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Certification of Trace and Rare Earth Element Mass Fractions in Estuarine Sediment IAEA-158A

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CERTIFICATION OF TRACE AND RARE EARTH ELEMENT MASS FRACTIONS IN ESTUARINE SEDIMENT IAEA-158A

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INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The IAEA assists its Member States in the understanding, monitoring and protection of the marine environment. In order to assess the impact of land based and sea based pollution sources on marine coastal environments, it is critical to ensure the quality of the analytical data generated by national and regional pollution monitoring programmes. For this purpose, the IAEA has assisted national laboratories and regional laboratory networks since the early 1970s through its activities relating to reference products for science and trade. This is accomplished through the production of certified reference materials, training in quality assurance and the evaluation of measurement performance through worldwide and regional interlaboratory comparison exercises and proficiency tests.

This publication describes the production of certified reference material IAEA-158A, which is based on a new characterization study of the existing reference material IAEA-158, produced by the IAEA in 2008. IAEA-158A was produced following the requirements of the international standards ISO 17034:2016 and ISO Guide 35:2017. This certified reference material is an estuarine sediment with certified mass fractions for trace elements, methylmercury and rare earth elements. The assigned values and their associated uncertainties were derived from the results provided by selected laboratories with demonstrated technical and quality competencies, following the guidance given in international standards for the production of reference materials.

The IAEA is grateful to the Government of Monaco for its support and wishes to thank the laboratories involved in the characterization study of this reference material. The IAEA officers responsible for this publication were S. Azemard and A.M. Orani of the Division of Marine Environment Laboratories.

CONTENTS

1   INTRODUCTION

1.1   BACKGROUND

The Marine Environmental Studies Laboratory (MESL) of the IAEA Marine Environment Laboratories (IAEA-NAML) provides assistance to Member States' laboratories to enhance the quality of analytical measurement results for trace element and organic contaminants in marine environment samples. This is achieved through the production of certified reference materials (CRM), the organization of interlaboratory comparisons (ILCs) and proficiency tests (PT), and by conducting training courses on the analysis of contaminants in marine samples. This activity is undertaken in the framework of NAML's subprogramme "Production of IAEA Certified Reference Materials and Proficiency Tests for the quality assurance of contaminant analysis in marine samples". The availability of matrix CRM, certified at fit for purpose concentration levels in a matrix matching monitoring sample, is of crucial importance for producing reliable and comparable results. Sediments represent a suitable matrix to perform long–term studies, useful for potential contamination detection, and are largely used in environmental studies. Therefore, as the availability of such CRM is limited, a new marine sediment CRM characterised for trace elements (TEs), methylmercury (MeHg) and rare earth elements (REEs) was produced by MESL.

Trace elements may be toxic, persistent and abundant contaminants affecting the marine environment. Considering that increasing coastal population and urban activities have contributed to increased trace elements inputs in the marine environment, quantifying trace elements in sediment is important to understand natural environmental processes and monitor the degree of anthropogenic disturbance.

MeHg is a bioaccumulating neurotoxin, affecting human health. However, because the main vector for MeHg exposure in humans is fish and shellfish consumption, the links between MeHg bioaccumulation in marine ecosystems and human exposure need to be better understood. There are three potential regions of methylation in marine ecosystems—coastal and slope sediments, low-oxygen waters below productive ocean waters, and deep ocean sediments. Producing reliable and comparable analytical results underpins a better understanding of the global mercury and other trace element cycles.

REEs are an extremely coherent group in terms of (geo) chemical behaviour and have become useful tracers in geological and hydrological systems [1, 2]. REEs are becoming increasingly important as they have found application in several fields such as chemical engineering, metallurgy, nuclear energy, laser materials, superconductors, secondary battery among others [3, 4]. As a consequence of their increased widespread use, the potential anthropogenic influence on the natural distribution of REEs has extended their application from geochemistry into the field of environmental chemistry [5, 6]. REEs are nowadays considered contaminants of emerging concern.

1.2   OBJECTIVE

In order to strengthen data quality assurance for the determination of trace elements, methylmercury and REEs in sediment in the frame of pollution assessment, MESL has produced an estuarine sediment CRM, IAEA-158A, characterized for trace elements, methylmercury and REEs mass fractions.

1.3 SCOPE

The scope of this publication is to describe the re-certification process for trace elements, methylmercury and REEs mass fractions in estuarine sediment sample. The new CRM IAEA-158A is produced following the requirements of the ISO 17034:2016 standard [7] and can be used in laboratory practice for quality control and method validation purposes. It has been produced to satisfy the needs of laboratories dealing with environmental analyses.

1.4 STRUCTURE

This publication is structured in five sections, the first being the Introduction. Section 2 reports the methodology used for the preparation of the reference material, including the selection of laboratories for the characterization campaign, and all procedures for the homogeneity, stability, and characterization of the material. This provides a foundation for Section 3 which covers the results and discussions on the determination of the assigned values and their expanded uncertainties. Then, Section 4 provides information on the metrological traceability and commutability of the CRM. Finally, Section 5 provides the conclusions.

2   METHODOLOGY

2.1 COLLECTION AND PREPARATION OF THE MATERIAL

In November 2004, a large quantity of marine sediment was collected from Kilbrannan Sound, southeast of the island of Arran, in the Clyde River estuary, Scotland, UK. The material was collected and supplied to the IAEA through collaboration with the QUASIMEME Laboratory Performance Studies Programme. The dried material was hand sieved (315 µm) by MESL staff. The sieving cut-off value chosen was a compromise value selected to ensure that the physical properties of the material were sufficiently uniform whilst retaining sufficient material to make an adequate number of units. The particle size distribution profile of the bottled material was measured using particle size analyser. Approximately 70% of particles had sizes below 100 µm. More details about the preparation of IAEA-158 are given in Ref. [8]

IAEA-158A was prepared by rebottling 200 units of IAEA-158 in amber borosilicate bottles into acid cleaned polypropylene containers. The content of each bottle of IAEA-158 was divided into two polypropylene containers after manual shaking. Preliminary investigations of the within- and between- bottles homogeneity of IAEA-158 indicated that the starting material was homogeneous and did not need additional homogenization before rebottling.

2.2 ANALYTICAL METHODOLOGIES

Analytical methods used for homogeneity and stability studies conducted at the IAEA MESL are described below. These methods were previously validated in the IAEA MESL inorganic chemistry laboratories.

For all analytes (except for Hg and MeHg), subsamples of 0.25g were mineralized in a microwave with 5 ml concentrated nitric acid (Trace Metal Grade), 2ml of hydrofluoric acid (Trace Metal Grade) and 2 ml of hydrogen peroxide (Trace Metal Grade). The digestion was performed in self-regulating pressure control vessels. The microwave program was set to 195 °C for 15 min with ramping time of 20 minutes, followed by cooling to room temperature. To remove the excess of HF and fluoride precipitates, digested samples were treated with 10 ml of 4% (w/v) boric acid and then heated at 170°C for 15 min with 10 min ramping time.

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Additional 10 ml of the same H_3BO_3 solution were added before final dilution. Two procedural blanks and duplicates of matrix CRM IAEA-475 were included in each digestion batch. For Ag, As, Cd, Co, Cs, Mo, Pb, Rb, Sb, Se, Sn, Th, U, V and REEs, measurements were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Sr, Ti and Zn measurements were performed by Flame Atomic Absorption Spectrometry (FAAS).

The determination of total Hg was performed by solid mercury analyzer using 0.25g solid subsamples. Internal calibration was verified using CRM IAEA-456 at regular intervals during the runs.

Methylmercury determination was performed by Gas Chromatography coupled to Atomic Fluorescence Spectroscopy after purge and trap. Subsamples of 0.25g were extracted in dichloromethane after leaching in 5ml of H_2SO_4 (5% v/v) /KBr (15% w/v) and 1ml of 1M $CuSO_4$ and back extracted in 2mM thiosulfate solution before derivatization with sodium tetraethyl borate. Two procedural blanks and duplicates of matrix CRM IAEA-456 were included in each batch of extracted samples.

The results were corrected for the moisture content determined in each unit at the time of analyses, by using the procedure described in Section 2.5.2.

2.3 HOMOGENEITY ASSESSMENT

In the context of a certified reference material, it is important that the material is finely divided and physically as homogeneous as possible, such that sub-samples are as representative as possible of the whole material. In other words, each distributed unit is the same, within the stated uncertainty, for each certified property values and the material within each unit is uniform [9]. Consequently, ISO 17034:2016 [7] requires reference material producers to quantify the between- and within- unit variation.

2.3.1 Between-units homogeneity assessment

The between-units homogeneity was evaluated using 12 polypropylene containers selected using random stratified sampling from the whole batch. Duplicate subsamples from each bottle were prepared and analyzed for their total element, REEs and methylmercury mass fractions in the inorganic chemistry laboratories of MESL as described in Section 2.2.

The measurements were performed in one analytical run under repeatability conditions and in a randomized way to be able to separate a potential analytical trend from a bottling and or trend from over the storage time.

Potential trend in the analytical sequence was tested by regression analyses. As the analytical sequences were randomized (i.e., not correlated with unit number and/or storage time at different conditions (Table 1)), any significant (95%) trend between run position and mass fraction were corrected using Eq. (1). Correction of trend is expected to reduce analytical variation improving the evaluation of potential between unit inhomogeneity.

Corrected result = Measured Result – ($b\times i$)   (1)

With:

b being the slope of the linear model

i being the position of the analyzed subsample in the run

Results (analytical trend corrected if needed) are then tested for processing bottling trend, using regression between unit number and results. At the time of IAEA-158 production, units were not labelled in production order, so it was not possible to test for the initial potential bottling trend. The evaluated trend only account for potential effect of the rebottling sequence. If a significant processing trend at 95% confidence level was observed, the estimate of heterogeneity between bottles (u_{Trend}) was modeled as the half width of a rectangular distribution following Eq. (2).

$$u_{Trend} = \frac{highe\quad result - lowes\quad result}{2\sqrt{3}} \tag{2}$$

Grubbs and Dixon tests were performed to identify potential outlying individual results or unit means. In case of a significant outlying mean at 95% confidence level, between bottle heterogeneity (u_{Out}) was modeled as the rectangular distribution limited by the outlying average using Eq. (3).

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

With:

y being the average of all results.

Otherwise, quantification of between-units heterogeneity was done by one way analysis of variance (ANOVA) which can separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter accounts for method repeatability and within unit inhomogeneity.

As a prerequisite for the application of ANOVA for the estimation of uncertainty arising from homogeneity, it was verified whether the individual results and unit means followed a normal distribution, or the data set had a single mode of distribution.

ANOVA allows the calculation of the within-unit standard deviation s_{wb} and the between-units standard deviation s_{bb} from mean squares (MS) of within- and between-groups, and enable the estimation of associated uncertainty components, by applying Eqs (4) and (5).

$$s_{wb} = \sqrt{MS_{wb}} \tag{4}$$

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$$s_{bb} = u_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{n}} \qquad (5)$$

With:

n being the number of replicates sub-samples per bottle

u_{bb} being the estimation of between bottle heterogeneity uncertainty.

s_{bb} and s_{wb} are estimates of the standard deviations and are subject to random fluctuations. Therefore, the mean square between groups (MS_{bb}) can be smaller than the mean square within groups (MS_{wb}), resulting in negative arguments under the square root used for the estimation of the between -units 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 in Ref. [10].

$$u^*_{bb} = \sqrt{\frac{s_{wb}}{n}} \sqrt[4]{\frac{2}{v_{MSwb}}} \qquad (6)$$

With:

n being the number of replicates sub-samples per bottle

v_{MSwb} being the degrees of freedom of MS_{wb}.

2.3.2 Within-unit homogeneity assessment

ISO Guide 35:2017 [9] recommends specific assessment of within-unit variation when the minimum sample intake is significantly lower than the unit size, which is the case for this study (10g units and sample size 0.25g).

For the within-unit study, 6 subsamples from the same unit were analyzed in triplicates for their total element, REEs and methylmercury mass fractions in the inorganic chemistry laboratories of MESL as described in Section 2.2. The measurements were performed under repeatability conditions in three runs using randomized block design, each subsample being measured once in each run randomly.

For Hg, the measurement on a same subsample cannot be repeated as the measurement was performed using a destructive technique. Therefore, the within bottle study was performed by measurements of 15 sub-samples from the same unit.

Potential trend in each analytical sequence was tested by regression analyses, significant trend (95%) between run position and mass fraction were corrected using Eq. (1). Results corrected for sequence trend were checked for single outlier and subsample mean outlier applying Grubbs and Dixon tests. In case of an outlying subsample mean, significant at 95% confidence level,

within bottle heterogeneity was modeled as the rectangular distribution limited by the outlying average using Eq. (3).

As a prerequisite for the application of ANOVA for the estimation of uncertainty, arising from homogeneity, it was verified whether the individual results and unit means followed a normal distribution and if not, whether as a minimum the distribution of the data had a single mode.

The quantification of uncertainty arising from within-unit homogeneity (u_{wb})was done by one-way ANOVA which in this case can separate within-bottle variation (Eq. (8)) from the measurement variation applying (Eq. (7)). The between-group mean square (MS_{wb}) represents the within-bottle variance while the within-group mean square (MS_{method}) represents the analytical variation. For total Hg, as only one measurement can be performed per subsample, s_{method} is obtained from validation and is estimated as 2.5%.

$$s_{\text{method}} = \sqrt{MS_{\text{method}}} \qquad (7)$$

$$s_{wb} = u_{wb} = \sqrt{\frac{MS_{wb} - MS_{met}}{n}} \qquad (8)$$

The significance of a between-run effect was evaluated using two-way ANOVA. In the case of randomized block design with one observation per subsample per run, the two-way ANOVA leads to between-run mean square, between-subsample mean square and a residual mean square equivalent to analytical variation. If the difference between runs was significant at 95% confidence level, the within-unit heterogeneity uncertainty was estimated using mean squares from two-way ANOVA in equations above using between-subsample mean square instead of MS_{wb} and using residual mean square instead of MS_{method}, otherwise one-way ANOVA was applied as described above.

2.4 STABILITY STUDY

Stability tests are necessary for the establishment of conditions for storage (long–term stability) as well as conditions for the transportation of the units to the customers (short–term stability).

The stability studies were carried out using an isochronous design [11]. 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). Analysis of the material (after various exposure times and temperatures) under repeatability conditions significantly improves the sensitivity of the stability tests.

Based on experience with similar matrix reference materials, no degradation was expected; for this reason, units used for long–term, short–term stability and homogeneity studies have been combined to optimize the number of analyses, as shown in Table 1.

This approach requires to verify the absence of significant difference linked with storage conditions. This was carried out using an F test (unbalanced ANOVA) with results obtained on

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units stored at -20°C in 2006, units stored at 20°C over 16 years and units exposed to 60°C for 1, 2 or 3 weeks after having been stored at 20°C for 16 years.

Evaluation of data was then carried out by performing a linear regression on the determined mass fractions versus time (for long─ and short–term study).

TABLE 1. COMBINED UNITS FOR HOMOGENEITY AND STABILITY STUDIES

Name	Bottle Number	Time at 20°C (year)	Time at 60°C (week)
IAEA-158A Reference condition	7	0	0
IAEA-158A Reference condition	9	0	0
IAEA-158A Reference condition	12	0	0
IAEA-158 A # 31 Short–term 1W	31	16	1
IAEA-158 A # 67 Short–term 2W	67	16	2
IAEA-158 A # 113	113	16	0
IAEA-158 A # 156 Short–term 1W	156	16	1
IAEA-158 A # 204 Short–term 3W	204	16	3
IAEA-158 A # 235 short–term 2W	235	16	2
IAEA-158 A # 253	253	16	0
IAEA-158 A # 362	362	16	0
IAEA-158 A # 397 Short–term 3W	397	16	3

2.4.1 Long–term stability

Original material IAEA-158 was prepared and bottled in 2006, at the time of bottling some bottles (10) were stored under so called "reference" condition: (-20 ± 2) °C in the dark. The other produced units were stored under "normal" conditions: (20 ± 5) C° in the dark. To evaluate the potential degradation of the material over 16 years, 3 bottles stored under "reference" conditions and 9 bottles stored under "normal" conditions were randomly selected. Two subsamples from each bottle were analyzed for their total element mass fractions, as described in Section 2.2. It should be noted that units stored at -20°C in 2006 were rebottled as described in Section 2.1. at the beginning of the process.

2.4.2 Short–term stability

In order to evaluate potential degradation of the material during transportation, six bottles were stored at (60 ± 3) °C. Two bottles were selected after 1, 2 and 3 weeks, respectively, and placed under "reference" condition (-20 ± 2) °C. Duplicate subsamples from each bottle were analyzed for their total element, REEs and methylmercury mass fractions as describe in Section 2.2.

2.5 CHARACTERIZATION

The characterization refers to the process of determining reference values and was based on the results of an intercomparison exercise, organised with selected laboratories and IAEA MESL.

2.5.1 Selection of participants

Invitations to participate to the characterisation campaign were sent to laboratories with demonstrated measurements capabilities in former IAEA ILCs and/or characterisation campaigns. In addition, for REEs, some laboratories previously reporting REEs results in IAEA-158 [8] and/or with peer reviewed scientific publication record on REEs were also invited.

In April 2022, letters of invitation were sent out to 43 laboratories from 24 IAEA Member States. The invitation letter underlined that only technically acceptable results reported with their measurement uncertainties and demonstrated traceability would be considered for the final characterisation process.

Positive responses were received from 24 laboratories from 17 IAEA Member States, and samples were duly dispatched to them. Results were reported by 16 laboratories from 12 IAEA member states. The list of laboratories participating in the characterization study is presented on page 45 of this report.

2.5.2 Study set up

Each laboratory received one bottle of candidate CRM, accompanied by an information sheet and a reporting form. In addition, each participant received 1 bottle of IAEA-475 (Marine sediment, IAEA) and 1 bottle of BCR® - 667 (Estuarine sediment, EC-JRC-IRMM) as blind quality control samples (QA blind) for trace metal (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Cs, Fe, Hg, K, Li, MeHg, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, Ti, U, V and Zn) and REEs (Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sc, Sm, Ta, Tb, Tm, Y and Yb) respectively.

All results received were treated confidentially. Each participant or working group are identified with a code number and the identity of this number were revealed only to the respective participant. Participants were requested to provide 3 to 5 independent results using validated analytical methods, expanded uncertainty, information on the applied quality control procedures as well as the information on the standard calibration solutions used in the measurement step.

Laboratories were requested to provide moisture corrected results. As the moisture content in the sample is an operationally dependent parameter, the method for moisture determination was preliminary prescribed to all participating laboratories to ensure comparability of measurement results. The prescribed protocol in this case is the following: 1 g sub-samples should be heated in a ventilated dry oven at 105ºC ± 3 ºC until constant weight (usually at least 24 hours).

3   RESULTS AND DISCUSSION

3.1   RESULTS OF HOMOGENEITY STUDY

The results of homogeneity studies for within and between units have been evaluated separately as describe in Section 2.3.

3.1.1   Results of between-unit homogeneity

As a first step it was verified that results obtained for units stored under different storage conditions did not show any trend or significant statistical differences (see Section 2.4.), as this would invalidate the possibility to use the combined data sets for homogeneity.

