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IAEA Analytical Quality in Nuclear Applications Series No. 47

Certification of Trace Elements and Methyl Mercury Mass Fractions in IAEA-470 Oyster Sample

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CERTIFICATION OF TRACE ELEMENTS AND METHYL MERCURY MASS FRACTIONS IN IAEA-470 OYSTER SAMPLE

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CERTIFICATION OF TRACE ELEMENTS AND METHYL MERCURY MASS FRACTIONS IN IAEA-470 OYSTER SAMPLE

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FOREWORD

The primary goal of the IAEA Environment Laboratories is to assist Member States in the use of both stable and radioisotope analytical techniques to understand, monitor and protect the marine environment. In this context, the major impact of large coastal cities on marine ecosystems is an issue of primary concern for the IAEA and the IAEA Environment Laboratories. The marine pollution assessments required to understand such impacts depend on accurate knowledge of contaminant concentrations in various environmental compartments. The IAEA Environment Laboratories have been assisting national laboratories and regional laboratory networks since the early 1970s through their reference products for science and trade programme.

Quality assurance, quality control and associated good laboratory practice are essential components of all marine environmental monitoring studies. Quality control procedures are commonly based on the analysis of certified reference materials and reference samples. This process helps to validate analytical methods used in monitoring studies and to assess reliability and comparability of measurement data. Data that are not based on adequate quality assurance and quality control can be erroneous, and their misuse can lead to poor environmental management decisions.

This publication describes the production of the IAEA-470 certified reference material, which was produced following ISO Guide 34:2009, General Requirements for the Competence of Reference Material Producers. A sample of approximately 10 kg of dried oysters was taken from oysters collected, dissected and freeze-dried by the Korean Ocean Research and Development Institute, and was further processed at the IAEA Environment Laboratories to produce a certified reference material. The sample contained certified mass fractions for arsenic, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, methyl mercury, rubidium, selenium, silver, sodium, strontium, vanadium and zinc. The produced vials containing the processed oyster sample were carefully capped and stored for further certification studies.

Between-unit homogeneity and stability during dispatch and storage were quantified in accordance with ISO Guide 35:2006, Reference Materials — General and Statistical Principles for Certification. The material was characterized by laboratories with demonstrated competence and adhering to ISO/IEC 17025:2005. Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (JCGM 100:2008), including uncertainty associated with heterogeneity and instability of the material, and with the characterization itself. The material is intended for the quality control and assessment of method performance. As with any reference material, it can also be used for control charts or validation studies.

The IAEA wishes to thank all the participants and laboratories that took part in this characterization study. The IAEA is also grateful to the Government of Monaco for its support. The IAEA officers responsible for this report were E. Vasileva and S. Azemard of the IAEA Environment Laboratories.

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CONTENTS

1. INTRODUCTION

Many laboratories are involved in the production of local or regional environmental data leading, in many cases, to wider assessments. These laboratories may develop and validate new analytical methods, study the environmental impact of human activities, provide services to other organizations, etc. The importance of having base scientific conclusions based on valid and internationally comparable data and to provide policy-makers with correct information on the state of the environment, it is indispensable to ensure the quality of the data produced by each laboratory.

The Marine Environmental Studies Laboratory (MESL) of the IAEA's Environment Laboratories (IAEA-EL) has the programmatic responsibility to provide assistance to Member States' laboratories in maintaining and improving the reliability of analytical measurement results, both in trace elements and organic pollutants. This is accomplished through the provision of certified reference materials of marine origin, validated analytical procedures, training in the implementation of internal quality control, and through the evaluation of measurement performance by the organization of world-wide and regional interlaboratory comparisons (ILC). IAEA's subprogramme 'Reference Products for Science and Trade' represents an important benchmark in upgrading the quality of laboratory performances and assessing the validity of the analytical methods used for marine monitoring studies in the member states.

Laboratories need to be able to check the performance of their methods for the determination of trace elements in difficult matrices such as marine biota. This is also true for standardized methods, the use of which does not guarantee accurate results. It is widely accepted that laboratories need to demonstrate their proficiency in the applicability of standard methods, for example, by using certified reference materials (CRMs).

While there are several CRMs certified for trace elements, there is still a noticeable lack of matrix CRMs.

The work presented in this report refers exclusively to the certification of the mass fractions of 19 trace elements (Ag, As, Ca, Cd, CH_3Hg, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Pb, Rb, Se, Sr, V and Zn) in oyster sample.

The CRM IAEA-470 has been developed to satisfy the demands of laboratories dealing with environmental and food safety analyses.

2. METHODOLOGY

2.1. COLLECTION AND PREPARATION OF THE MATERIAL

A sample of 10 kg of dried oysters was delivered by the Korean Ocean Research and Development Institute (KORDI).

The homogenization of the material was performed by dividing the total mass of oyster material to 12 lots, each of them with the weight of 1.5 kg. The material of each lot was transferred into clean plastic bottles and mixed using a shaker (Turbula, Switzerland) for 24 hours at 20°C and humidity of 50%. Aliquots of about 20 g were packed into pre-cleaned polyethylene bottles with secured screw caps immediately after stopping the mixing operation. The process was repeated 12 times and bottles were labeled with lot and bottle numbers.

The sample material was labeled as IAEA-470. The average moisture content of the sample after bottling was determined by oven drying of then subsamples (1 g each) to a constant mass at 85°C.

Particle size distribution was checked from the beginning to the end of the processing by using a particle analyser (Mastersizer, Malvern Instruments, Germany) on randomly selected units. The resulting material showed 90% particle size below 100 µm (Figure 1).

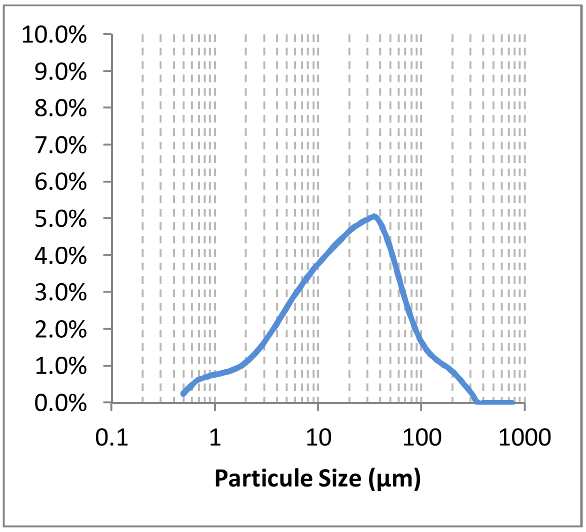

FIG. 1. Particle size measurements for IAEA-470 sample.

2.2. SELECTION OF LABORATORIES FOR THE CHARACTERIZATION STUDY

The selection of participants for this characterization study was based on the measurement performances demonstrated by laboratories in the previous IAEA characterization studies and ILC on marine biota. Only results of laboratories having a quality system in place, using validated methods, applying uncertainty and traceability concepts and providing good results in the previous IAEA ILC were accepted for the calculation of the assigned values and their uncertainties.

Each laboratory received one bottle of oyster sample, accompanied by an information sheet and a reporting form. Participants were requested to analyse Ag, Al, As, Cd, CH_3Hg, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sn, Se, V and Zn using a validated analytical method; results for other elements were also welcome. The second request was to report the measurement results (three replicates and average value) along with the expanded uncertainty in addition to the information about the applied quality control procedure. The second request was to report results for the trace elements in a CRM with a matrix similar to the candidate reference material. As a result for moisture in the oyster sample is operationally dependent, the method for moisture determination was prescribed to all participating laboratories.

The list of laboratories participating in the characterization study is presented page 48.

2.3. HOMOGENEITY ASSESSMENT

A key requirement for any reference material is the equivalence between various units. Extensive homogeneity tests were carried out on this material in order to ensure its suitability as a certified reference material and to estimate the uncertainty associated with homogeneity of the sample.

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. The between-unit homogeneity was tested by the determination of the mass fractions of some typical elements (As, CH_3Hg, Cr, Cu, Fe, Hg, Mn, Ni and Zn) in the oyster sample.

In total, one bottle from each lot was selected (12 bottles in total) using random stratified sampling. Care was taken to ensure that the order of measurements did not correspond to the filling sequence of the bottles, which enables the differentiation between potential trend in the filling sequence and analytical drift. Three subsamples from each bottle were analysed for their total element mass fractions. For all elements except Hg and CH_3Hg, subsamples of 0.2 g were mineralized with 5 ml conc. HNO_3 in a microwave oven. The final measurements were performed by flame and graphite furnace atomic absorption spectrometry under repeatability conditions, and in a randomized way, in order to be able to separate a potential analytical drift from a trend in the filling sequence. The determination of the total Hg was done in solid subsamples (50 mg) with solid mercury analyser. Methyl mercury was determined by gas chromatography coupled with atomic fluorescence spectrometer (GC-AFS) after alkaline digestion and room temperature derivatization.

Results for Ag, Cd, Co, Pb, and Sr obtained by ICP-MS and for CH_3Hg by GC-AFS in the frame of long-term stability studies, were also used for homogeneity assessment. The use of the long-term stability study data for homogeneity evaluation in this particular case was appropriate since no sign of instability of oyster sample with the time has been detected (see 3.2.2.)

All methods used for homogeneity studies were previously validated in MESL, IAEA Inorganic Chemistry Laboratory.

2.4. STABILITY STUDY

Stability testing is necessary to establish conditions for dispatching the IAEA-470 sample to customers (short-term stability) as well as conditions for storage (long-term stability) of the material.

Time, temperature and light were regarded as the most relevant parameter affecting stability of the oyster sample. The influence of light was minimized by the choice of the container (i.e., amber bottles placed in aluminized sachet). In addition, the material was stored in the dark, thus practically eliminating the possibility of degradation by light. Therefore, only the influences of time and temperature were further investigated.

The stability studies for IAEA-470 were carried out using an isochronous approach. In this approach, selected units are stored for a certain time at different temperature conditions. Afterwards, the units are moved to conditions where further degradation can be assumed to be negligible (reference conditions), effectively 'freezing' the degradation status of the materials. At the end of the isochronous storage, the units are analysed simultaneously under repeatability conditions, improving in this way the sensitivity of the stability tests.

2.4.1. Short-term stability

One isochronous study over four weeks was applied in order to evaluate short term stability of the materials during the transportation. 8 bottles were stored in the dark at +20°C immediately after the bottling and eight bottles at +60°C for 1, 2, 3 and 4 weeks respectively. After each of above mentioned time intervals two bottles kept at +20°C and another two kept at +60°C were transferred to -20°C temperature, considered as reference temperature for this study. Two independent measurements per bottle were performed under repeatability conditions. The obtained results were compared with the results from samples kept at -20°C during the entire period of the stability study.

The measurements were performed by flame atomic absorption for Cu, Fe, Mn, Zn; by graphite furnace for As, Ni and Cr and by Advance Mercury Analyser for total Hg. The measurements were performed under repeatability conditions, and in a randomized manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each unit by using the procedure in the section 2.6.

2.4.2. Long-term stability

In the same way, an isochronous study over 24 months was performed to evaluate long-term stability of the materials under prescribed storage conditions. Eight bottles were stored in the dark at +20°C for 6, 12, 18 and 24 months respectively. Reference temperature was kept at -20°C. Two independent measurements per bottle were performed under repeatability conditions. The obtained results were compared with the results from samples kept at -20°C during the entire period of the stability study.

The measurements were performed by ICP-MS for Ag, As, Cd, Co, Cu, Mn, Ni, Pb, Sr, Zn; by Advance Mercury Analyser for total Hg and by gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) for CH_3Hg. The measurements were performed under repeatability conditions and in a randomized manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each unit by using the procedure in the section 2.6.

2.5. CHARACTERIZATION

Characterization refers to the process of determining the certified values. The material was initially analysed in the IAEA-EL in Monaco. The final characterization was based on the results delivered by selected laboratories with demonstrated measurement capabilities, based on criteria that comprised both technical and quality management aspects. The characterization of the trace element mass fraction in the oyster sample was based on the application of different analytical techniques as summarized in Figure 2 on page 6. Abbreviations used in this report for description of applied in the characterization study instrumental techniques are given in Table 1.

All participating laboratories have been requested to use validated methods for the determination of requested trace elements in the oyster sample. In addition, they provided results from the analysed CRM with matrix composition similar to the candidate reference material, and information on standard calibration solutions used in the measurement step. The results of laboratories not reporting any quality assurance data were excluded from further evaluation.

Combined uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [1], including uncertainties of characterization, estimated heterogeneity and instability.

All participating laboratories claimed traceability of provided results to the International System of Units (SI) via standard calibration solutions and CRM applied as a part of their analytical procedures.

