IAEA/AQ/50

IAEA Analytical Quality in Nuclear Applications Series No. 50

Certification of Trace Elements and Methylmercury Mass Fractions in Tuna Fish Flesh Homogenate IAEA-436A

IAEA
International Atomic Energy Agency

CERTIFICATION OF TRACE ELEMENTS AND METHYLMERCURY MASS FRACTIONS IN TUNA FISH FLESH HOMOGENATE IAEA-436A

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ANGOLA
ANTIGUA AND BARBUDA
ARGENTINA
ARMENIA
AUSTRALIA
AUSTRIA
AZERBAIJAN
BAHAMAS
BAHRAIN
BANGLADESH
BARBADOS
BELARUS
BELGIUM
BELIZE
BENIN
BOLIVIA, PLURINATIONAL STATE OF
BOSNIA AND HERZEGOVINA
BOTSWANA
BRAZIL
BRUNEI DARUSSALAM
BULGARIA
BURKINA FASO
BURUNDI
CAMBODIA
CAMEROON
CANADA
CENTRAL AFRICAN REPUBLIC
CHAD
CHILE
CHINA
COLOMBIA
CONGO
COSTA RICA
CÔTE D'IVOIRE
CROATIA
CUBA
CYPRUS
CZECH REPUBLIC
DEMOCRATIC REPUBLIC OF THE CONGO
DENMARK
DJIBOUTI
DOMINICA
DOMINICAN REPUBLIC
ECUADOR
EGYPT
EL SALVADOR
ERITREA
ESTONIA
ETHIOPIA
FIJI
FINLAND
FRANCE
GABON
GEORGIA
GERMANY
GHANA
GREECE
GUATEMALA
GUYANA
HAITI
HOLY SEE
HONDURAS
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN, ISLAMIC REPUBLIC OF
IRAQ
IRELAND
ISRAEL
ITALY
JAMAICA
JAPAN
JORDAN
KAZAKHSTAN
KENYA
KOREA, REPUBLIC OF
KUWAIT
KYRGYZSTAN
LAO PEOPLE'S DEMOCRATIC REPUBLIC
LATVIA
LEBANON
LESOTHO
LIBERIA
LIBYA
LIECHTENSTEIN
LITHUANIA
LUXEMBOURG
MADAGASCAR
MALAWI
MALAYSIA
MALI
MALTA
MARSHALL ISLANDS
MAURITANIA
MAURITIUS
MEXICO
MONACO
MONGOLIA
MONTENEGRO
MOROCCO
MOZAMBIQUE
MYANMAR
NAMIBIA
NEPAL
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGER
NIGERIA
NORWAY
OMAN
PAKISTAN
PALAU
PANAMA
PAPUA NEW GUINEA
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
QATAR
REPUBLIC OF MOLDOVA
ROMANIA
RUSSIAN FEDERATION
RWANDA
SAN MARINO
SAUDI ARABIA
SENEGAL
SERBIA
SEYCHELLES
SIERRA LEONE
SINGAPORE
SLOVAKIA
SLOVENIA
SOUTH AFRICA
SPAIN
SRI LANKA
SUDAN
SWAZILAND
SWEDEN
SWITZERLAND
SYRIAN ARAB REPUBLIC
TAJIKISTAN
THAILAND
THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
TOGO
TRINIDAD AND TOBAGO
TUNISIA
TURKEY
TURKMENISTAN
UGANDA
UKRAINE
UNITED ARAB EMIRATES
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED REPUBLIC OF TANZANIA
UNITED STATES OF AMERICA
URUGUAY
UZBEKISTAN
VANUATU
VENEZUELA, BOLIVARIAN REPUBLIC OF
VIET NAM
YEMEN
ZAMBIA
ZIMBABWE

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world''.

IAEA/AQ/50

IAEA Analytical Quality in Nuclear Applications Series No. 50

CERTIFICATION OF TRACE ELEMENTS AND METHYLMERCURY MASS FRACTIONS IN TUNA FISH FLESH HOMOGENATE IAEA-436A

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2017

COPYRIGHT NOTICE

All IAEA scientific and technical publications are protected by the terms of the Universal Copyright Convention as adopted in 1952 (Berne) and as revised in 1972 (Paris). The copyright has since been extended by the World Intellectual Property Organization (Geneva) to include electronic and virtual intellectual property. Permission to use whole or parts of texts contained in IAEA publications in printed or electronic form must be obtained and is usually subject to royalty agreements. Proposals for non-commercial reproductions and translations are welcomed and considered on a case-by-case basis. Enquiries should be addressed to the IAEA Publishing Section at:

Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
http://www.iaea.org/books

For further information on this publication, please contact:

IAEA Environment Laboratories, Monaco
Radiometrics Laboratory
International Atomic Energy Agency
4a Quai Antoine 1er, MC 98000
Principality of Monaco

CERTIFICATION OF TRACE ELEMENTS AND METHYLMERCURY MASS FRACTIONS
IN TUNA FISH FLESH HOMOGENATE IAEA-436A
IAEA, VIENNA, 2017
IAEA/AQ/50
ISSN 2074–7659

© IAEA, 2017

Printed by the IAEA in Austria
September 2017

FOREWORD

The primary goal of the IAEA Environment Laboratories is to assist Member States in the use of both stable and radioactive isotope analytical techniques to understand, monitor and protect the marine environment. The major impact of large coastal cities on marine ecosystems is a primary concern for the IAEA. The Marine Environment Studies Laboratory, as a part of IAEA Environment Laboratories in Monaco, acts as the analytical support centre for Member State laboratories and is the pillar of the quality assurance programme for the determination of non-nuclear pollutants, trace elements and organic contaminants in the marine environment. The marine pollution assessments required to understand such impacts depend on accurate knowledge of contaminant concentrations in various environmental compartments.

Good laboratory practice and quality assurance and control are essential components of the analytical process for the production of data. Quality control procedures are commonly based on analyses of certified reference materials to assess reproducibility and measurement biases and uncertainties. Certified reference materials are key tools for quality assurance. They are used to validate analytical methods and to establish traceability to internationally agreed references. They are cornerstones for laboratory accreditation and the correct implementation of national and international regulations. In the development and validation of new methods, certified reference materials play a vital role in state of the art technologies where measurements are critical.