Table 2 shows results of the between-unit study data evaluation as described in Section 2.3.1. As it can be seen the majority of u_{bb} (~50%) were estimated using $u*$ (Eq. (6)) due to method repeatability and/or within bottle heterogeneity being higher than between bottle variation. Few single outliers were detected but none of them were rejected based on the absence of technical justifications. As well, all observed outlying units were retained and treated as described in Section 2.3.1. using Eq. (3). For analytes with u_{bb} estimated as S_{bb} or $u*$ it was verified that unit means follow normal or at least unimodal distribution.

Results observed for Cu, Mo, Sb and Sn suggested some lack of homogeneity of the material. For Hg, as already observed at the time of production of IAEA-158 [8], the homogeneity of the material was impacted by some extreme outliers, resulting in unacceptable u_{bb} uncertainty. It is assumed that the sample contains "highly" contaminated particulates (hot spots) that cannot be homogenously distributed in the sample. Results obtained for MeHg demonstrate that the phenomenon is only observed for inorganic mercury. For all other analytes, the uncertainty component arising from between bottle homogeneity at 250 mg sample intake was found to be <5%.

TABLE 2. SUMMARY OF BETWEEN-BOTTLE HOMOGENEITY STUDY

Analyte	Analytical trend	Outliers single data	Outliers bottle mean	Bottling trend	u_{bb}	u_{bb} type
Al	no	no	no	no	1.7%	$u*$ Eq. (6)
Ag	yes	no	no	no	2.2%	$u*$ Eq. (6)
As	yes	1	no	no	2.0%	$u*$ Eq. (6)
Ba	no	no	no	no	1.6%	$u*$ Eq. (6)
Ca	yes	no	no	no	1.0%	$u*$ Eq. (6)
Cd	no	no	no	no	3.5%	S_{bb} Eq. (5)
Ce	no	no	no	no	0.9%	S_{bb} Eq. (5)
Co	yes	1	no	no	2.2%	$u*$ Eq. (6)
Cr	no	no	no	no	2.8%	$u*$ Eq. (6)
Cs	yes	no	no	no	1.4%	$u*$ Eq. (6)
Cu	no	2	2	no	12%	u_{Out} Eq. (3)
Dy	no	no	no	no	0.8%	S_{bb} Eq. (5)
Er	no	1	no	no	1.7%	S_{bb} Eq. (5)
Eu	no	no	no	no	1.4%	$u*$ Eq. (6)
Fe	no	no	no	no	1.3%	$u*$ Eq. (6)
Gd	no	no	no	no	1.7%	$u*$ Eq. (6)
Hf	yes	no	no	no	1.7%	$u*$ Eq. (6)

TABLE 2. SUMMARY OF BETWEEN-BOTTLE HOMOGENEITY STUDY (CONT.)

Analyte	Analytical trend	Outliers single data	Outliers bottle mean	Bottling trend	u_{bb}	u_{bb} type
Hg	no	4	3	no	30%	u_{Out} Eq. (3)
Ho	no	no	no	no	1.6%	u^* Eq. (6)
K	yes	no	no	no	1.5%	u^* Eq. (6)
La	no	no	no	no	2.2%	S_{bb} Eq. (5)
Li	no	no	no	no	1.1%	u^* Eq. (6)
Lu	no	1	1	no	3.1%	u_{Out} Eq. (3)
MeHg	yes	1	no	yes	3.6%	u_{Trend} Eq. (2)
Mg	yes	no	1	no	1.4%	u_{ROut} Eq. (3)
Mn	yes	no	no	no	1.0%	u^* Eq. (6)
Mo	yes	no	1	no	11%	u_{Out} Eq. (3)
Na	no	no	no	no	1.1%	u^* Eq. (6)
Nd	no	no	no	no	2.0%	S_{bb} Eq. (5)
Ni	no	no	no	no	1.1%	S_{bb} Eq. (5)
Pb	no	no	no	yes	3.4%	u_{Trend} Eq. (2)
Pr	no	no	no	no	1.6%	S_{bb} Eq. (5)
Rb	yes	no	no	no	1.6%	u^* Eq. (6)
Sb	no	no	no	no	6.7%	u^* Eq. (6)
Sc	yes	no	1	no	3.6%	u_{Out} Eq. (3)
Se	yes	1	1	no	6.7%	u_{Out} Eq. (3)
Sm	no	1	no	no	1.6%	S_{bb} Eq. (5)
Sn	no	no	no	yes	8.5%	u_{Trend} Eq. (2)
Sr	yes	1	no	no	1.6%	S_{bb} Eq. (5)
Ta	yes	no	no	no	0.9%	S_{bb} Eq. (5)
Tb	no	no	no	no	1.6%	u^* Eq. (6)
Th	no	1	no	no	2.8%	u^* Eq. (6)
Ti	no	no	no	no	2.4%	u^* Eq. (6)
Tm	no	1	1	no	3.4%	u_{Out} Eq. (3)
U	no	no	1	no	2.5%	u_{Out} Eq. (3)
V	yes	1	no	no	1.7%	u^* Eq. (6)
Y	no	no	no	no	0.9%	S_{bb} Eq. (5)
Yb	no	1	1	no	4.6%	u_{Out} Eq. (3)
Zn	yes	no	1	no	4.6%	u_{Out} Eq. (3)

3.1.2 Results of within-unit homogeneity

Table 3 shows results of the within-unit study data evaluation as described in Section 2.3.2. As it can be seen the majority of u_{wb} (~60%) were estimated using two-way ANOVA, due to significant run effect. Few single outliers were detected but none of them were rejected based on the absence of technical justifications. Outlying means (i.e., average of three measurement of the same solution) detected for As, Co, Cr, Hg, Rb, Ti, V and Yb were also retained and u_{wb} was estimated using Eq. (3). For Cd, one digested solution was contaminated, therefore it was decided to reject results of this specific solution before applying ANOVA calculations.

For Cu, despite not being detected as outlier, the three observed single results outliers were from the same subsample solution and the observed distribution of individual results was not unimodal. Consequently, it was decided to model heterogeneity within-bottles as the half width of a rectangular distribution following Eq. (3).

For Hg, as for between-bottle study, some extreme outliers were detected confirming the inhomogeneity of the material. For Fe and K it was not possible to estimate u_{wb} due to negative argument (i.e. $MS_{method} > MS_{sb}$ in Eq. (5).), u_{wb} was estimated as describe in Section 3.1.1 using $u*$ calculated with Eq. (6). The within-bottle inhomogeneity was found to be significant for a large majority of analytes and varied from 0.2 to 11% (except for Hg).

TABLE 3. SUMMARY OF WITHIN-BOTTLE HOMOGENEITY STUDY

Analyte	Analytical trend	Outliers single data	Outliers mean	Run effect	S_{method}	u_{wb}	u_{wb} type
Ag	no	no	no	yes	1.4%	6.1%	S_{wb} Eq. (8)
Al	no	no	no	no	0.8%	1.2%	S_{wb} Eq. (8)
As	yes	1	1	yes	1.3%	3.0%	u_{Out} Eq. (3)
Ba	yes	no	no	yes	1.4%	3.5%	S_{wb} Eq. (8)
Ca	yes	no	no	no	1.5%	0.3%	S_{wb} Eq. (8)
Cd	no	1	1	no	2.4%	2.6%	S_{wb} Eq. (8)
Ce	no	no	no	yes	2.0%	2.8%	S_{wb} Eq. (8)
Co	yes	3	1	no	0.9%	4.3%	u_{Out} Eq. (3)
Cr	no	no	1	no	1.9%	3.7%	u_{Out} Eq. (3)
Cs	no	no	no	yes	0.8%	3.2%	S_{wb} Eq. (8)
Cu	no	3	no	yes	0.5%	8.0%	u_{Out} Eq. (3)
Dy	no	no	no	yes	1.1%	3.1%	S_{wb} Eq. (8)
Er	no	1	no	no	2.0%	1.6%	S_{wb} Eq. (8)
Eu	no	no	no	yes	1.1%	2.8%	S_{wb} Eq. (8)
Fe	no	no	no	yes	1.6%	0.8%	$u*$ Eq. (6)
Gd	no	no	no	yes	1.1%	3.5%	S_{wb} Eq. (8)
Hf	no	no	no	yes	1.8%	3.4%	S_{wb} Eq. (8)
Hg	no	3	n.a.	n.a.	2.5%	47%	u_{Out} Eq. (3)
Ho	no	1	no	yes	1.9%	2.0%	S_{wb} Eq. (8)
K	no	no	no	no	6.1%	2.9%	$u*$ Eq. (6)
La	no	no	no	yes	0.9%	4.2%	S_{wb} Eq. (8)
Li	yes	no	no	no	1.6%	2.5%	S_{wb} Eq. (8)
Lu	no	no	no	no	2.3%	2.2%	S_{wb} Eq. (8)
MeHg	yes	no	no	no	1.3%	1.8%	S_{wb} Eq. (8)
Mg	yes	no	no	yes	1.0%	0.3%	S_{wb} Eq. (8)
Mn	no	no	no	no	1.3%	1.8%	S_{wb} Eq. (8)
Mo	yes	no	no	no	2.0%	5.9%	S_{wb} Eq. (8)
Na	yes	no	no	yes	2.7%	0.5%	S_{wb} Eq. (8)
Nd	no	no	no	yes	1.1%	4.0%	S_{wb} Eq. (8)
Ni	yes	no	no	yes	1.8%	1.8%	S_{wb} Eq. (8)
Pb	no	no	no	no	1.2%	5.1%	S_{wb} Eq. (8)
Pr	no	no	no	yes	2.1%	3.1%	S_{wb} Eq. (8)
Rb	yes	no	1	no	1.8%	2.8%	u_{Out} Eq. (3)
Sb	no	1	no	no	3.8%	8.9%	S_{wb} Eq. (8)
Sc	yes	no	no	yes	2.0%	2.1%	S_{wb} Eq. (8)
Se	yes	no	1	yes	5.2%	3.6%	u_{Out} Eq. (3)
Sm	no	no	no	yes	1.2%	4.2%	S_{wb} Eq. (8)

TABLE 3. SUMMARY OF WITHIN-BOTTLE HOMOGENEITY STUDY (CONT.)

Analyte	Analytical trend	Outliers single data	Outliers mean	Run effect	S_{method}	u_{wb}	u_{wb} type
Sn	no	no	no	no	2.2%	10.6%	S_{wb} Eq. (8)
Sr	no	no	no	yes	0.7%	5.2%	S_{wb} Eq. (8)
Ta	no	no	no	yes	1.9%	3.4%	S_{wb} Eq. (8)
Tb	no	no	no	yes	1.3%	2.2%	S_{wb} Eq. (8)
Th	no	no	no	yes	5.4%	1.1%	S_{wb} Eq. (8)
Ti	yes	3	1	yes	1.8%	7.5%	u_{Out} Eq. (3)
Tm	no	no	no	yes	2.3%	1.6%	S_{wb} Eq. (8)
U	no	no	no	yes	1.5%	4.3%	S_{wb} Eq. (8)
V	yes	no	1	yes	1.3%	2.5%	u_{Out} Eq. (3)
Y	no	no	no	yes	1.5%	2.4%	S_{wb} Eq. (8)
Yb	no	no	1	yes	0.8%	3.0%	u_{Out} Eq. (3)
Zn	no	no	no	yes	1.0%	4.1%	S_{wb} Eq. (8)

3.1.3   Estimates of inhomogeneity uncertainties

Final uncertainty u_{hom} associated to inhomogeneity of the material at the prescribed minimum sample size (0.25g) was estimated by Eq. (9).

$$u_{hom} = \sqrt{u_{wb}^2 + u_{bb}^2} \qquad\qquad (9)$$

For Cu, Hg, Mo, Sb and Sn estimated u_{hom} are above 10% indicating some inhomogeneity of the material probably linked with the final sieving through a 315μm sieve and potential "contaminated" particulates not evenly distributed in the sample. Most other analytes, as shown in Table 5, and specifically MeHg and REEs showed very good homogeneity with u_{hom} being less than 5%.

3.2   RESULTS FOR STABILITY STUDY

The results of long and short─term stability studies have been evaluated separately as describe in Section 2.4.

3.2.1   Long–term stability

Evaluation of data was carried out by performing a linear regression on the determined mass fractions versus time. No significant slope at 99% level of confidence was detected for any of the investigated trace elements in the long–term stability study at +20°C. The approach proposed in ISO Guide 35 [9] was followed, an uncertainty contribution related with possible instability of the candidate reference material (u_{lt}) was estimated as the standard error of the slope multiplied by the selected shelf life of 5 years. Obtained u_{lt} ranged from 0.3 to 4.9%.In addition, obtained values during this study were in very good agreement with values available in the reference sheet of IAEA-158. This comparison additionally confirmed the stability of the material over the last 16 years.

It should be highlighted that this study did not consider the potential effect of the change of containers material (i.e., stored in glass for 20 years before transfer to polypropylene containers). The IAEA-158A material will be checked for stability at regular intervals in line with the NAML internal standard operating procedure to evaluate potential impact of this change of storage containers.

Some CRM produced previously in polypropylene containers [12, 13] have been demonstrated to be stable with exception of MeHg in a sediment sample. It should be noted that the observed instability of MeHg at ultralow level concentration in IAEA-475 was not related to the storage container material. As a precautionary approach, and despite demonstration of long—term stability of MeHg in IAEA-158A, MeHg is given as an information value until data on long—term stability in new containers is demonstrated.

3.2.2   Short–term stability

Evaluation of data was carried out by performing a linear regression on the determined mass fractions versus time of storage at 60°C. No significant slope at 99% level of confidence was detected for any of the investigated trace elements in the short–term stability study. As no degradation was observed, 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.

3.3   RESULTS OF CHARACTERIZATION

Results obtained during the characterization campaign have been evaluated based on below criteria.

3.3.1   Evaluation of reported results

The obtained measurement results were first checked for compliance with the certification requirements, and then for their validity based on technical judgment. After reception of the data sets, the results were subjected to evaluation according to the following criteria.

3.3.1.1   *Review of minimum requirements:*

As requested in the invitation letter and information sheet, it was mandatory for participants to report a minimum of 3 independent results, an uncertainty statement, and results for their internal quality control (QC) sample. In addition, participants were to answer a questionnaire with detailed information regarding the used method and traceability assessment. Laboratory code 18 was excluded from the characterization exercise as not reporting three independent results for any of the analytes.

In addition, the fitness for purpose of the applied procedures was checked for the characterization exercise of total trace elements in a sediment sample. All participating laboratories applied either acid digestion with hydrofluoric acid or non-destructive techniques, both being considered suitable for the determination of total mass fraction of trace elements.

3.3.1.2 *Review of reported values for QA blind samples:*

For CRM IAEA-475, As, Co, Cr, Cu, Fe, Hg, Ni, Pb, and Zn results were evaluated against certified values while Ag, Al, Cd, Li, Mn and Sr were evaluated against information values. For analytes with no information on the certificate, if at least 5 results were available it was decided to calculate an assigned value following ISO 13528:2022 [14]. Therefore, for Ba, Ca, K, Mg, Na, Rb, Sb, Ti, and V results were evaluated against consensus values calculated as median of reported results. Associated uncertainty for the assigned consensus values were estimated using Eq. (10).

$$U_{ass} = k \times \sqrt{u_{hom}^2 + u_{char}^2} \qquad\qquad (10)$$

With:

u_{char} being the standard error of the median

u_{hom} being set at 5 %.

Results reported for Cs, MeHg, Mo, Se and Sn could not be evaluated as no consensus value could be estimated (less than 5 results reported) and no values were available in the certificate.

For CRM BCR® - 667, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Yb, Th and U results were evaluated against certified values while Ta results were evaluated against the information value. Results reported for Hf and Y could not be evaluated as no values were available in the certificate and no consensus value could be estimated (less than 5 results reported).

The evaluation was performed using Zeta scores calculated using Eq (11).

$$\text{Zeta score} = \frac{x_{lab} - X_{ass}}{\sqrt{u_{lab}^2 + u_{ass}^2}} \qquad\qquad (11)$$

With:

x_{lab} being the measurement result reported by participant

X_{ass} being the assigned value

u_{ass} being the standard uncertainty of the assigned value

u_{lab} being the standard uncertainty reported by participant.

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If a laboratory received |Zeta score| > 2 for more than half of its reported results or extreme |Zeta score| (i.e. > 7) for more than 2 analytes, the entire dataset sent by the laboratory was rejected. Based on these criteria, laboratory 20 was excluded from the dataset.

If results reported for the blind QA sample received a |Zeta score| > 2, reported results for the analyte were excluded. About 25% of reported results were excluded based on this criterion.

3.3.1.3   Review of reported uncertainties and analytical precision:

It was considered that results reported with expanded uncertainties exceeding 20% were not fit for the purpose of the study and were therefore excluded. As well, the relative standard deviations (RSD) of individual reported results (minimum of 3) were scrutinized and values were excluded if RSD exceeded 20%.

After exclusion as mentioned above, the number of results per analytes varied from 1 to 9. For analytes with more than 5 values available, data sets were checked for outlying results using the Grubbs and Dixon test. Normality of the distribution of the reported means were tested using the Shapiro-Wilk Test. All tested analytes were normally distributed with at least 99% confidence. Only the Zn result reported by laboratory 1 was detected as an outlier at 95 and 99% confidence level. Despite not having a technical reason to explain this result, it was decided to reject it as it was almost twice higher than the other reported results. Datasets not complying with the preliminary defined requirements or considered as not technically valid are listed in Table 4.

TABLE 4. DATASET EXCLUDED FROM FURTHER EVALUATION AFTER TECHNICAL REVIEW

Lab code	Analyte
1	Ba, Tb, Zn
4	Co, Dy, Eu, Pb, Ta, Tb, U
7	As, Cd, Co Hg, Li, Pb, U, V
8	Ca, Ce, Co, Cs, Dy, Sb, Sr, Ta, Tb
9	As, Dy, Mg, Pr, Sm, Tb
13	Al, Co, Fe, K, Mo, Na, Sb, Ti,
14	Cr
15	Dy, Er, Gd, Lu, Pr, Tm, U, Yb
16	Al, Cr, Cu, Fe, Mn, Na, Ni, Pb, Zn
18	All
19	K, Mo, Ta, Zn
20	All

3.3.2   Analytical methods

The characterization of trace elements, methylmercury and REEs mass fractions in the material was based on the application of several analytical techniques and sample preparation presented in Table 9 of Appendix I. Acronyms for analytical methodologies used further in the text and in figures are also shown in this Table.

3.4 DETERMINATION OF ASSIGNED VALUES AND THEIR UNCERTAINTIES

For analytes where at least five results were available after technical evaluation in Section 3.3.1, assigned values were estimated as the mean of means of reported results. The uncertainties associated with the assigned values were calculated according to ISO Guide 35 [9]. The relative combined uncertainty of the CRM's certified value consists of uncertainty contributors related to its characterization (u_{char}), sample heterogeneity (u_{hom}), long–term stability (u_{lt}) and short–term stability (u_{st}). These different contributions were combined and multiplied with a coverage factor k, to estimate the expanded uncertainty as shown in Eq. (12).

