wb} = \sqrt{\frac{MS_{wb} - MS_{metho}}{n}} \tag{6}$$

The uncertainty u_{hom} associated with homogeneity of the material at the prescribed minimum sample size was estimated by Eq. 7 and presented in Table 4 [3].

$$u_{hom} = \sqrt{u_{wb}^2 + u_{bb}^2} \tag{7}$$

The conclusion from the obtained results was that the homogeneity of the sediment sample complied with the requirements given by the ISO Guide 35 [3] at the sample sizes of masses used in the present study. Sample masses of 0.05 g for Hg and 0.2 g for other trace element were set up as a minimum sample intake

TABLE 4. THE ESTIMATE OF HOMOGENEITY CONTRIBUTIONS TO THE TOTAL UNCERTAINTY FOR THE CERTIFIED TRACE ELEMENTS

Element	$u_{bb,rel}$	$u_{wb, rel}$	$u_{hom, rel}$
Ag	1.0%	0.6%	1.2%
Al	1.3%	3.3%	3.5%
As	1.3%	0.6%	1.4%
Cd	2.5%	5.4%	6.0%
Co	1.2%	1.2%	1.7%
Cr	1.5%	1.0%	1.8%
Cu	1.5%	2.0%	2.5%
Fe	1.1%	1.3%	1.7%
Hg	1.9%	1)	1.9%
MeHg	4.9%	7.1%	7.8%
Li	1.7%	0.5%	1.8%
Mn	2.7%	1.2%	3.0%
Ni	1.4%	0.8%	1.6%
Pb	1.4%	1.0%	1.7%
Sr	1.0%	2.0%	2.2%
Zn	1.3%	2.2%	2.6%

1) negative argument in Eq. 6

3.2. RESULTS FOR STABILITY STUDY

The samples selected for short term stability study were analysed and each of the elements was evaluated individually. Regression analyses were performed to evaluate potential trends in the analytical run.

Significant analytical sequence trends were found for Ni and Sr. A linear model was chosen as a reasonable approximation for the correction of both datasets. The correction of biases, even if they were statistically not significant, were found to combine the smallest uncertainty with the highest probability to cover the true value [4]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking the potential instability. Before applying any statistical analysis, trends significant at, at least a 95 % confidence level, were corrected following Equation 1.

Grubbs and Dixon tests at 95% and 99% confidence levels were performed to identify individual outlying results. One individual result was detected as outlier for Hg, but as no technical reason was found and results were normally distributed, all data were taken for further evaluation.

Evaluation of data was carried out by performing a linear regression on the determined mass fractions versus time. The tested properties showed no significant trend at +60°C storage temperature within four weeks. No significant slope at 95% level of confidence was detected for any of investigated trace elements in the short term stability study. As no degradation was observed under applied conditions, it was concluded that no special precautions regarding temperature control during shipment are necessary. The uncertainty associated with short term stability was set to 0. Graphical representations of the short term stability study are displayed in the Appendix I (Figures 3 – 17).

Ten units have been placed at -20°C (reference temperature) at the time of bottling and the long term stability of the material will be checked at regular interval as planned by the NAEL internal standard operation procedure. Based on experience of long term monitoring study (more than 10 years) on the previous IAEA reference material of the same matrix kept under "normal" conditions ((20 ± 3)°C, in the dark), the material is expected to be stable and the uncertainty associated with its stability (u_{stab}) was set to zero [3].

3.3. DETERMINATION OF ASSIGNED VALUES AND THEIR UNCERTAINTIES

The characterization campaign resulted in 3 to 9 measurement results for the selected trace elements. The obtained measurement results were first checked for compliance with the certification requirements, and then for their validity based on technical reasoning. All accepted set of results were submitted to the following statistical tests: Grubbs and Dixon's test to detect outliers and Kolmogorov-Smirnov's test for Normal distribution. No results were detected as outlier and all datasets were normally distributed.

The medians and unweighted mean of the means were calculated and compared. No significant differences were observed, and the reference values obtained with the mean of the mean approach was further used. These values are considered to be the most reliable estimates of the property values of the selected trace elements in IAEA-475.

The uncertainties associated with the assigned values were calculated according to ISO Guide 35 [3]. The relative combined uncertainty of the certified value of the CRM consists of uncertainty related to its characterization (u_{char}), sample heterogeneity (u_{hom}) and long term stability (u_{stab}). These different contributions were combined to estimate the expanded uncertainty.

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \tag{8}$$

Where

k: coverage factor equaling 2, representing a level of confidence of about 95%

u_{hom} was estimated as described in section 3.1

u_{stab} was estimated at zero as described in section 3.2

u_{char} was estimated as described in ISO 35 [3] using Eq. (9):

$$u_{char} = \frac{s}{\sqrt{p}} \tag{9}$$

Where: s is the standard deviation of the mean; p is the number of datasets.

Means values, their relative expanded uncertainties (k=2) and uncertainty contributions from the characterization and homogeneity are presented in Table 5 for all trace elements.

TABLE 5. MEAN OF THE MEANS AND UNCERTAINTIES

Element	Mean of the means mg kg^{-1}	$u_{char,rel}$	$u_{hom,rel}$	$U_{,rel}$ (k=2)
Ag	0.121	14.8%	1.2%	29.6%
Al	73.1×10^3	3.5%	3.5%	9.8%
As	12.6	2.5%	1.4%	5.8%
Cd	0.066	8.6%	6.0%	21.0%
Co	12.4	1.3%	1.7%	4.3%
Cr	65.8	1.3%	1.8%	4.4%
Cu	27.8	2.2%	2.5%	6.7%
Fe	34.2×10^3	2.2%	1.7%	5.6%
Hg	0.030	1.6%	1.9%	5.0%
MeHg[1]	0.199×10^{-3}	2.3%	7.0%	15%
Li	41.2	2.3%	1.8%	5.8%
Mn	573	1.1%	3.0%	6.4%
Ni	28.5	1.1%	1.6%	3.9%
Pb	29.9	1.7%	1.7%	4.9%
Sr	251	2.4%	2.2%	6.5%
Zn	100	1.9%	2.6%	6.5%

[1] as Hg

The results for the mass fractions of the trace elements as reported by the participants in this characterization study, grouped by the applied analytical methods are presented in Appendix II. In all figures the reported results are plotted versus the laboratory code, and the mean of the means value denoted by a bold line, while the dashed lines represent the mean of the means ± its associated expanded uncertainty (*k*=2) (Eq. 8). The error bars represent the expanded uncertainties, reported by participants.

As shown previously on Figure 2 and on Figures 19–34, methods with different quantification principles (Graphite Furnace-AAS, AFS, ICP-MS) as well as methods without sample preparation step, such as neutron activation or solid sampling AAS, were used for the characterization of the candidate reference material. A good agreement within the stated uncertainty was observed for results obtained with different methods, therefore all of them were considered in the process of calculation of the assigned values. The agreement between results confirms the absence of any significant method bias and demonstrates the identity of the analyte.

Certified values were calculated as the mean of the means of accepted dataset for the elements fulfilling the following criteria: i.) at least 5 results from 2 different methods were available and ii.) relative expanded uncertainties of the assigned value were less than 15% (*k*=2).

These criteria were fulfilled for As, Co, Cr, Cu, Fe, Hg, MeHg, Ni, Pb and Zn. The assigned certified values are presented in Table 6, together with their expanded uncertainty (*k*=2).

TABLE 6. CERTIFIED VALUES FOR TRACE ELEMENT MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k*=2) IN IAEA-475

Element	Unit	Certified value[1]	Expanded uncertainty (*k*=2)[2]
As	$mg\ kg^{-1}$	12.6	0.7
Co	$mg\ kg^{-1}$	12.4	0.5
Cr	$mg\ kg^{-1}$	65.8	2.9
Cu	$mg\ kg^{-1}$	27.8	1.8
Fe	$mg\ kg^{-1}$	34.2×10^{3}	1.9×10^{3}
Hg	$mg\ kg^{-1}$	29.9×10^{-3}	1.5×10^{-3}
MeHg	$mg\ kg^{-1}$ as Hg	0.199×10^{-3}	0.034×10^{-3}
Ni	$mg\ kg^{-1}$	28.5	1.1
Pb	$mg\ kg^{-1}$	29.9	1.5
Zn	$mg\ kg^{-1}$	100	6

[1] The value is the mean of the means of the accepted sets of data, each set being obtained by different laboratory. The certified values are reported on dry mass basis and are traceable to the SI.

[2] The uncertainty is expressed as a combined standard uncertainty with a coverage factor *k*=2, corresponding to the level of confidence of about 95%, estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [8], and ISO Guide 35 [3].

The criteria were not fulfilled for Ag, Al, Cd, Li, Mn and Sr and as a result only information values were provided. The information values for Ag, Al, Cd, Li, Mn and Sr are presented in Table 7.

TABLE 7. INFORMATION VALUES FOR TRACE ELEMENTS MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k*=2) IN IAEA-475

Element	Unit	Information value[1]	Expanded uncertainty (*k*=2)[2]
Ag	mg kg^{-1}	0.121	0.036
Al	mg kg^{-1}	73.1×10^3	7.2×10^3
Cd	mg kg^{-1}	0.066	0.014
Li	mg kg^{-1}	41.2	2.4
Mn	mg kg^{-1}	573	37
Sr	mg kg^{-1}	251	16

[1] The value is the mean of the means of accepted sets of data.

[2] The uncertainty is expressed as a combined standard uncertainty with a coverage factor *k*=2, corresponding to the level of confidence of about 95%, estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [8], and ISO Guide 35 [3].

4. METROLOGICAL TRACEABILITY AND COMMUTABILITY

Pure metal standard solutions (CRMs) with stated purity were employed for calibration by all laboratories, participating in this characterization study. As stated in the respective certificates from all CRM producers, the mass fractions of the trace element in the respective standard solutions were measured against another CRM (i.e. National Institute of Standard and Technology, Bundesanstalt für Materialforschung und -prüfung) with demonstrated SI traceability, followed by gravimetric preparation and calibrated with SI traceable weights analytical balances.

Only validated methods applied within stated scope were used by participating laboratories in this characterization study. Matrix CRMs with stated SI traceability purchased from National Institute of Standard and Technology, Institute for reference material and measurement, National Research Council of Canada and IAEA were used for validation of the methods applied in this study.