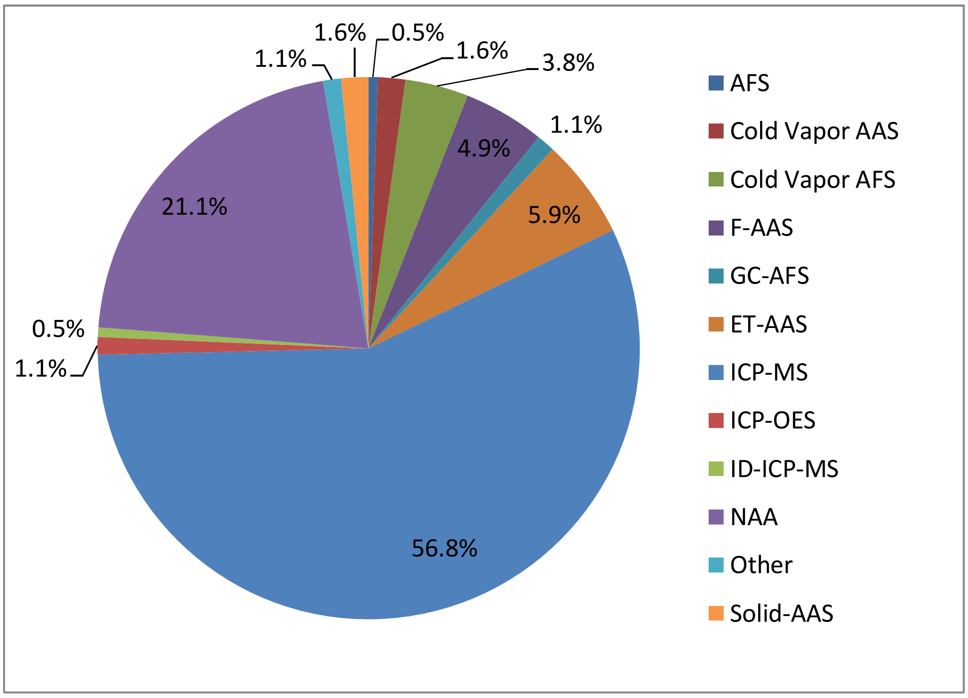

FIG. 2. Analytical methods used for the characterization of trace elements in the IAEA-470 oyster sample.

TABLE 1. INSTRUMENTAL TECHNIQUES

Method code	Instrumental technique
AFS	Atomic Fluorescence Spectrometry
CV-AAS	Cold Vapour - Atomic Absorption Spectrometry
CV-AFS	Cold Vapour - Atomic Fluorescence Spectrometry
F-AAS	Atomic Absorption Spectrometry – Flame
GC-AFS	Gas Chromatography coupled with Atomic Fluorescence Spectrometry
ET-AAS	Atomic Absorption Spectrometry - Graphite furnace
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Optical Emission Spectrometry
ID ICP-MS	Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
NAA	Neutron Activation Analysis
Solid AAS	Solid Sampling Atomic Absorption Spectrometry

2.6. MOISTURE DETERMINATION

The determination of the moisture content of the samples is to some extent an ‘operationally defined’ parameter. In view of the comparability of results, the protocol for the correction of the moisture was developed at IAEA-EL and prescribed to other participants. The drying procedure at 85(±2)°C was established after experimental evaluation of sample stability. Correction for dry mass was obtained from separate portions of the material of minimum mass of 0.5 g (10 sub samples from 5 bottles). The weighing and repeated drying were performed until constant mass was attained. Moisture, determined at 85°C, was found to be 6.5(±0.5) % for bottles kept at 20°C.

3. RESULTS AND DISCUSSION

3.1. RESULTS OF THE HOMOGENEITY STUDY

3.1.1. Between-unit homogeneity

For the homogeneity study, 12 units (about 2% of the total batch) of oyster sample were selected by using a random stratified sample picking scheme and analysed for their trace elements contents in triplicate. Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence.

Results of Cu and Hg have shown significant trend in the bottling sequence at 95% but also 99% confidence level.

Grubbs-tests at 95% and 99% confidence levels were also performed to identify potentially outlying individual results as well as outlying bottle means. As presented in Table 2 on page 10, few individual results were detected as outliers at 95% and 99% confidence levels. Additionally one outlying unit mean was found for Zn. No technical reasons were identified for outlying results, and all data were retained for statistical analysis. It was checked whether the retained individual results and unit means followed a normal distribution or are unimodally distributed. It was found out that the series of results for investigated trace elements were normally distributed.

Quantification of between-unit homogeneity was done by analysis of variance (ANOVA) which can separate the between-unit variation (s_{bb}) 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 [2]. ANOVA allows the calculation of within-unit standard deviation s_{wb} and also between-units standard deviation s_{bb}:

$$s_{wb} = u_{wb} = \sqrt{MS_{wb}} \tag{1}$$

$$s_{bb} = u_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{n}} \tag{2}$$

s_{bb} and s_{wb} are estimates of the true standard deviations and are therefore subject to random fluctuations. Therefore, the mean square between groups (MS_{bb}) can be smaller than the mean squares within groups (MS_{wb}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum heterogeneity that could be hidden by method repeatability, was calculated as described by Linsinger et al. [3]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum heterogeneity that might be undetected by the given study setup.

For As, Co, Ni and Sr; ANOVA mean square between units was smaller than MS_{wb} (ANOVA mean square within units) and $s_{bb.}$ could not be calculated. Instead, u^*_{bb}, the homogeneity was calculated as described by Linsinger et al. [3]:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwb}}} \tag{3}$$

Where: n is the number of replicate sub-samples per bottle; and $\nu_{MSw\mathit{b}}$ is the degrees of freedom of MS_{wb}.

For Zn for which outlying unit average was detected, between-unit homogeneity was modelled as a rectangular distribution limited by the largest outlying unit average, and the standard uncertainty of homogeneity was estimated as:

$$u_{bb} = \frac{|outlier - y|}{\sqrt{3}} \tag{4}$$

y : average of all results of the homogeneity study

It should be mentioned that the outlying unit averages are a result of presence of outlying individual values and do not necessarily reflect the real distribution of these elements in the material.

For Cu and Hg where bottling sequence trends have been detected, between-unit variation was modelled as the half width of a rectangular distribution between the highest and the lowest bottle average,

$$u_{bb} = \frac{|highest\ result - lowest\ results|}{2\sqrt{3}} \tag{5}$$

For nickel the within bottle variation (s_{wb}) was higher than typical method repeatability (4%), which could indicate that within unit homogeneity is not sufficient at the sample intake used for the study (200 mg) and the calculated u^*_{bb} might underestimate the real uncertainty associated with sample heterogeneity. The between-units homogeneity could have been quantified due to the good repeatability of the method used with the exception of Ni.

The between-unit variations were between 1.5 and 3.6%, small enough to ensure the homogeneity of the material. The uncertainty contributions due to the between-unit homogeneity were estimated according to ISO Guide 35 [2] as the maximum values obtained with Eq. 3, Eq. 4, Eq. 5 or Eq. 6. The uncertainty from homogeneity for elements not included in the homogeneity study (Al, Ca, Cr, Mg, Na, Rb, Se and V) was set at 3.6%.

TABLE 2. THE ESTIMATE OF INHOMOGENEITY CONTRIBUTIONS TO THE TOTAL UNCERTAINTY FOR THE CERTIFIED TRACE ELEMENTS

	Individual outliers		Mean outliers		s_{wb}	s_{bb}	u^*_{bb}	u_{bb}	u_{homo}
	95%	99%	95%	99%	%	%	%	%	%
Ag	0	0	0	0	2.5	0.2	1.1	-	1.1
As	0	0	0	0	3.9	1)	1.2	-	1.2
Cd	0	0	0	0	2.3	1.5	1.0	-	1.5
CH_3Hg	0	0	0	0	6.8	2.4	3.6	-	3.6
Co	0	0	0	0	3.9	1)	1.8	-	1.8
Cr	0	0	0	0	2.8	2.6	0.9	-	2.6
Cu	0	0	0	0	1.3	1.3	0.4	1.3	1.3
Fe	3	2	0	0	1.7	1.6	0.5	-	1.6
Hg	0	0	0	0	1.9	2.8	0.6	2.6	2.8
Mn	2	2	0	0	2.0	1.2	0.62	-	1.2
Ni	0	0	0	0	9.4	1)	3.0	-	3.0
Pb	2	1	0	0	5.5	3.4	2.6	-	3.4
Sr	2	0	0	0	2.9	1)	1.4	-	1.4
Zn	1	1	2	2	1.4	1.0	0.4	1.1	1.1

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

3.1.2. Within-unit homogeneity

The within-unit homogeneity is closely related with the minimum sample intake. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

In this study, the minimum sample intake was assessed by using the method information supplied by the laboratories participating in the characterization study. The smallest sample intake that still yielded results with acceptable trueness to be included in the respective studies was taken as minimum sample intake.

The minimum sample intake for all certified elements in this study was set to 50 mg for Hg and 200 mg for all other elements.

The conclusion from the presented results was that the homogeneity of the candidate reference material complied with the provisions given by the ISO Guide 35, at the range of weights used. A minimum sample intake of 0.2 g was set, based on the smallest sample intake used in the characterization study.

3.2. RESULTS FOR STABILITY STUDY

3.2.1. Short term stability study

The samples selected for short term stability study were analysed and each of the elements (As, Cr, Cu, Fe, Hg, Mn, Zn) was evaluated individually. The obtained data were evaluated individually for each temperature (20°C and 60°C).

No outliers were found and the evaluation of data was further carried out by performing a linear regression on the determined mass fractions versus time. The test material showed no significant trend of degradation over the timeframe at different temperatures: +20°C and +60°C. No significant slope at 99% level of confidence was detected for any of investigated trace elements in the short-term stability study. As no degradation could be observed under any of applied conditions it was concluded that no special precautions regarding temperature control during shipment are necessary. The uncertainty of the short-term stability (u_{sts}) estimated as described by Linsinger et al. [4] for 2 weeks was less than 1% for all studied elements. It is considered to be negligible since no degradation was expected during this short time.

3.2.2. Long-term stability study

The samples selected for short-term stability study were analysed and each of the elements (Ag, As, Cd, CH_3Hg, Co, Cu, Hg, Mn, Ni, Pb, Sr, Zn) was evaluated individually. As presented in Table 3 few individual outliers were found at 95% but also at 99%, but since no technical reasons were identified for outlying results (with only exception – data for Ni) , all data were retained for statistical analysis.

The evaluation of data was further carried out by performing a linear regression on the determined mass fractions versus time. The test material showed no significant trend of degradation over the timeframe at prescribed storage conditions (+20C° in the dark). No significant slope at 95% level of confidence was detected for any of the investigated analytes in the long-term study.

Failure to detect degradation, however, does not prove stability. The uncertainty of stability u_{stab} describes the potential degradation which still can be reconciled with the data, even if the slope is not statistically and significantly different from zero. Although under these conditions an expansion of the total uncertainty of the certified values is generally not encouraged, in this case the approach of ISO Guide 35 [2] was followed, mainly due to the lack of sound alternatives. An uncertainty contribution related with the stability of the candidate reference material ($u_{stab)}$ was estimated as uncertainty of the regression line with a slope of 0 multiplied with the chosen shelf life, as described by Linsinger et al. [4]. Graphical representations of the long–term stability study are displayed in Appendix 2 (Figures 3–14). The estimated standard uncertainty of long-term stability varies from 1.8 to 6.8%. In the case of CH_3Hg (6.8%) and Pb (6.2%) the relatively high uncertainty observed for long term stability is related with the lower repeatability of the analytical methodology used for characterisation, typically observed at this low level. For Ni, u_{stab} was estimated at 16.5%, but this high value is most probably linked with the lack of homogeneity of sample.

The uncertainty from long-term stability for elements not included in the study was set as the average estimate uncertainty: 3.5%.

TABLE 3. THE ESTIMATE CONTRIBUTION OF UNCERTAINTY ON STABILITY TO THE TOTAL UNCERTAINTY OF THE CERTIFIED TRACE ELEMENTS

	Individual outliers 95%	Individual outliers 99%	Slope significance (95%)	u_{stab} %
Ag	0	0	No	1.8
As	0	0	No	2.9
Cd	0	0	No	2.1
CH_3Hg	0	0	No	6.8
Co	0	0	No	3.4
Cu	1	0	No	3.5
Hg	0	0	No	1.3
Mn	0	0	No	2.8
Ni	3	1	No	16.5
Pb	2	1	No	6.2
Sr	0	0	No	2.1
Zn	0	0	No	2.2

3.3. DETERMINATION OF CERTIFIED VALUES AND UNCERTAINTIES

The characterization campaign resulted in 1–15 results for the 34 elements but only 21 elements with more than 5 reported results were further considered for certification. The obtained data 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 test to detect single and double outliers, Dixon's test to detect outlying laboratory means and Kolmogorov-Smirnov's test for normal distribution. Few individual outliers were found at 95% for Cd, CH_3Hg, Co, Cr, Fe, Hg and V but also at 99% for CH_3Hg and Co. Since no technical reasons were identified for outlying results, all data were retained for statistical analysis. All data sets were normally distributed.

Robust statistics as described in ISO 13528 [5] were used for the determination of the assigned values. The robust mean and robust standard deviations were calculated as per Algorithm A, i.e., as described in ISO 13528, Annex C.21 [5].

Briefly, individual results were ranked in increasing order:

(x_1, x_2, x_i,...x_p)

Initial values of the robust average x^* and robust standard deviation s^* were calculated as:

$$x^* = \text{median of } x_i \quad (\text{i}=1,2,3\cdots.\text{p}) \tag{6}$$

$$s^* = 1.483 \times \text{median } |x_i - x^*| \quad (\text{i}=1,2,3\cdots..\text{p}) \tag{7}$$

The initial values x^* and s^* were updated by calculating:

$$\delta = 1.5 \times s^* \tag{8}$$

For each x_i $(i = 1,2,3 \ldots.p)$ calculate

$$x_i^* = \begin{Bmatrix} x_i^* = x^* - \delta, & \text{if } x_i < x^* - \delta \\ x_i^* = x^* + \delta, & \text{if } x_i > x^* + \delta \\ x_i^* = x^*, & \text{otherwise} \end{Bmatrix} \tag{9}$$

New values for x^* and s^* were calculated as:

$$x^* = \frac{\sum_1^p x_i^*}{p} \tag{10}$$

$$s^* = 1.134\sqrt{\frac{(x_i - x^*)^2}{(p-1)}} \tag{11}$$

The robust estimates of x^* and s^* were calculated by iteration by updating the values of x* and s* until they converged to the third significant figure.