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

With:

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

u_{hom} being estimated as described in Section 3.1

u_{lt} being estimated as described in Section 3.2.1

u_{st} being estimated as zero as described in Section 3.2.2

u_{char} bieng estimated as described in ISO Guide 35 [9] using Eq. (13).

$$u_{char} = \frac{s}{\sqrt{p}} \qquad (13)$$

With:

s being the standard deviation of the mean

p being the number of datasets.

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

Expanded uncertainties associated to assigned mass fractions were below 15% except for Cu, Hg, Mo, Sb and Ti. In addition, as shown in Table 5 and Appendix, for all analytes, methods with different quantification principles (ICP-MS, ICP – OES, F-AAS, NAA) as well as methods without a sample preparation step, such as neutron activation, were used for characterization of the material. For all studied analytes, the good agreement within the stated uncertainty confirms the absence of any significant method bias and demonstrates the identity of the analyte. Therefore the mass fractions and associated uncertainties presented in Table 6 for Al, As, Ba, Ca, Cd, Ce, Co, Cr, Eu, Fe, K, La, Li, Mg, Mn, Na, Nd, Ni, Pb, Rb, Sm, Sr, U,

V, Y, Yb and Zn are considered as certified values, while mass fraction of Cu, Mo, Sb and Ti could only be given as additional information. For Hg due to extreme outliers observed during homogeneity study, the uncertainty of the assigned mass fraction is over 100%, therefore no information on Hg mass fraction will be given for the material.

TABLE 5. MEAN OF THE MEANS AND UNCERTAINTIES

Analyte	Mean of the means (mg kg^{-1})	$u_{char,rel}$	$u_{hom,rel}$	$u_{lt,rel}$	p	Number of Methods	U_{rel} (k=2)
Al	52.2×10^3	0.9%	2.1%	0.5%	6	4	5%
As	12.0	2.2%	3.6%	0.6%	7	3	9%
Ba	1031	0.9%	3.9%	0.5%	9	4	8%
Ca	65.3×10^3	1.9%	1.0%	0.3%	8	4	4%
Cd	0.361	3.9%	4.4%	0.7%	5	3	12%
Ce	54.1	4.2%	2.9%	0.6%	5	2	10%
Co	9.19	1.6%	4.6%	0.7%	7	3	10%
Cr	77.0	2.4%	4.6%	0.9%	11	4	11%
Cu	46.5	2.1%	15%	2.4%	9	3	30%
Eu	1.10	2.2%	3.1%	0.4%	5	2	8%
Fe	26.6×10^3	1.7%	1.5%	0.4%	9	4	5%
Hg	0.141	4.3%	56%	4.9%	6	2	112%
K	20.5×10^3	1.6%	3.3%	0.5%	6	4	7%
La	28.5	2.6%	4.7%	0.5%	5	2	11%
Li	33.5	4.1%	2.7%	0.3%	5	3	10%
MeHg*	0.0018	6.1%	4.0%	0.6%	6	2	15%
Mg	10.9×10^3	2.2%	1.4%	0.3%	7	4	5%
Mn	367	1.5%	2.1%	0.4%	10	4	5%
Mo	4.91	3.6%	12%	1.4%	6	3	26%
Na	23.9×10^3	1.3%	1.2%	0.3%	8	4	4%
Nd	25.1	2.7%	4.5%	0.5%	5	2	11%
Ni	31.1	2.5%	2.1%	0.4%	8	3	7%
Pb	41.0	1.6%	6.1%	0.7%	6	3	13%
Rb	87.4	2.5%	3.2%	0.5%	8	3	8%
Sb	1.36	5.1%	11%	2.2%	5	2	25%
Sm	4.64	3.2%	4.4%	0.5%	5	2	11%
Sr	478	1.4%	5.5%	0.5%	9	4	11%
Ti	3.29×10^3	4.4%	7.9%	0.7%	7	4	18%
U	2.40	4.6%	5.0%	0.5%	5	2	14%
V	74.1	1.7%	3.0%	0.5%	9	3	7%
Y	17.1	1.9%	2.5%	0.5%	6	2	7%
Yb	2.02	1.8%	5.4%	0.7%	6	2	12%
Zn	141	1.4%	6.2%	0.6%	9	4	13%

*as Hg

TABLE 6. CERTIFIED VALUES FOR TRACE ELEMENT MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k=2*) IN IAEA-158A

Element	Certified value[1] (mg kg^{-1})	U (*k=2*)[2] (mg kg^{-1})
Al	52.2×10^3	2.4×10^3
As	12.0	1.0
Ba	1.031×10^3	0.083×10^3
Ca	65.3×10^3	2.8×10^3
Cd	0.361	0.043
Ce	54.1	5.6
Co	9.19	0.90
Cr	77.0	8.2
Eu	1.098	0.085
Fe	26.6×10^3	1.2×10^3
K	20.5×10^3	1.5×10^3
La	28.5	3.1
Li	33.5	3.3
Mg	10.86×10^3	0.58×10^3
Mn	367	19
Na	23.91×10^3	0.88×10^3
Nd	25.1	2.6
Ni	31.1	2.1
Pb	41.0	5.2
Rb	87.4	7.2
Sm	4.64	0.52
Sr	478	54
U	2.40	0.33
V	74.1	5.2
Y	17.1	1.1
Yb	2.02	0.24
Zn	141	18

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

[2] The uncertainty is expressed as an expanded uncertainty with a coverage factor *k=2*, corresponding to a 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 [15], and ISO Guide 35 [9].

For analytes for which less than 5 values were available after technical evaluation of reported data (Section 3.3.1) mean of the means of all reported values were calculated (i.e., including values excluded in Section 3.3.1, Table 1). Mean of the means, their relative expanded uncertainties (*k=2*) and uncertainty contributions from the characterization, homogeneity and stability are presented in Table 7 along the number of results and independent analytical methods. Those consensus values are considered as additional information and are presented in Table 8 along other information values.

The results for the mass fractions of the certified analytes, as reported by the participants in this study are presented in Appendix II. The information for the analytes with information values is reported in Appendix III. In all figures the reported results are plotted versus the assigned value denoted by a bold line, while the dashed lines represent the expanded uncertainty (*k=2*) associated with assigned value. The error bars represent the expanded uncertainty as reported by participants, and excluded values based on technical review (Section 3.3.1) are shown in red.

TABLE 7. MEANS OF THE MEANS AND UNCERTAINTIES

Analyte	Mean of the means (mg kg^{-1})	$u_{char,rel}$	$u_{hom,rel}$	$u_{lt,rel}$	p	Number of methods	U_{rel} (k=2)
Ag	0.219	2.9%	6.5%	0.6%	3	1	14%
Cs	3.58	2.8%	3.5%	0.4%	5	2	9.0%
Dy	3.35	5.2%	3.2%	0.5%	6	2	12%
Er	2.04	4.5%	2.3%	0.6%	4	1	10%
Gd	4.47	5.4%	3.9%	0.5%	4	1	13%
Hf	5.54	0.7%	3.8%	0.5%	4	2	7.8%
Ho	0.692	4.7%	2.6%	0.5%	5	1	11%
Lu	0.307	1.9%	3.8%	0.6%	6	2	8.6%
Pr	6.59	8.7%	3.5%	0.6%	3	1	19%
Sc	8.20	2.9%	4.2%	0.5%	5	2	10%
Se	0.625	8.6%	7.6%	0.8%	2	1	23%
Sn	7.904	5.3%	13.6%	2.0%	4	2	29%
Ta	0.984	6.2%	3.5%	0.8%	6	2	14%
Tb	0.633	4.0%	2.7%	0.5%	8	2	10%
Th	8.39	2.2%	3.0%	0.8%	5	2	7.6%
Tm	0.298	4.0%	3.8%	0.6%	4	1	11%

TABLE 8. INFORMATION VALUES FOR TRACE ELEMENT MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (k=2) IN IAEA-158A

Element	Information value[1] (mg kg^{-1})	U (k=2)[2] (mg kg^{-1})
Ag	0.219	0.031
Cs	3.58	0.32
Cu	47	14
Dy	3.35	0.41
Er	2.04	0.21
Gd	4.47	0.60
Hf	5.54	0.43
Ho	0.692	0.074
Lu	0.307	0.026
MeHg[3]	1.80×10^{-3}	0.26×10^{-3}
Mo	4.9	1.3
Pr	6.6	1.2
Sb	1.36	0.34
Sc	8.20	0.84
Se	0.63	0.14
Sn	7.9	2.3
Ta	0.984	0.14
Tb	0.633	0.061
Th	8.39	0.64
Ti	3.29×10^{3}	0.59×10^{3}
Tm	0.298	0.033

[1] The value is the mean of the means of sets of data, each set being obtained by a different laboratory. The information values are reported on dry mass basis and are traceable to the SI.
[2] The uncertainty is expressed as an expanded uncertainty with a coverage factor k=2, corresponding to a 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 [15], and ISO Guide 35 [9].
[3] as Hg

4   METROLOGICAL TRACEABILITY AND COMMUTABILITY

All standard solutions employed for calibration by laboratories participating in the characterization study were CRM which implies that the mass fractions of the trace elements in the respective standard solutions are traceable to the international system of units (SI), i.e., by comparative measurement against another CRM with established SI traceability. In addition, IAEA-475 and BCR®-667 matrix CRM, were used for validation of the methods applied in this study for most of the analytes. Therefore, results used to obtain the certified values are considered as individually traceable to SI, inferring the traceability of certified values.

The trust in the certified values and their trueness are further underpinned by the agreement among the technically accepted datasets obtained with different analytical methods as shown in Figures 1 - 27. Results obtained from nondestructive methodologies confirm the absence of bias arising from sample digestion.

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 describe this concept, ISO is defining it as: "the ability of the reference material, characterized by one measurement procedure (usually a reference procedure) to act as a calibrator or quality control material for a second measurement or testing procedure applied to routine test materials. "

The demonstration of commutability of matrix CRMs is not mandatory [9] especially if matrix and handling are similar to routine sample. IAEA-158A 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-158A characterization study confirms the absence of any significant method bias and demonstrates commutability of the material for all certified trace elements.

5   CONCLUSIONS

This certification campaign enabled the assignment of certified values for Al, As, Ba, Ca, Cd, Ce, Co, Cr, Eu, Fe, K, La, Li, Mg, Mn, Na, Nd, Ni, Pb, Rb, Sm, Sr, U, V, Y, Yb and Zn with associated uncertainties following relevant ISO standard requirement. The certified values are derived from measurement results provided by laboratories with demonstrated measurement performances, participating in the characterization study. As the certified values are derived from SI traceable individual results, they are also traceable to the International System of Units (SI). The new CRM IAEA-158A can be successfully applied for quality assurance and the validation of procedures used in environmental monitoring of trace metals and REEs in marine sediments.

APPENDIX I.

ANALYTICAL METHODS USED IN THE CHARACTERIZATION

TABLE 9. ANALYTICAL METHOD AND SAMPLE PREPARATION REPORTED BY PARTICIPANTS

Lab Code	Method	Sample preparation	Analytes
1	Neutron activation (NAA) k_0 standardize method	n.a.	As, Ba, Ca, Co, Cr, Cs, Fe, Mo, Na, Rb, Sb, Sr, Th, U, Zn, Ce, Eu, Hf, La, Nd, Sc, Sm, Ta, Tb, Yb
4	NAA k_0 standardize method	n.a.	Al, As, Ba, Co, Cr, Cs, Fe, Mg, Mn, Na, Rb, Sb, Sr, Th, Ti, U, V, Zn, Ce, Dy, Eu, Hf, La, Lu, Nd, Sc, Sm, Ta, Tb, Yb
	Xray Fluorescence (XRF)	Pressurized pellets	Pb, Y
7	ICP-MS	Microwave digestion (HNO_3, HCl, HF) followed by boric acid	As, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, U, V, Zn
	Solid Hg analyser	n.a.	Hg
8	NAA	n.a.	Al, As, Ba, Ca, Co, Cr, Cs, Fe, K, Mn, Na, Rb, Sb, Sr, Th, Ti, U, V, Ce, Dy, Eu, La, Sc, Sm, Ta, Tb, Yb
9	Inductively coupled plasma mass spectrometry (ICP-MS)	Hot plate digestion (HNO_3, HCl, HF) followed by evaporation	As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, U, V, Zn, Ce, Dy, Er, Eu, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb
	Inductively coupled plasma atomic emission spectrometry (ICP-OES)	As above	Ba, Ca, Fe, K, Mg, Na, Sr, Ti
10	Solid Hg analyser	n.a.	Hg
10	Purge and trap gas chromatography, pyrolysis atomic fluorescence spectroscopy (PT-GC-AFS)	Distillation followed by $NaBEtH_4$ derivatisation	MeHg

TABLE 9. ANALYTICAL METHOD AND SAMPLE PREPARATION REPORTED BY PARTICIPANTS (CONT.)

Lab Code	Method	Sample preparation	Analytes
13	ICP-MS	Lithium borate fusion	Ba, Co, Cu, Mn, Mo, Ni, Rb, Sb, Sn, Sr, V, Zn
	ICP-OES	As above	Al, Ca, Cr, Fe, K, Mg, Na, Ti
14	Flame atomic absorption spectroscopy (F-AAS)	Open hot plate digestion (HNO_3, HF, $HClO_4$)	Cr, Cu, Fe, Mn, Pb, Zn
	Graphite furnace atomic absorption spectroscopy (ET-AAS)	As above	Cd
	Cold vapour absorption spectroscopy (CV-AAS)	Closed hot plate (HNO_3)	Hg
15	ICP-MS	Microwave digestion (HNO_3, HCl, HF) followed by boric acid	Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Ti, U, V, Zn, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb
	CV-AAS	Closed hot plate digestion (HNO_3, HCl, HF)	Hg
	PT-GC-AFS	Acidic (H_2SO_4/KBr) solvent extraction (CH_2Cl_2) followed by extraction in water by evaporation and $NaBEtH_4$ derivatisation	MeHg
16	ICP-OES	Microwave digestion (HNO_3, HCl, HF)	Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, V, Zn
18	ICP-MS	Closed hot plate digestion (HNO_3, HCl, HF)	Ag, al, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, V, Zn, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Tb, Tm, Yb
19	ICP-MS	Closed hot plate digestion (HNO_3, HCl, HF) followed by evaporation	Ag, As, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Rb, Se, Sr, U, V, Zn
	ICP-OES	As above	Al, Ba, Ca, Fe, K, Mg, Na, Ti
	Solid Hg analyser	n.a.	Hg

TABLE 9. ANALYTICAL METHOD AND SAMPLE PREPARATION REPORTED BY PARTICIPANTS (CONT.)

Lab Code	Method	Sample preparation	Analytes
20	NAA	n.a.	As, Ba, Ca, Co, Cs, Fe, K, Mg, Mn, Na, Rb, Sb, Th, V, Zn, Ce, Eu, Hf, La, Lu, Nd, Sc, Sm, Ta, Tb, Yb
21	Solid Hg analyser	n.a.	Hg
	PT-GC-AFS	Acidic (H_2SO_4/KBr) solvent extraction (CH_2Cl_2) followed by extraction in water by evaporation and $NaBEtH_4$ derivatisation	MeHg
23	Isotope dilution (ID) PT-GC-ICP-MS	Distillation followed by $NaBEtH_4$ derivatisation	MeHg
24	PT-GC-AFS	Acidic (H_2SO_4/KBr) solvent extraction (CH_2Cl_2) followed by extraction in water by evaporation and $NaBEtH_4$ derivatisation	MeHg
IAEA	ICP-MS	Microwave digestion (HNO_3, HCl, HF) followed by boric acid	Ag, As, Cd, Co, Cr, Cs, Cu, Mo, Ni, Pb, Rb, Sb, Se, Sn, Th, V, U, Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sc, Sm, Ta, Tb, Tm Yb, Y
	F-AAS	As above	Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Rb, Sr, Ti, Zn
	ICP-OES	As above	Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, Zn
	PT-GC-AFS	Acidic (H_2SO_4/KBr) solvent extraction (CH_2Cl_2) followed by extraction in thiosulfate and $NaBEtH_4$ derivatisation	MeHg