In addition, the agreement between the results confirms the absence of any significant method bias and demonstrates the identity of the measurand. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias.

As the certified values are combinations of agreeing results, individually traceable to the SI, the certified quantity values are also traceable to the SI system of units. The trust in the certified values and their trueness are further underpinned by the agreement among the technically accepted datasets.

The degree of equivalence in the analytical behavior of real samples and a CRM with respect to various measurement procedures (methods) is summarized in a concept called 'commutability of a reference material'.

Various definitions define this concept. For instance, the CLSI Guideline C53-A [8] recommends the use of the following definition for the term commutability: "The equivalence of the mathematical relationships among the results of different measurement procedures for an reference material and for representative samples of the type intended to be measured." The commutability of a CRM defines its fitness for use and is, therefore, a crucial characteristic when applying different measurement methods.

Commutability is a property of a reference material, demonstrated by the closeness of agreement between the relation among the measurement results for a stated quantity in this material, obtained according to two given measurement procedures, and the relation obtained among the measurement results for other specified materials [9].

Commutability is a critical requirement to avoid introducing unintended, and sometimes undetected, bias results when using one CRM. Commutable CRMs should exhibit an analytical behavior for a given method similar to a real laboratory sample. However, CRMs might show behavior different from that of real samples, in particular during digestion, due to their small particle size in contrast to the possible larger particle size for the real laboratory samples. IAEA -475 is a natural marine sediment sample. The analytical behavior should be the same as for a routine sediment sample. The agreement between results obtained with different analytical methods selected for the IAEA-475 characterization study confirms the absence of any significant method bias and demonstrates commutability of the material for all certified trace elements and methods applied in this study.

5. CONCLUSIONS

This certification campaign allowed the assignment of certified values with their associated uncertainties for As, Co, Cr, Cu, Fe, Hg, MeHg, Ni, Pb and Zn mass fractions in marine sediment sample. The certified values were derived from measurement results provided by the laboratories participating in the characterization study. Participating in the characterization of the IAEA - 475 CRM laboratories applied only validated analytical methods. As the certified values are combinations of SI traceable individual results, they are also traceable to the International System of Units.

APPENDIX I

RESULTS FROM THE SHORT TERM STABILITY STUDY AT 60°C:

Figures 3 – 18 present unit averages mass fractions per time point. The error bars represent the standard deviation of all results (two bottles per time, analysed in duplicate). In all figures the results are plotted versus storage duration at elevated temperature. In addition, the certified (or informative) value is plotted as a bold line, while the dashed lines represent the certified (or informative) value ± its expanded uncertainty (*k*=2) associated.

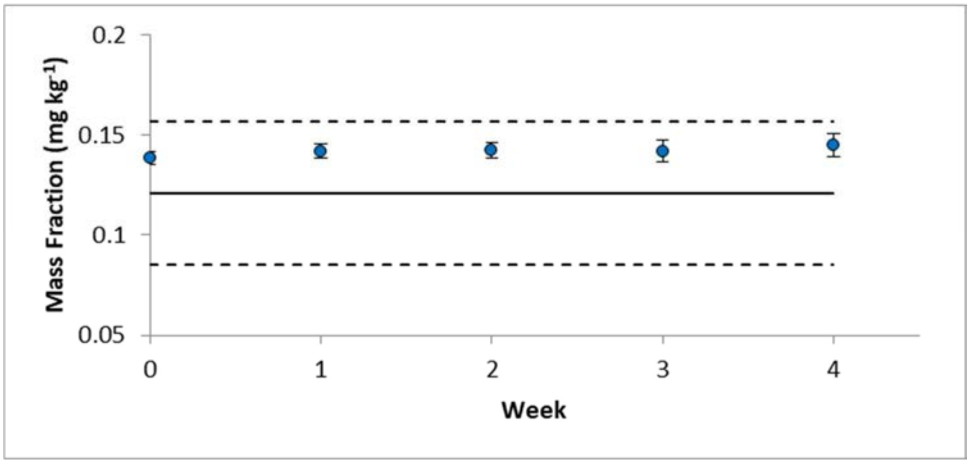

FIG. 3. Results of short term stability study for silver.

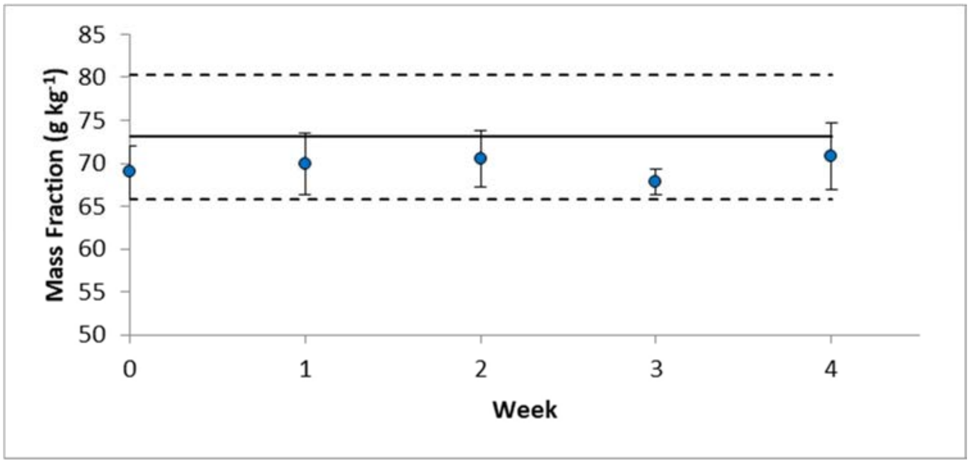

FIG. 4. Results of short term stability study for aluminium.