The IAEA supports the development and production of environmental certified reference materials for monitoring laboratories in Member States. The reference material IAEA-436, characterized for trace elements and methylmercury mass fractions in tuna fish flesh homogenate, was produced by the IAEA in Monaco in 2006. This publication describes the production of certified reference material IAEA-436A, which is based on the new characterization of IAEA-436, and which was produced following international guidelines and characterized by laboratories with demonstrated measurement competence.

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

EDITORIAL NOTE

This publication has been prepared from the original material as submitted by the contributors and has not been edited by the editorial staff of the IAEA. The views expressed remain the responsibility of the contributors and do not necessarily reflect those of the IAEA or the governments of its Member States.

Neither the IAEA nor its Member States assume any responsibility for consequences which may arise from the use of this publication. This publication does not address questions of responsibility, legal or otherwise, for acts or omissions on the part of any person.

The use of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of names of specific companies or products (whether or not indicated as registered) does not imply any intention to infringe proprietary rights, nor should it be construed as an endorsement or recommendation on the part of the IAEA.

The IAEA has no responsibility for the persistence or accuracy of URLs for external or third party Internet web sites referred to in this publication and does not guarantee that any content on such web sites is, or will remain, accurate or appropriate.

CONTENTS

1. INTRODUCTION 1
2. METHODOLOGY 2
   2.1. PREPARATION OF THE MATERIAL 2
   2.2. SELECTION OF LABORATORIES 2
   2.3. HOMOGENEITY ASSESSMENT 2
   2.4. STABILITY STUDY 3
   2.5. CHARACTERIZATION 4
   2.6. MOISTURE DETERMINATION 4
3. RESULTS AND DISCUSSION 5
   3.1. RESULTS OF HOMOGENEITY STUDY 5
3.1.1. Between-unit homogeneity 5
3.1.2. Within-unit homogeneity 7
   3.2. RESULTS FOR STABILITY STUDY 8
   3.3. DETERMINATION OF ASSIGNED VALUES AND THEIR UNCERTAINTIES 8
4. METROLOGICAL TRACEABILITY 12
5. CONCLUSIONS 13

APPENDIX I 15

APPENDIX II 23

APPENDIX III 35

REFERENCES 47

LIST OF PARTICIPANTS 49

CONTRIBUTORS TO DRAFTING AND REVIEW 51

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 or provide services to other organizations. Because of the needs to base scientific conclusions 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 measurement results produced by each laboratory.

The Marine Environmental Studies Laboratory (MESL) of the International Atomic Energy Agency 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 worldwide and regional inter-laboratory comparison (ILC). The IAEA Subprogramme of Reference Products for Science and Trade, encompassing also reference material production 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 IAEA Member States.

CRM IAEA-436A will assist laboratories in validating their analytical methods and controlling the quality of produced analytical results for the determination of trace elements and methyl mercury in marine sediment samples [1]. The CRM IAEA-436A will be used for strengthening of mercury monitoring efforts of marine environment, in order to assess mercury contamination, as well as to control the efficiency of the control measures undertaken, particularly for the Member States adopting Minamata convention.

The work presented in this report refers exclusively to the re-certification of the mass fractions of trace elements and methylmercury in tuna fish flesh homogenate. The CRM IAEA-436A has been produced to satisfy the demands of laboratories dealing with environmental and food safety analyses.

2. METHODOLOGY

2.1. PREPARATION OF THE MATERIAL

In 2004 a large quantity of tuna fish filet was obtained commercially. It was deep-frozen, freeze-dried, and then ground and sieved. The material was homogenized by mixing in a stainless steel rotating drum for 15 days. The sample material was packed into cleaned amber borosilicate glass bottles with Teflon lined screw caps. More details about the preparation of IAEA-436, used for the production of CRM IAEA-436A are given in the reference [2].

2.2. SELECTION OF LABORATORIES

The selection of participants for the characterization study was based on the measurement performances demonstrated by laboratories in the previous ILC, organized by the IAEA. Only results of laboratories having a quality system in place, using validated methods, applying uncertainty and traceability concepts were accepted for the calculation of the assigned values and their uncertainties [3].

Each laboratory received one bottle of tuna fish flesh homogenate sample, accompanied by an information sheet and a reporting form. Participants were requested to analyse Ag, Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, CH_3Hg, Li, Mn, Ni, Pb, Sn, Sr and Zn using validated analytical methods from their laboratory practice. They were asked to report measurement results (three replicates and average value), expanded uncertainty and the information on the applied quality control procedures. The second request was to report results for the trace elements in one CRM with a matrix similar to the matrix of the candidate reference material. As the result for the moisture content in the fish sample is operationally dependent, the method for moisture determination was prescribed to all participating laboratories. Participants were requested to send the results for additional trace elements, they are determining on a regular basis.

The list of laboratories participating in the characterization study is presented on page 49.

2.3. HOMOGENEITY ASSESSMENT

A key requirement for any certified reference material is the equivalence between various units. Extensive homogeneity tests were carried out on the tuna fish homogenate in order to estimate the uncertainty contribution coming from the homogeneity of the sample and to ensure its suitability as a certified reference material.

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 Ag, Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, CH3Hg, Mn, Ni, Pb, Sr and Zn in the sample.

In total, 10 bottles from the whole batch were selected, using random stratified sampling. Three subsamples from each bottle were analysed for their total element mass fractions. For all analytes except Hg and CH_3Hg, subsamples of 0.2 g were mineralized with 5 ml conc. HNO3 in a microwave oven. The final measurements were performed by inductively coupled plasma-mass spectrometry (ICP-MS) under repeatability conditions, and in a randomized way. The determination of the total Hg was done in solid subsamples (50 mg) with advanced mercury analyser. Methyl mercury was determined by gas chromatography-atomic fluorescence spectrometry (GC-AFS) after alkaline digestion and room temperature derivatization.

The measurement repeatability for the ICP-MS and GC-AFS was estimated as the relative standard deviation of 9 independent measurements of investigated trace elements, performed on the same digested solution over the entire sequence (several hours). The measurement repeatability for Hg was the relative standard deviation from 10 measurement results, obtained for Hg mass fraction in CRM.