RESULTS OF THE CHARACTERIZATION MEASUREMENTS

The results reported by the participating laboratories, their expanded uncertainty and measurement techniques are presented in Figures 1 to 27. Results not considered after technical evaluation (3.3.1) are in red. The certified value for the respective analyte and its expanded uncertainty (k=2) are presented as line and dashed lines respectively.
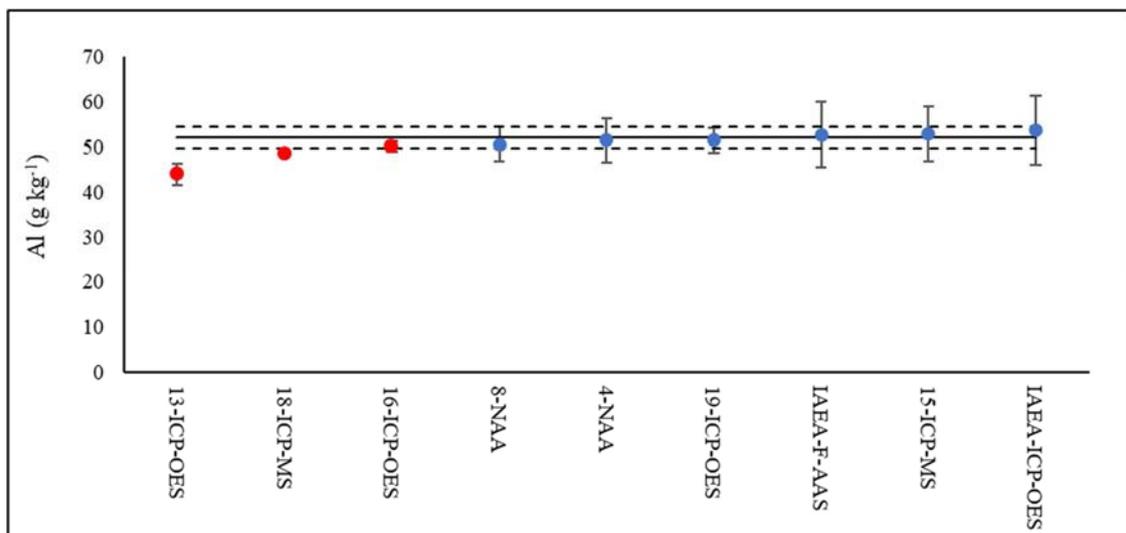
FIG. 1. Laboratory results for aluminum mass fraction (g kg^{-1}) in IAEA-158A.
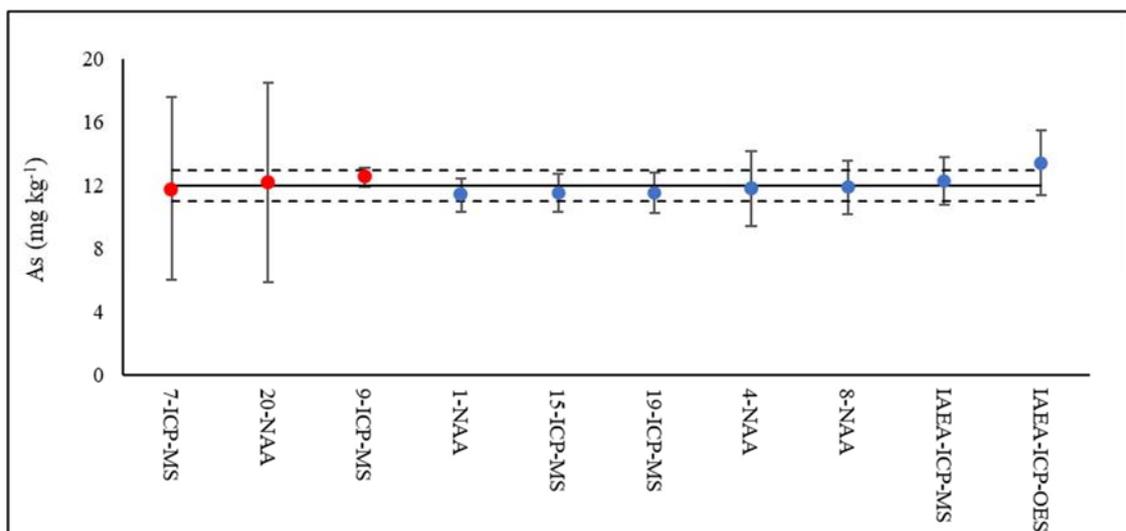
FIG. 2. Laboratory results for arsenic mass fraction (mg kg^{-1}) in IAEA-158A.
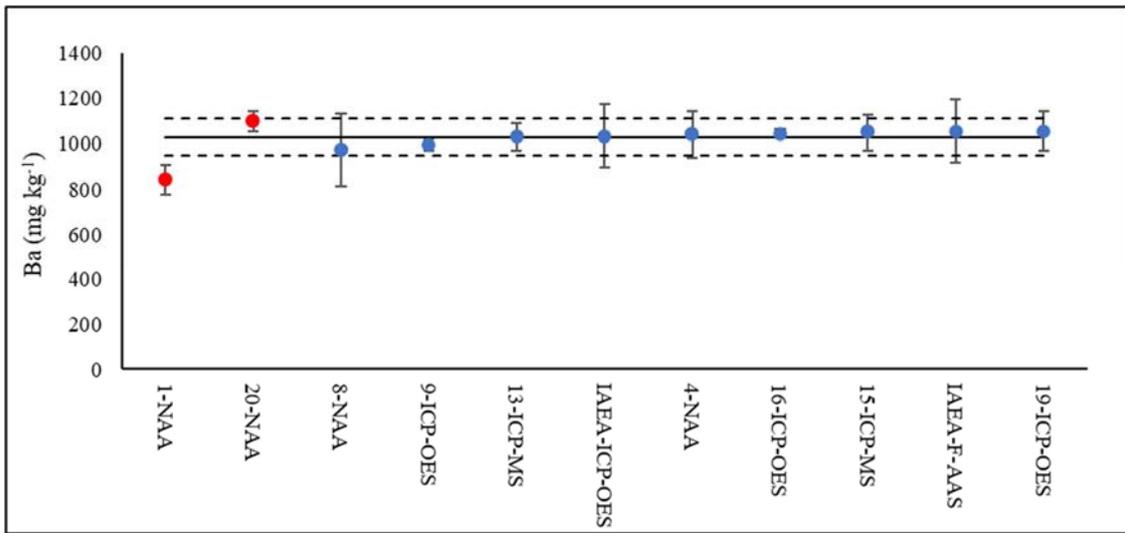
FIG. 3. Laboratory results for barium mass fraction (mg kg⁻¹) in IAEA-158A.
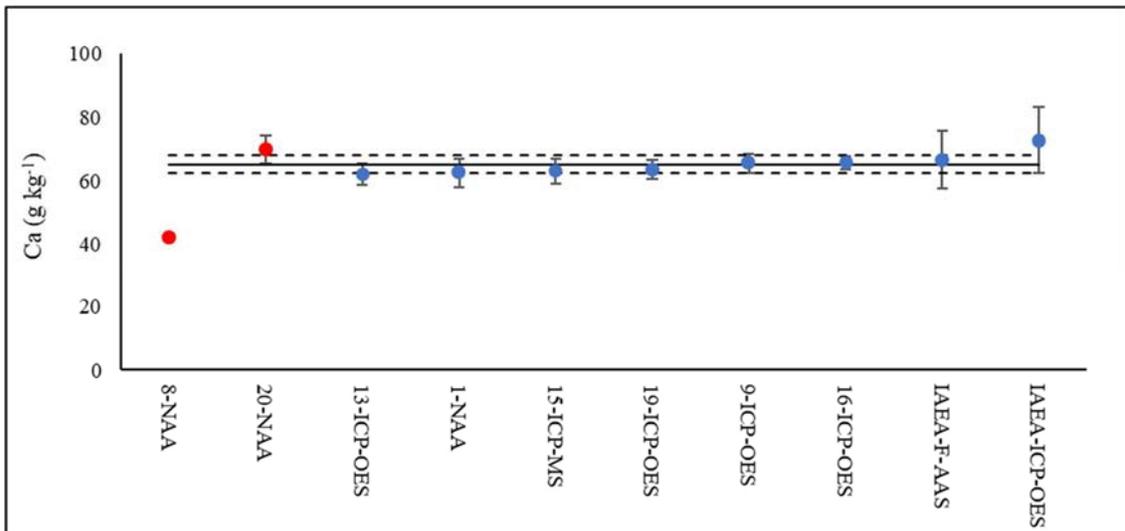
FIG. 4. Laboratory results for calcium mass fraction (g kg⁻¹) in IAEA-158A.
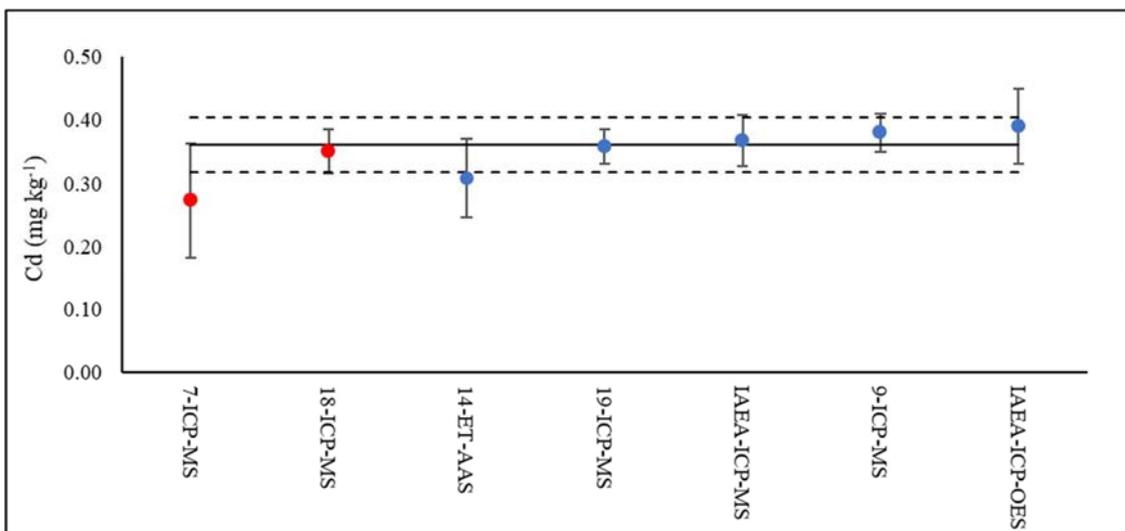
FIG. 5. Laboratory results for cadmium mass fraction (mg kg⁻¹) in IAEA-158A.