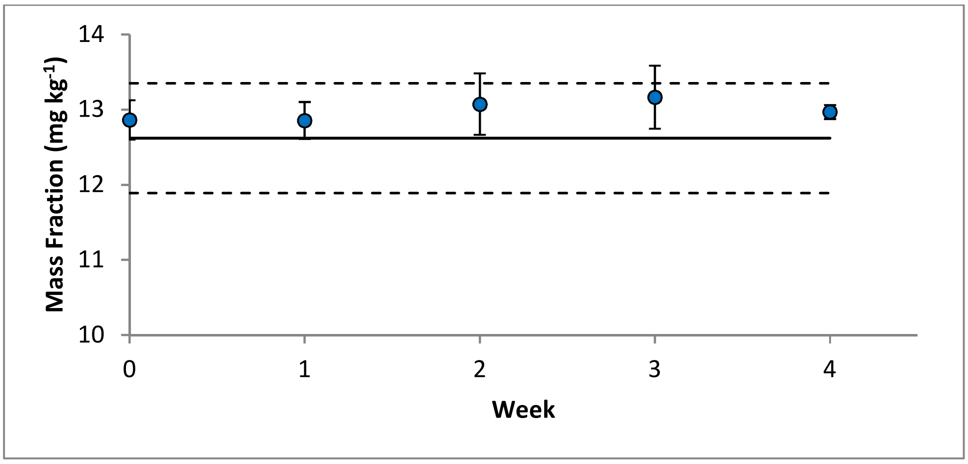

FIG. 5. *Results of short term stability study for arsenic.*

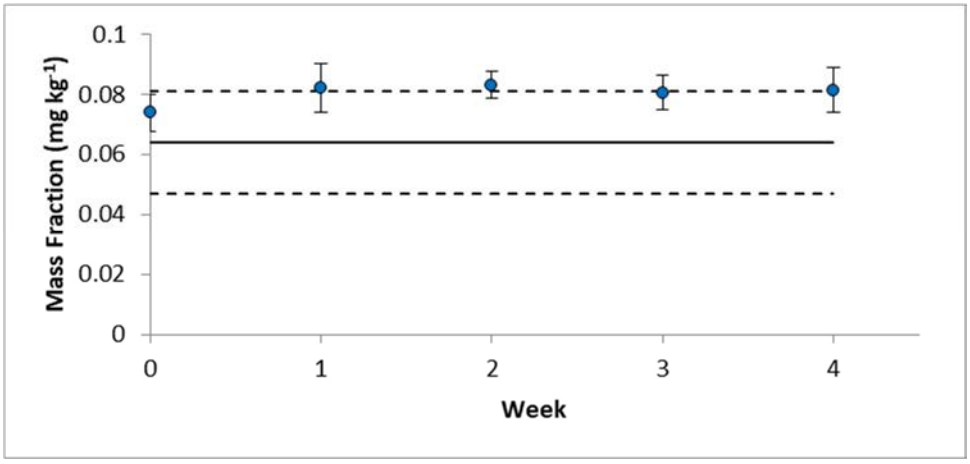

FIG. 6. *Results of short term stability study for cadmium.*

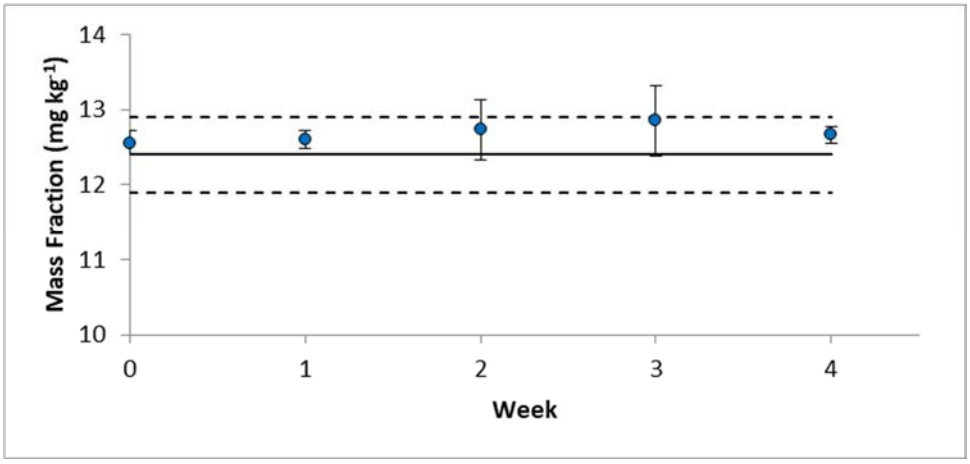

FIG. 7. *Results of short term stability study for cobalt.*

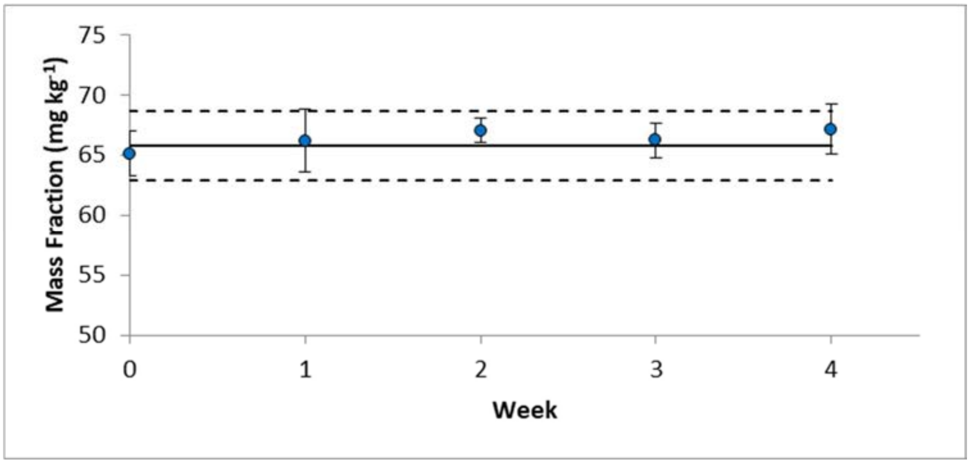

FIG. 8. Results of short term stability study for chromium.

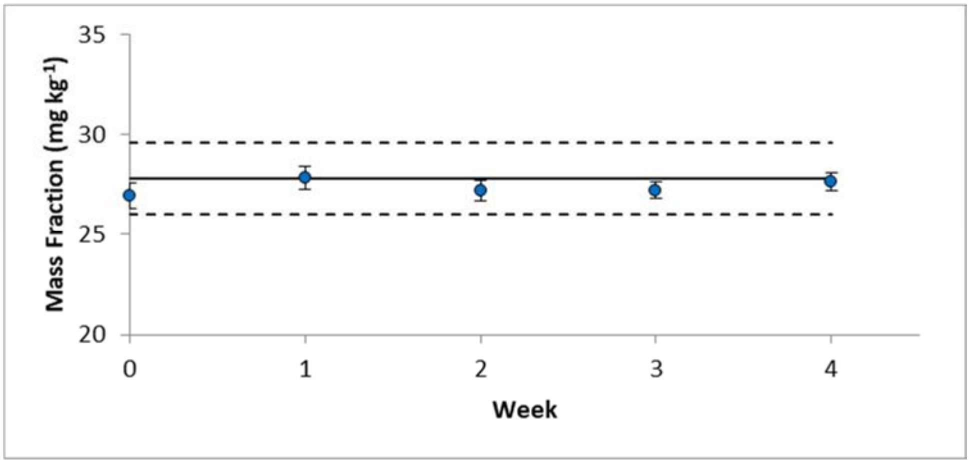

FIG. 9. Results of short term stability study for copper.

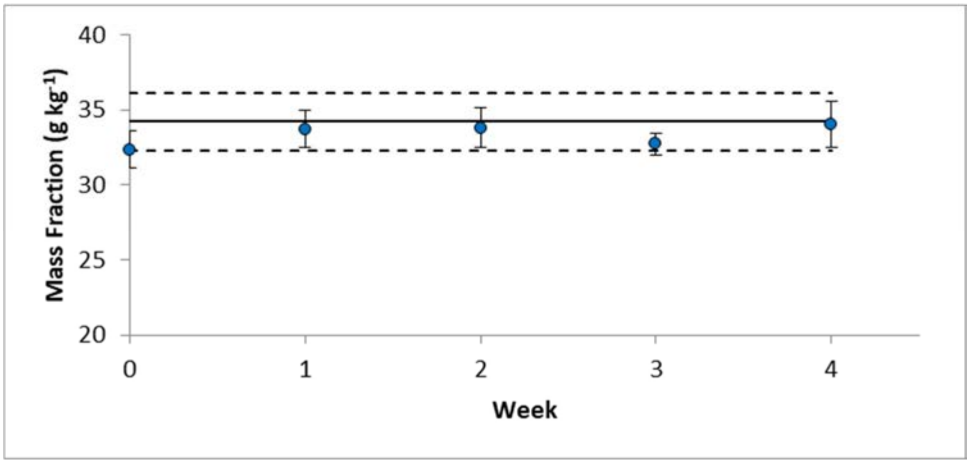

FIG. 10. Results of short term stability study for iron.

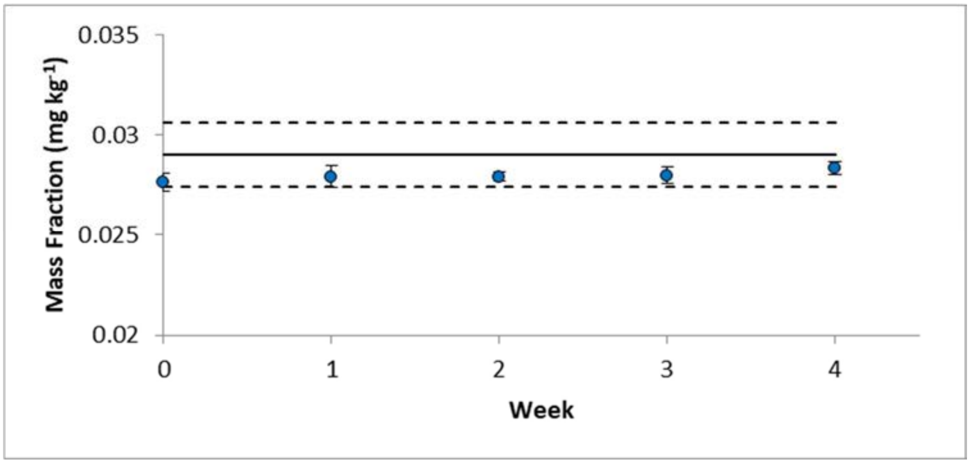

FIG. 11. Results of short term stability study for mercury.

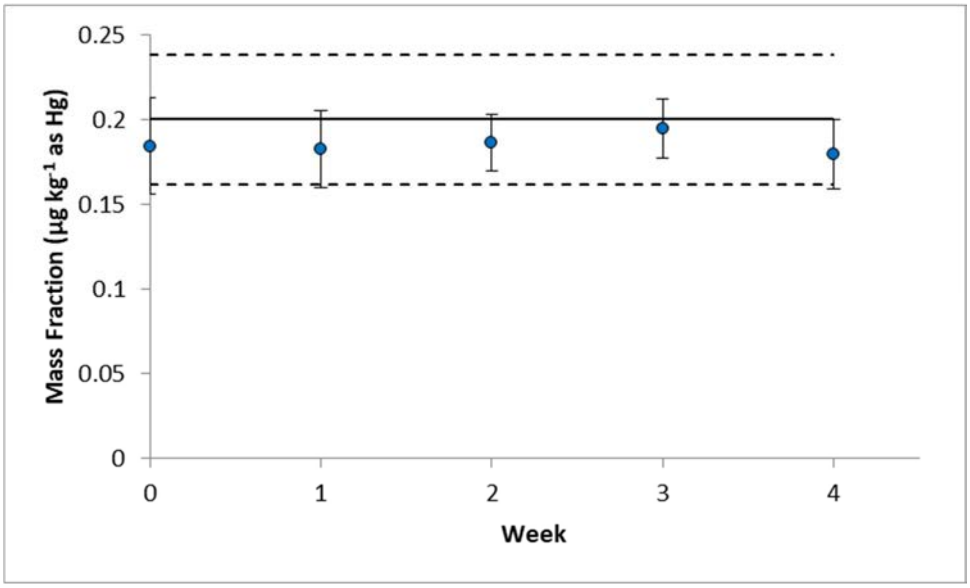

FIG. 12. Results of short term stability study for methylmercury.

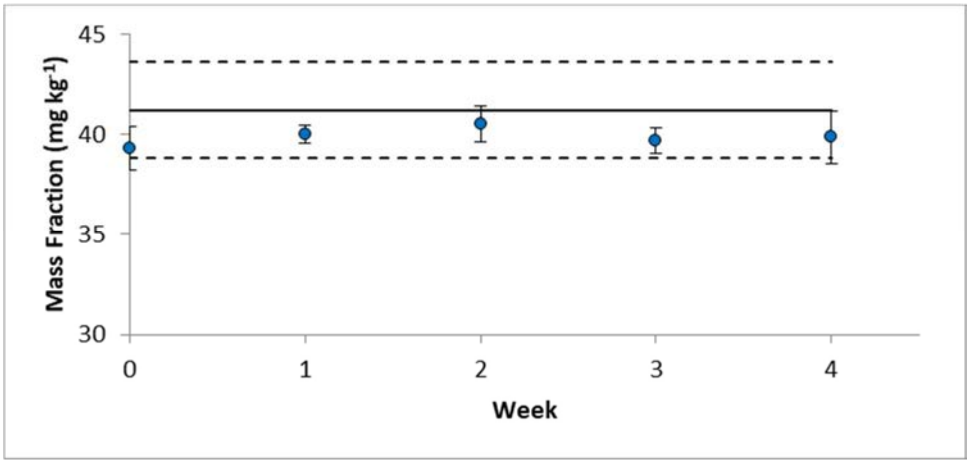

FIG. 13. Results of short term stability study for lithium.