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

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

2.4. STABILITY STUDY

IAEA-436 has been prepared and bottled in 2004, at the time of bottling some bottles (10) have been stored under so called “reference” condition: -20 ± 2°:C in the dark. The other produced unit were then stored under “normal” conditions: +20 ± 3 C° in the dark.

To evaluate potential degradation of the material over 12 years, 5 bottles stored under “reference” conditions and 5 bottles stored under “normal” conditions were randomly selected. Three subsamples from each bottle were analysed for their total element mass fractions as describe in Section 2.3.

The measurements were performed under repeatability conditions and in randomized way in order to be able to separate a potential analytical drift from a trend over the storage time. The results were corrected for the water content determined in each unit by using the protocol described in Section 2.6.

2.5. CHARACTERIZATION

The tuna fish sample 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. The characterization of the trace elements mass fractions in the tuna sample was based on the application of several analytical techniques. They are summarized on Figure 1. Abbreviations used in this report for the 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 tuna fish flesh homogenate sample and to report the results with their expanded uncertainty. In addition, they were requested to provide results for the mass fractions of the analysed trace elements in one CRM with matrix composition similar to the candidate reference material, as well as the information on the standard calibration solutions used in the measurement step.

The results of laboratories not fulfilling the above described requirements were excluded from the further evaluation.

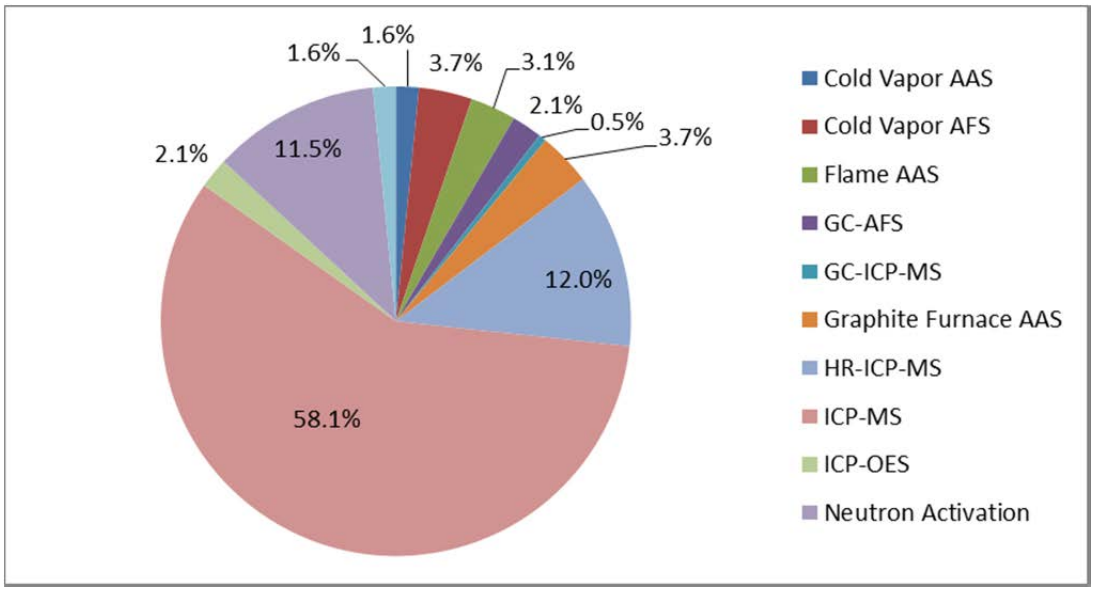

FIG. 1. Analytical methods used for the characterization of trace elements in the IAEA-436A.

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 the IAEA 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, the weighing and repeated drying were performed until constant mass was attained (generally 24 hours). Moisture, determined at 85°C, at MESL (10 subsamples from 5 bottles) was found to be 5.1(±0.5) % for bottles kept at 20°C.

TABLE 1. ABBREVIATION FOR INSTRUMENTAL TECHNIQUES

Abbreviation	Instrumental technique
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
GC	Gas Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
HR-ICP-MS	High Resolution Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Optical Emission Inductively Coupled Plasma Mass Spectrometry
ET-AAS	Graphite Furnace Atomic Absorption Spectrometry
NAA	Neutron Activation

3. RESULTS AND DISCUSSION

3.1. RESULTS OF HOMOGENEITY STUDY

3.1.1. Between-unit homogeneity

For the homogeneity study, 10 units of tuna 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. No trends for the bottling and analytical sequences were detected for all measurement datasets.

Obtained results are presented in Table 2.

Grubbs-tests at 95% and 99% confidence levels were also performed to identify potentially outlying individual results or bottle means. As presented in Table 2, some individual results were detected as outliers at 95% and 99% confidence levels, but no outlying bottle means was found out. It was checked whether the retained individual results and unit means follow 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 (sbb) from the within-unit variation (swb). The

latter is equivalent to the method repeatability, if the individual aliquots are representative for the whole unit.

ANOVA allows the calculation of within-unit standard deviation s_{wb} and also between-units standard deviation s_{bb}:

$$s_{wb} = u_{wb} = \sqrt{MS_{wb}} \quad (1)$$

$$s_{bb} = u_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{n}} \quad (2)$$

s_{bb} and s_{wb} are estimates of the 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. [5]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum heterogeneity that might be undetected by the applied experimental setup.

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

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

The uncertainty contributions due to the between-unit homogeneity were estimated according to the ISO Guide 35 [4] as the maximum values obtained with Eq. 2 or Eq. 3 and presented in Table 2. As can be seen in Table 2 the between-unit variations for Ag, As, Ca, Cd, Cu, Fe, Hg, CH_3Hg, Mn, Rb, Se, Sr and Zn were sufficiently small to demonstrate the homogeneity of the material for specified sample mass.

The between-unit variations for Al, Co, Cr, Ni and Pb were in the range 7.0-14.4% and for those elements only recommended values were provided.