The medians and unweighted mean of the means were also calculated and compared with the respective robust mean. No significant differences were observed and the reference values obtained with the robust mean approach were further used. These values are considered to be the most reliable estimates of the property values.

The uncertainties associated with the reference values were calculated according to ISO Guide 35 [2]. The relative combined uncertainty of the certified value of the CRM consists of uncertainty related to characterization u_{char}, between-unit heterogeneity (u_{bb}) and long-term stability (u_{stab}),while uncertainty component due to short term stability was demonstrated to be negligible. These different contributions were combined to estimate the expanded uncertainty.

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \qquad (12)$$

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

u_{hom} was estimated as described in section.

u_{stab} was estimated as described in section 3.2.2.

u_{char} was estimated as described in ISO 13528 [5] using Eq. 13:

$$u_{char} = 1.25 \times \frac{s^*}{\sqrt{p}} \qquad (13)$$

Where: s^* is the robust standard deviation calculated by Eq. 11; p is the number of laboratories.

Robust means and uncertainties are presented in Table 4.

As shown previously in Figure 1on page 2, methods with different quantification steps (AAS, ET-AAS, AFS, ICP-MS) as well as methods without sample preparation step such as INAA, Solid Sampling AAS and X ray Fluorescence were used for characterization of the material. The agreement between results confirms the absence of any significant method bias and demonstrates the identity of the analyte.

The results provided by participants for trace element mass fractions grouped by methods are displayed in Figures 15–34 and in Tables 7–26 (Appendix III). In all figures, the reported results are plotted versus the robust mean denoted by a bold line, while the dashed lines represent the expanded uncertainty (*k=2*) associated with the robust mean (as calculated in Eq. 13). The error bars represent the expanded uncertainty as reported by participants.

For all elements results from at least 2 independent analytical methods were available. A good agreement within the stated uncertainty was observed for results obtained with different methods. Therefore, all of them were considered in deriving certified values.

The certified values are presented in Table 5, together with their expanded uncertainty.

For Ni the relative expanded uncertainty (34.3%) reflects the heterogeneity of sample at prescribed minimum sample size (200 mg) consequently only information value is provided from this characterization study.

TABLE 4. ROBUST MEANS AND UNCERTAINTIES

Element	Robust mean mg kg^{-1}	u_{char}, %	u_{hom}, %	u_{stab}, %	U (*k*=2) %
Ag	1.29	3.3	1.1	1.8	7.9
As	11.8	1.9	1.2	2.9	7.3
Ca	2430	3.0	3.5	3.5	11.6
Cd	3.14	2.8	1.5	2.1	7.7
CH_3Hg^*	0.00522	3.1	3.6	6.8	16.6
Co	0.201	5.0	1.8	3.4	12.6
Cr	0.965	3.9	2.6	3.5	11.7
Cu	146	2.3	1.3	3.5	8.8
Fe	131	2.3	1.6	3.5	8.9
Hg	21.1	3.9	2.8	1.3	9.9
Mg	3080	4.0	3.5	3.5	12.8
Mn	66.7	2.6	1.2	2.8	8.0
Na	19700	3.1	3.5	3.5	11.7
Ni	0.849	3.6	3	16.5	34.3
Pb	0.361	1.8	3.4	6.2	14.6
Rb	5.14	2.9	3.5	3.5	11.5
Se	3.06	2.3	3.5	3.5	10.9
Sr	20.6	3.0	1.4	2.1	7.8
V	0.899	5.3	3.5	3.5	14.4
Zn	727	2.2	1.1	2.2	6.6

* mg kg^{-1} as Hg

4. METROLOGICAL TRACEABILITY AND COMMUTABILITY

If the results obtained by different laboratories are to be compared, it is essential that all results are based on reliable measurement standards the values of which are linked to the same reference.

Only validated methods applied within stated scope were used by participating laboratories in this characterization study. Matrix CRMs with stated SI traceability purchased from NIST, EC JRC IRMM, NRC-CNRC and IAEA were used for validation of the methods applied in this study.

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 of 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 Standards and Technology, Federal Institute for Materials Research, USA and Testing, Germany or Swiss Federal Laboratories for Materials Science and Technology, Switzerland) with demonstrated International System of Units (SI) traceability, followed by gravimetric preparation using balances calibrated with SI-traceable weights.

In addition, the agreement between the results confirms the absence of any significant method bias and demonstrates the identity of the measurand. Measurands are clearly defined as total element mass fractions and independent of the measurement method. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias.

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

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

Commutability is a property of an RM, 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 [6].

The appropriate characterization of CRMs, especially those materials intended to be used with routine measurement procedures, must carefully address fitness-for-use for all methods which the material is intended to be used for. Commutability is a critical requirement to avoid introducing unintended, and sometimes undetected, bias results when using a CRM.

Commutable CRMs should exhibit an analytical behaviour for a given method similar to a real laboratory sample. However, CRMs might show behaviour 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 real laboratory samples. IAEA-470 is a natural marine biota sample. The analytical behaviour should be the same as for a routine sample of dried biota samples. The agreement between results obtained with different analytical methods selected for the IAEA-470 characterization study confirms the absence of any significant method bias and demonstrates commutability of the material for all certified trace elements.

TABLE 5. CERTIFED VALUES FOR TRACE ELEMENT MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k=2*) IN THE IAEA-470 OYSTER SAMPLE

Element	Unit	Certified value[1]	Expanded uncertainty (*k=2*)[2]
Ag	mg kg-1	1.29	0.10
As	mg kg-1	11.9	0.9
Ca	mg kg-1	2430	282
Cd	mg kg-1	3.14	0.24
CH_3Hg	µg kg-1 as Hg	5.22	0.87
Co	mg kg-1	0.201	0.025
Cr	mg kg-1	0.965	0.113
Cu	mg kg-1	146	13
Fe	mg kg-1	131	12
Hg	µg kg-1	21.1	2.1
Mg	mg kg-1	3080	390
Mn	mg kg-1	66.7	5.3
Na	mg kg-1	19700	2300
Pb	mg kg-1	0.361	0.053
Rb	mg kg-1	5.14	0.59
Se	mg kg-1	3.06	0.33
Sr	mg kg-1	20.6	1.6
V	mg kg-1	0.899	0.130
Zn	mg kg-1	727	48

[1] The value is the robust mean of 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] Expanded uncertainty with a coverage factor *k*=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

TABLE 6. INFORMATION VALUES FOR TRACE ELEMENTS MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k=2*) IN THE IAEA-470 OYSTER SAMPLE

Element	Unit	Information value[1]	Expanded uncertainty (k=2)[2]
Ni	mg kg^{-1}	0.849	0.291

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory.

[2] Expanded uncertainty with a coverage factor *k=2* estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

5. CONCLUSIONS

This exercise allows assignment of certified values for Ag, As, Ca, Cd, CH_3Hg, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Pb, Rb, Se, Sr, V and Zn with associated uncertainties following ISO guidelines. The certified values are derived from measurement results provided by the laboratories participating in this characterization study. Only validated methods were applied in the characterization of the biota sample. As the certified values are combinations of SI traceable individual results, they are themselves traceable to SI. The produced oyster sample is suitable for quality control, and as any certified reference material it can be used for validation studies.

APPENDIX I

RESULTS OF THE LONG-TERM STABILITY STUDY:

Figures 3–15 present individual mass fractions measured at each time-point relative to the mean at time zero, against the time that the samples were held at 20 ± 2 ºC. Dashed lines represent expanded uncertainty of measurements.

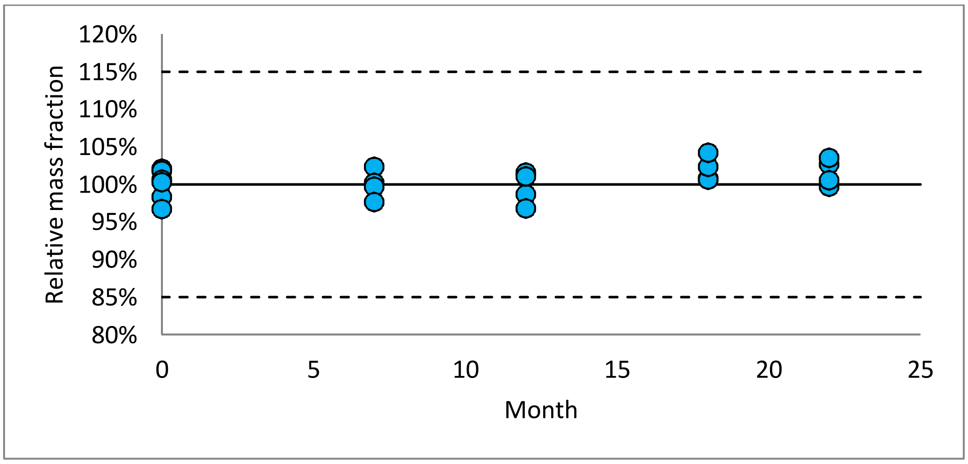

FIG. 3. Results of long-term stability study for silver.

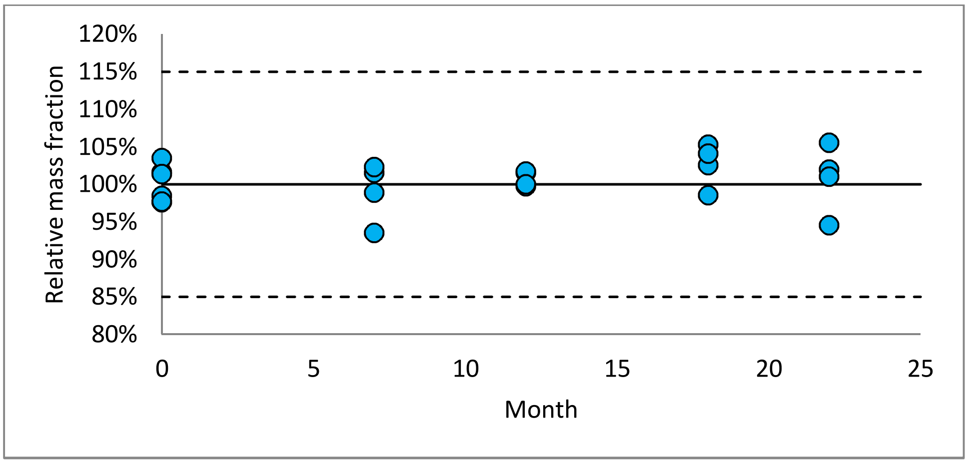

FIG. 4. Results of long-term stability study for arsenic.

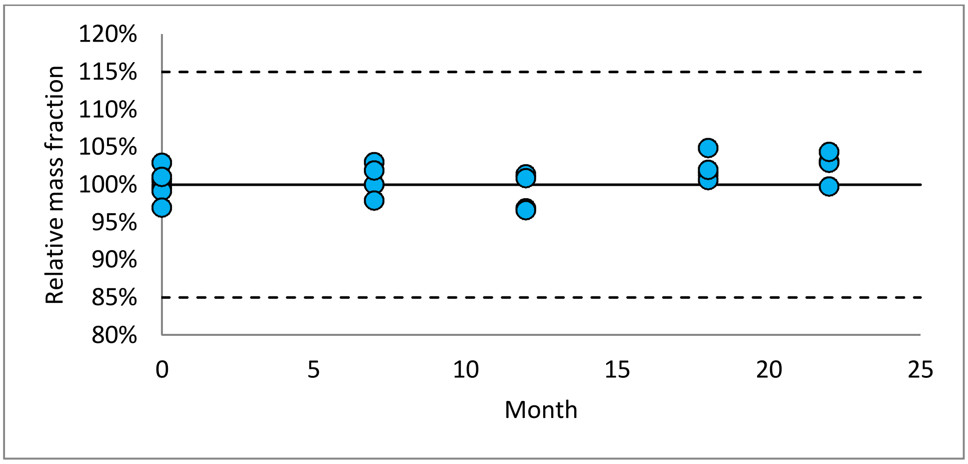

FIG. 5. Results of long-term stability study for cadmium.

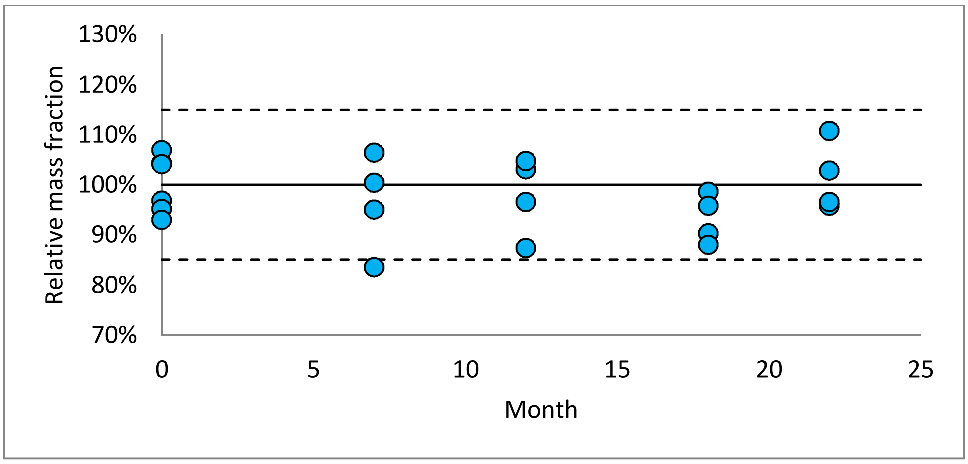

FIG. 6. Results of long-term stability study for methyl mercury.