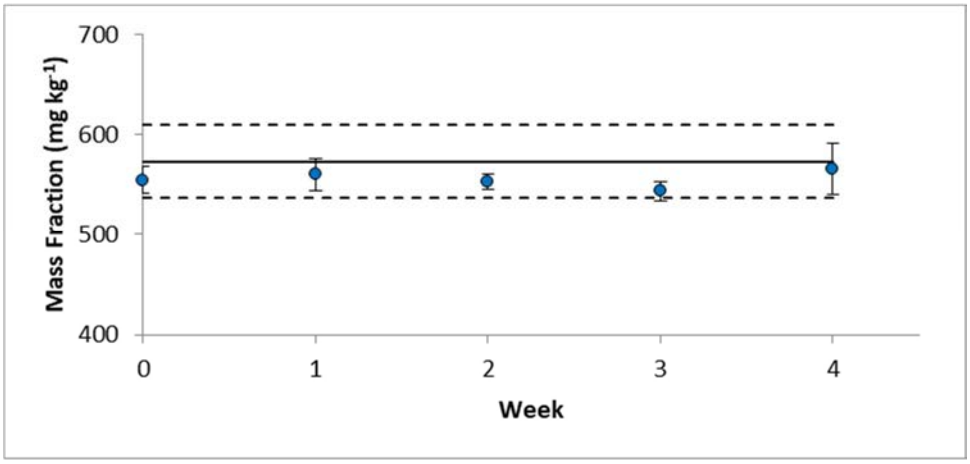

FIG. 14. Results of short term stability study for manganese.

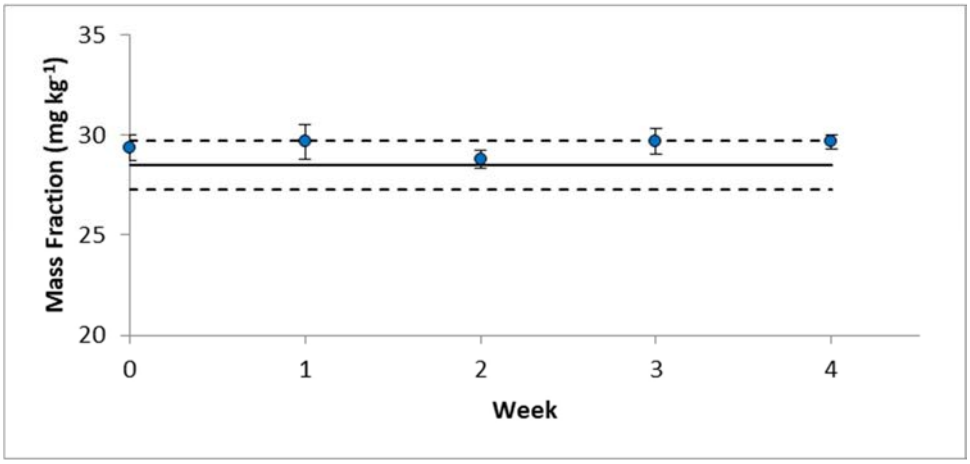

FIG. 15. Results of short term stability study for nickel.

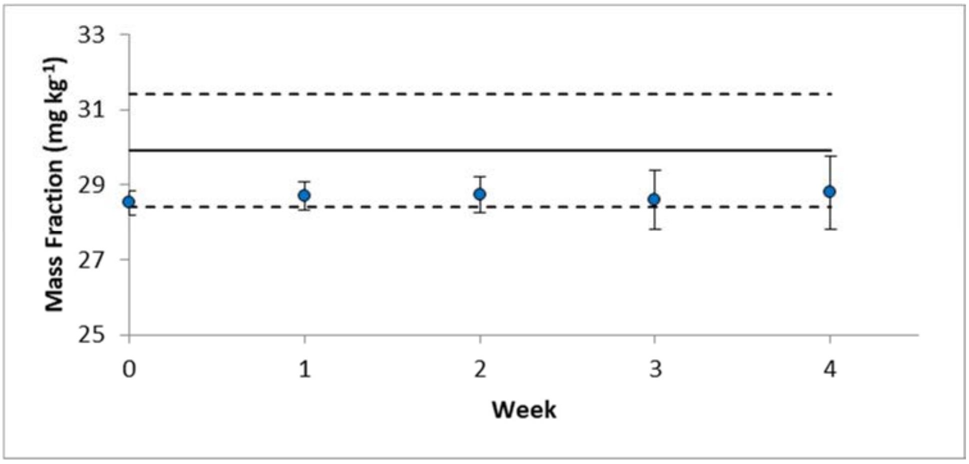

FIG. 16. Results of short term stability study for lead.

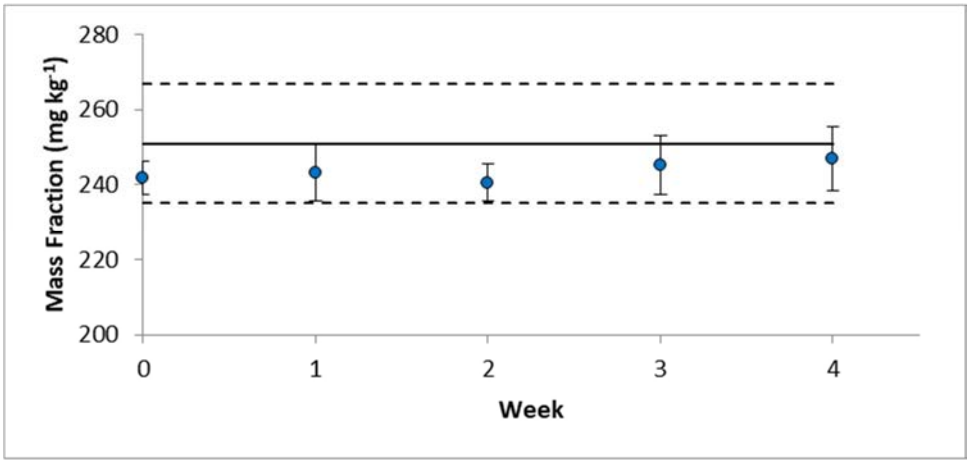

FIG. 17. Results of short term stability study for strontium.

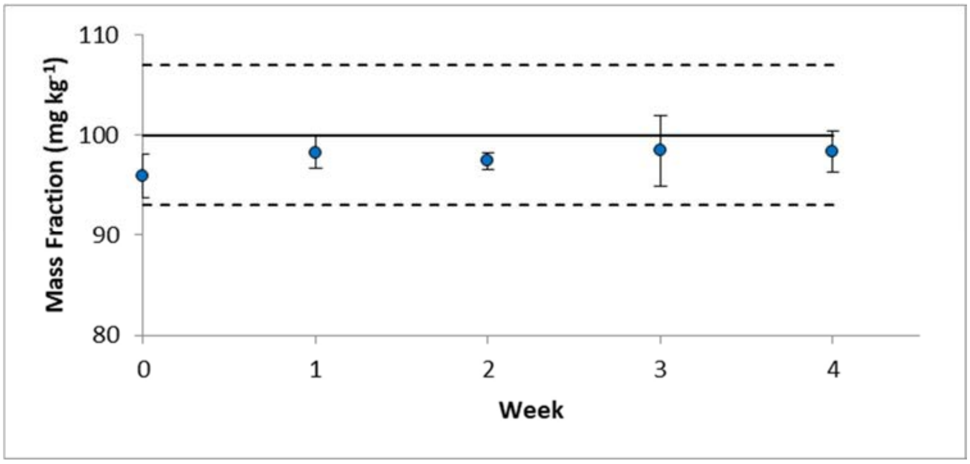

FIG. 18. Results of short term stability study for zinc.

APPENDIX II

RESULTS OF THE CHARACTERIZATION MEASUREMENTS

The results reported by participants together with their expanded uncertainty and measurement techniques are presented in Tables 8-23. Figures 19–34 provide graphical presentation of the individual results and their expanded uncertainties as well as the assigned value for the respective trace element and its expanded uncertainty (*k*=2).

TABLE 8. SILVER: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
7	ICP-MS	0.085	0.020
13	ICP-MS	0.135	0.035
IAEA-1	ICP-MS	0.142	0.022

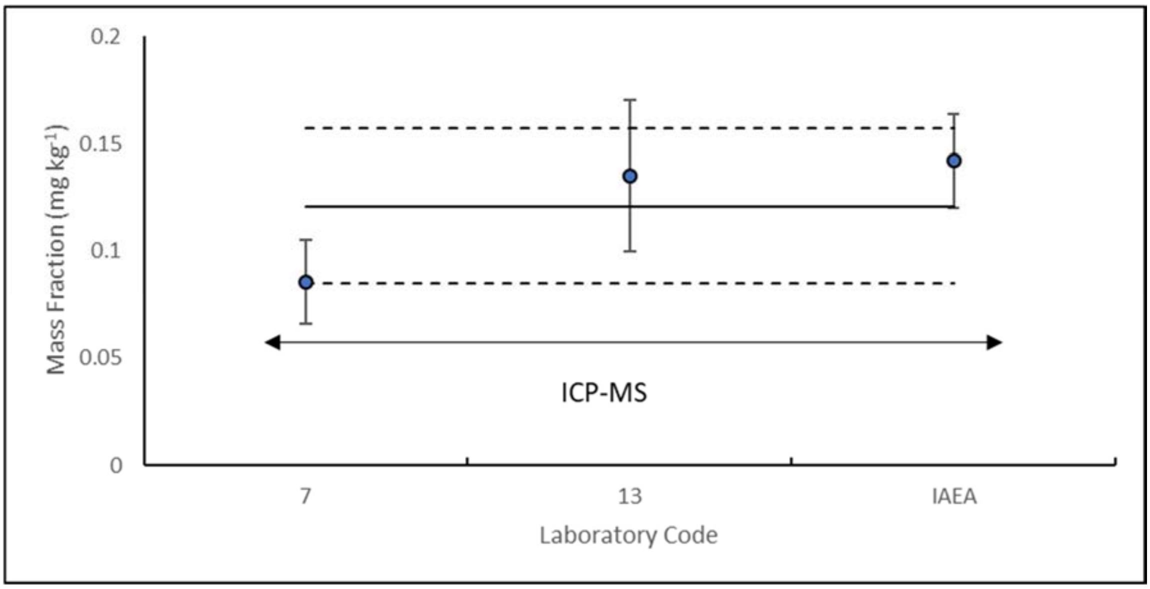

FIG. 19. Laboratory results for silver mass fraction (mg kg^{-1}) in IAEA-475.