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

Element	Individual outliers (Grubbs test)		$s_{wb,rel}$	$s_{bb,rel}$	$u^*_{bb,rel}$	$u_{hom,rel}$	Measurement repeatability
	95%	99%	%	%	%	%	%
Ag	2	2	9.9	4.1	3.3	4.1	3.0
Al	6	5	31.0	12.0	10.0	12.0	8.0
As	0	0	3.6	2.9	1.2	2.9	4.0
Ca	2	2	11.0	[1)]	4.1	4.1	3.5
Cd	0	0	3.6	1.5	1.2	1.5	3.0
Co	0	0	14.4	7.0	4.7	7.0	3.0
Cr	0	0	13.5	9.1	4.4	9.1	7.0
Cu	0	0	3.2	2.3	1.0	2.3	4.0
Fe	2	2	3.7	2.3	1.2	2.3	2.6
Hg	0	0	2.0	[1)]	0.7	0.7	4.0
CH_3Hg	5	0	10.7	0.8	3.5	3.5	5.0
Mn	0	0	1.1	0.7	0.4	0.7	5.0
Ni	3	1	23.3	20.8	7.6	14.4	5.0
Pb	2	1	20.5	13.9	6.7	14.0	3.0
Rb	2	2	2.8	1.8	0.9	1.8	3.3
Se	0	0	2.6	3.2	0.9	3.2	2.8
Sr	1	1	5.0	3.5	1.6	3.5	4.7
Zn	2	0	2.8	2.2	0.9	2.2	2.0

[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 assigned value within its stated uncertainty. During characterization study the minimum sample size was prescribe to participant (0.05g for Hg and 0.2g for other trace element), based on preliminary homogeneity study.

The conclusion from the presented results was that the homogeneity of the tuna sample complied with the provisions given by the ISO Guide 35 [4] at the range of weights used. A minimum sample intake of 0.2 g for Ag, As, Ca, Cd, Cu, Fe, CH_3Hg, Mn, Rb, Se, Sr and Zn and 0.05g for Hg was set.

3.2. RESULTS FOR STABILITY STUDY

The samples selected for long term stability study were analysed and each of the elements (Ag, Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, CH3Hg, Mn, Ni, Pb, Sr and Zn) was evaluated individually.

The evaluation of data was further carried out by performing a t-test assuming equal variance. Except for Ni no statistical differences were detected between results obtained in units stored under “normal” or “reference” conditions.

Failure to detect degradation, however, does not prove stability. Although under these conditions an expansion of the total uncertainty of the assigned values is generally not encouraged, in this case the approach of ISO Guide 35 [4] was followed, mainly due to the lack of sound alternatives. An uncertainty contribution related with the stability of the candidate reference material (ustab) was estimated as the measurement method repeatability observed during the study (Table 2). Graphical representations of the long–term stability study are displayed in Appendix I (Figures 2– 19).

3.3. DETERMINATION OF ASSIGNED VALUES AND THEIR UNCERTAINTIES

The characterization campaign resulted in 2 to 11 measurement results for the requested trace elements. The obtained measurement results were first checked for compliance with the certification requirements, and then for their validity based on technical reasoning. All accepted set of results were submitted to the following statistical tests: Grubbs test to detect single and double outliers, Dixon’s test to detect outlying laboratory means and Kolmogorov-Smirnov’s test for normal distribution. As shown in Table 3, two outliers (95%) were found for Zn and all data sets were normally distributed. Since no technical reasons were identified for outlying results, all data were retained for statistical analysis.

The medians, unweighted mean of the means and robust mean were calculated and compared (Table 3). Robust estimations were calculated only if at least 4 measurement results were available. No significant differences were observed and the reference values obtained with the mean of the mean approach was further used. These values are considered to be the most reliable estimates of the property values of the selected trace elements in tuna fish homogenate.

TABLE 3. COMPARISON OF DIFFERENT MEAN

Element	Robust Mean** (mg kg^{-1})	Median (mg kg^{-1})	Mean of the means (mg kg^{-1})	Outlier 95%	Outlier 99%	Distribution
As	1.97	1.97	1.98	0	0	normal
Ca	127	126	129	0	0	normal
Cd	0.0496	0.0502	0.0492	0	0	normal
Cu	1.74	1.74	1.74	0	0	normal
Fe	87.9	88.1	88.0	0	0	normal
Hg	4.25	4.27	4.26	0	0	normal
CH_3Hg*	3.61	3.64	3.62	0	0	normal
Mn	0.215	0.213	0.222	0	0	normal
Rb	2.37	2.39	2.32	0	0	normal
Se	4.43	4.40	4.43	0	0	normal
Sr	0.502	0.500	0.530	0	0	normal
Zn	18.0	17.9	18.0	2	0	normal

* mg kg^{-1} as Hg

** robust means were calculated as described in the ISO guide 13528 [6].

The uncertainties associated with the assigned values were calculated according to ISO Guide 35 [4]. 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}). These different contributions were combined to estimate the expanded uncertainty.

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \quad (4)$$

Where

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

u_{hom} was estimated as described in Section 3.1.1.

u_{stab} was estimated as described in Section 3.2

u_{char} was estimated as described in ISO 35 [5] using Eq. (5):

$$u_{char} = \frac{s}{\sqrt{p}} \quad (5)$$

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

Means values, their expanded uncertainties (k=2) and uncertainty contributions from the characterization, homogeneity and stability studies are presented in Table 4 for all trace elements (including the elements with information values).

TABLE 4. MEAN OF THE MEAN AND UNCERTAINTIES

Element	Mean of the mean mg kg^{-1}	$u_{char,rel}$ %	$u_{hom,rel}$ %	$u_{stab,rel}$ %	$U_{,rel}$ (k=2) %
Ag	$5.42 .10^{-3}$	22.9	4.1	10.0	50.6
Al	3.92	24.1	12.0	8.0	56.2
As	1.98	1.3	2.9	4.0	10.2
Ba	0.0552	1.5	4.0	4.0	11.7
Ca	129	3.3	4.0	3.5	12.5
Cd	0.0492	2.7	1.5	3.0	8.7
Co	0.0436	4.2	7.0	3.0	17.4
Cr	0.134	5.3	9.0	7.0	25.1
Cs	0.188	3.2	4.0	4.0	13.0
Cu	1.74	2.9	2.3	4.0	10.9
Fe	88.0	1.3	2.3	2.6	7.4
Hg	4.26	1.3	0.7	4.0	8.5
K	$12.3.10^{3}$	2.1	4.0	4.0	12.1
CH_3Hg*	3.62	2.2	3.5	5.0	13.0
Mg	$1.06.10^{3}$	1.4	4.0	4.0	11.7
Mn	0.222	2.8	0.7	5.0	11.6
Na	$1.46.10^{3}$	2.4	4.0	4.0	12.3
Ni	0.0700	8.7	14.4	5.0	46.2
Pb	0.0124	5.4	14.0	3.0	30.6
Rb	2.32	3.2	1.8	3.3	9.8
Se	4.43	1.7	3.2	2.8	9.2
Sr	0.530	3.6	3.5	4.7	13.7
Zn	18.0	2.0	2.2	2.0	7.2

* mg kg^{-1} as Hg

The results for the mass fractions of the certified trace elements as reported by the participants in this certification and grouped by methods are presented in Appendix II. In Appendix III is presented the information for the trace elements with information values. 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 (as calculated in Eq. 4). The error bars represent the expanded uncertainty as reported by participants.