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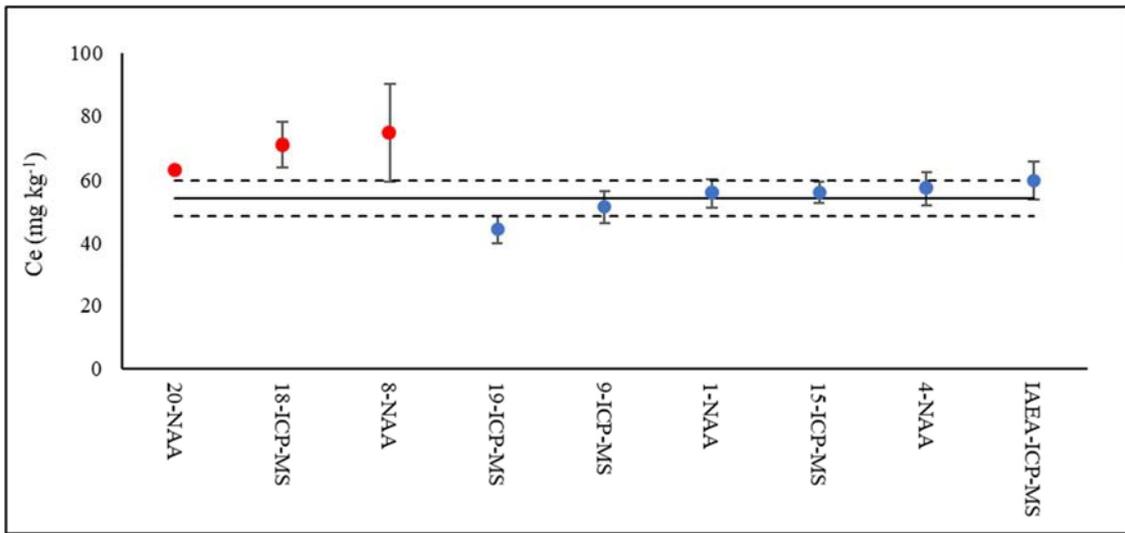
FIG. 6. Laboratory results for cerium mass fraction (mg kg^{-1}) in IAEA-158A.
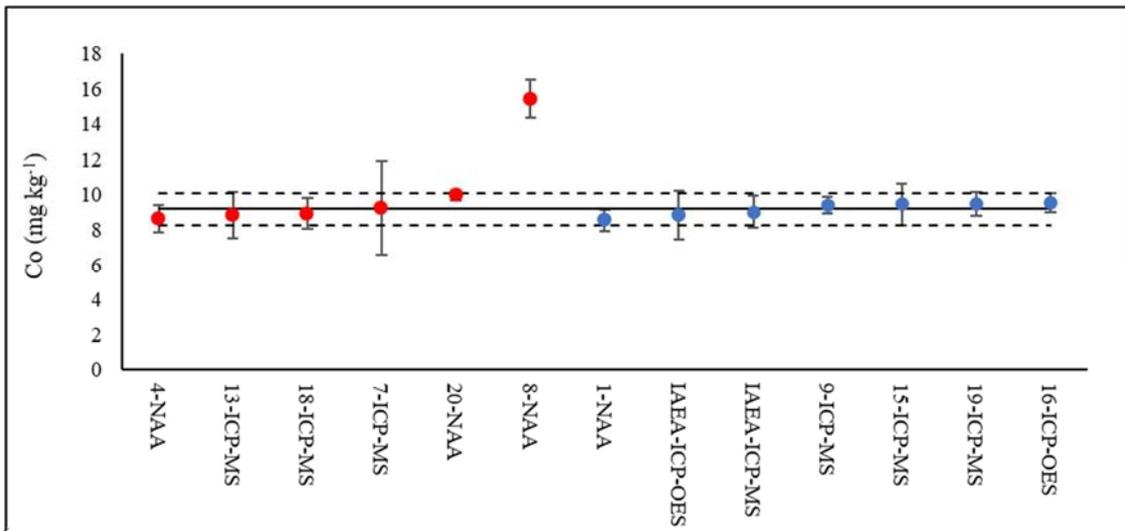
FIG. 7. Laboratory results for cobalt mass fraction (mg kg^{-1}) in IAEA-158A.
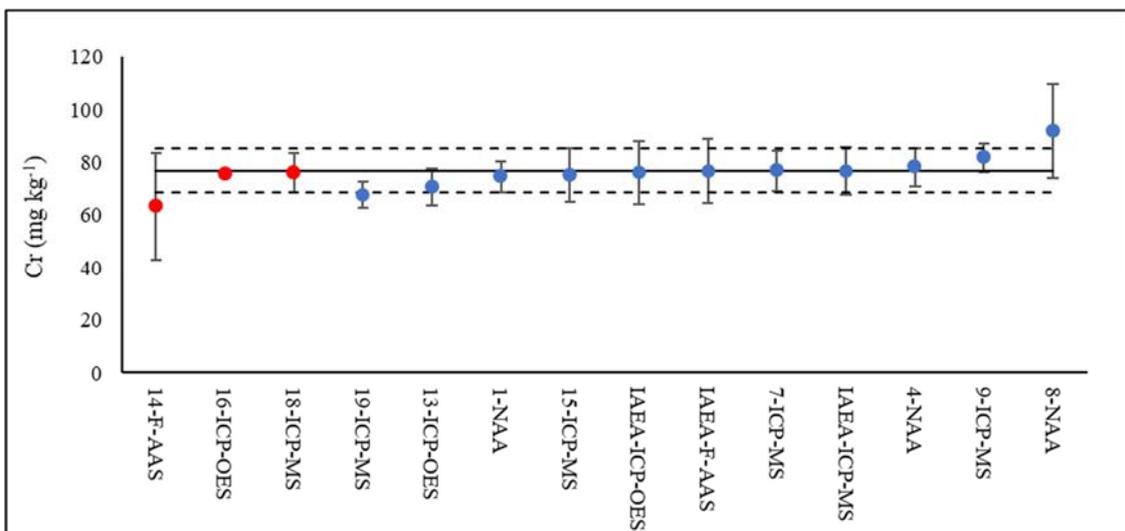
FIG. 8. Laboratory results for chromium mass fraction (mg kg^{-1}) in IAEA-158A.
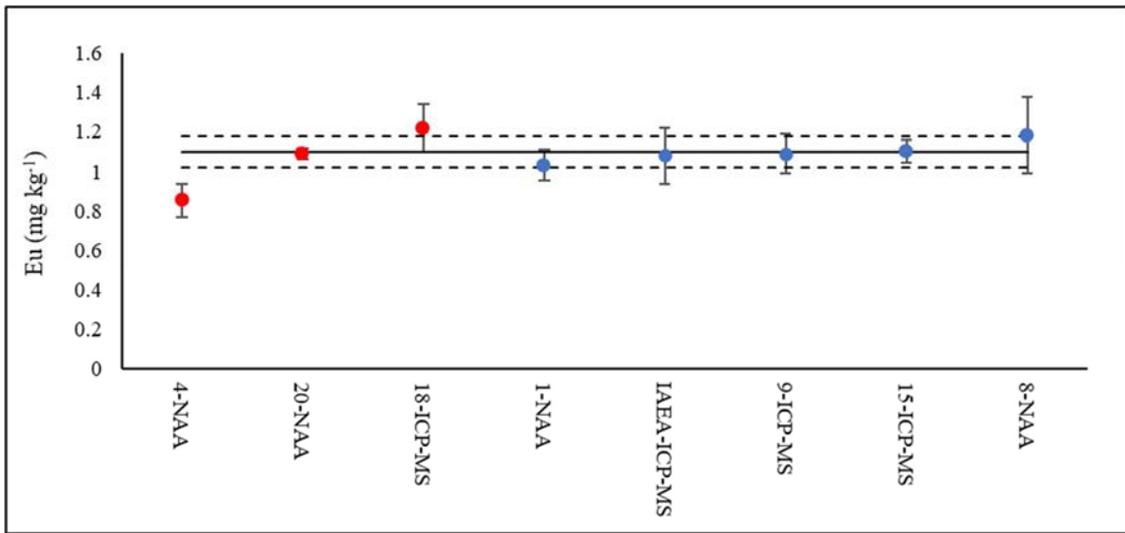
FIG. 9. Laboratory results for europium mass fraction (mg kg^{-1}) in IAEA-158A.
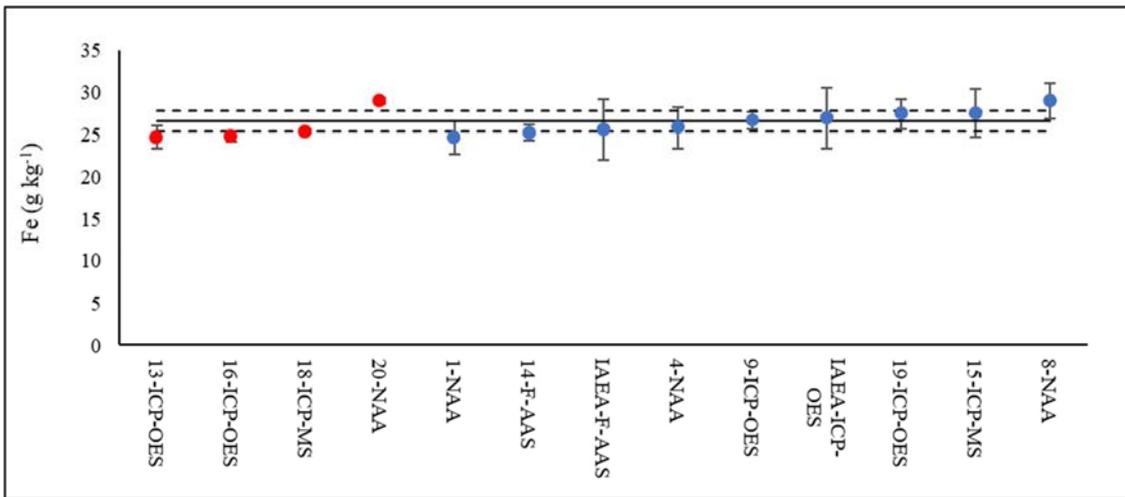
FIG. 10. Laboratory results for iron mass fraction (g kg^{-1}) in IAEA-158A.
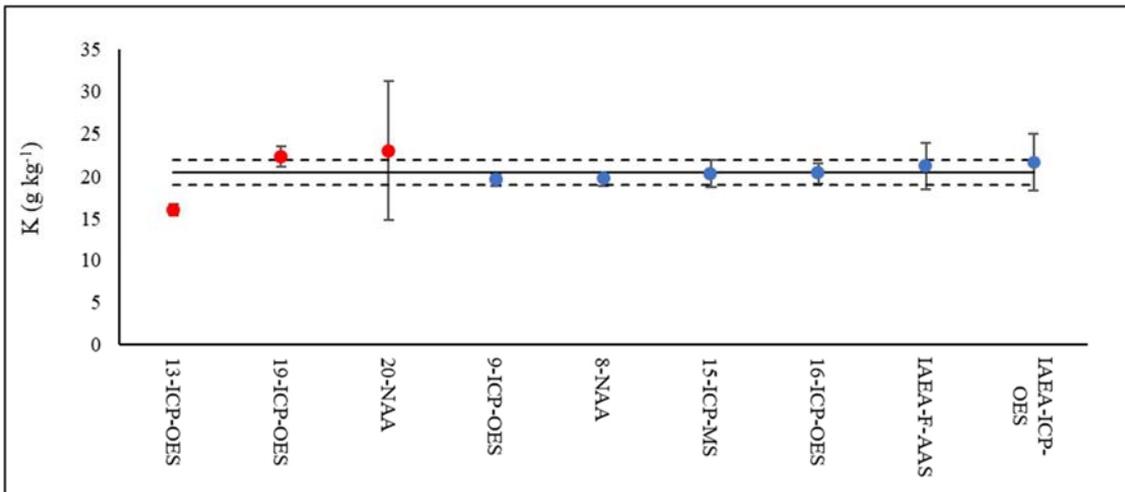
FIG. 11. Laboratory results for potassium mass fraction (g kg^{-1}) in IAEA-158A.
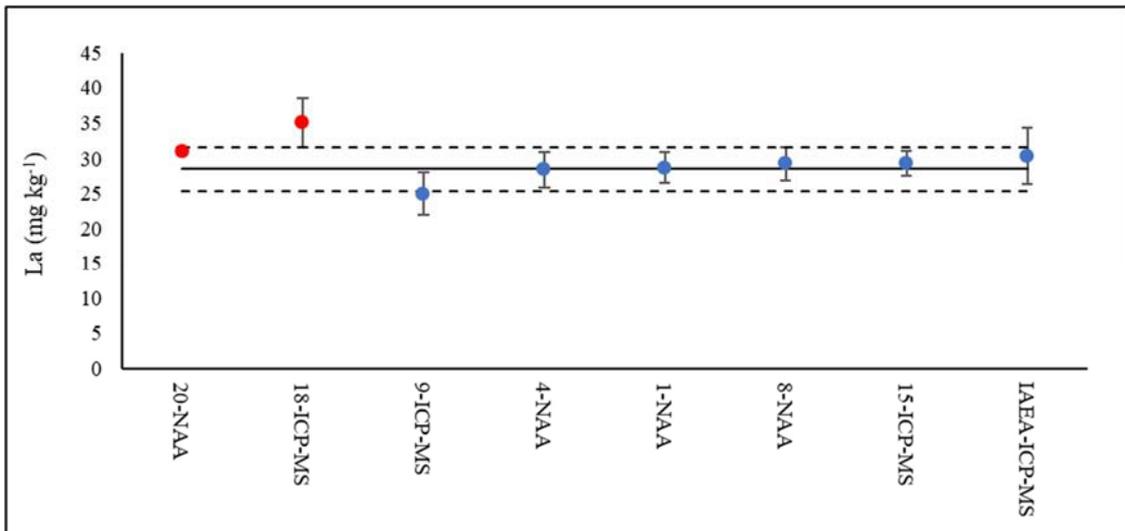
FIG. 12. Laboratory results for lanthanum mass fraction (mg kg^{-1}) in IAEA-158A.
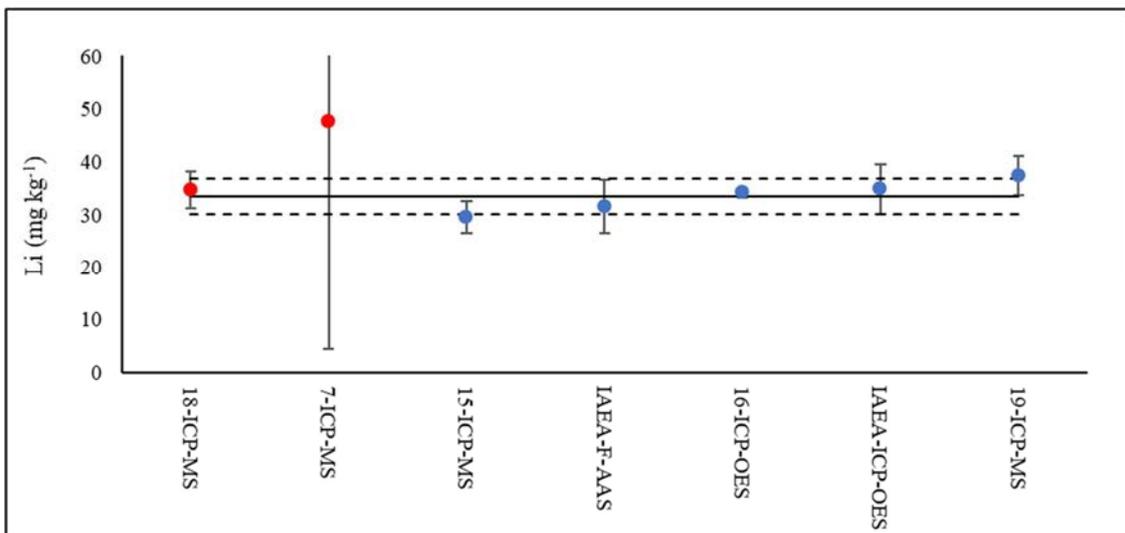
FIG. 13. Laboratory results for lithium mass fraction (mg kg^{-1}) in IAEA-158A.
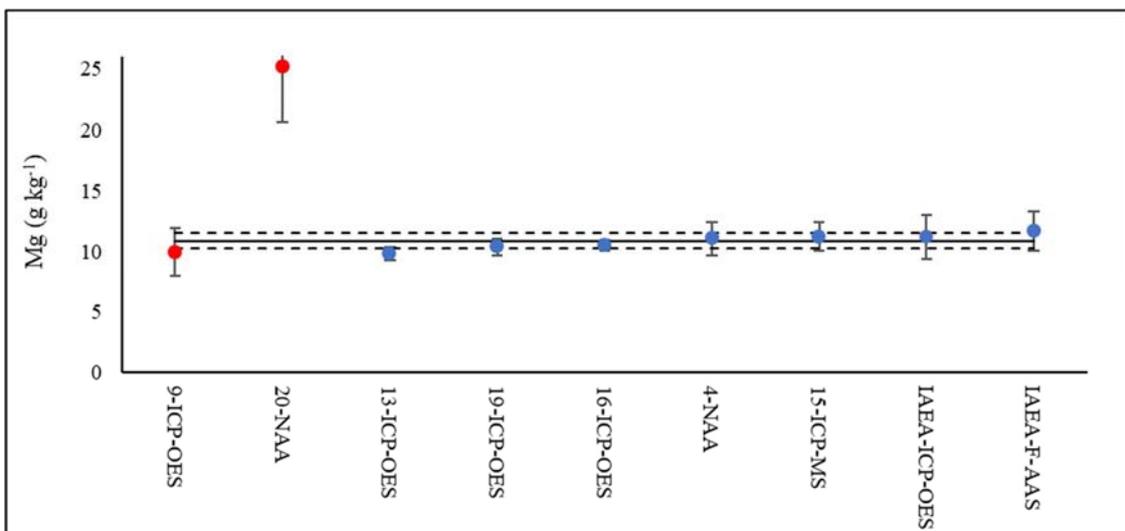
FIG. 14. Laboratory results for magnesium mass fraction (g kg^{-1}) in IAEA-158A.
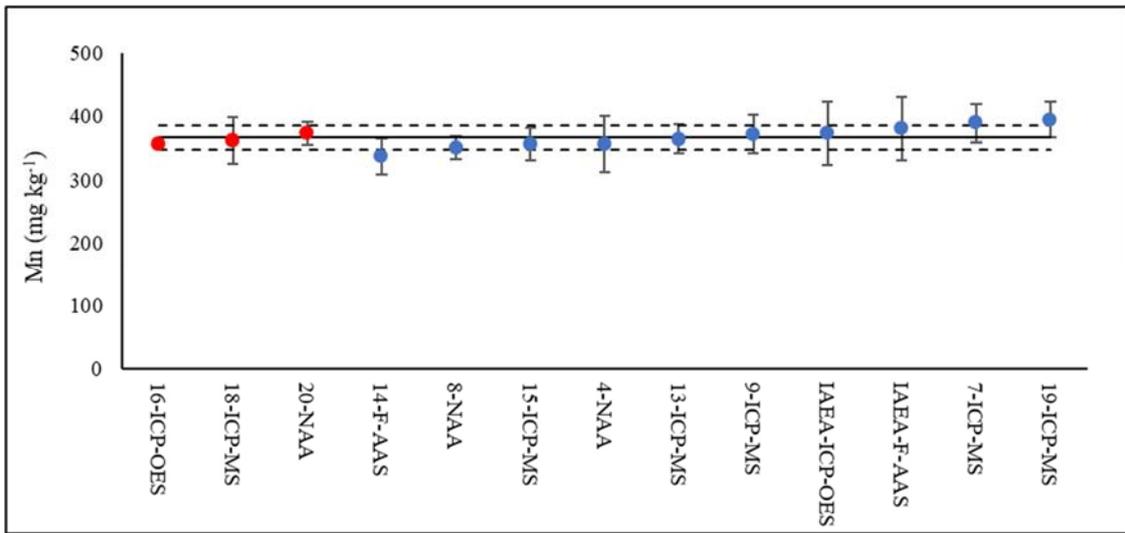
FIG. 15. Laboratory results for manganese mass fraction (mg kg⁻¹) in IAEA-158A.
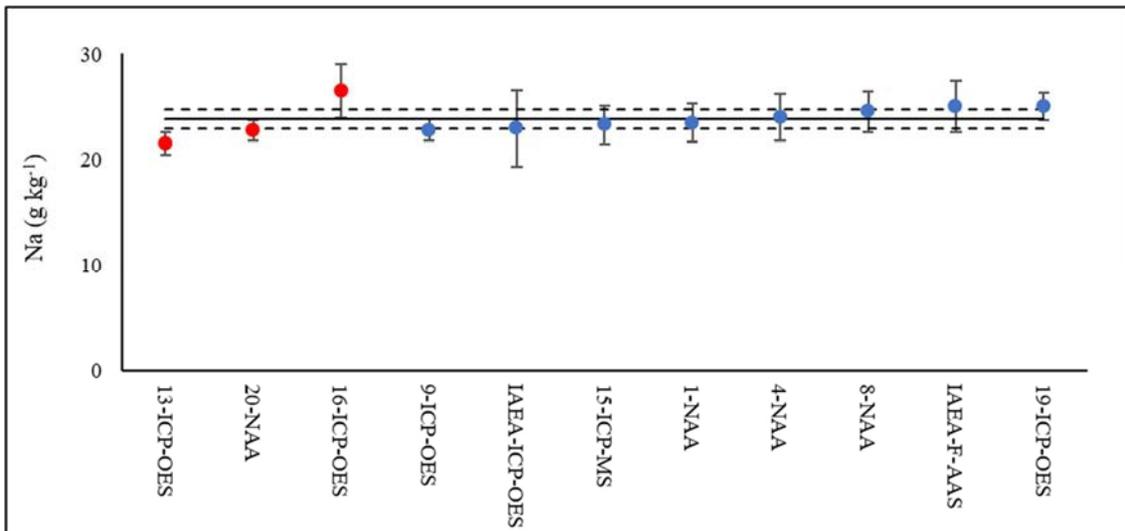
FIG. 16. Laboratory results for sodium mass fraction (g kg⁻¹) in IAEA-158A.
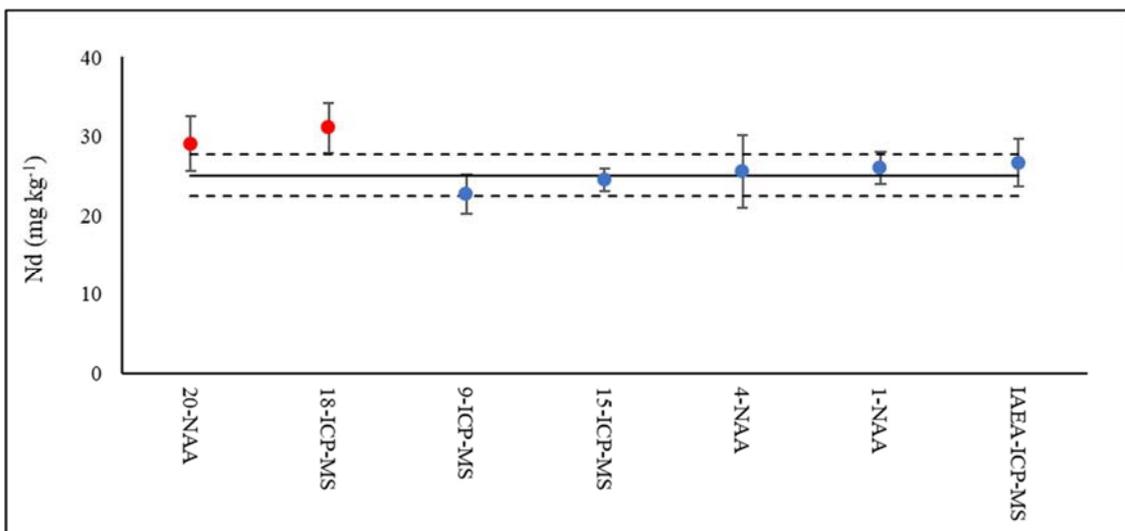
FIG. 17. Laboratory results for neodymium mass fraction (mg kg⁻¹) in IAEA-158A.

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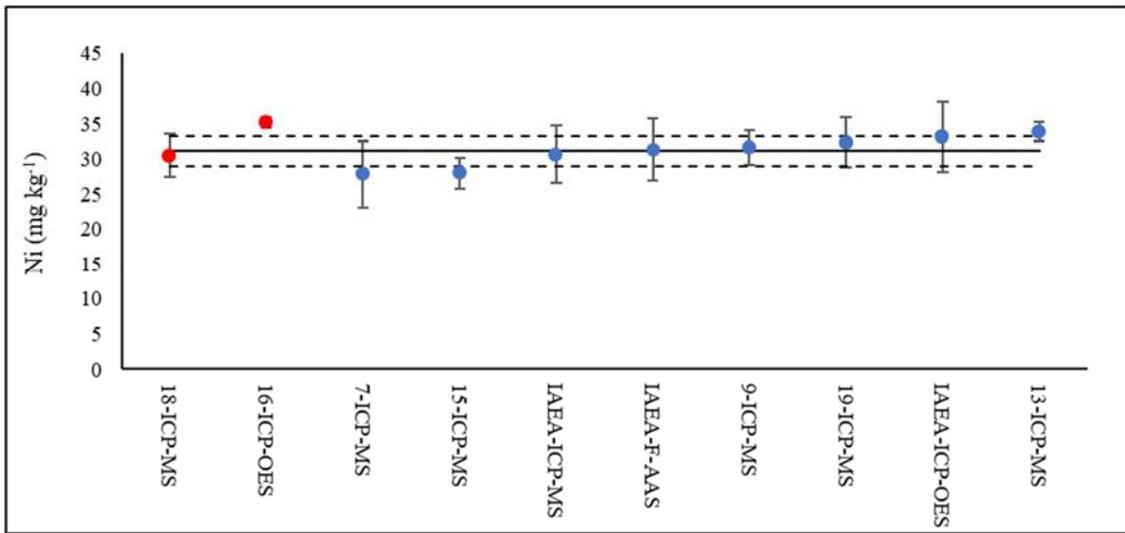
FIG. 18. Laboratory results for nickel mass fraction (mg kg^{-1}) in IAEA-158A.
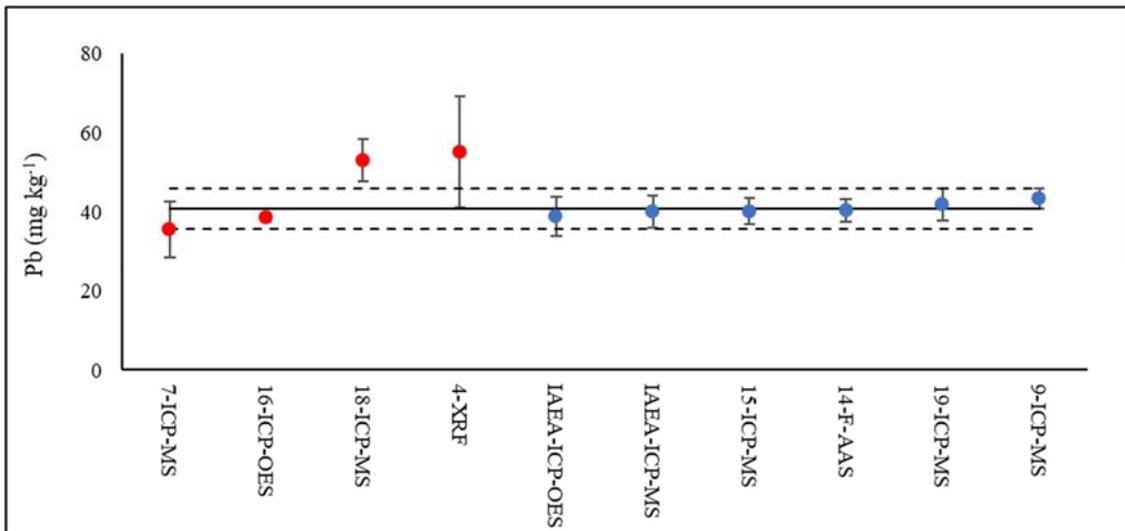
FIG. 19. Laboratory results for lead mass fraction (mg kg^{-1}) in IAEA-158A.
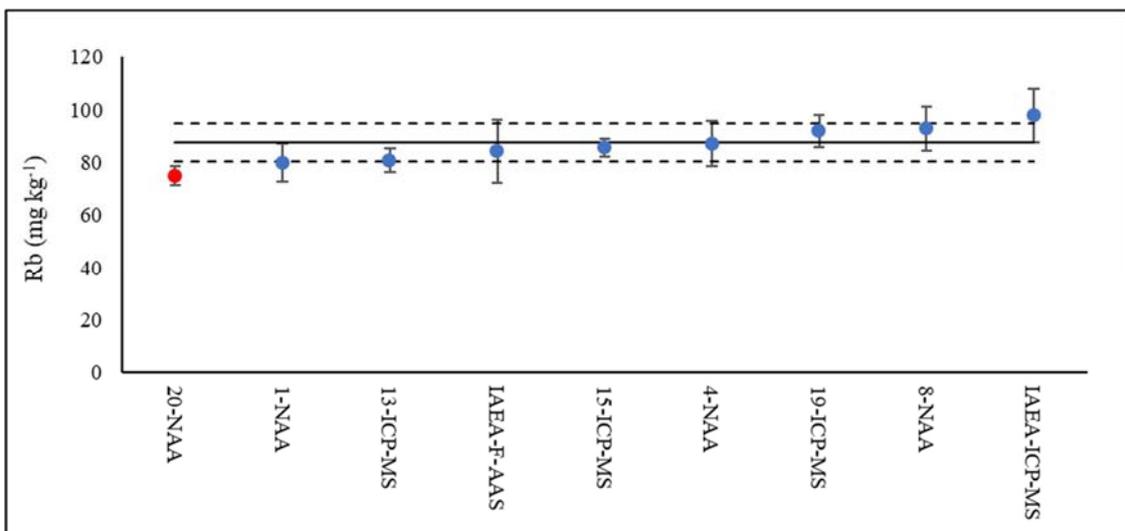
FIG. 20. Laboratory results for rubidium mass fraction (mg kg^{-1}) in IAEA-158A.
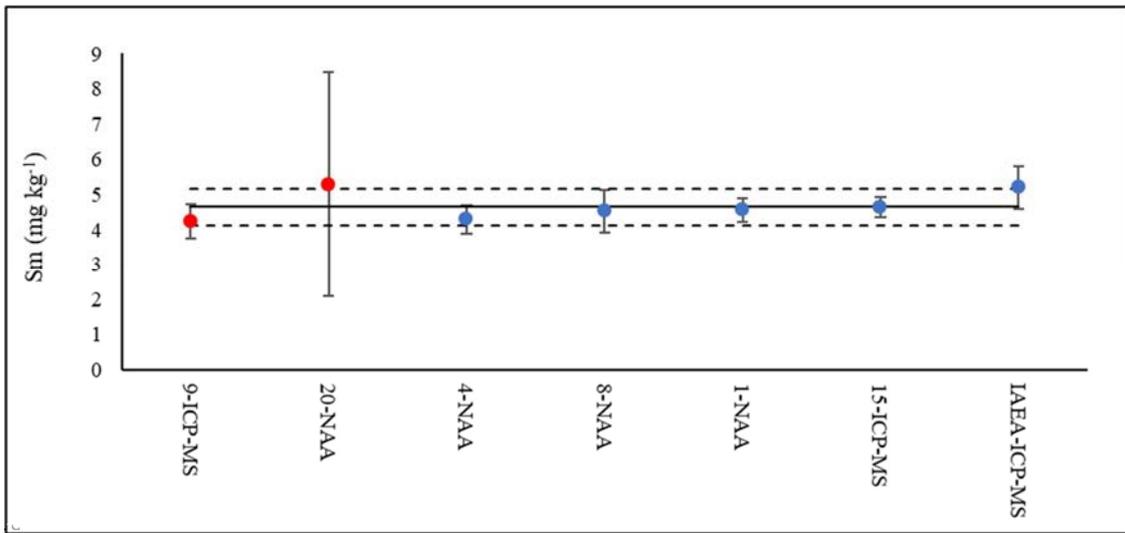
FIG. 21. Laboratory results for samarium mass fraction (mg kg⁻¹) in IAEA-158A.
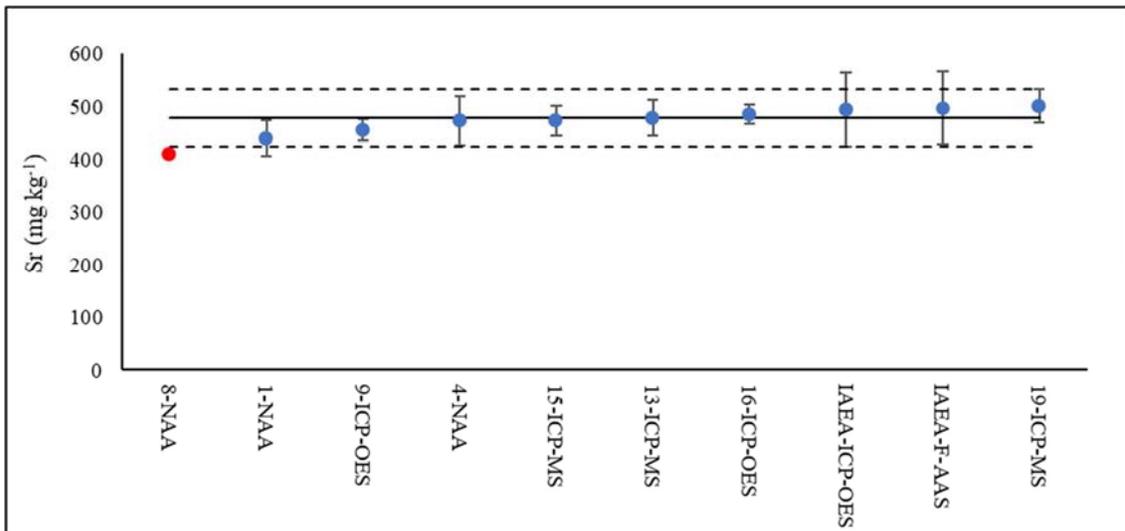
FIG. 22. Laboratory results for strontium mass fraction (mg kg⁻¹) in IAEA-158A.
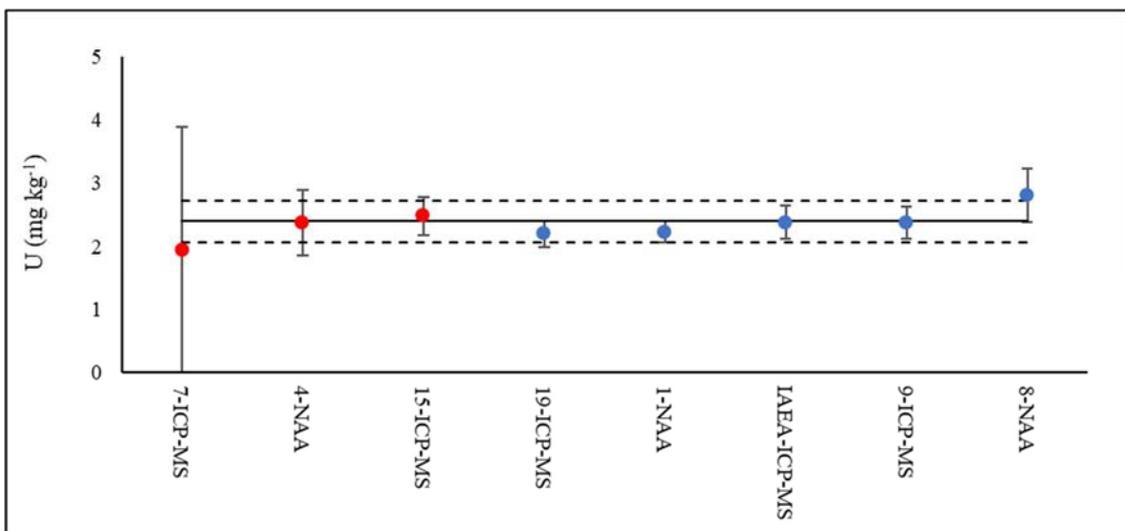
FIG. 23. Laboratory results for uranium mass fraction (mg kg⁻¹) in IAEA-158A.