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TABLE 9. ALUMINIUM: RESULTS AS REPORTED BY PARTICIPANTS (g kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
13	ICP-MS	68.8	2.6
2	ICP-MS	70.3	21.1
IAEA-1	Flame AAS	73.2	11.7
15	Neutron Activation	80.2	4.7

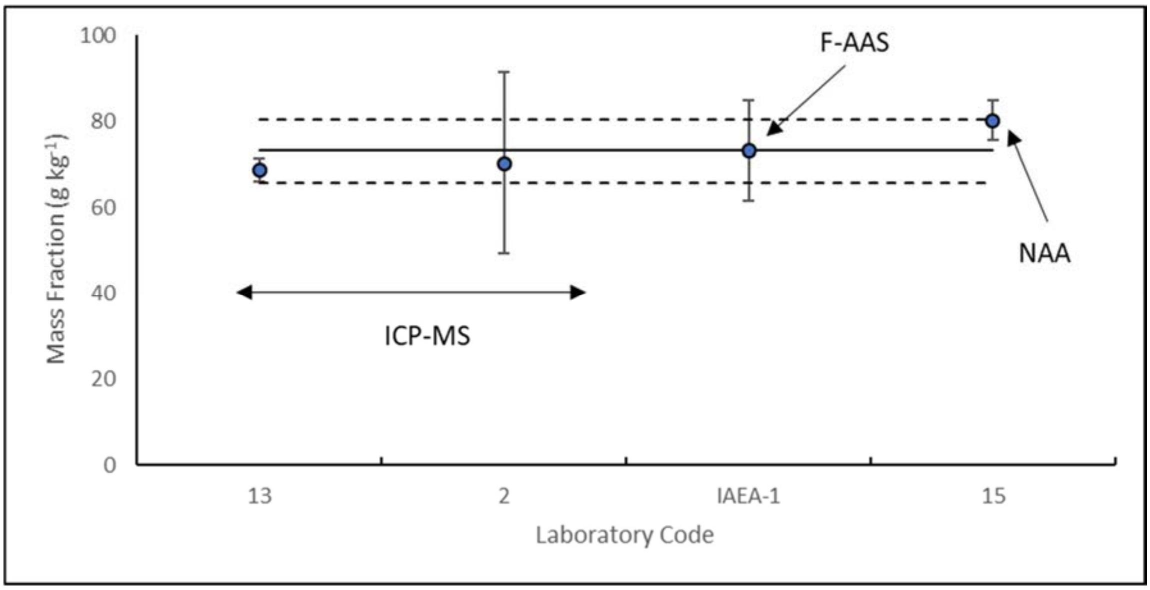

FIG. 20. Laboratory results for aluminum mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 10. ARSENIC: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Graphite Furnace AAS	12.2	2.0
IAEA-1	ICP-MS	12.1	2.0
13	ICP-MS	12.2	1.4
IAEA-2	ICP-MS	13.8	1.0
10	Neutron Activation (k_0-INAA)	12.8	1.0
Results not used in certification			
7	ICP-MS	14.7	3.2
15	Neutron Activation	12.9	0.8

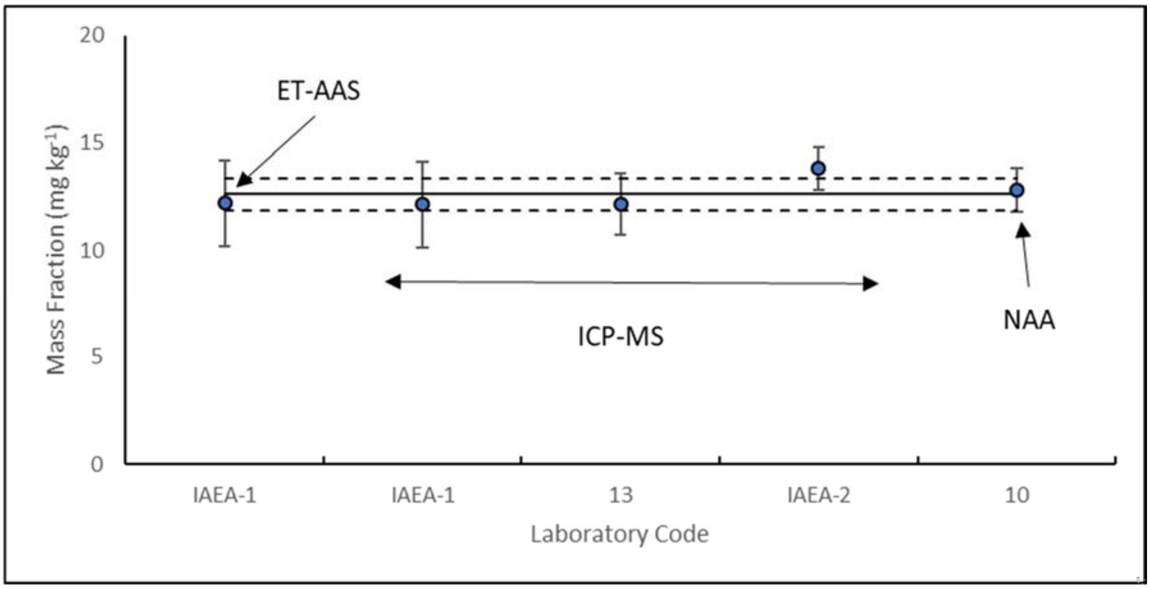

FIG. 21. Laboratory results for arsenic mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 11. CADMIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Graphite Furnace AAS	0.065	0.010
IAEA-1	ICP-MS	0.049	0.008
2	ICP-MS	0.054	0.022
13	ICP-MS	0.056	0.019
7	ICP-MS	0.094	0.017
IAEA-1	Isotope Dilution ICP-MS	0.068	0.002
IAEA-1	Solid-AAS	0.072	0.008

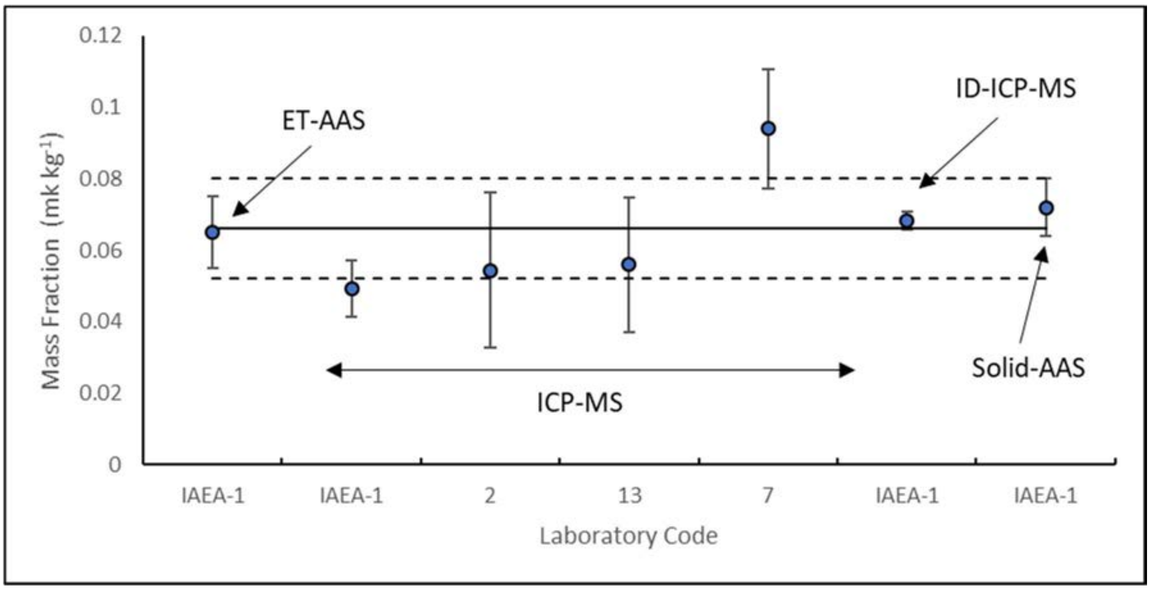

FIG. 22. Laboratory results for cadmium mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 12. COBALT: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA -1	Graphite Furnace AAS	12.3	2.0
IAEA -1	ICP-MS	11.7	2.0
2	ICP-MS	12.2	1.8
13	ICP-MS	12.3	0.6
7	ICP-MS	12.4	1.5
IAEA -2	ICP-MS	12.9	0.6
15	Neutron Activation	13.1	0.6
10	Neutron Activation (k_0-INAA)	12.0	0.8

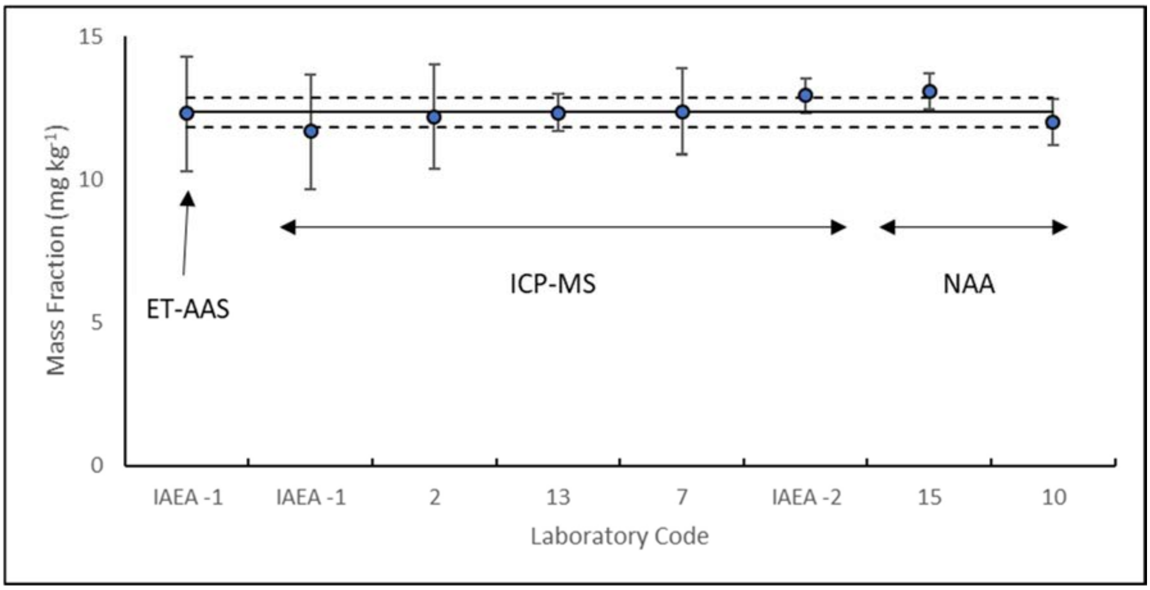

FIG. 23. Laboratory results for cobalt mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 13. CHROMIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA -1	Flame AAS	65.6	9.2
IAEA -1	Graphite Furnace AAS	69.6	9.7
IAEA -1	ICP-MS	62.7	10.0
13	ICP-MS	62.7	1.8
IAEA -2	ICP-MS	65.4	3.7
2	ICP-MS	65.5	9.8
7	ICP-MS	66.0	2.0
15	Neutron Activation	69.6	3.3
10	Neutron Activation (k$_0$-INAA)	64.9	4.6