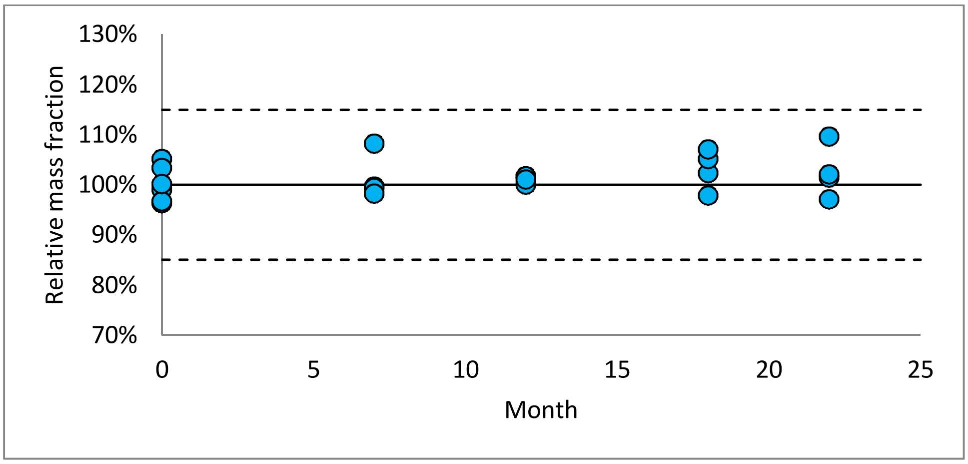

FIG. 7. Results of long-term stability study for cobalt.

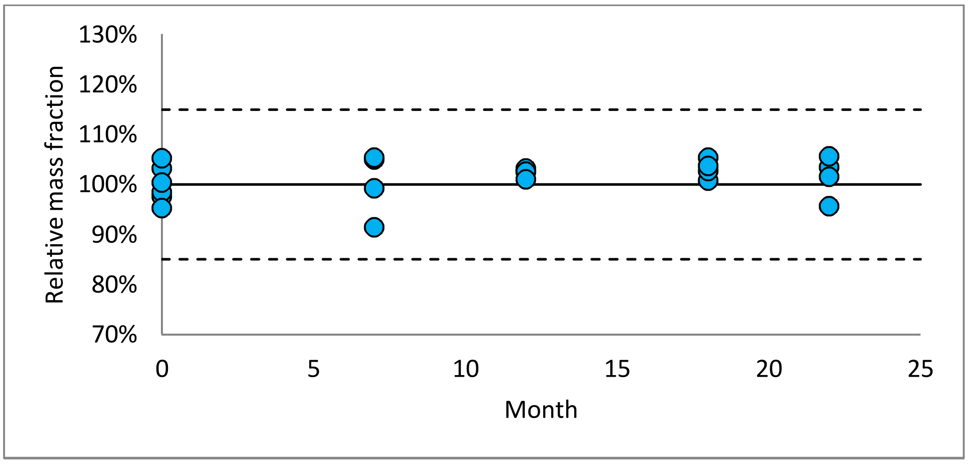

FIG. 8. Results of long-term stability study for cupper.

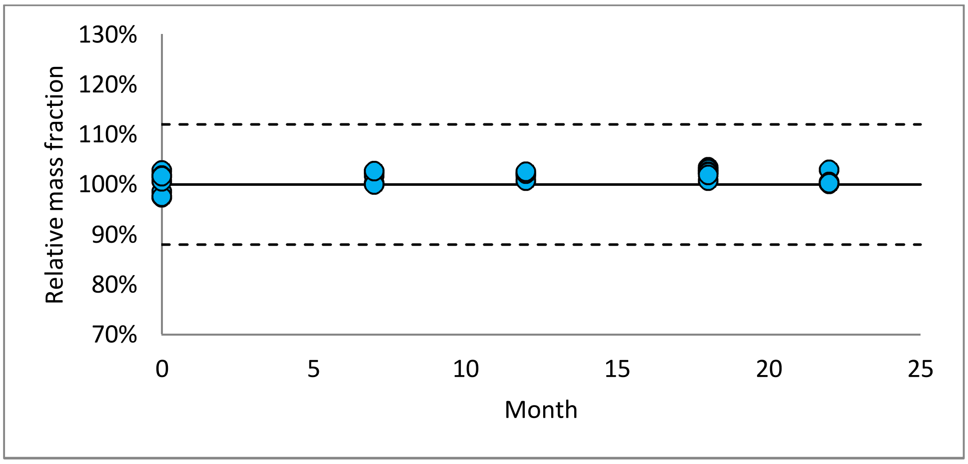

FIG. 9. Results of long-term stability study for total mercury.

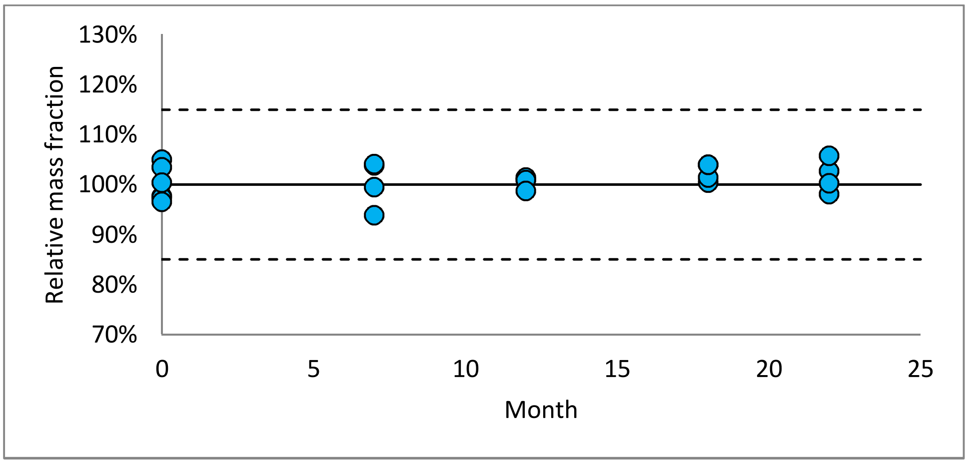

FIG. 10. Results of long-term stability study for manganese.

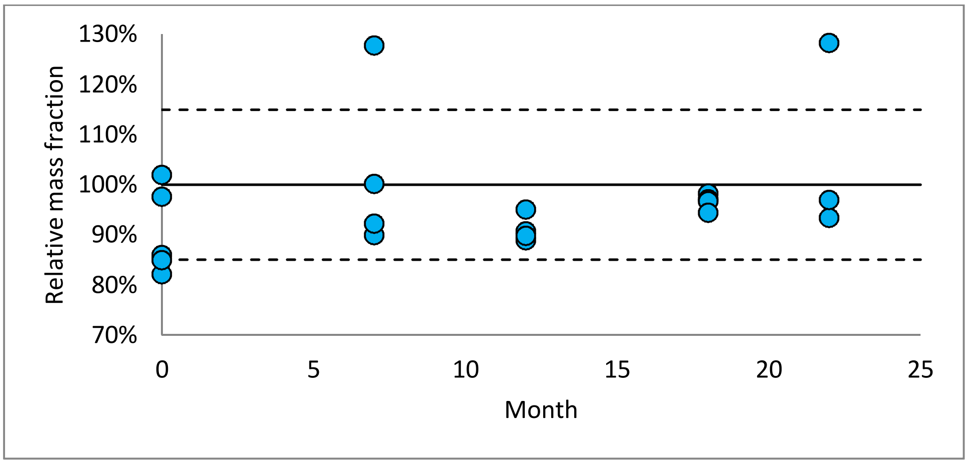

FIG. 11. *Results of long-term stability study for nickel.*

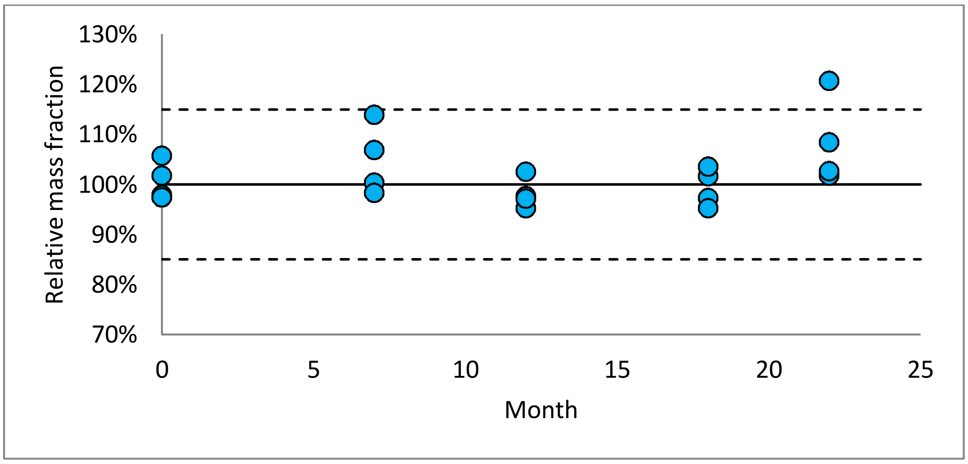

FIG. 12. *Results of long-term stability study for lead.*

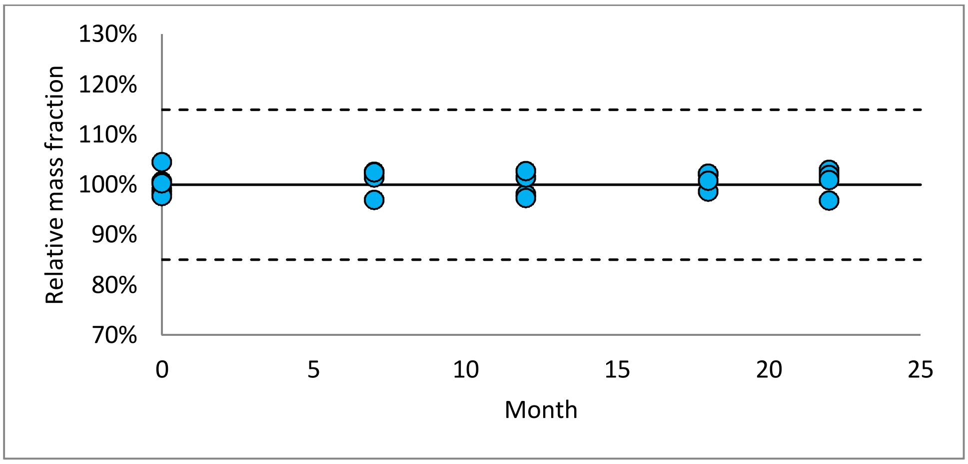

FIG. 13. *Results of long-term stability study for strontium.*

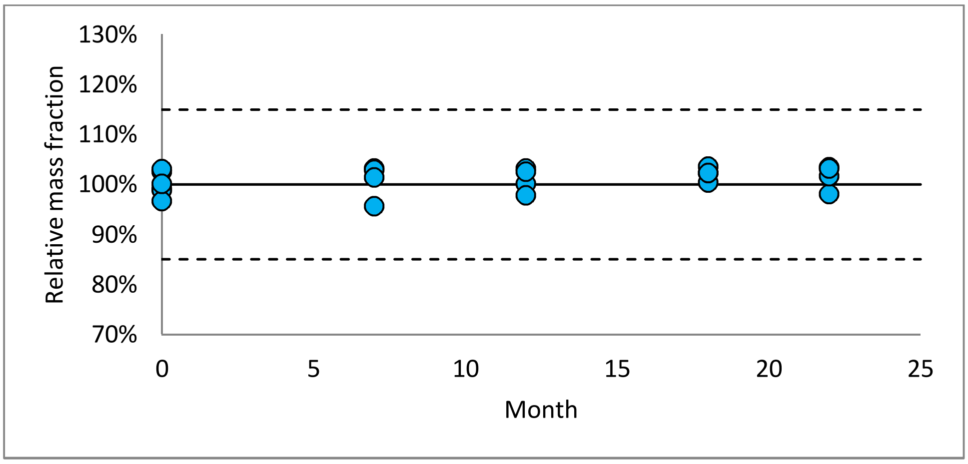

FIG. 14. Results of long-term stability study for zinc.