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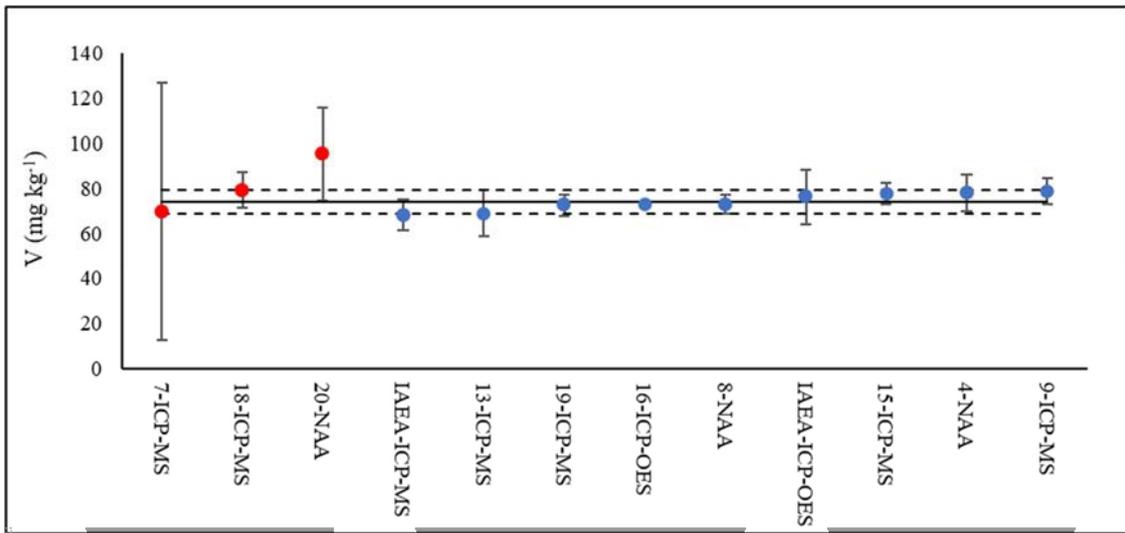
FIG. 24. Laboratory results for vanadium mass fraction (mg kg⁻¹) in IAEA-158A.
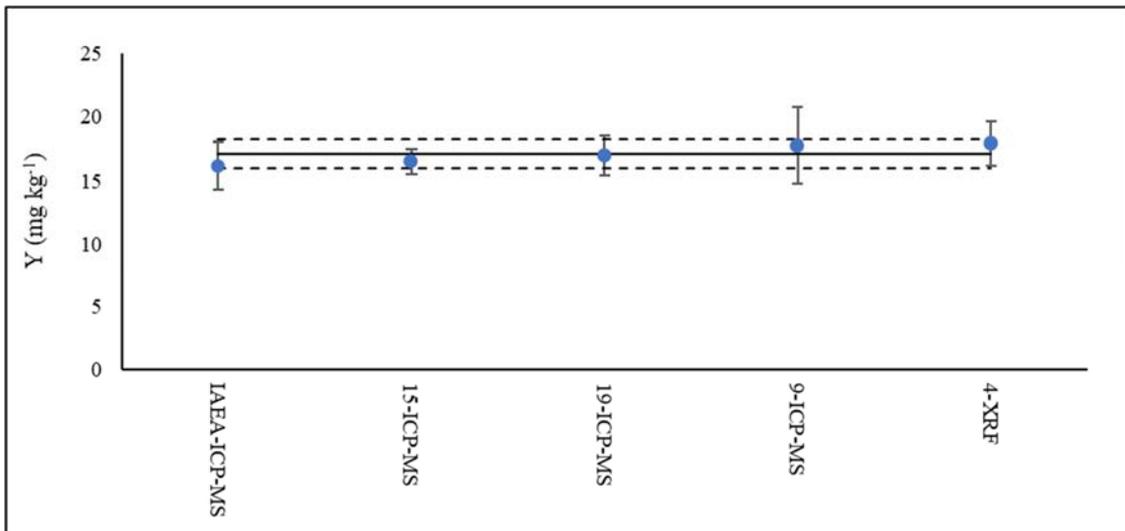
FIG. 25. Laboratory results for yttrium mass fraction (mg kg⁻¹) in IAEA-158A.
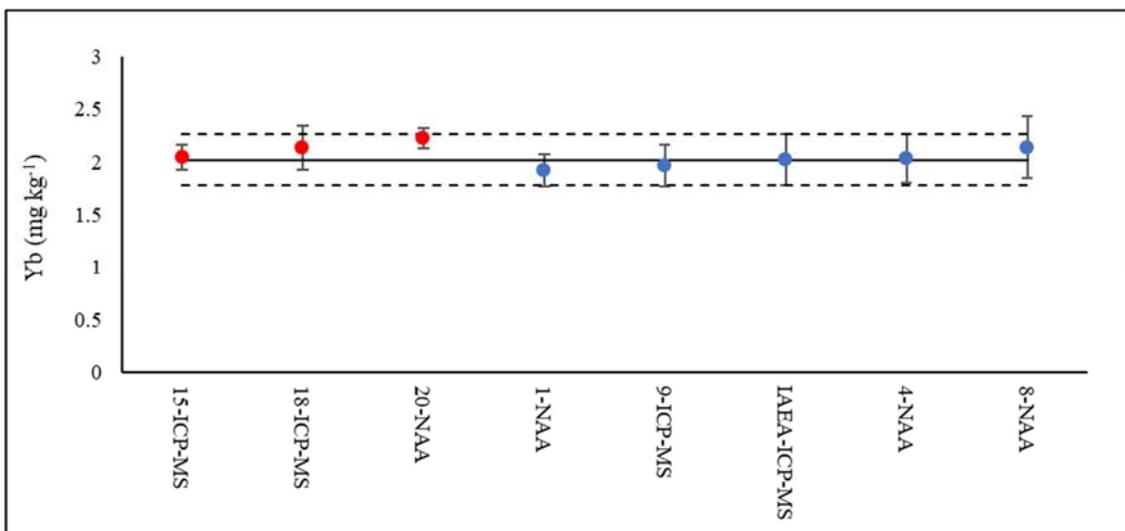
FIG. 26. Laboratory results for ytterbium mass fraction (mg kg⁻¹) in IAEA-158A.
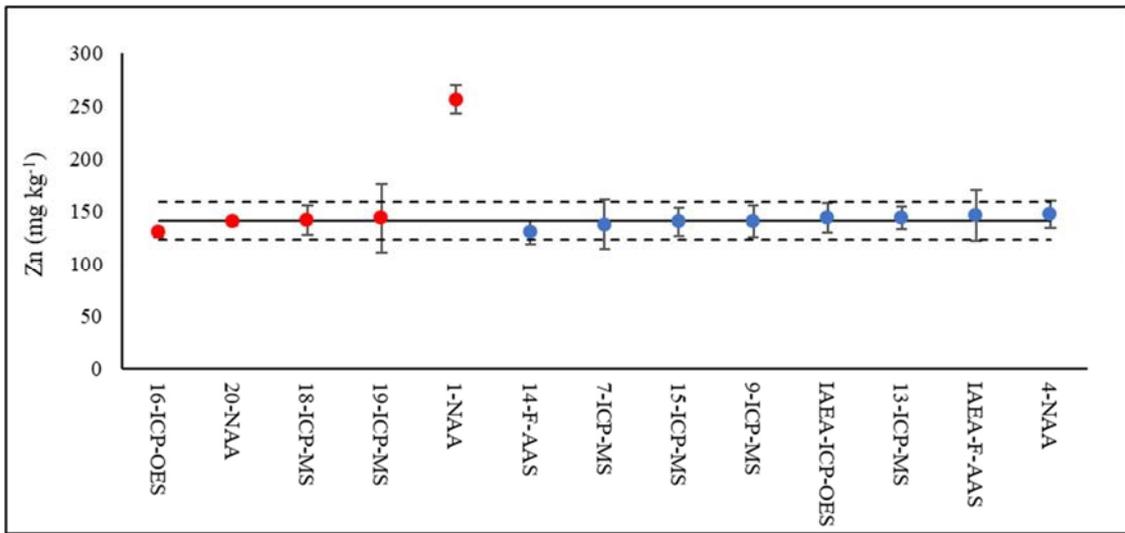
FIG. 27. Laboratory results for zinc mass fraction (mg kg^{-1}) in IAEA-158A.