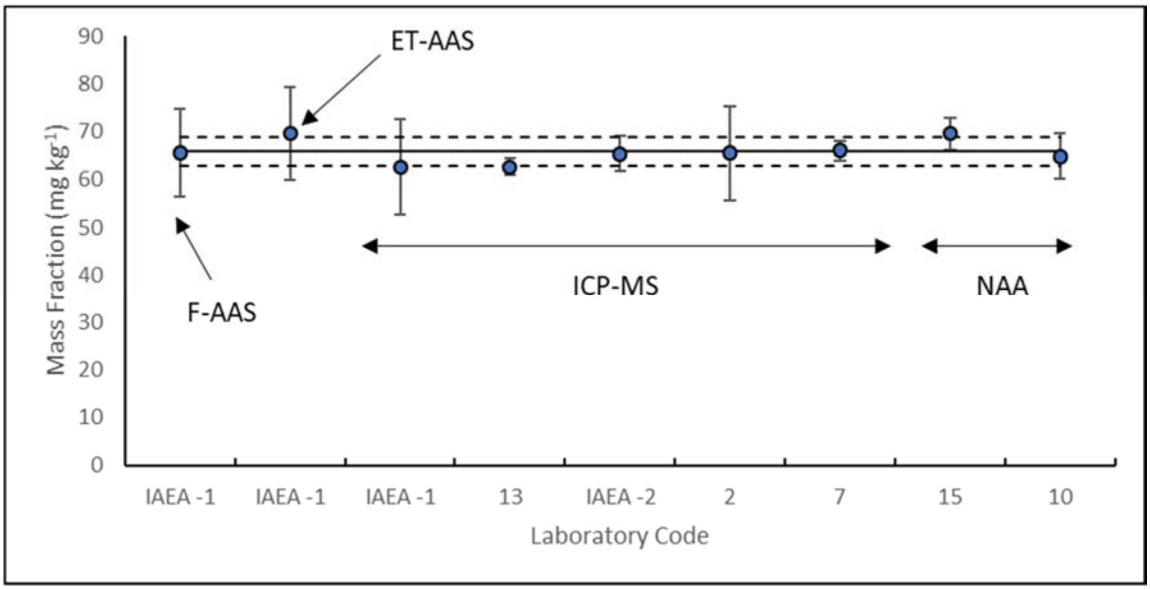

FIG. 24. Laboratory results for chromium mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 14. COPPER: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Flame AAS	27.8	4.4
IAEA-1	Graphite Furnace AAS	28.9	4.6
IAEA-1	ICP-MS	25.0	5.6
2	ICP-MS	26.7	4.0
7	ICP-MS	28.0	2.0
13	ICP-MS	28.1	1.1
IAEA-2	ICP-MS	30.0	1.6

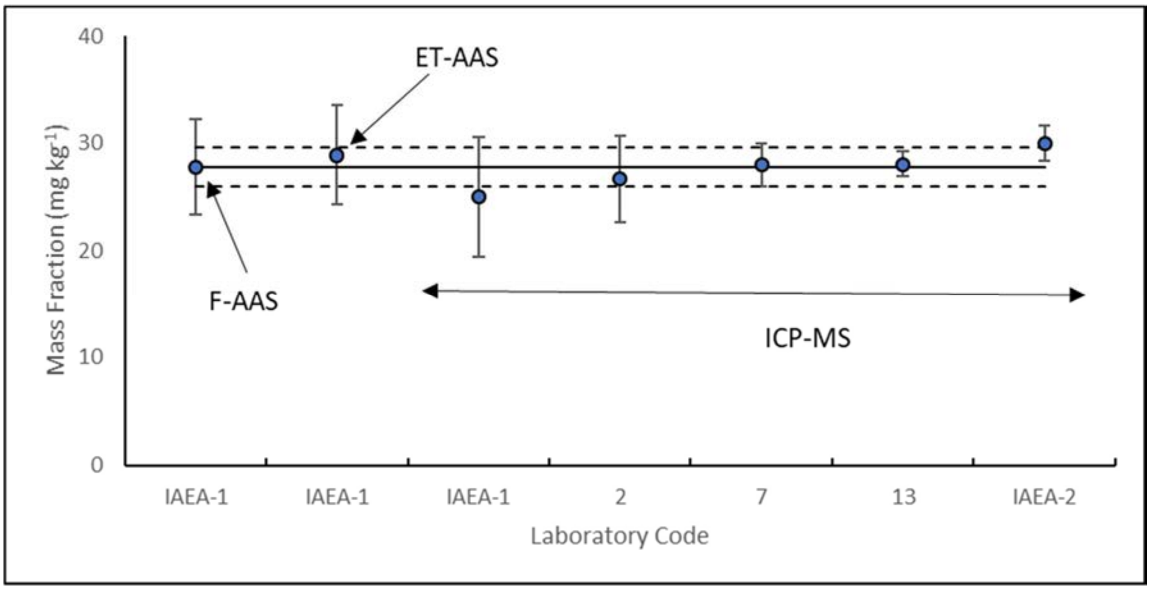

FIG. 25. Laboratory results for copper mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 15. IRON: RESULTS AS REPORTED BY PARTICIPANTS (g kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Flame AAS	32.5	4.5
7	Flame AAS	35.4	0.8
13	ICP-MS	32.6	0.8
10	Neutron Activation (k_0-INAA)	33.9	2.4
15	Neutron Activation	36.4	1.7
Results not used in certification			
2	ICP-MS	35.0	10.5

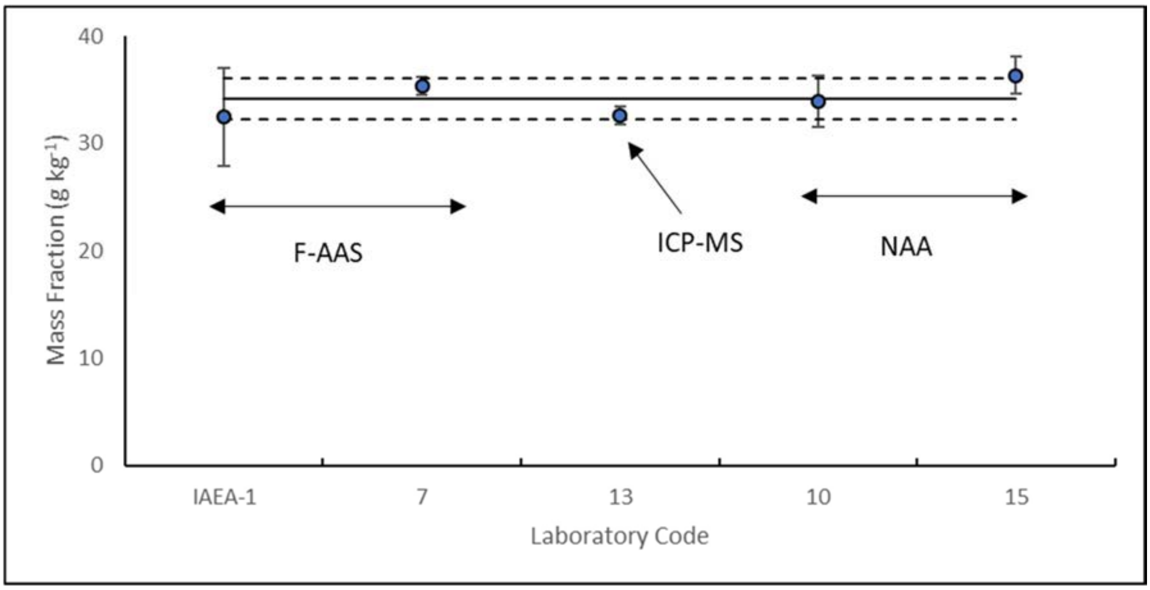

FIG. 26. Laboratory results for iron mass fraction (g kg^{-1}) in IAEA-475.

TABLE 16. MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
10	Cold Vapor AAS	0.0288	0.0026
7	Cold Vapor AAS	0.0310	0.0078
13	Cold Vapor AFS	0.0303	0.0033
8	Solid Hg analyser	0.0278	0.0047
IAEA-1	Solid Hg analyser	0.0300	0.0040
IAEA-1	Solid Hg analyser	0.0288	0.0040
IAEA-1	Cold Vapor ICP-MS	0.0321	0.0026
IAEA-1	Cold Vapor ID ICP-MS	0.0302	0.0013
Results not used in certification			
2	solid Hg analyser	0.0283	0.0085