As shown previously in Figure 1 and in Figures 7-29, methods with different quantification steps (graphite furnace-AAS, AFS, ICP-MS) as well as methods without sample preparation step such as neutron activation or solid sampling AAS were used for characterization of the material. The agreement between results confirms the absence of any significant method bias and demonstrates the identity of the analyte.

Certified values were calculated as the mean of the mean of accepted dataset for elements fulfilling the following criteria: at least 5 results from 2 methods were available and relative expanded uncertainties of the assigned value are less than 20%. The certified values are presented in Table 5, together with their expanded uncertainty.

The above conditions were not satisfied for Ag , for Al, Co, Cr, Ni and Pb and for some additionally reported by the participants in the characterization campaign elements as Ba,Cs, K and Na, the conditions for homogeneity were not fulfilled only information values are provided. They are presented in Table 6.

TABLE 5. ASSIGNED VALUES FOR TRACE ELEMENT MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k=2*) IN IAEA-436A

Element	Unit	Assigned value[1]	Expanded uncertainty (k=2)[2]
As	mg kg^{-1}	1.98	0.20
Ca	mg kg^{-1}	129	16
Cd	mg kg^{-1}	0.0492	0.0042
Cu	mg kg^{-1}	1.74	0.19
Fe	mg kg^{-1}	88.0	6.5
Hg	mg kg^{-1}	4.26	0.36
CH_3Hg	mg kg^{-1} as Hg	3.62	0.47
Mn	mg kg^{-1}	0.222	0.026
Rb	mg kg^{-1}	2.32	0.23
Se	mg kg^{-1}	4.43	0.41
Sr	mg kg^{-1}	0.530	0.073
Zn	mg kg^{-1}	18.0	1.3

[1] The value is the mean of the mean of accepted sets of data, each set being obtained by different laboratory. The assigned 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 [7], 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 IAEA-436A

Element	Unit	Information value[1]	Expanded uncertainty (k=2)[2]
Ag	mg kg^{-1}	$5.42.10^{-3}$	$2.7.10^{-3}$
Al	mg kg^{-1}	3.92	2.20
Ba	mg kg^{-1}	$55.1.10^{-3}$	$6.5.10^{-3}$
Co	mg kg^{-1}	$42.6.10^{-3}$	$7.4.10^{3}$
Cr	mg kg^{-1}	0.134	0.034
Cs	mg kg^{-1}	0.188	0.025
K	mg kg^{-1}	$12.3.10^{3}$	$1.5.10^{3}$
Mg	mg kg^{-1}	$1.06.10^{3}$	$0.12.10^{3}$
Na	mg kg^{-1}	$1.46.10^{3}$	$0.18.10^{3}$
Ni	mg kg^{-1}	$70.1.10^{-3}$	$3.2.10^{-3}$
Pb	mg kg^{-1}	$12.4.10^{-3}$	$3.8.10^{-3}$

[1] The value is the mean of the mean of accepted sets of data.
[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 [7], corresponding to the level of confidence of about 95%.

4. METROLOGICAL TRACEABILITY

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.

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. NIST, BAM or EMPA) with demonstrated SI traceability, followed by gravimetric preparation using balances calibrated with SI-traceable weights.

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.

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

As the certified values are combinations of agreeing results, individually traceable to the SI, the certified quantity values are also traceable to the SI system of units. Therefore individual

assigned results are traceable to the SI. The trust in the certified values and their trueness are further underpinned by the agreement among the technically accepted datasets.

5. CONCLUSIONS

This certification campaign allows assignment of certified values for As, Ca, Cd, Cu, Fe, Hg, CH_3Hg, Mn, Rb, Se, Sr and Zn with associated uncertainties following ISO guidelines. The certified values are derived from measurement results provided by the laboratories participating in the characterization study. Only validated methods were applied in the characterization of IAEA-436A CRM. As the certified values are combinations of SI traceable individual results, they are also traceable to the International System of Units.

APPENDIX I

RESULTS FROM THE LONG TERM STABILITY STUDY:

Figures 2–19 present individual mass fractions measured in unit kept 12 years at reference temperature (-20°C); at normal temperature (+20°C) and the results of previous characterization study performed in 2004.

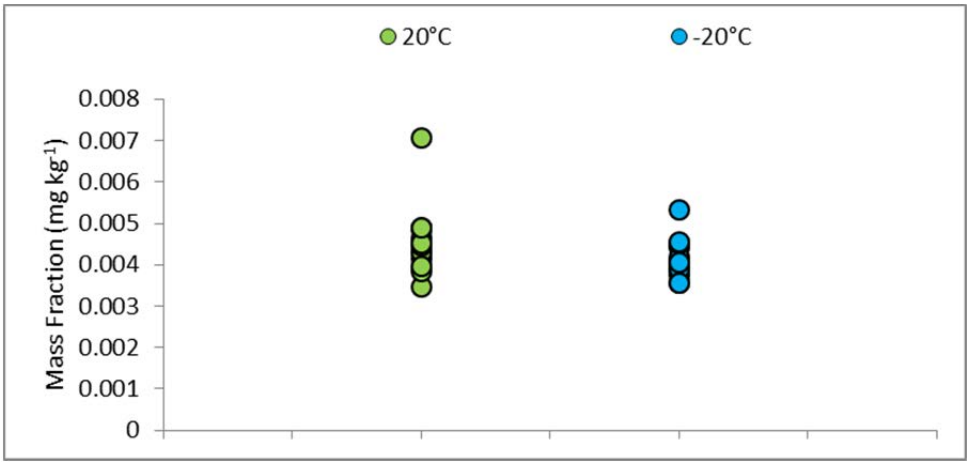

FIG. 2. Results of long term stability study for silver.