RESULTS OF THE CHARACTERIZATION MEASUREMENTS FOR ANALYTES WITH INFORMATION VALUES

The results reported by the participating laboratories, their expanded uncertainty and measurement techniques are presented in Figures 28 to 48. Results not considered after technical evaluation (3.3.1) are in red. The information value for the respective analyte and its expanded uncertainty (k=2) are presented as line and dashed lines respectively.
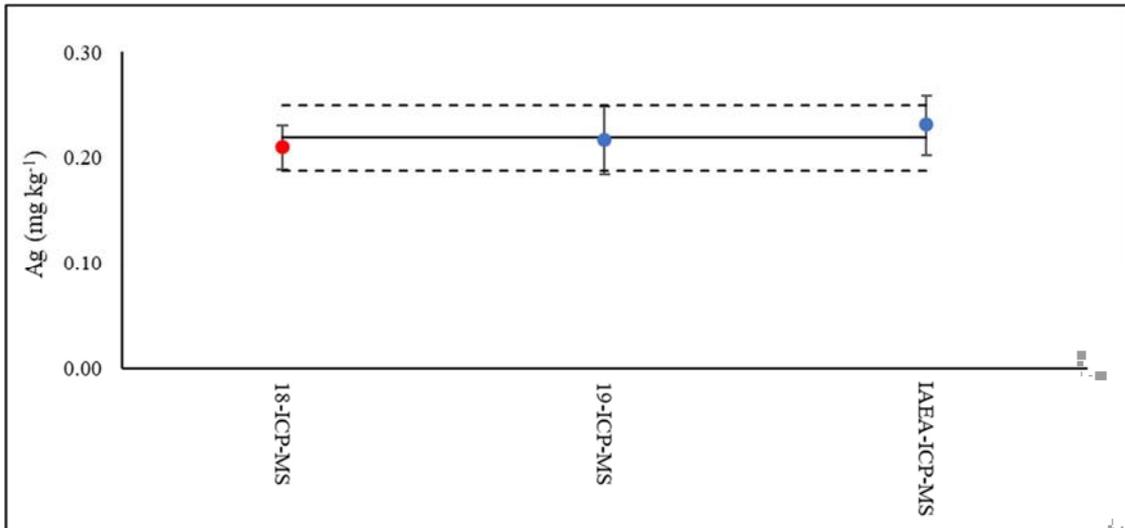
FIG. 28. Laboratory results for silver mass fraction (mg kg^{-1}) in IAEA-158A.
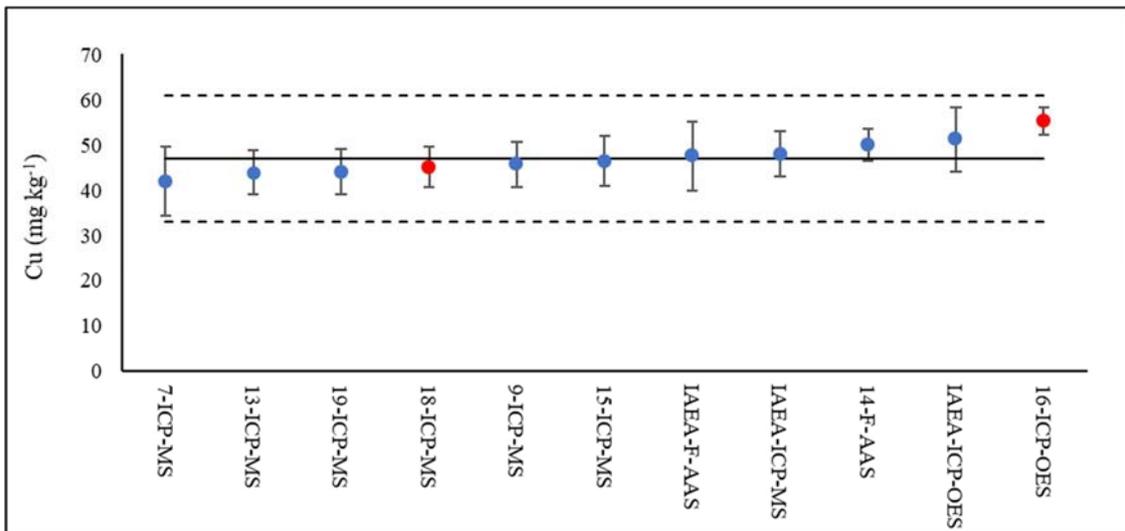
FIG. 29. Laboratory results for copper mass fraction (mg kg^{-1}) in IAEA-158A.
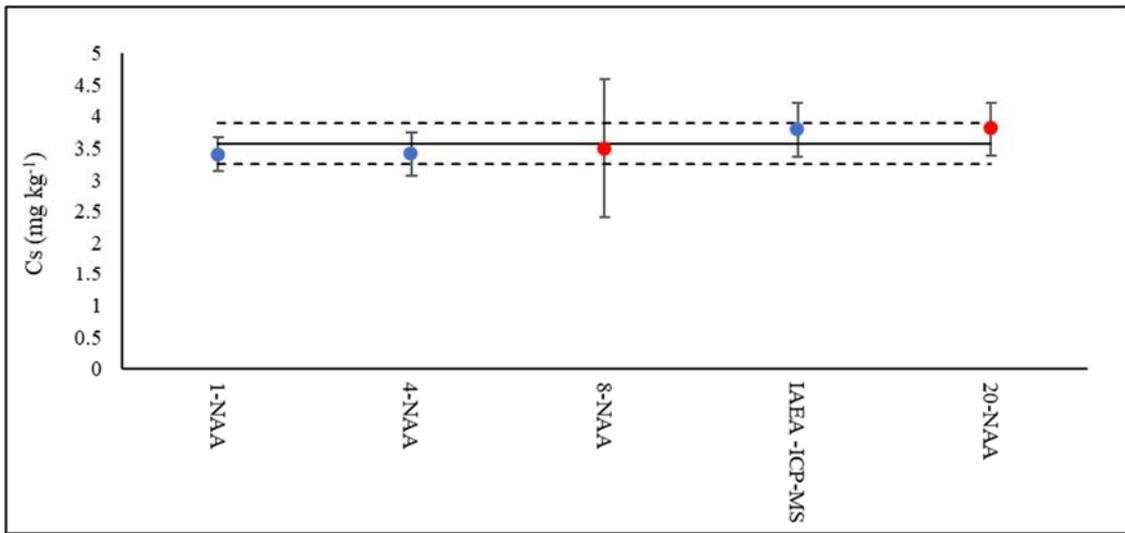
FIG. 30. Laboratory results for cesium mass fraction (mg kg^{-1}) in IAEA-158A.
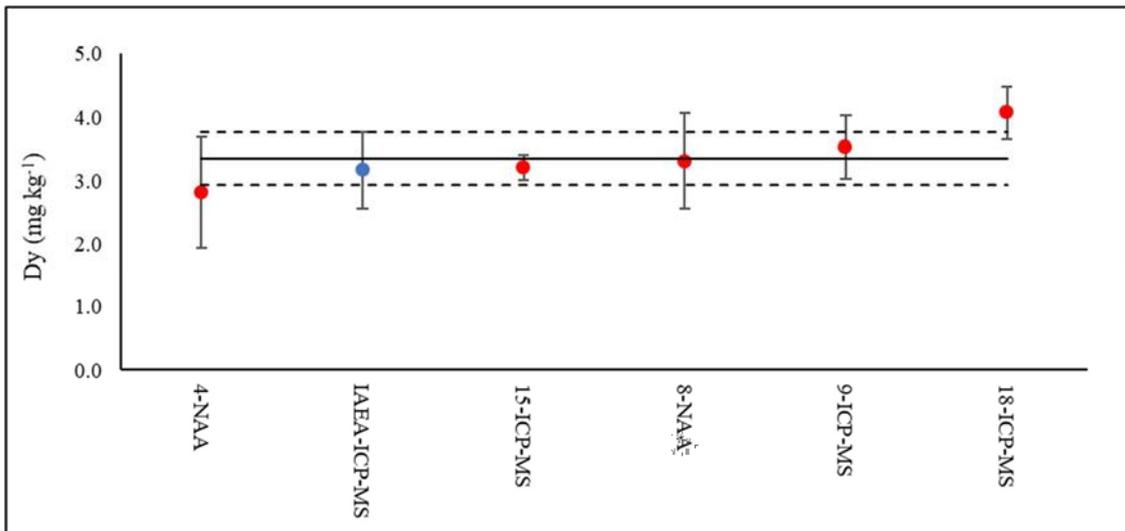
FIG. 31. Laboratory results for dysprosium mass fraction (mg kg^{-1}) in IAEA-158A.
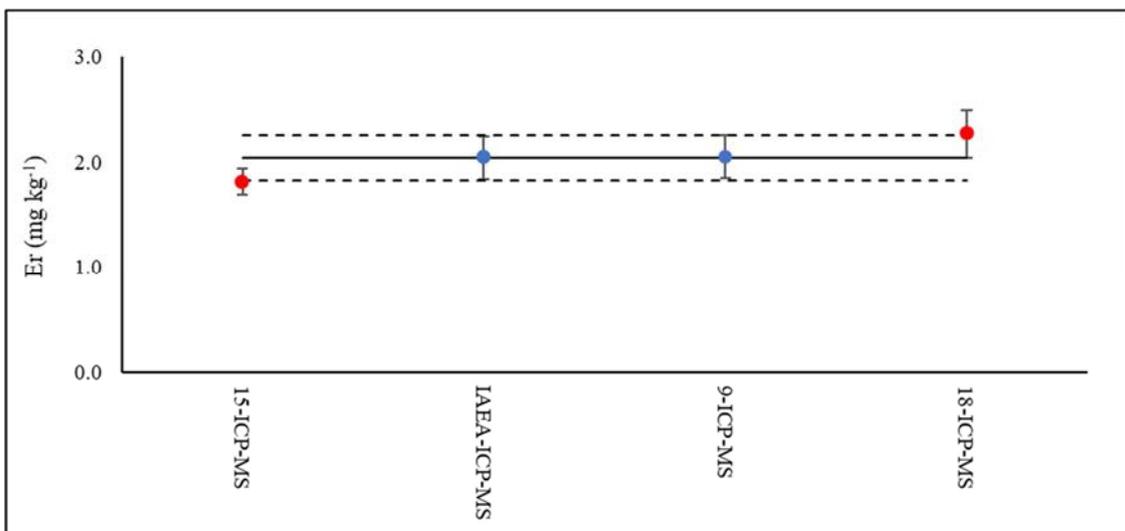
FIG. 32. Laboratory results for erbium mass fraction (mg kg^{-1}) in IAEA-158A.
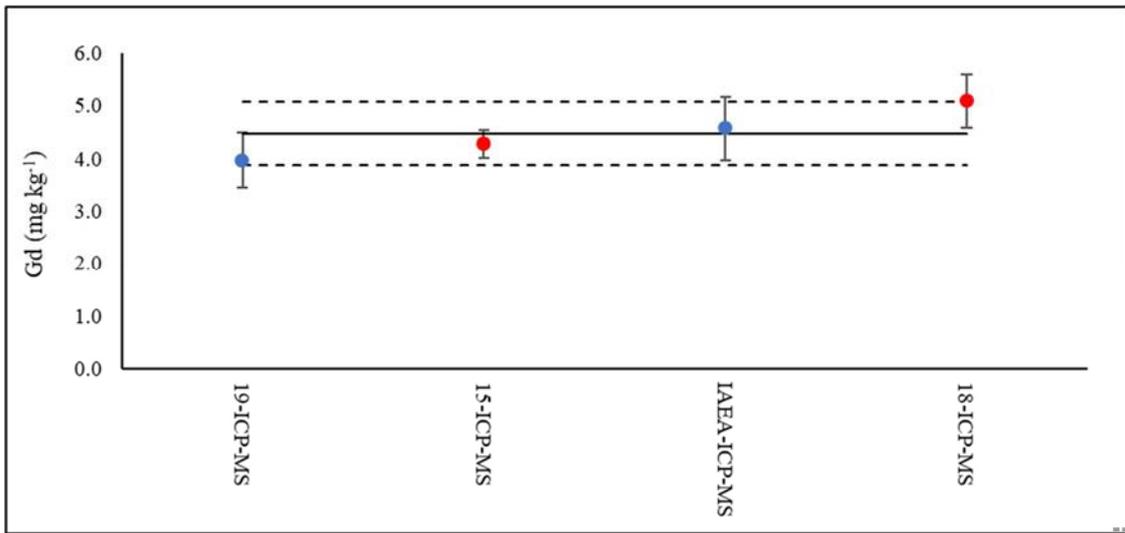
FIG. 33. Laboratory results for gadolinium mass fraction (mg kg^{-1}) in IAEA-158A.
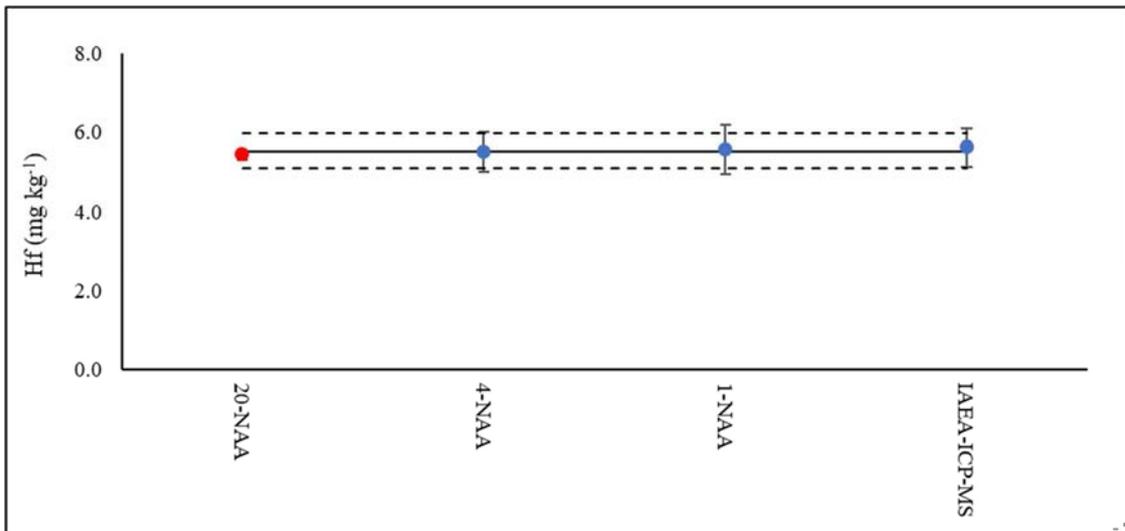
FIG. 34. Laboratory results for hafnium mass fraction (mg kg^{-1}) in IAEA-158A.
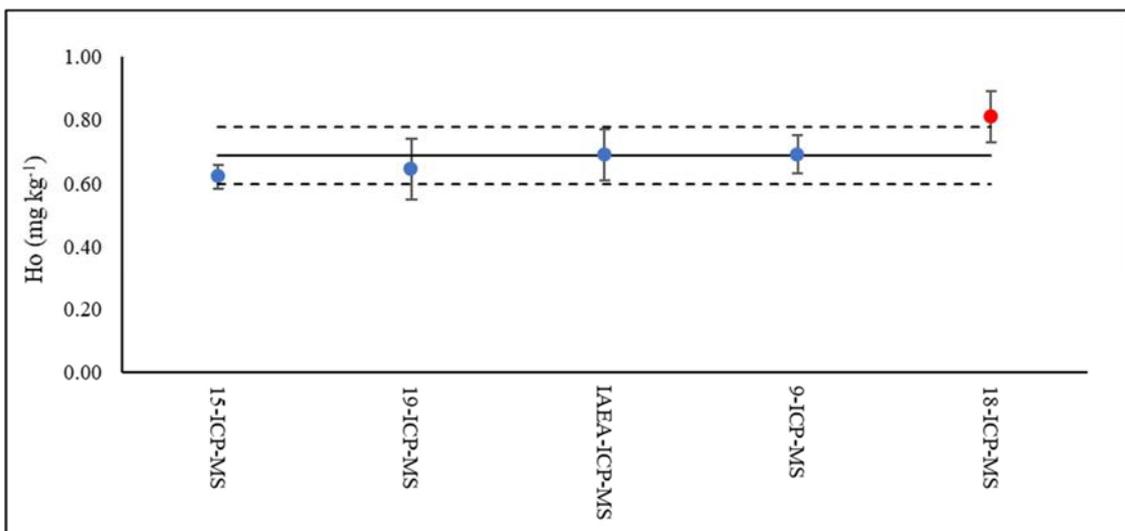
FIG. 35. Laboratory results for holmium mass fraction (mg kg^{-1}) in IAEA-158A.
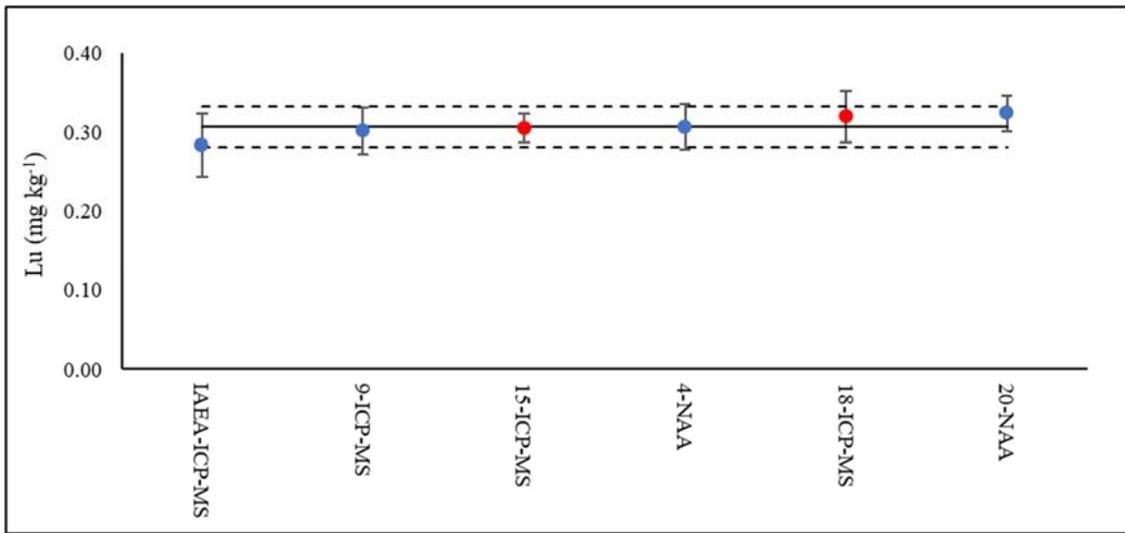
FIG. 36. Laboratory results for lutetium mass fraction (mg kg^{-1}) in IAEA-158A.