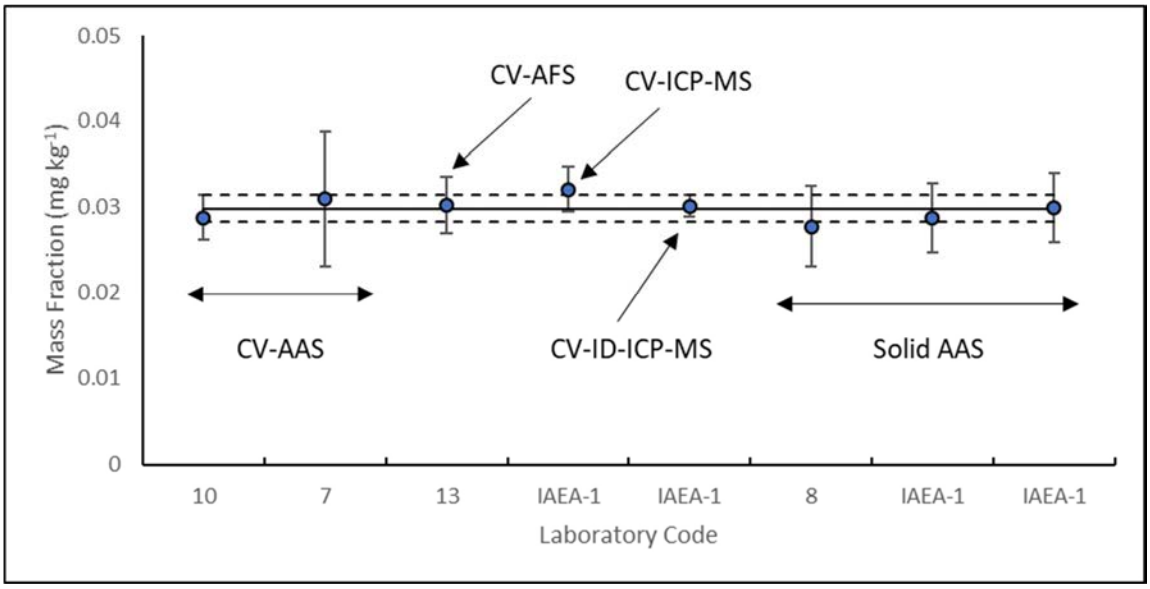

FIG. 27. Laboratory results for mercury mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 17. METHYL MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (µg kg^{-1} as Hg)

Laboratory Code	Method	Mean	Expanded uncertainty (U)
10	GC-AFS	0.2050	0.0240
8	GC-AFS	0.2200	0.0440
IAEA-1	GC-AFS	0.1885	0.0339
16	GC-Isotope Dilution-ICPMS	0.1887	0.0080
IAEA-1	HPLC- Isotope Dilution -ICPMS	0.1960	0.0080
Results not used in certification			
13	GC-AFS	0.144	0.144

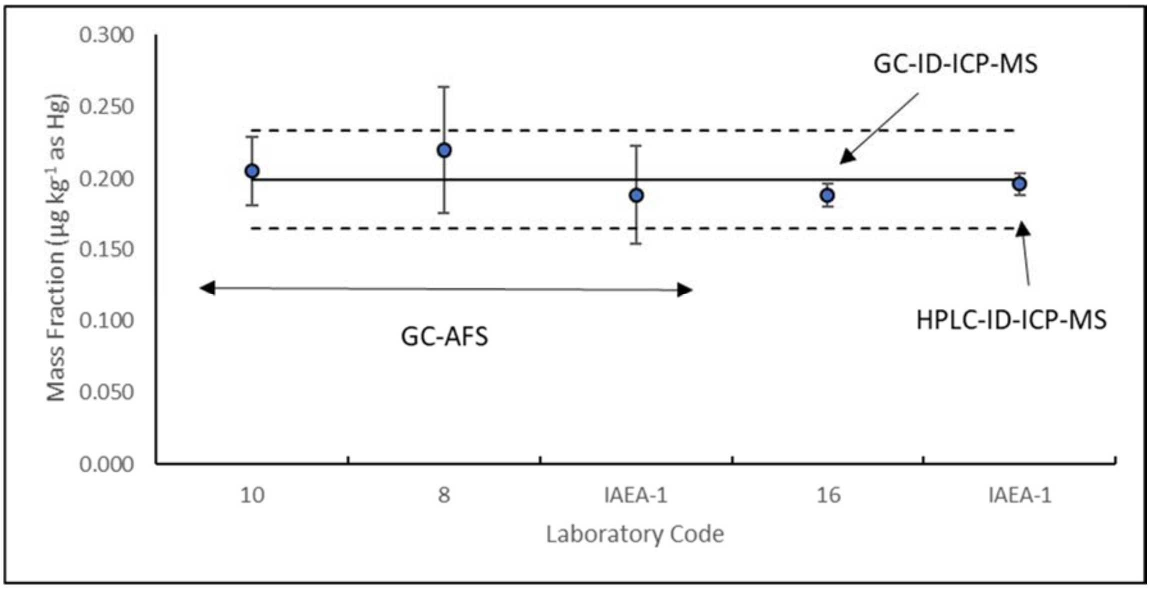

FIG. 28. Laboratory results for methyl mercury mass fraction (µg kg^{-1} as Hg) in IAEA-475.

TABLE 18. LITHIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Flame AAS	41.1	5.7
7	ICP-MS	39.0	2.6
IAEA-1	ICP-MS	41.0	6.0
2	ICP-MS	43.7	8.7

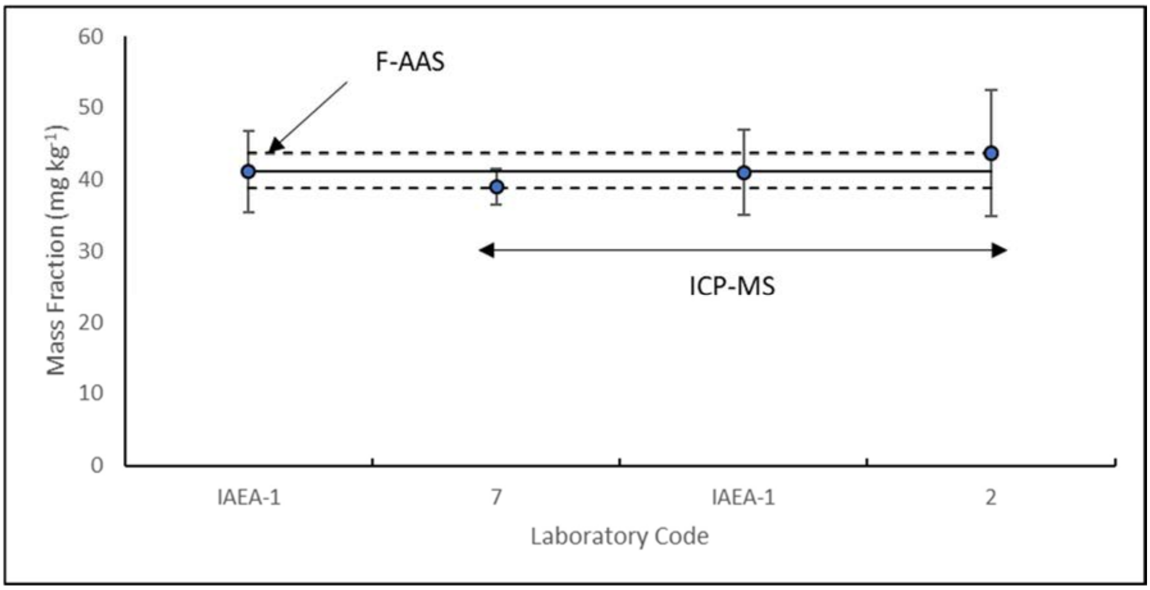

FIG. 29. Laboratory results for lithium mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 19. MANGANESE: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
7	Flame AAS	562	21
IAEA-1	Flame AAS	577	80
2	ICP-MS	563	84
IAEA-2	ICP-MS	589	42
Results not used in certification			
13	ICP-MS	555	36
15	Neutron Activation	563	32

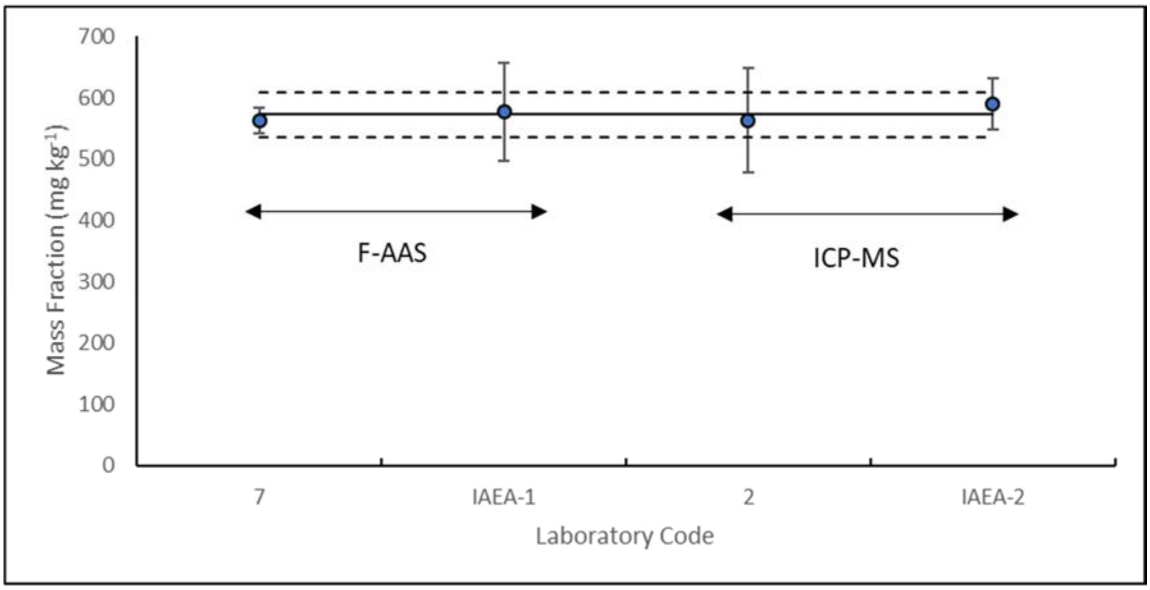

FIG. 30. Laboratory results for manganese mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 20. NICKEL: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Flame AAS	28.7	4.0
IAEA-1	Graphite Furnace AAS	27.6	3.9
IAEA-1	ICP-MS	27.7	4.0
2	ICP-MS	28.2	4.2
7	ICP-MS	28.8	2.4
IAEA-2	ICP-MS	30.1	1.5
IAEA-1	Isotope Dilution ICP-MS	28.6	0.6
Results not used in certification			
13	ICP-MS	24.7	2.2