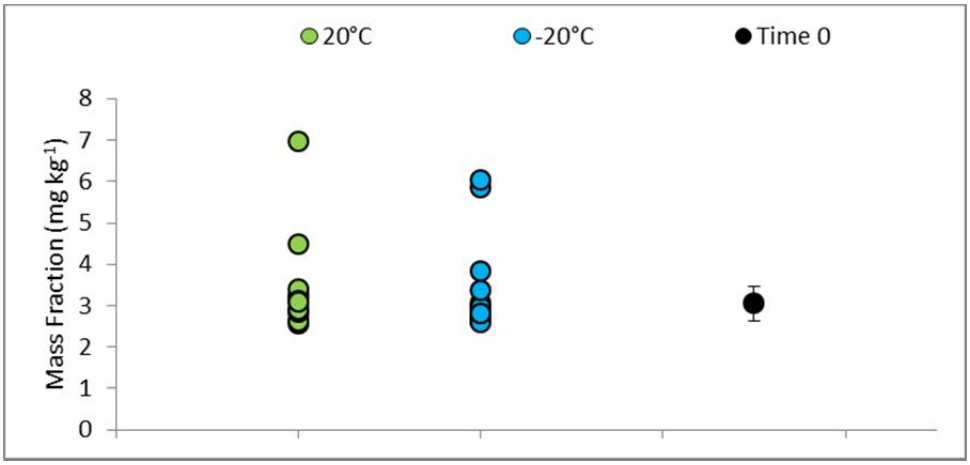

FIG. 3. Results of long term stability study for aluminium.

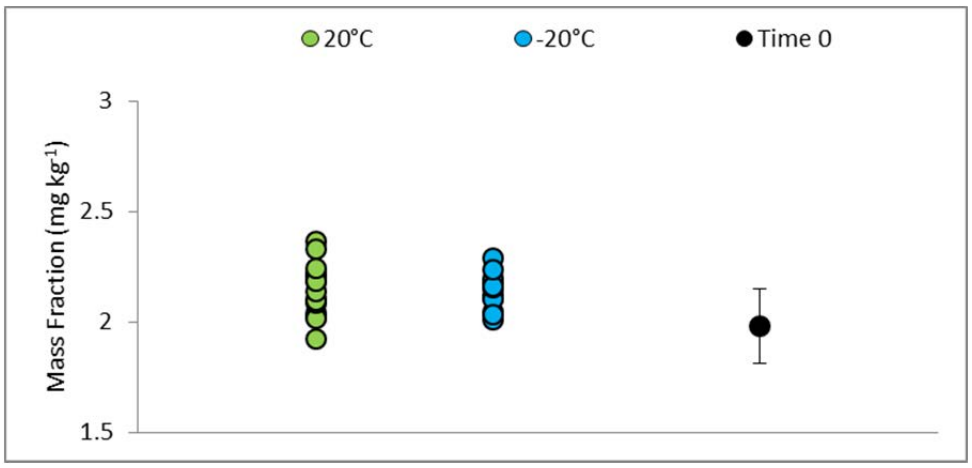

FIG. 4. Results of long term stability study for arsenic.

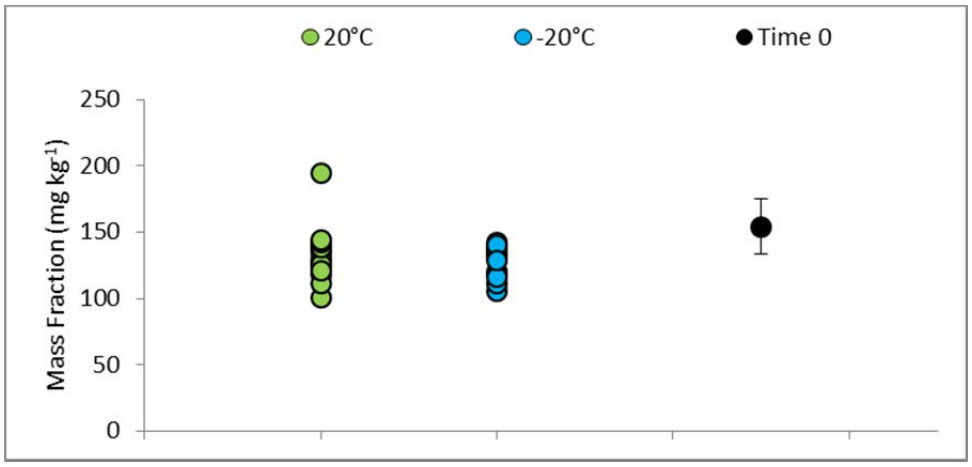

FIG. 5. Results of long term stability study for calcium.

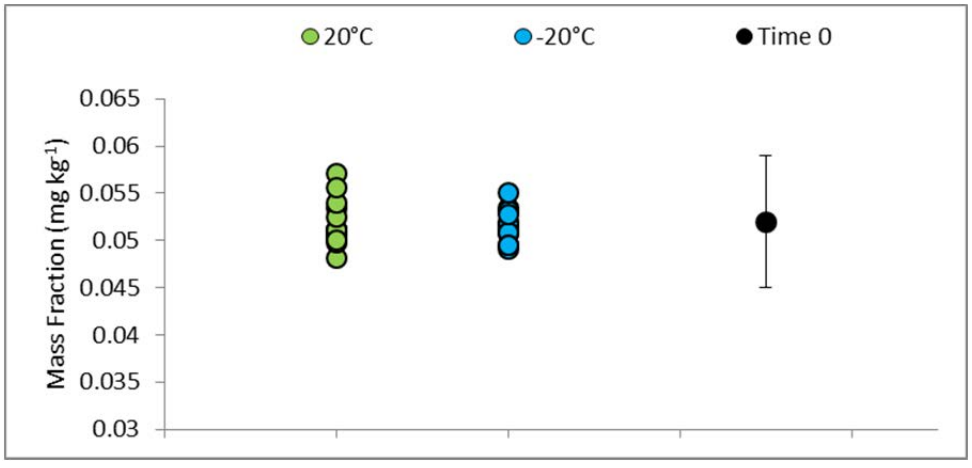

FIG. 6. Results of long term stability study for cadmium.