APPENDIX II

RESULTS OF THE CHARACTERIZATION MEASUREMENTS:

TABLE 7. SILVER: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	1.31	1.32	NIST 1566b	ICP-MS
8	1.36	0.14	SRM 1547	NAA
13	1.24	0.37	DORM-2	ICP-MS
19	1.31	0.20	SRM1566b	ICP-MS
22A	1.18	0.11	DOLT-4	NAA
25	1.47	0.07	SRM 1566b	NAA
28	1.20	0.04	ESA-2 Oyster	ICP-MS
IAEA	1.31	0.15	SRM 2976	ICP-MS

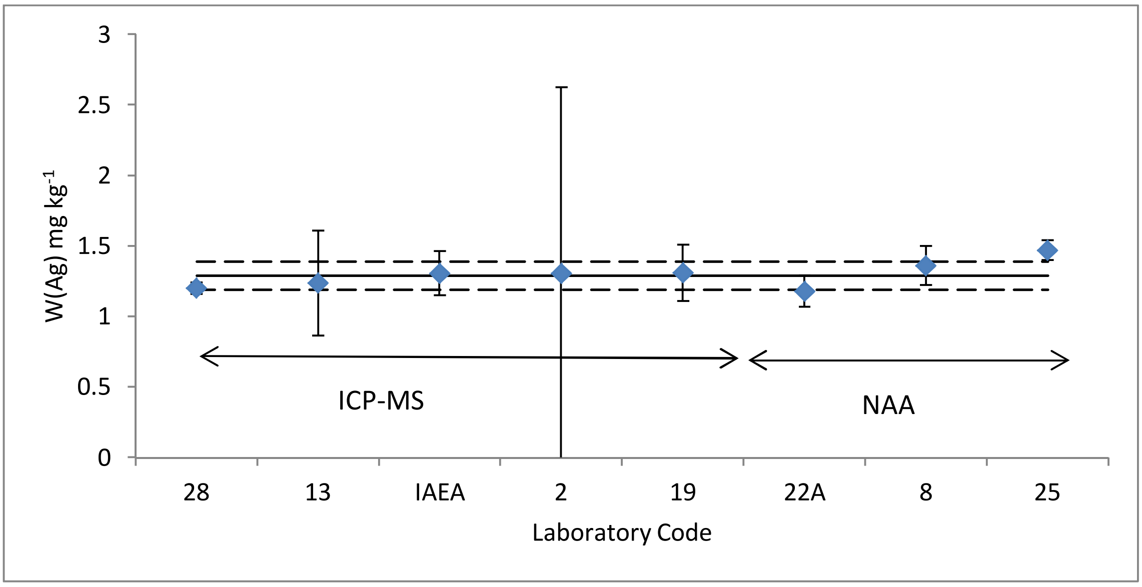

FIG. 15. Laboratory results for silver mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	12.4	1.0	NIST 1566b	ICP-MS
4	10.5	0.3	TORT-2	ICP-MS
5	12.4	0.3	DORM-3	ICP-MS
6	11.8	0.7	DORM-3	ET-AAS
8	11.8	1.0	SRM 1547	NAA
13	11.4	2.3	DORM-2	ICP-MS
14	11.2	0.8	SRM 2976	NAA
15	12.8	8.7	TORT-3	ICP-MS
22A	12.0	1.4	DOLT-4	NAA
25	12.0	0.6	SRM 1566b	NAA
28	10.6	1.2	ESA-2 Oyster	ICP-MS
IAEA	12.6	2.0	TORT-2	ET-AAS
IAEA	12.3	1.5	SRM 2976	ICP-MS

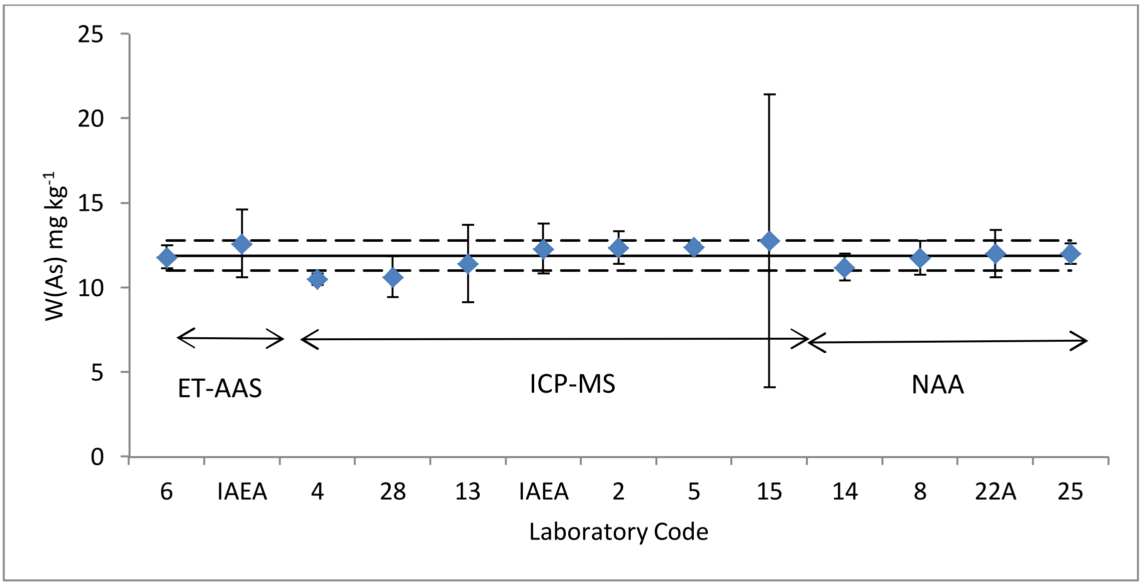

FIG. 16. Laboratory results for arsenic mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5	2530	15	SRM 1547	ICP-MS
8	2282	208	SRM 1547	NAA
14	2537	240	SRM 2976	NAA
15	2548	384	TORT-3	ICP-MS
25	2140	430	SRM 1566b	NAA
28	2393	60	ESA-2 Oyster	ICP-MS

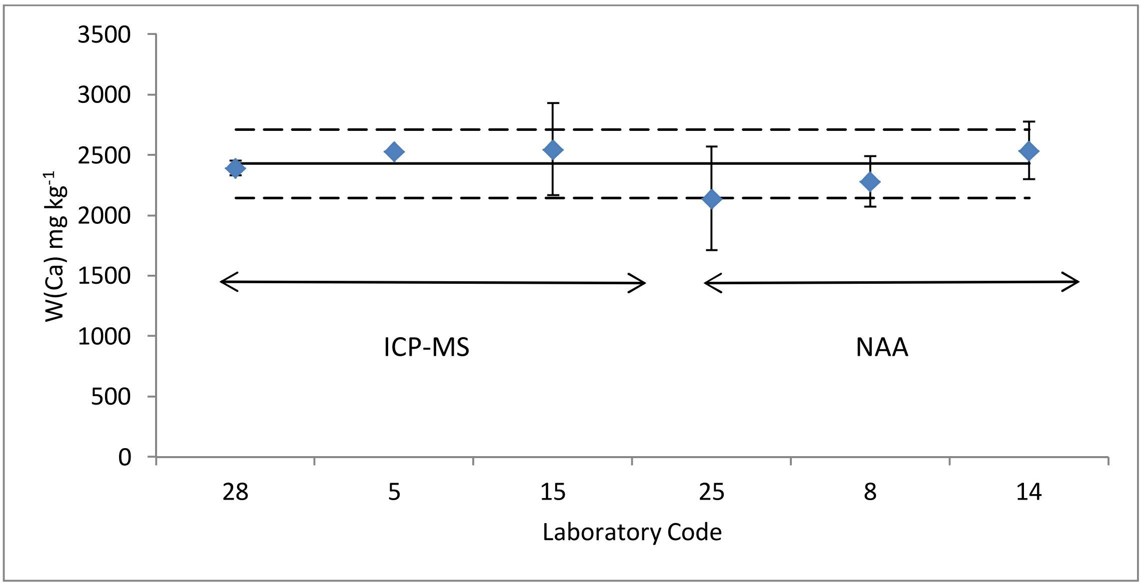

FIG. 17. Laboratory results for calcium mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	3.32	0.21	NIST 1566b	ICP-MS
4	3.10	0.22	TORT-2	ICP-MS
5	3.28	0.08	DORM-3	ICP-MS
6	2.92	0.14	NIST 1566b	F-AAS
13	3.26	0.65	IAEA-452	ICP-MS
14	2.46	0.19	SRM 2976	ET-AAS
15	3.46	0.58	TORT-3	ICP-MS
19	3.23	0.48	SRM1566b	ICP-MS
22B	2.47	0.12	NIST 1566B	ICP-MS
28	3.01	0.14	ESA-2 Oyster	ICP-MS
32	3.03	0.24	SRM 1566a	ICP-MS
IAEA	3.41	0.40	SRM 2976	ICP-MS

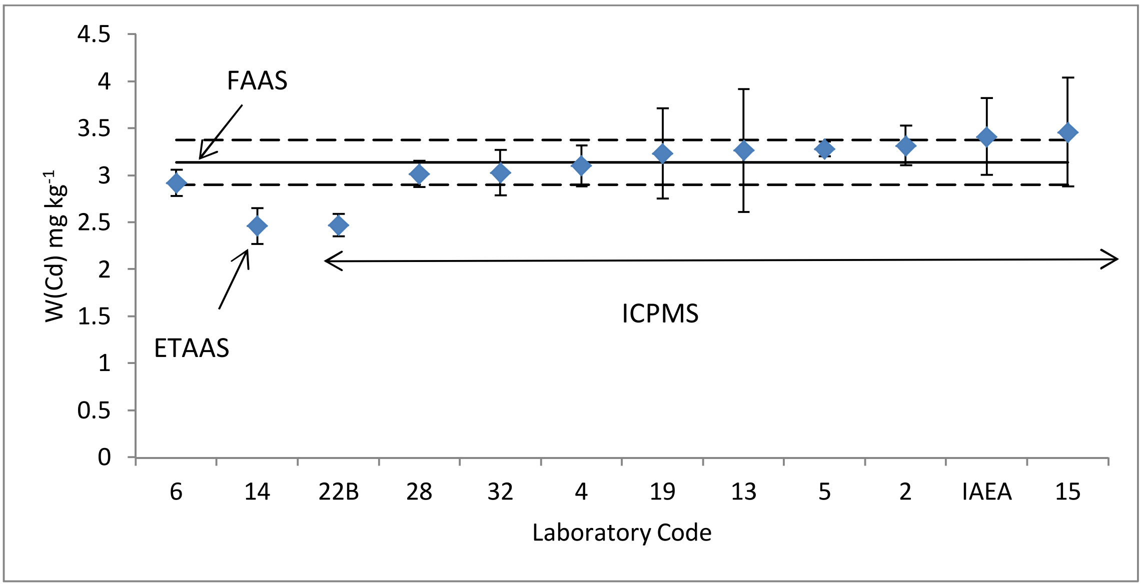

FIG. 18. Laboratory results for cadmium mass fraction (mg kg^{-1}) in the IAEA-470.

TABLE 11. METHYL MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (µg kg^{-1} as Hg)

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5	5.31	0.26	DOLT-4	CV-AFS
8	3.21	0.28	T-38	CV-AFS
12	5.29	1.06	DORM-2	CV-AFS
15	6.50	1.29	TORT-3	GC-AFS
IAEA	5.10	0.80	IAEA-452	Solid-AAS
IAEA	4.80	0.20	IAEA-461	ID ICP-MS
IAEA	5.36	0.80	IAEA-452	GC-AFS

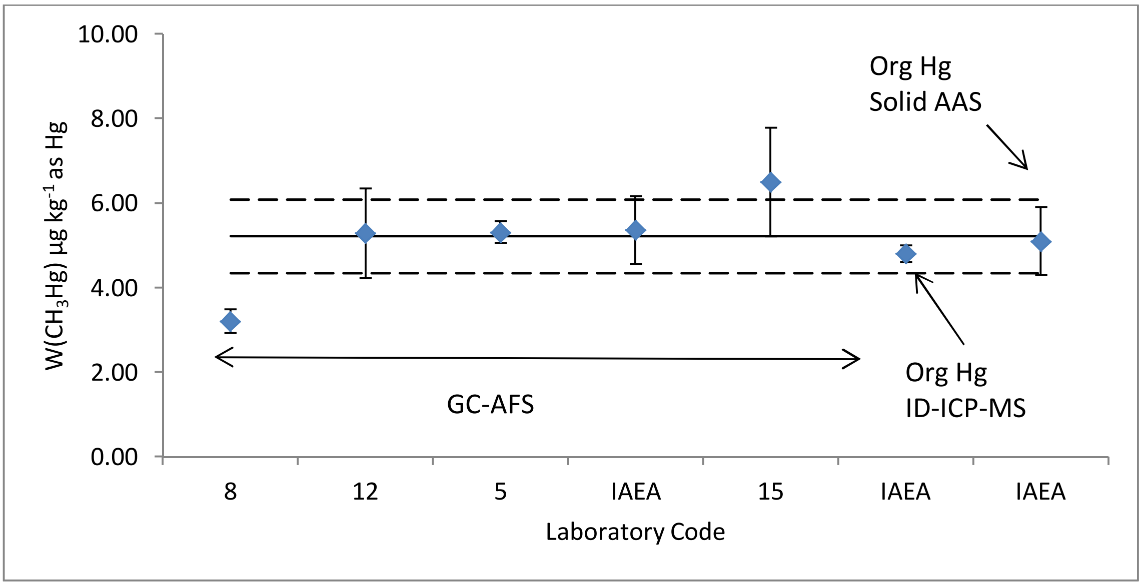

FIG. 19. Laboratory results for methyl mercury mass fraction (µg kg^{-1} as Hg) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	0.213	0.014	NIST 1566b	ICP-MS
4	0.162	0.015	TORT-2	ICP-MS
5	0.199	0.011	SRM 1547	ICP-MS
8	0.184	0.016	SRM 1547	NAA
13	0.199	0.040	DORM-2	ICP-MS
14	0.366	0.020	SRM 2976	NAA
15	0.206	0.035	TORT-3	ICP-MS
22B	0.245	0.018	NIST 1566B	ICP-MS
22A	0.182	0.016	DOLT-4	NAA
28	0.180	0.020	ESA-2 Oyster	ICP-MS
32	0.261	0.026	SRM 1566a	ICP-MS
IAEA	0.164	0.033	TORT-2	ET-AAS
IAEA	0.210	0.025	SRM 2976	ICP-MS