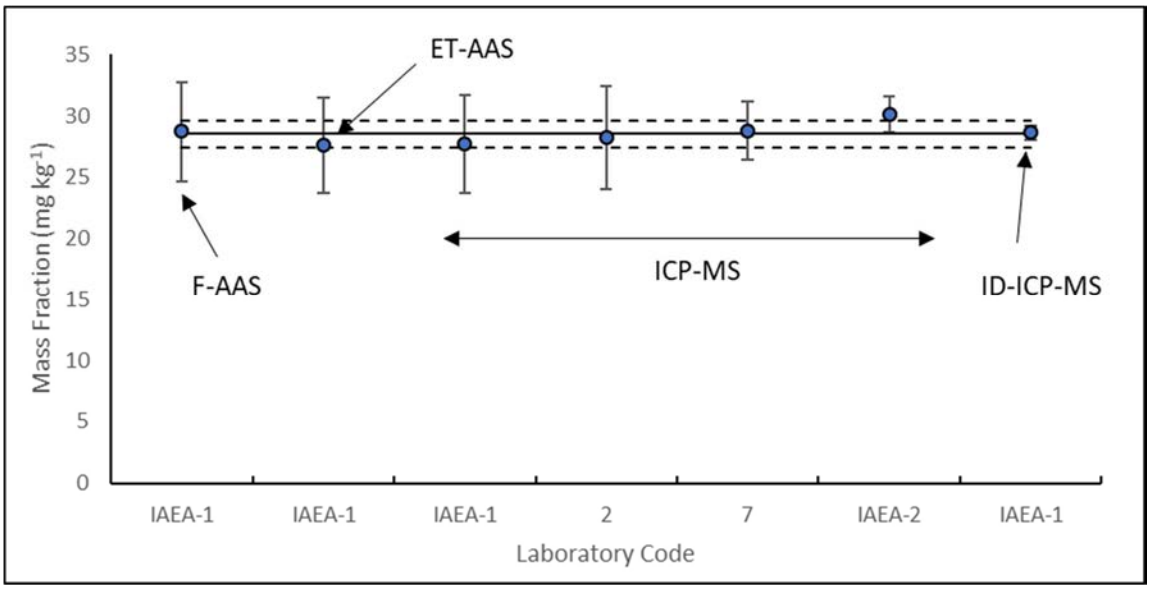

FIG. 31. Laboratory results for nickel mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 21. LEAD: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
7	ICP-MS	28.1	3.6
IAEA-1	ICP-MS	28.7	4.0
IAEA-2	ICP-MS	30.4	1.3
2	ICP-MS	31.0	4.7
13	ICP-MS	31.3	4.3
IAEA-1	Graphite Furnace AAS	30.1	4.2

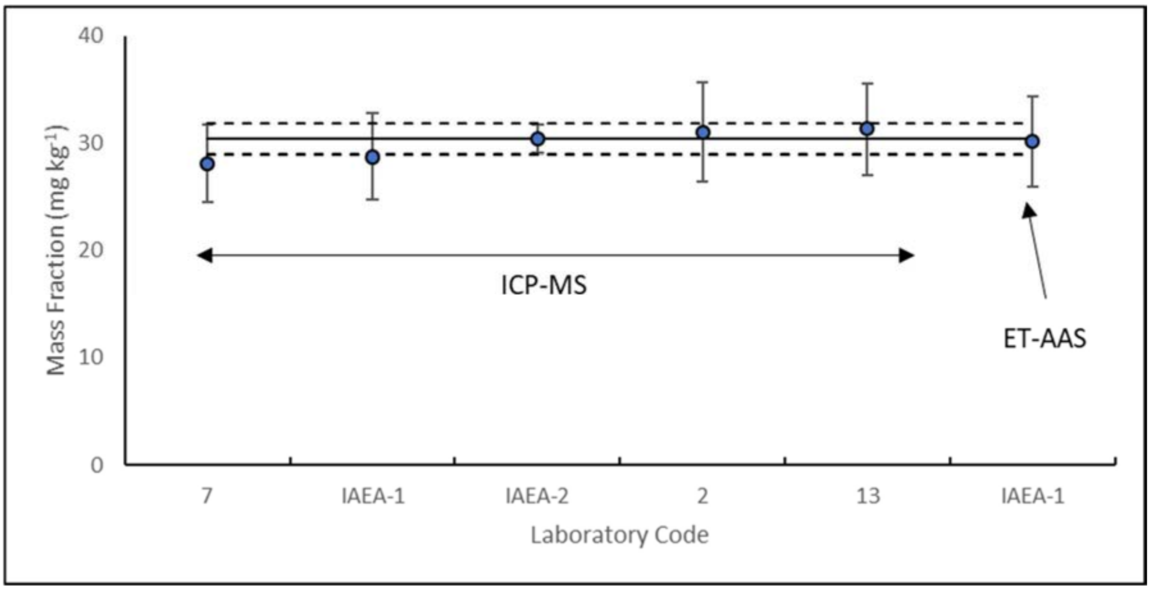

FIG. 32. Laboratory results for lead mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 22. STRONTIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
IAEA-1	Flame AAS	263	37
7	ICP-MS	235	21
IAEA-2	ICP-MS	256	11
10	Neutron Activation (k$_0$-INAA)	252	24
Results not used in certification			
13	ICP-MS	252	7

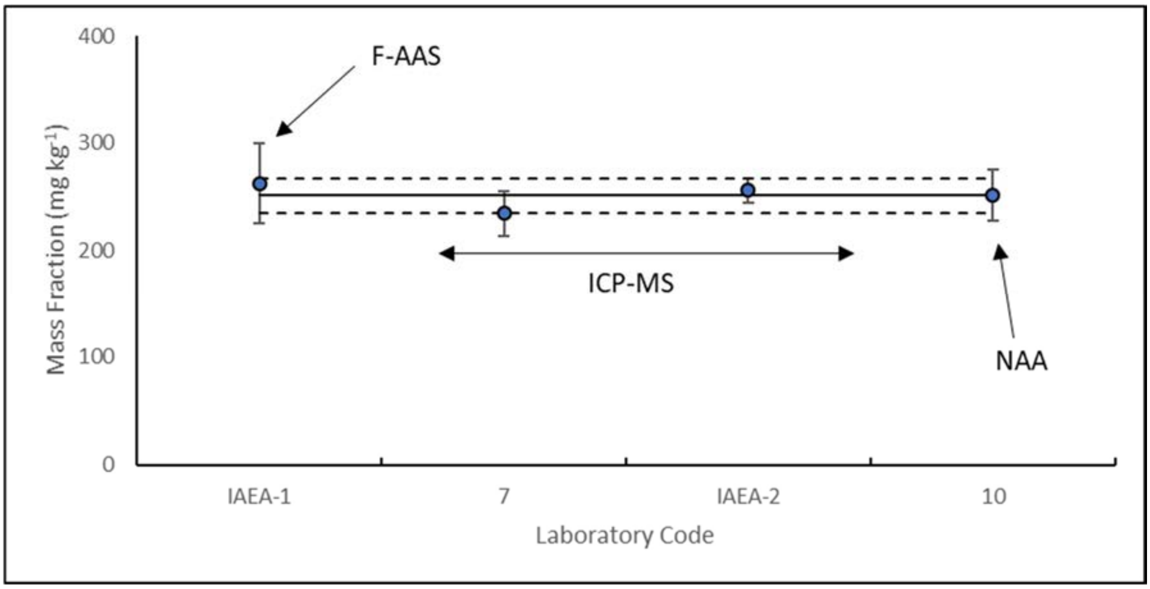

FIG. 33. Laboratory results for strontium mass fraction (mg kg^{-1}) in IAEA-475.

TABLE 23. ZINC: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory Code	Method	Mean	Expanded uncertainty (U)
7	Flame AAS	96.0	11.8
IAEA-1	Flame AAS	97.9	13.7
13	ICP-MS	95.7	9.5
2	ICP-MS	99.0	19.8
IAEA-2	ICP-MS	105	7
IAEA-1	Isotope Dilution ICP-MS	100	2
10	Neutron Activation (k_0-INAA)	95.6	7.0
15	Neutron Activation	111	5

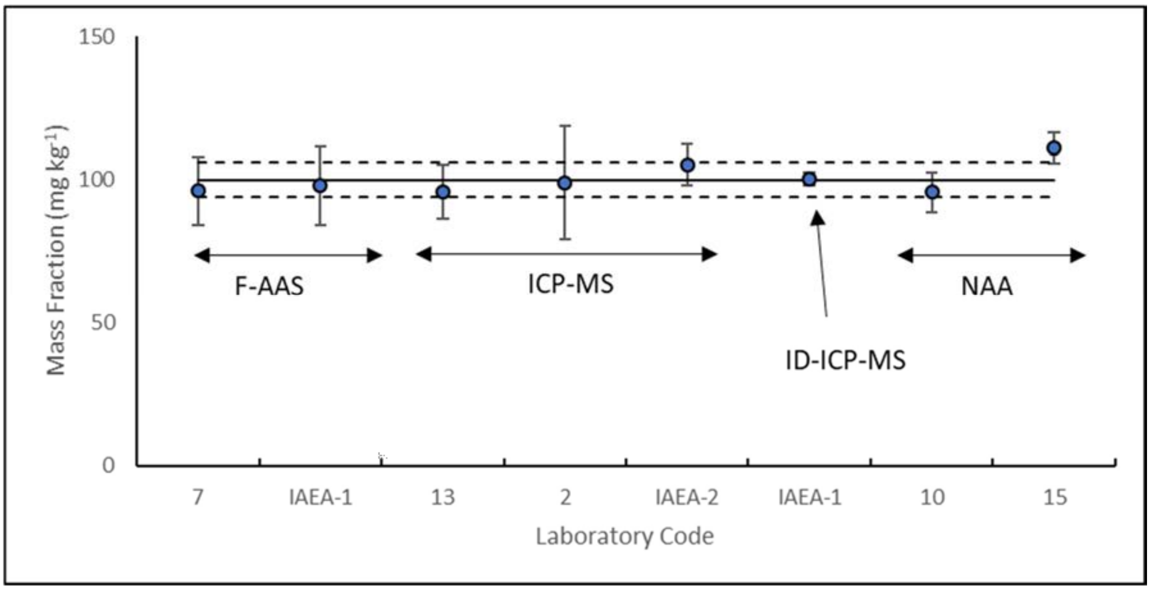

FIG. 34. Laboratory results for zinc mass fraction (mg kg^{-1}) in IAEA-475.

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