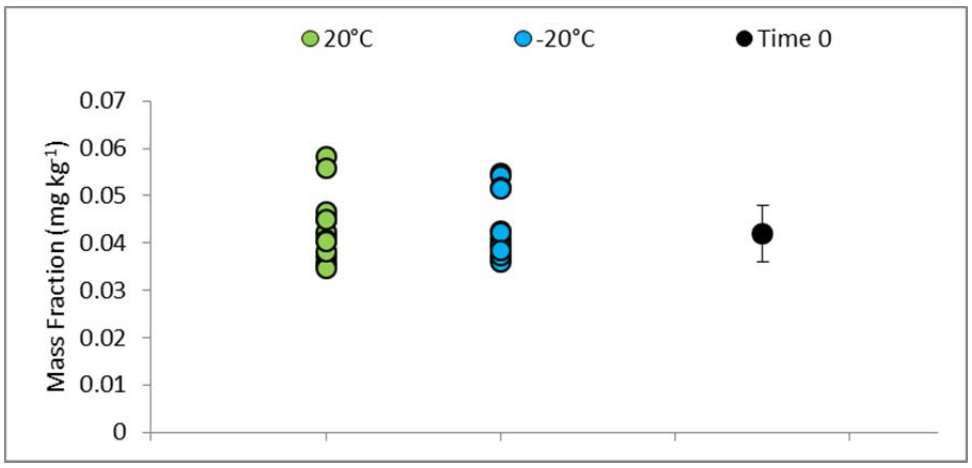

FIG. 7. Results of long term stability study for cobalt.

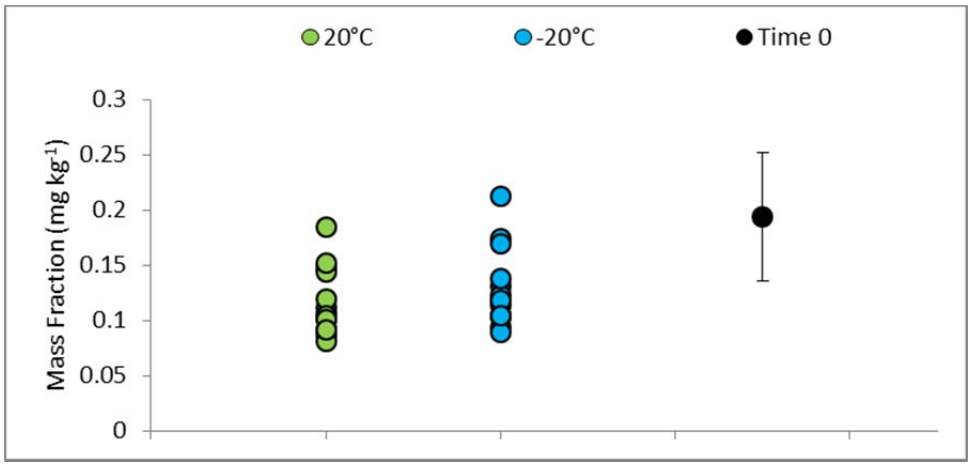

FIG. 8. Results of long term stability study for chromium.

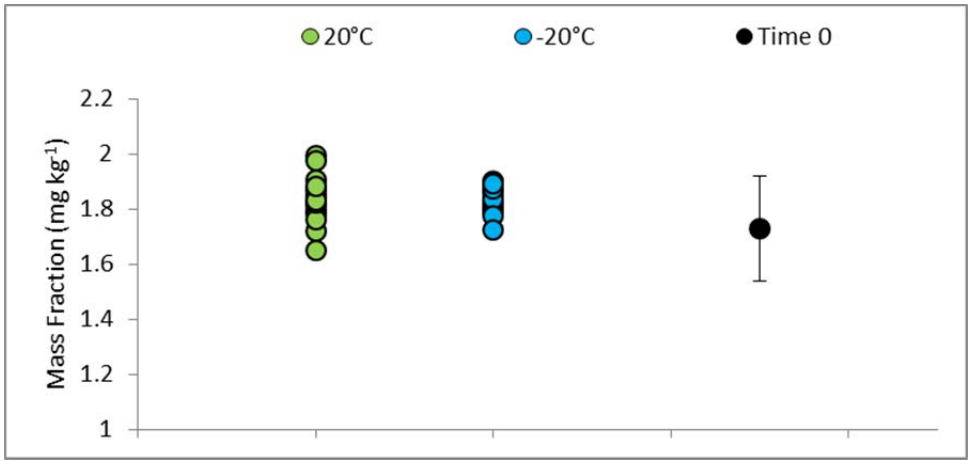

FIG. 9. Results of long term stability study for copper.

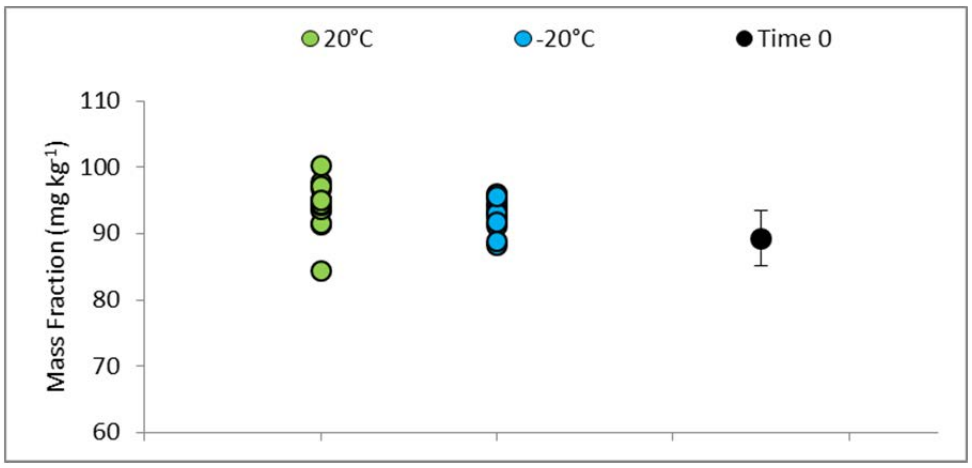

FIG. 10. Results of long term stability study for iron.