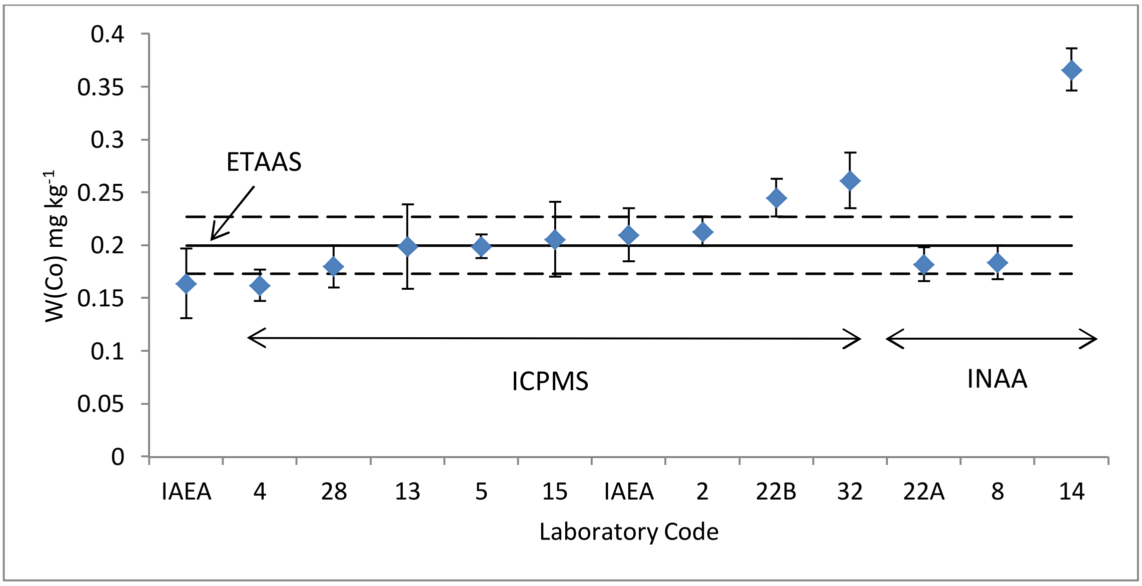

FIG. 20. Laboratory results for cobalt mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	1.22	0.10	NIST 1566b	ICP-MS
5	0.758	0.120	DORM-3	ICP-MS
8	0.977	0.120	SRM 1547	NAA
13	0.965	0.290	DORM-2	ICP-MS
14	0.840	0.120	SRM 2976	NAA
15	0.903	0.291	TORT-3	ICP-MS
22A	0.990	0.240	DORM-2	NAA
28	1.01	0.04	ESA-2 Oyster	ICP-MS
IAEA	1.03	0.20	TORT-2	ET-AAS

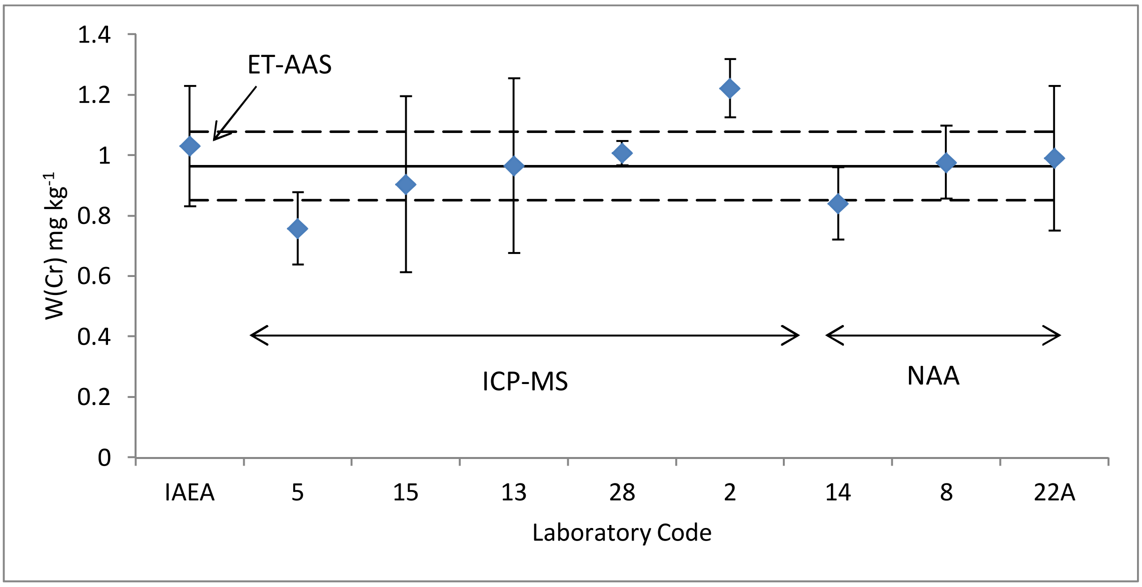

FIG. 21. Laboratory results for chromium mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	152	9	NIST 1566b	ICP-MS
4	130	9	TORT-2	ICP-MS
5	146	7	DORM-3	ICP-MS
6	143	4	DORM-3	F-AAS
13	145	22	IAEA-452	ICP-MS
15	155	24	TORT-3	ICP-MS
19	157	16	SRM1566b	ICP-MS
22B	140	6	NIST 1566B	ICP-MS
28	137	6	ESA-2 Oyster	ICP-MS
32	142	11	SRM 1566a	ICP-MS
IAEA	150	15	TORT-2	F-AAS
IAEA	153	18	SRM 2976	ICP-MS

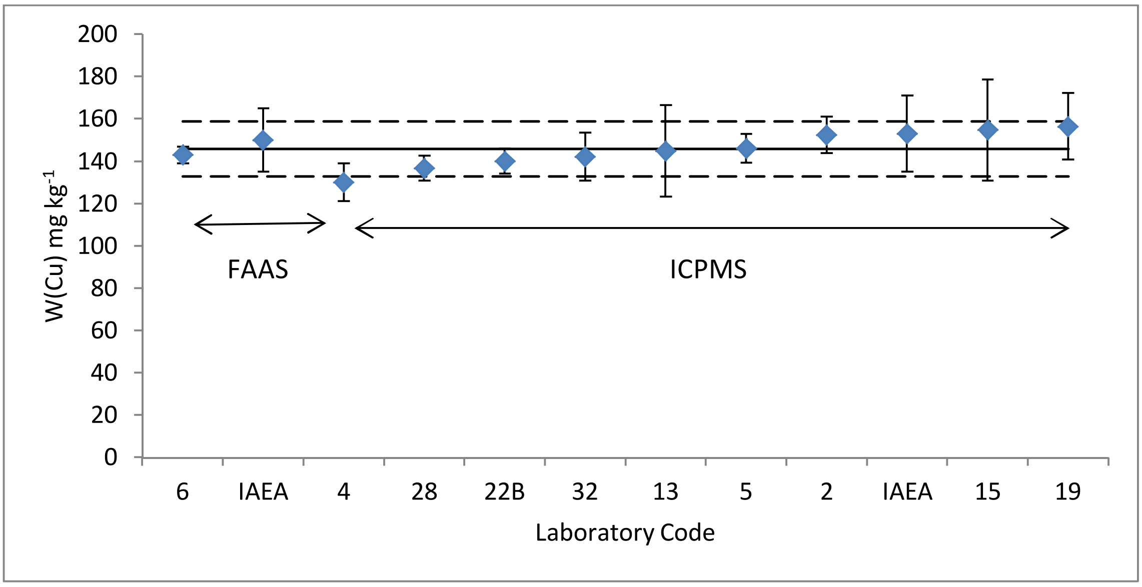

FIG. 22. Laboratory results for copper mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	124	10	NIST 1566b	ICP-MS
5	125	6	DORM-3	ICP-MS
6	131	3	DORM-3	F-AAS
8	133	10	SRM 1547	NAA
13	124	19	DORM-2	ICP-MS
14	123	8	SRM 2976	NAA
15	139	32	TORT-3	ICP-OES
22A	128	10	DOLT-4	NAA
25	136	10	SRM 1566b	NAA
28	169	4	ESA-2 Oyster	ICP-MS
32	141	17	SRM 1566a	ICP-MS
IAEA	131	23	TORT-2	F-AAS

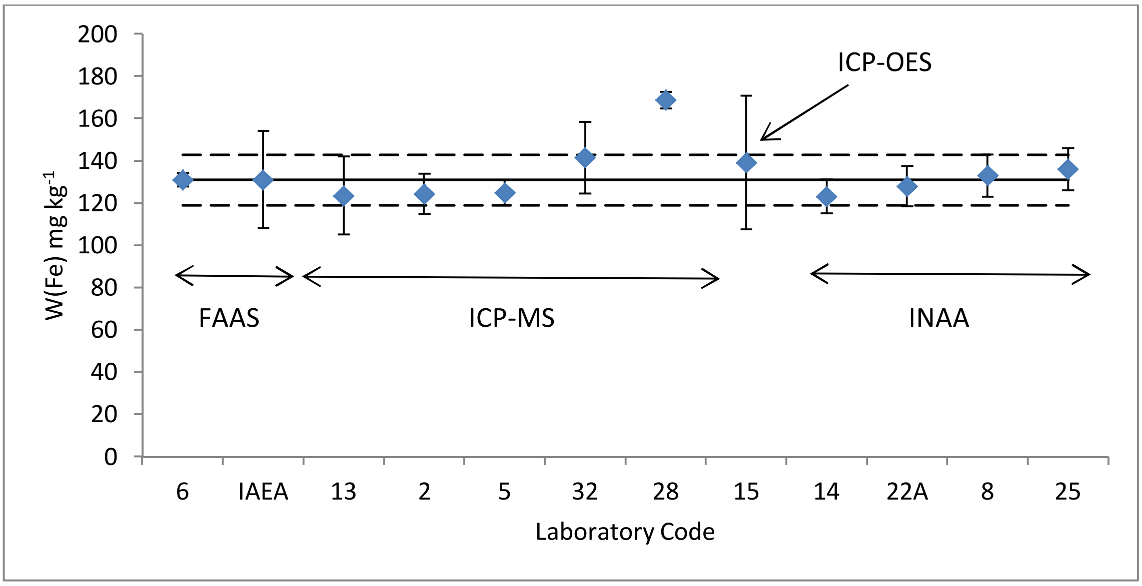

FIG. 23. Laboratory results for iron mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
8B	20.1	2.2	SRM 1566b	CV-AAS
19	21.0	3.0	IAEA-142	CV-AAS
14	23.7	4.3	NIST 1566b	CV-AAS
5	14.8	0.4	DORM-3	CV-AFS
12	18.7	3.4	DORM-3	CV-AFS
6	27.0	4.0	DORM-3	CV-AFS
8	19.9	1.0	SRM 1566b	Solid-AAS
28	20.2	0.4	ESA-2 Oyster	Solid-AAS
15	22.3	6.7	TORT-3	Solid-AAS
IAEA	22.5	1.8	SRM 2976	Solid-AAS
IAEA	21.3	1.1		ID ICP-MS

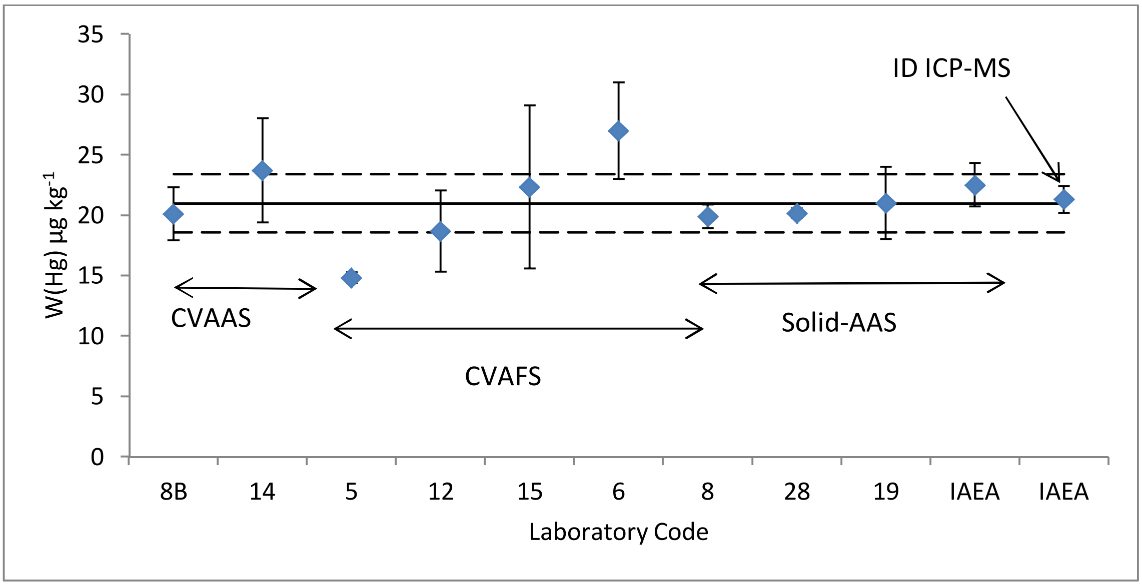

FIG. 24. Laboratory results for mercury mass fraction (mg kg^{-1}) in the IAEA-470.