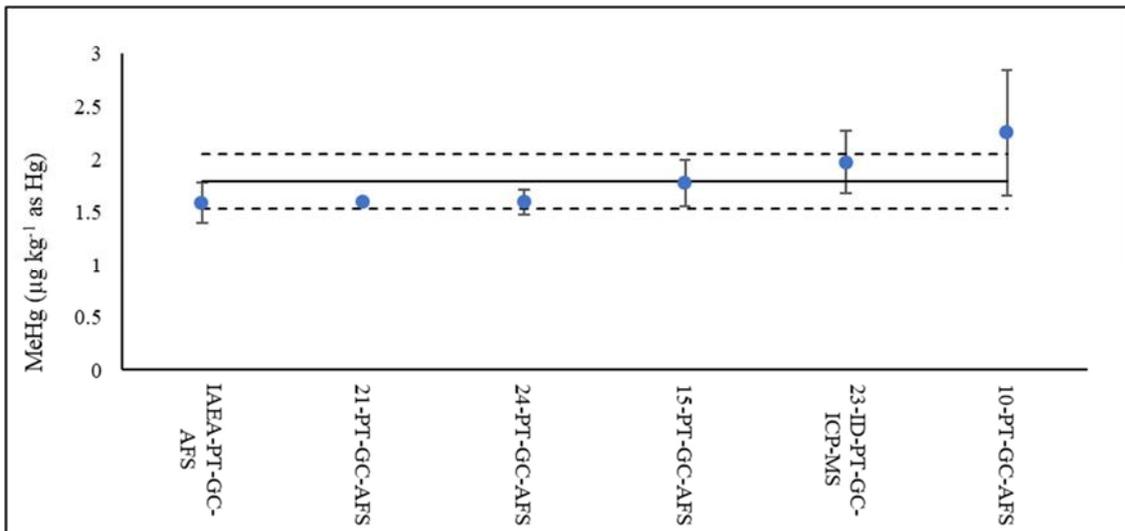
FIG. 37. Laboratory results for methylmercury mass fraction (μg kg^{-1} as Hg) in IAEA-158A.
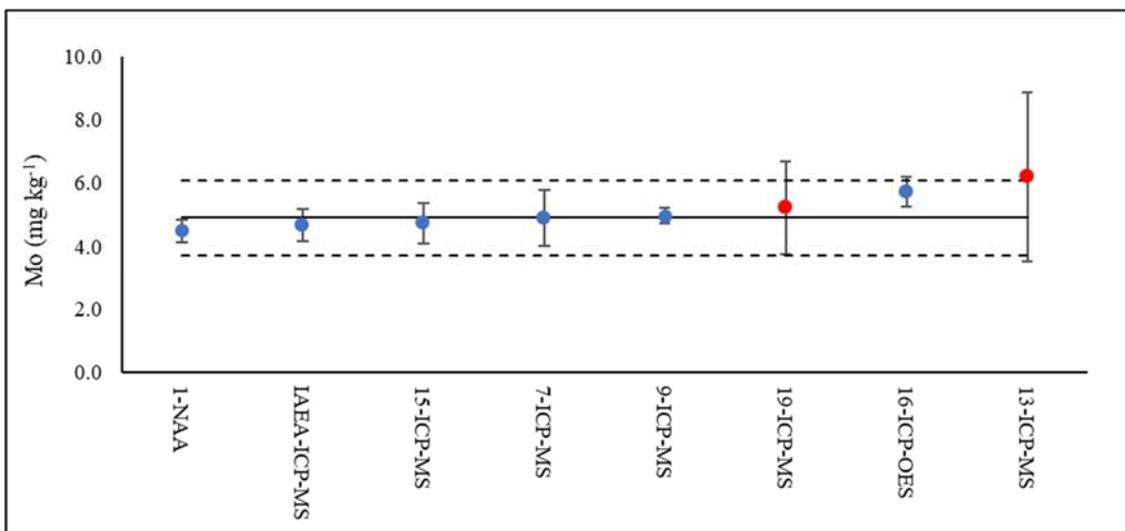
FIG. 38. Laboratory results for molybdenum mass fraction (mg kg^{-1}) in IAEA-158A.
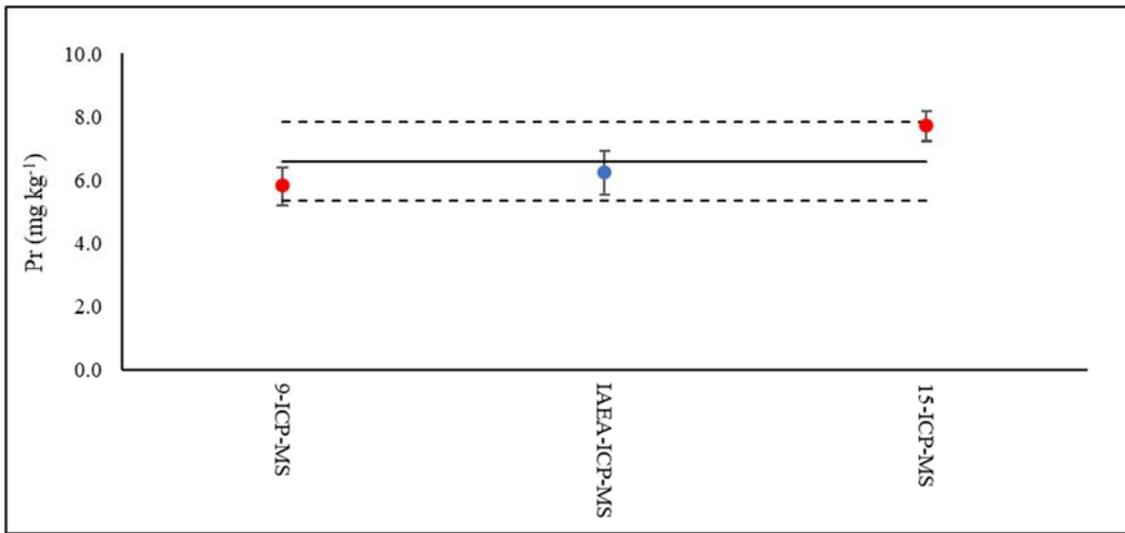
FIG. 39. Laboratory results for praseodymium mass fraction (mg kg⁻¹) in IAEA-158A.
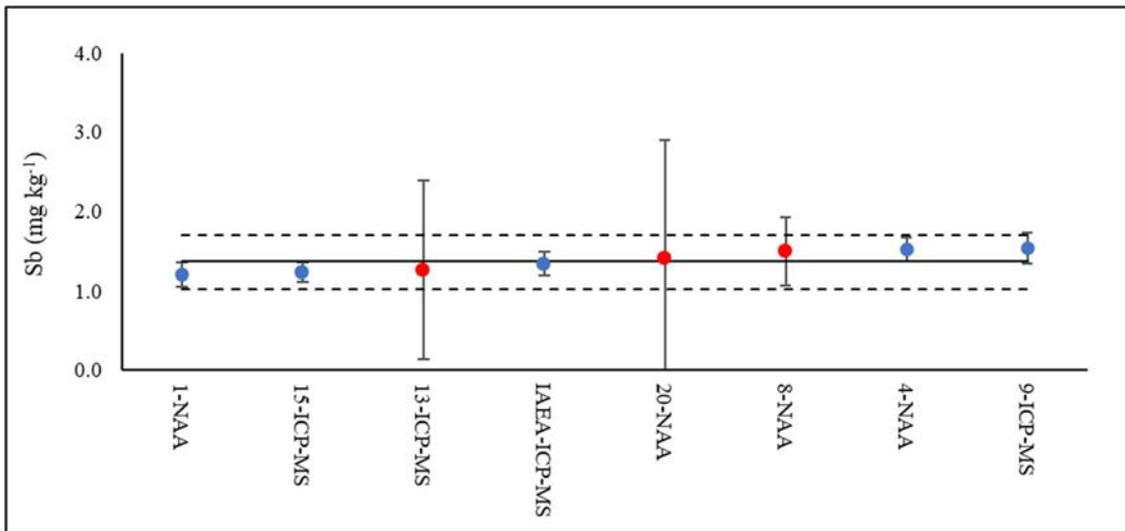
FIG. 40. Laboratory results for antimony mass fraction (mg kg⁻¹) in IAEA-158A.
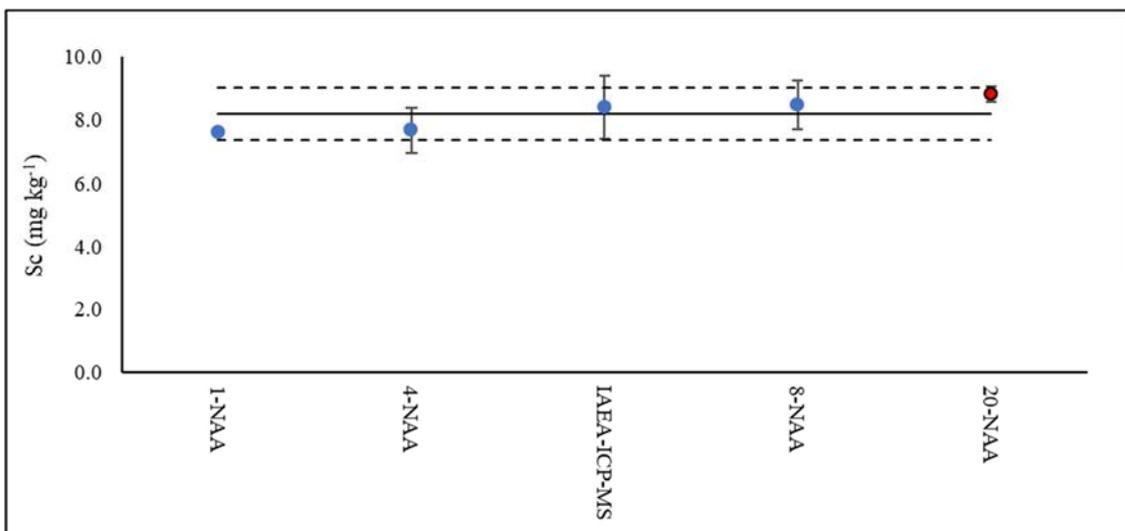
FIG. 41. Laboratory results for scandium mass fraction (mg kg⁻¹) in IAEA-158A.
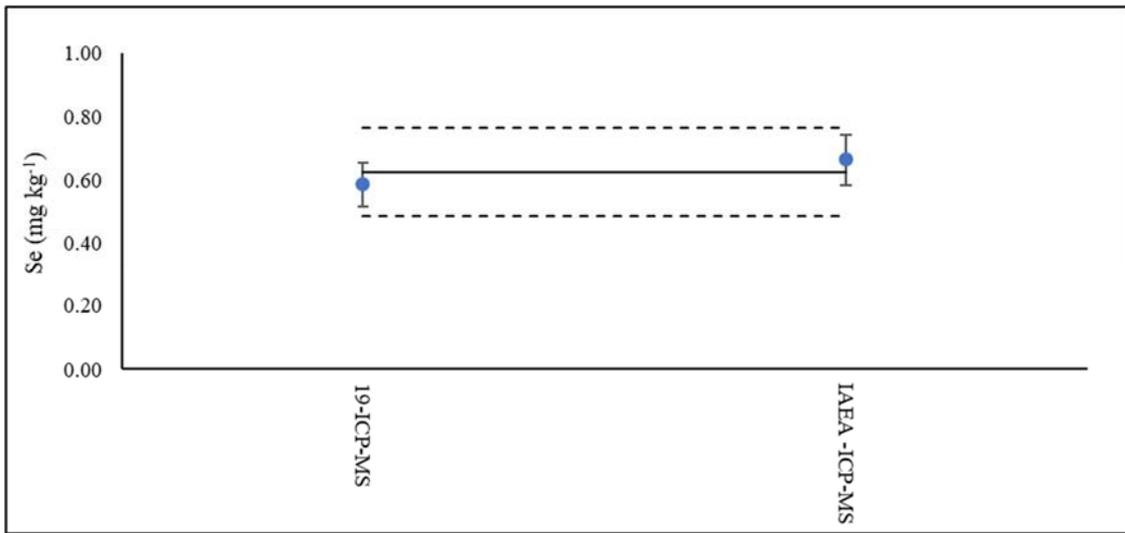
FIG. 42. Laboratory results for selenium mass fraction (mg kg⁻¹) in IAEA-158A.
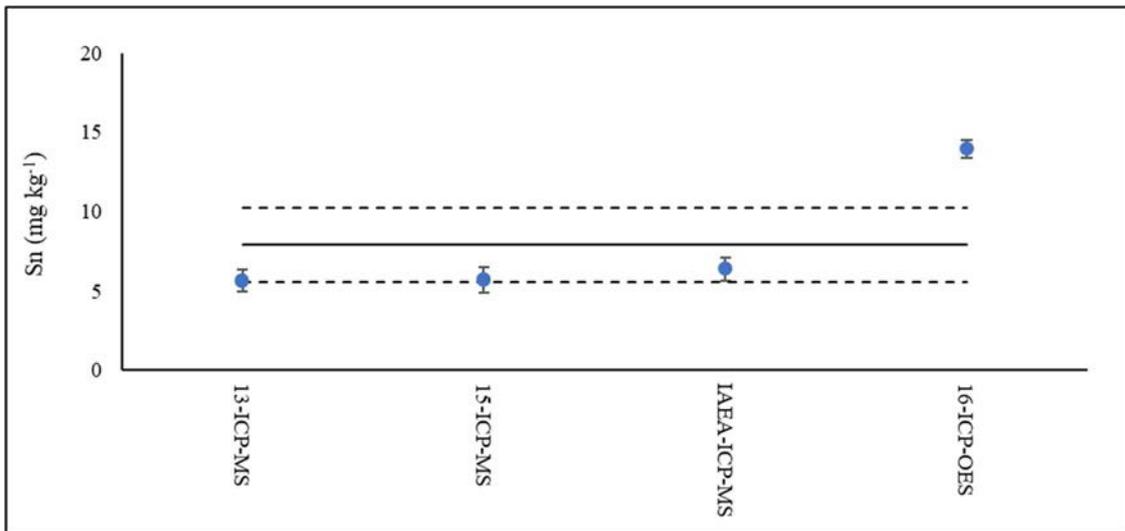
FIG. 43. Laboratory results for tin mass fraction (mg kg⁻¹) in IAEA-158A.
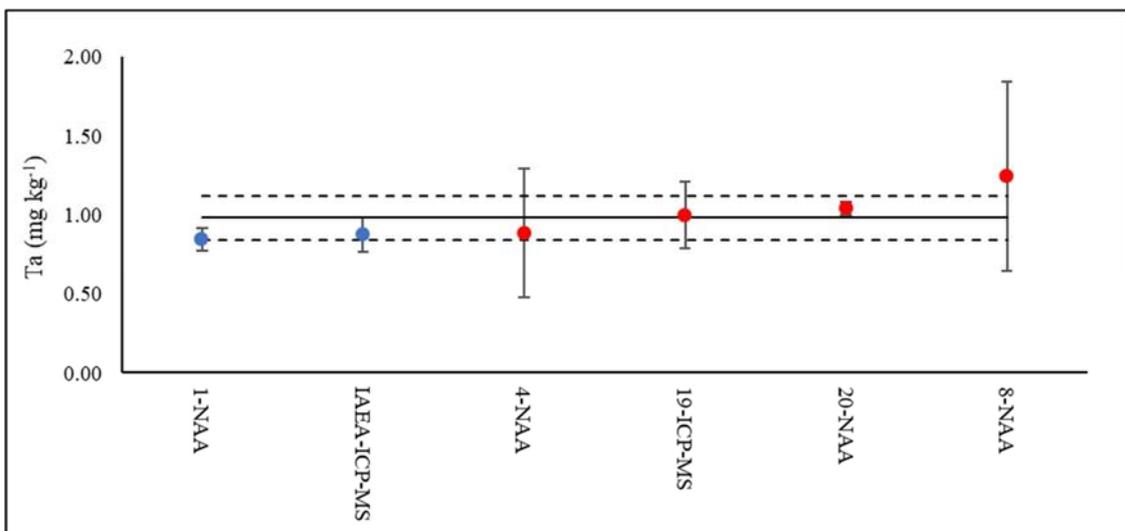
FIG. 44. Laboratory results for tantalum mass fraction (mg kg⁻¹) in IAEA-158A.
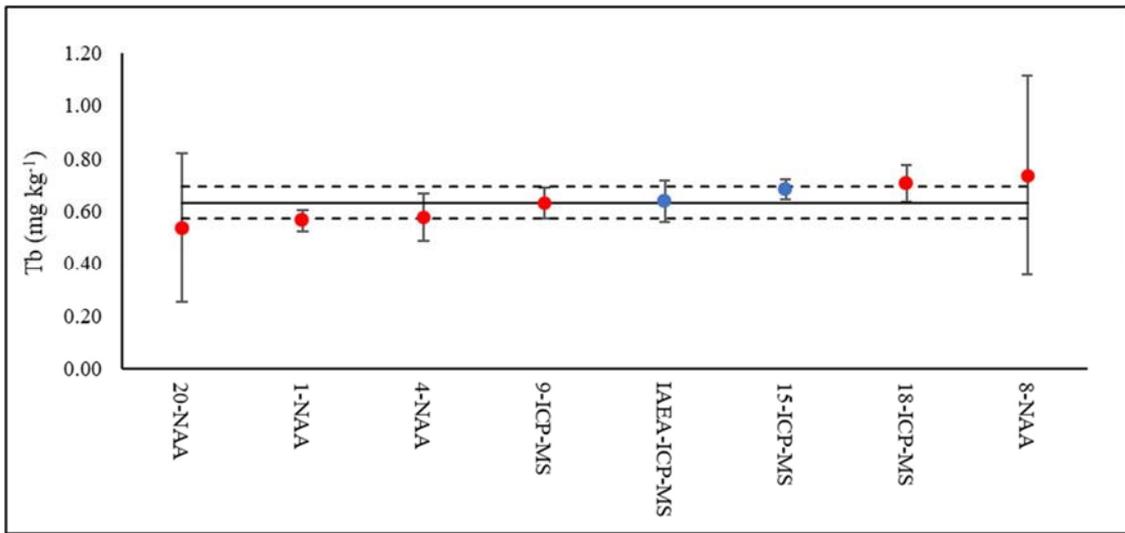
FIG. 45. Laboratory results for terbium mass fraction (mg kg⁻¹) in IAEA-158A.
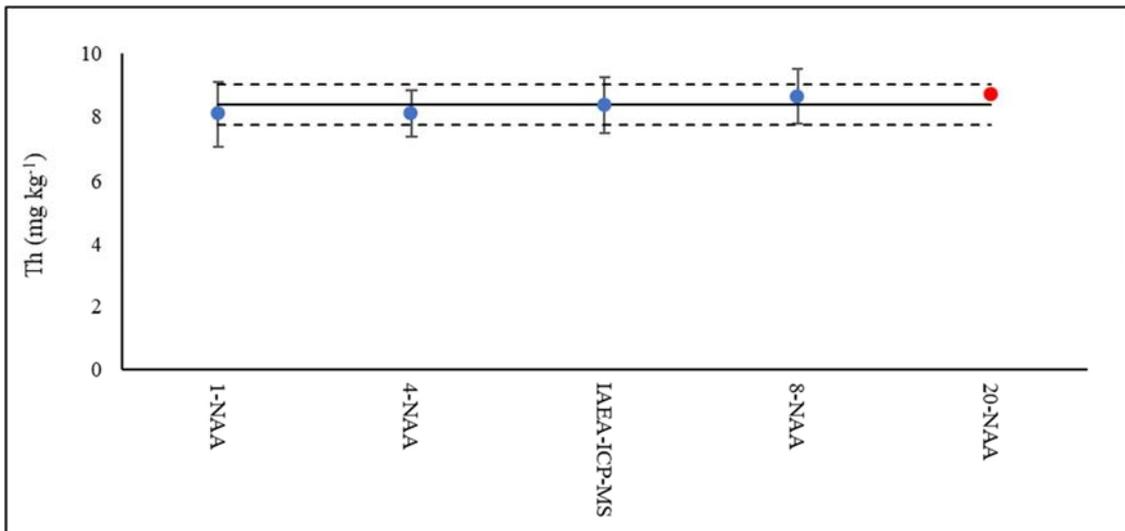
FIG. 46. Laboratory results for thorium mass fraction (mg kg⁻¹) in IAEA-158A.
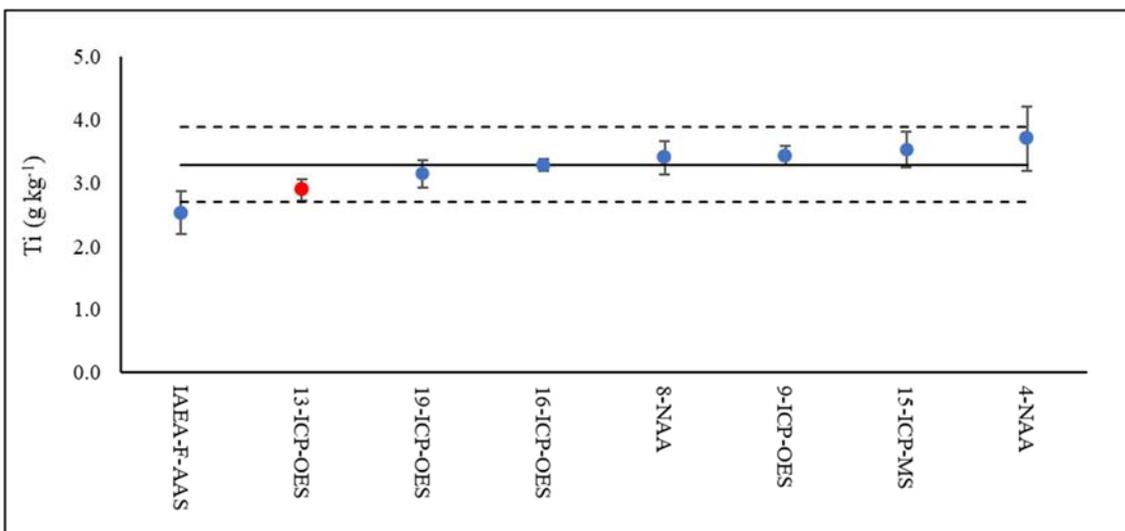
FIG. 47. Laboratory results for titanium mass fraction (mg kg⁻¹) in IAEA-158A.
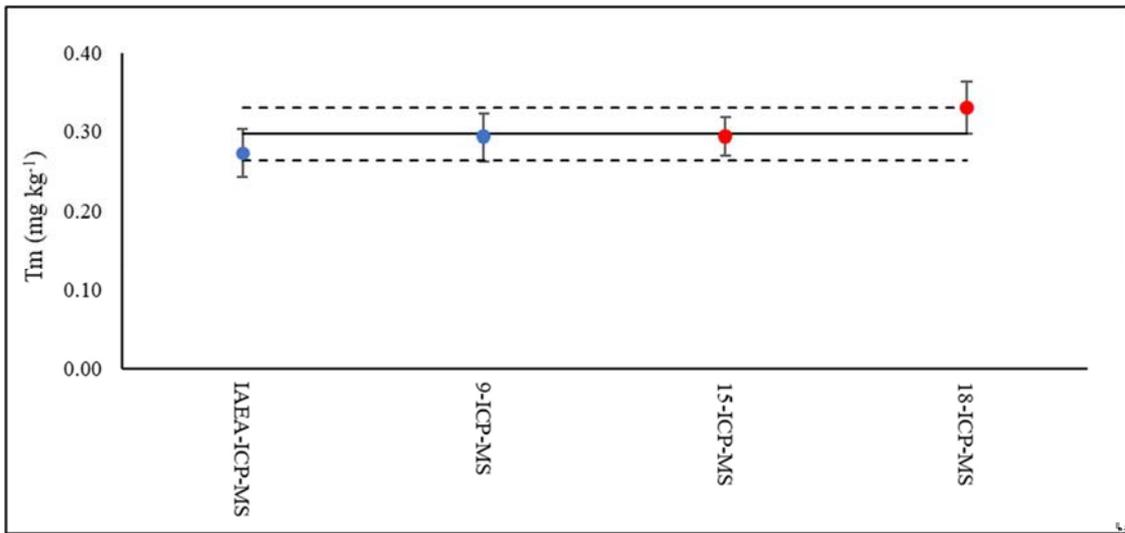
FIG. 48. Laboratory results for thulium mass fraction (mg kg⁻¹) in IAEA-158A.

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