TABLE 17. MAGNESIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	3208	182	NIST 1566b	ICP-MS
5	3030	146	SRM 1547	ICP-MS
15	3322	521	TORT-3	ICP-MS
25	2815	203	SRM 1566b	NAA
28	3007	120	ESA-2 Oyster	ICP-MS

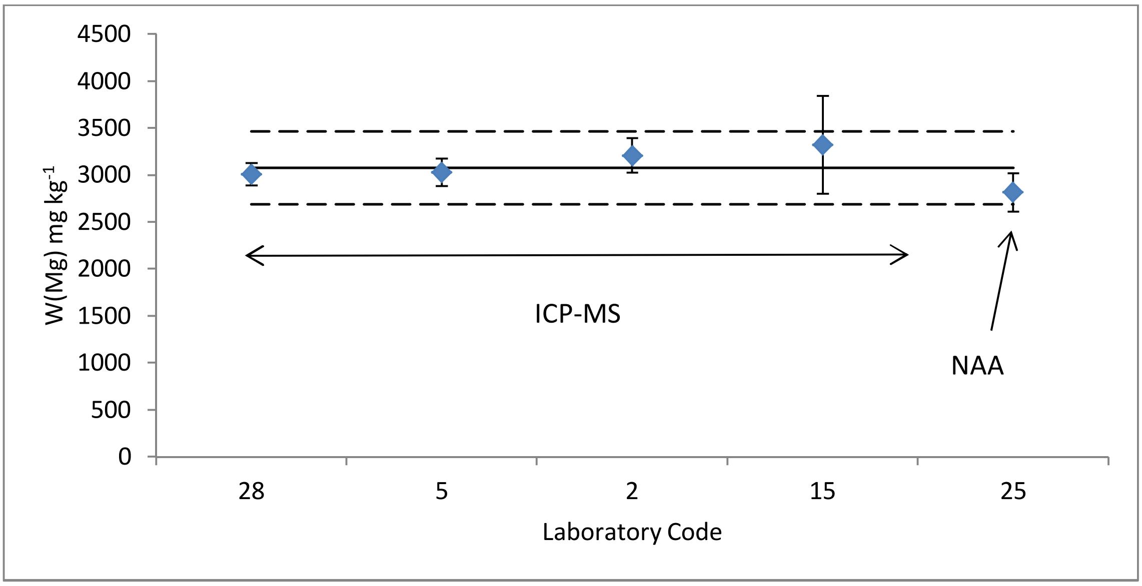

FIG. 25. Laboratory results for magnesium mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	66.7	3.4	NIST 1566b	ICP-MS
4	62.3	4.4	TORT-2	ICP-MS
5	64.7	0.7	SRM 1547	ICP-MS
6	66.3	3.3	NIST 1566b	F-AAS
13	67.9	6.8	IAEA-452	ICP-MS
15	73.3	10.1	TORT-3	ICP-MS
25	63.0	13.0	SRM 1566b	NAA
28	60.2	2.0	ESA-2 Oyster	ICP-MS
32	69.5	5.6	SRM 1566a	ICP-MS
IAEA	73.3	11.7	TORT-2	F-AAS
IAEA	66.9	8	SRM 2976	ICP-MS

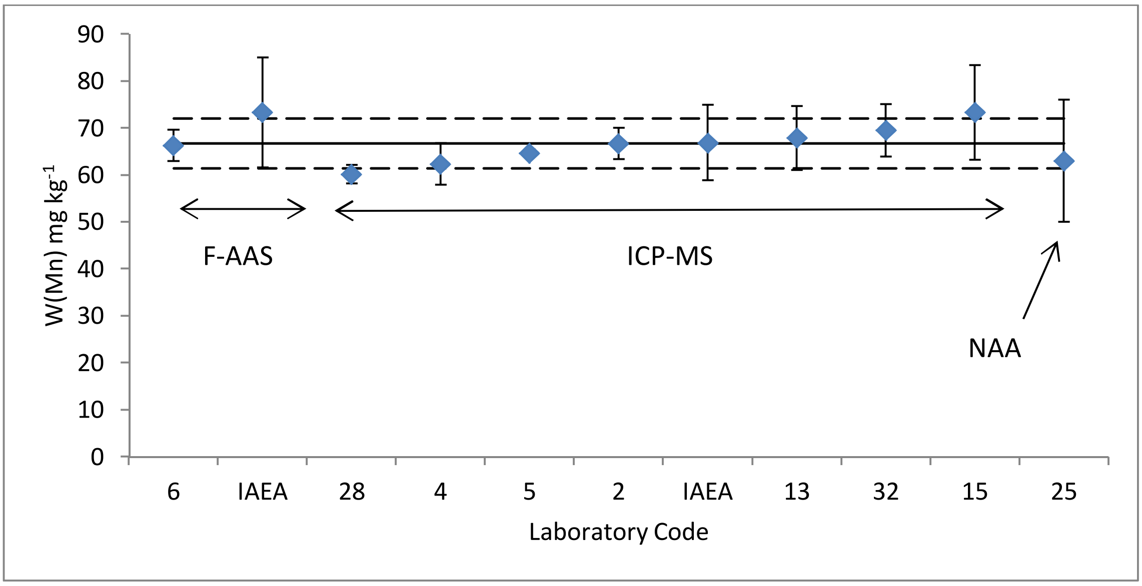

FIG. 26. Laboratory results for manganese mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	17.7	1.4	NIST 1566b	ICP-MS
8	20.6	1.7	SRM 1547	NAA
14	18.8	0.7	SRM 2976	NAA
15	22.2	3.3	TORT-3	ICP-OES
22A	19.6	1.8	IAEA-407	NAA
25	20.3	0.8	SRM 1566b	NAA
28	19.5	0.4	ESA-2 Oyster	ICP-MS

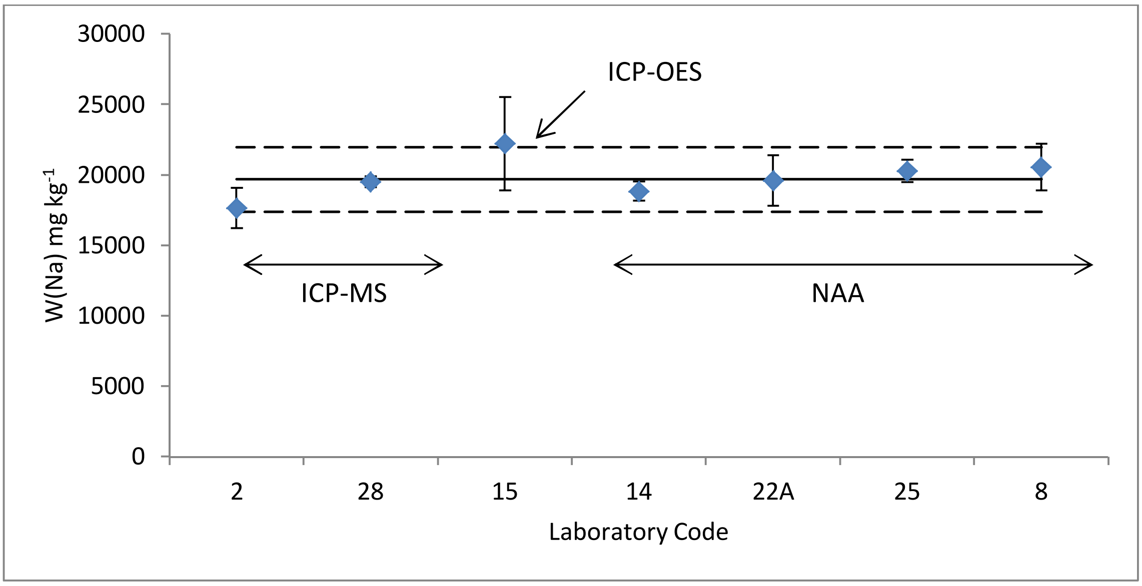

FIG. 27. Laboratory results for sodium mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	0.876	0.052	NIST 1566b	ICP-MS
5	0.660	0.020	DORM-3	ICP-MS
13	0.820	0.164	DORM-2	ICP-MS
15	0.776	0.348	TORT-3	ICP-MS
19	0.920	0.180	SRM1566b	ICP-MS
28	0.913	0.120	ESA-2 Oyster	ICP-MS
32	0.840	0.084	SRM 1566a	ICP-MS
IAEA	0.891	0.180	TORT-2	ET-AAS

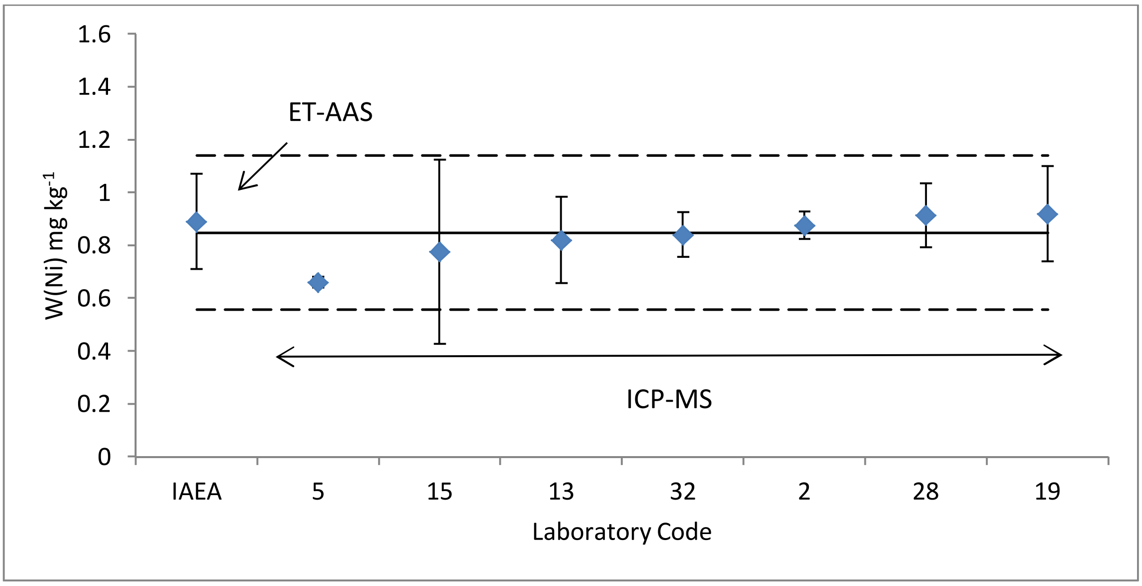

FIG. 28. Laboratory results for nickel mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	0.376	0.016	NIST 1566b	ICP-MS
5	0.355	0.010	SRM 1547	ICP-MS
6	0.333	0.022	DORM-3	ET-AAS
13	0.370	0.093	DORM-2	ICP-MS
14	0.381	0.076	SRM 2976	ET-AAS
15	0.370	0.265	TORT-3	ICP-MS
19	0.370	0.060	SRM1566b	ICP-MS
22B	0.310	0.026	NIST 1566B	ICP-MS
28	0.297	0.012	ESA-2 Oyster	ICP-MS
IAEA	0.362	0.026	SRM 2976	ICP-MS

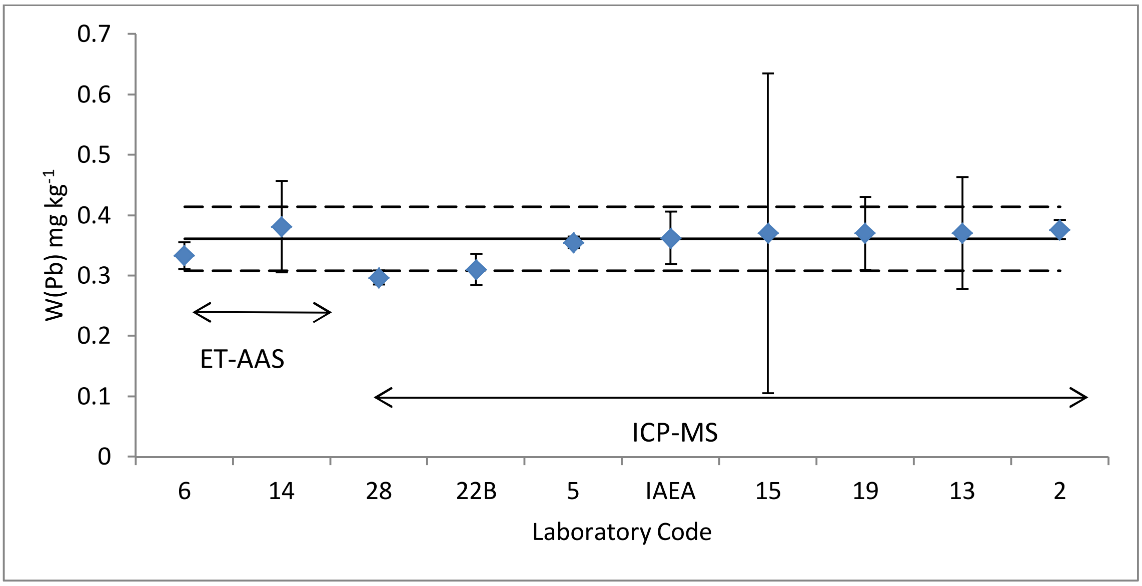

FIG. 29. Laboratory results for lead mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
8	5.13	0.38	SRM 1547	NAA
13	5.07	0.76	IAEA-452	ICP-MS
14	4.80	0.40	SRM 2976	NAA
15	5.41	1.02	TORT-3	ICP-MS
25	5.30	0.30	SRM 1566b	NAA

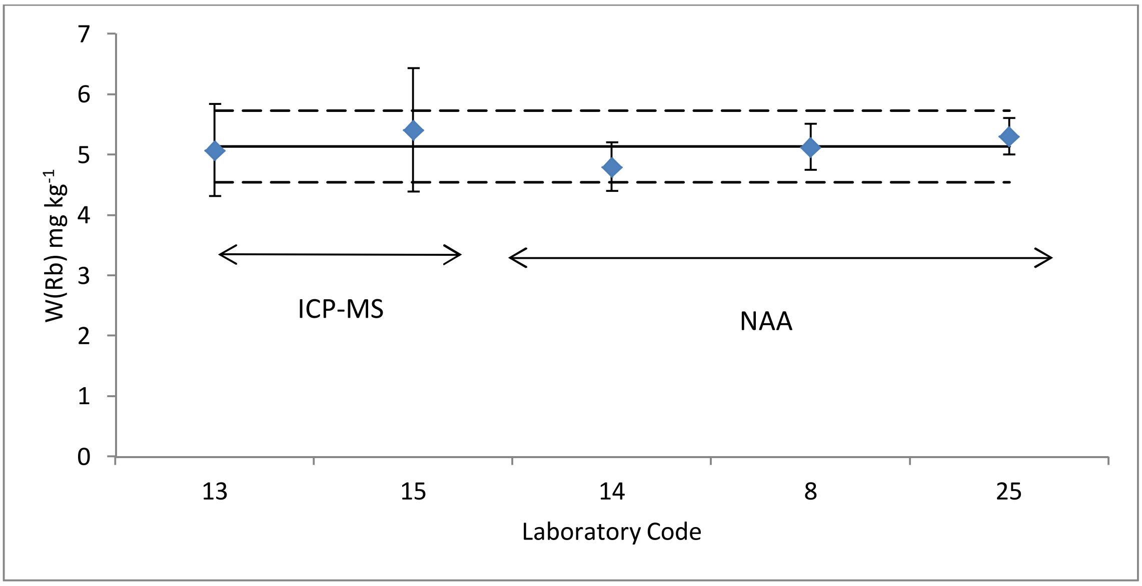

FIG. 30. Laboratory results for rubidium mass fraction (mg kg^{-1}) in the IAEA-470.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5	3.16	0.26	DORM-3	ICP-MS
8	3.22	0.26	SRM 1547	NAA
13	3.11	0.62	DORM-2	ICP-MS
14	2.90	0.40	SRM 2976	NAA
15	3.20	0.68	TORT-3	ICP-MS
22A	2.74	0.30	DOLT-4	NAA
25	3.20	0.16	SRM 1566b	NAA
28	2.64	0.04	ESA-2 Oyster	AFS
IAEA	2.99	0.60	TORT-2	ET-AAS

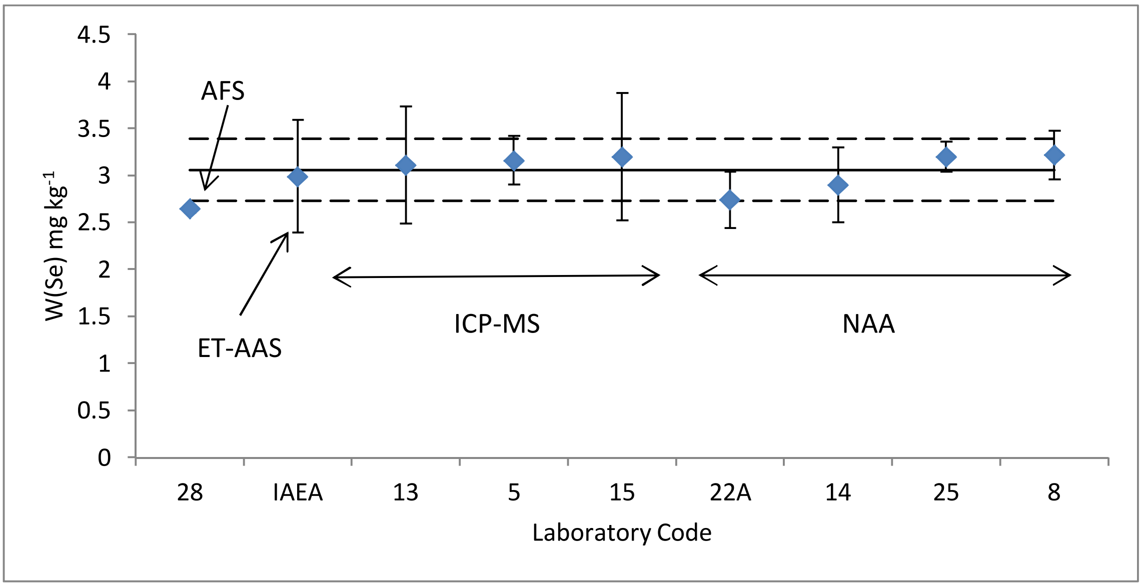

FIG. 31. Laboratory results for selenium mass fraction (mg kg^{-1}) in the IAEA-470.

TABLE 24. STRONTIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	21.1	1.1	NIST 1566b	ICP-MS
13	20.0	3.0	IAEA-452	ICP-MS
15	20.5	3.1	TORT-3	ICP-MS
22B	18.0	0.8	NIST 1566B	ICP-MS
28	18.9	1.0	ESA-2 Oyster	ICP-MS
32	21.7	1.7	SRM 1566a	ICP-MS
IAEA	21.1	3.4	TORT-2	ET-AAS
IAEA	22.3	2.7	SRM 2976	ICP-MS

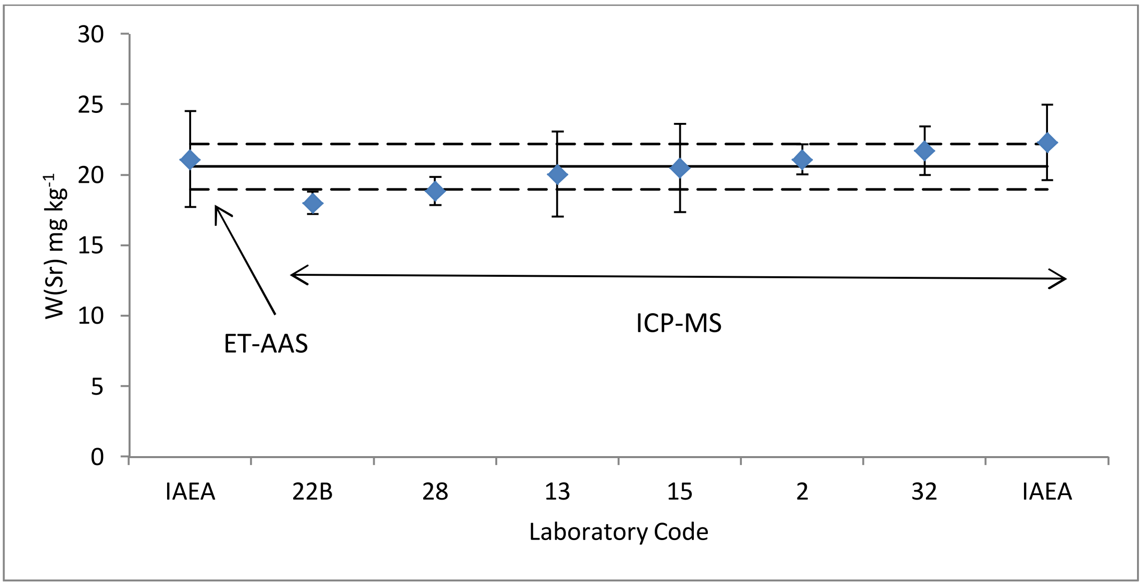

FIG. 32. Laboratory results for strontium mass fraction (mg kg^{-1}) in the IAEA-470.

TABLE 25. VANADIUM: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	0.977	0.073	NIST 1566b	ICP-MS
5	0.881	0.130	SRM 1547	ICP-MS
13	0.846	0.169	IAEA-452	ICP-MS
15	0.964	0.402	TORT-3	ICP-MS
25	0.800	0.040	SRM 1566b	NAA
28	0.880	0.040	ESA-2 Oyster	ICP-MS
32	1.16	0.09	SRM 1566a	ICP-MS
IAEA	0.785	0.157	TORT-2	ET-AAS

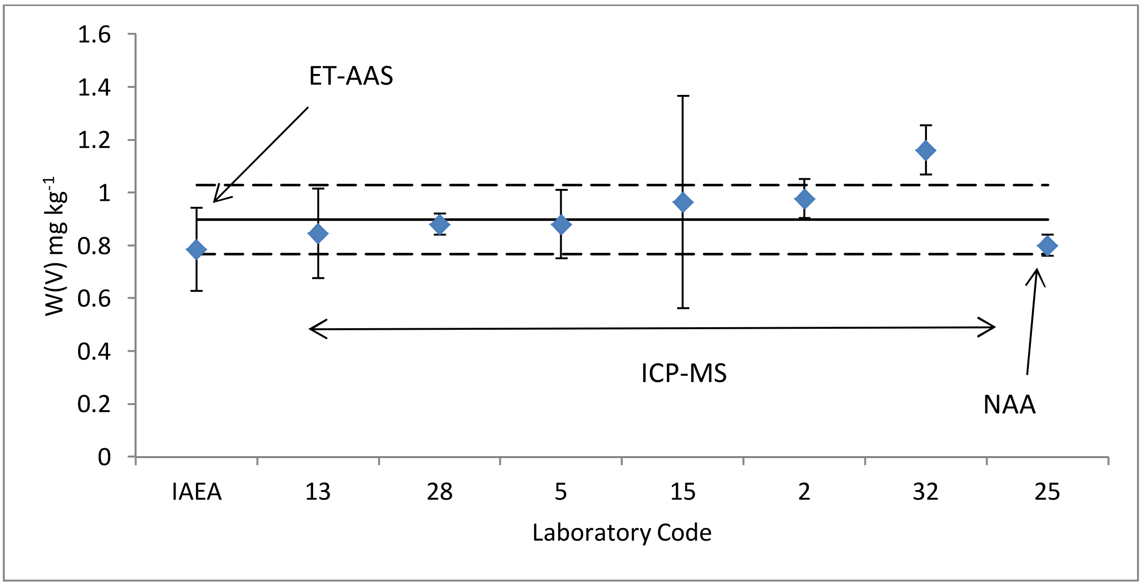

FIG. 33. Laboratory results for vanadium mass fraction (mg kg^{-1}) in the IAEA-470.

TABLE 26. ZINC: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
2	756	48	NIST 1566b	ICP-MS
4	683	30	TORT-2	ICP-MS
5	754	29	DORM-3	ICP-MS
6	682	41	DORM-3	F-AAS
8	756	52	SRM 1547	NAA
13	774	116	IAEA-452	ICP-MS
14	742	62	SRM 2976	NAA
15	778	109	TORT-3	ICP-MS
19	795	80	SRM1566b	ICP-MS
22B	621	26	NIST 1566B	ICP-MS
22A	700	36	DOLT-4	NAA
25	740	37	SRM 1566b	NAA
28	692	14	ESA-2 Oyster	ICP-MS
32	668	53	SRM 1566a	ICP-MS
IAEA	739	74	TORT-2	F-AAS

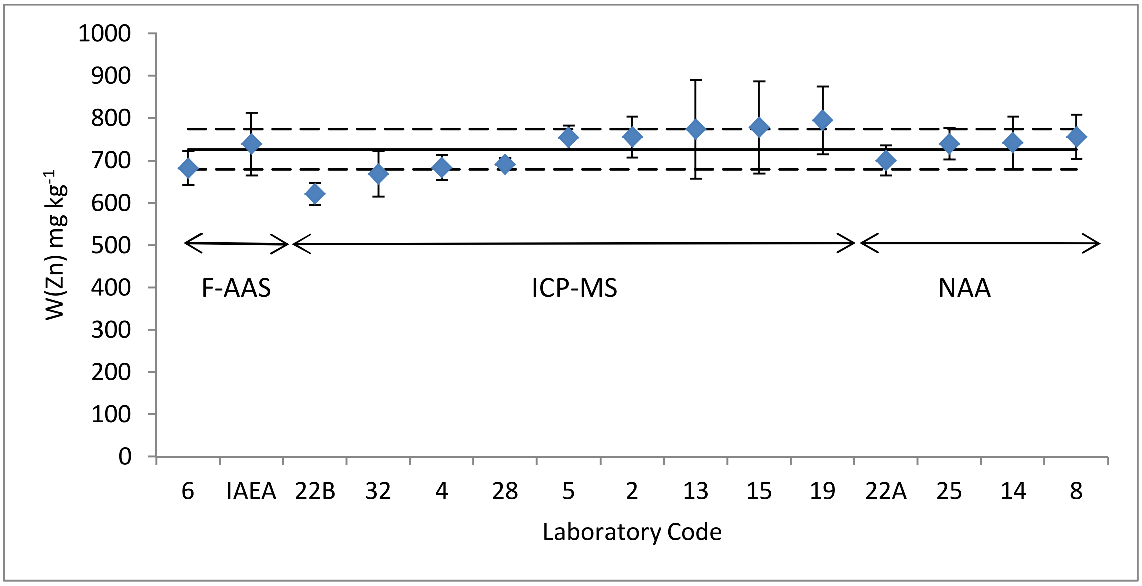

FIG. 34. Laboratory results for zinc mass fraction (mg kg^{-1}) in the IAEA-470.

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