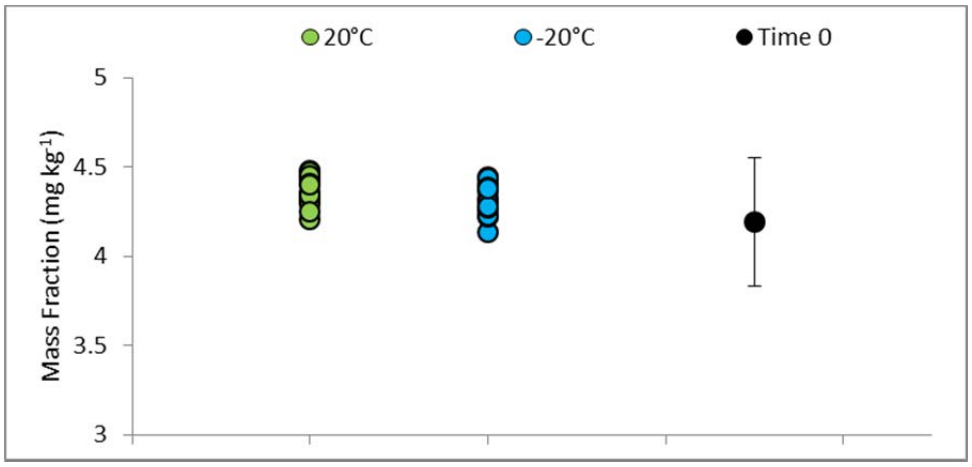

FIG. 11. Results of long term stability study for total mercury.

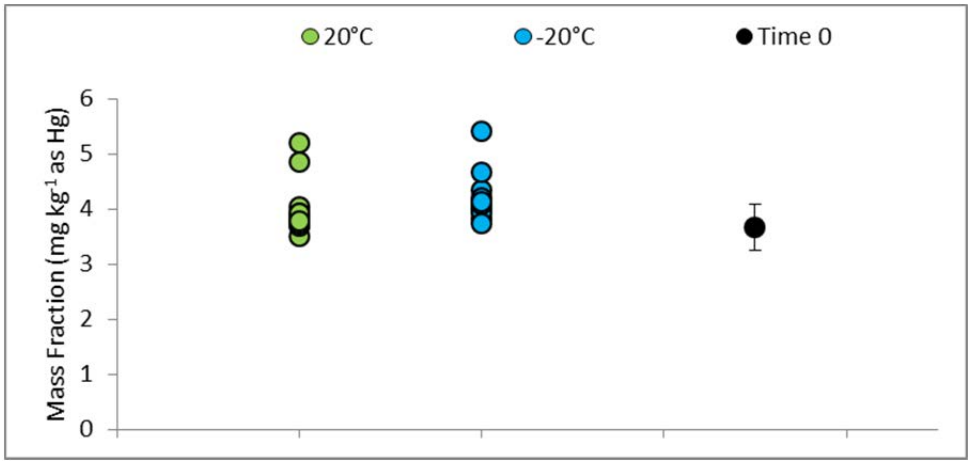

FIG. 12. Results of long term stability study for methyl mercury.

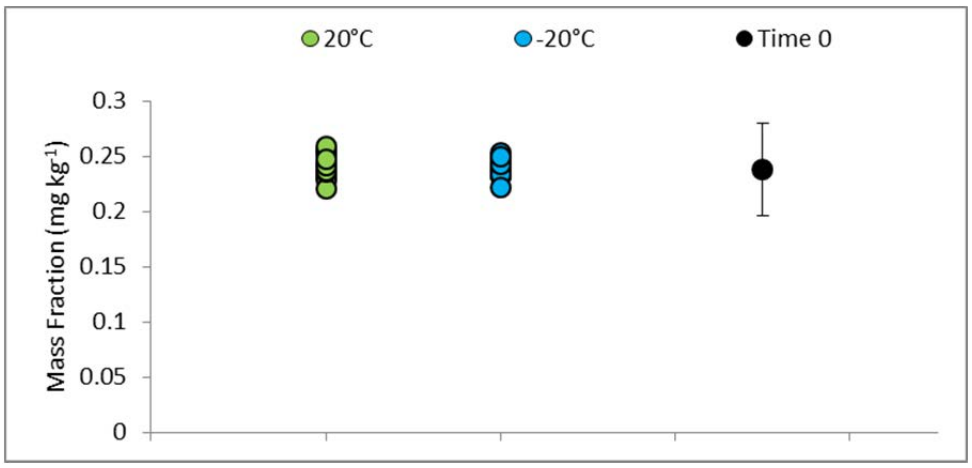

FIG. 13. Results of long term stability study for manganese.

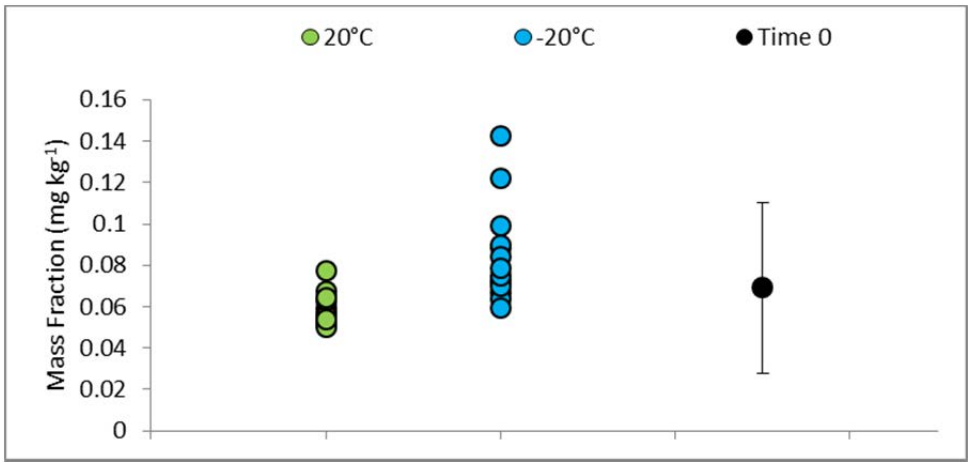

FIG. 14. Results of long term stability study for nickel.

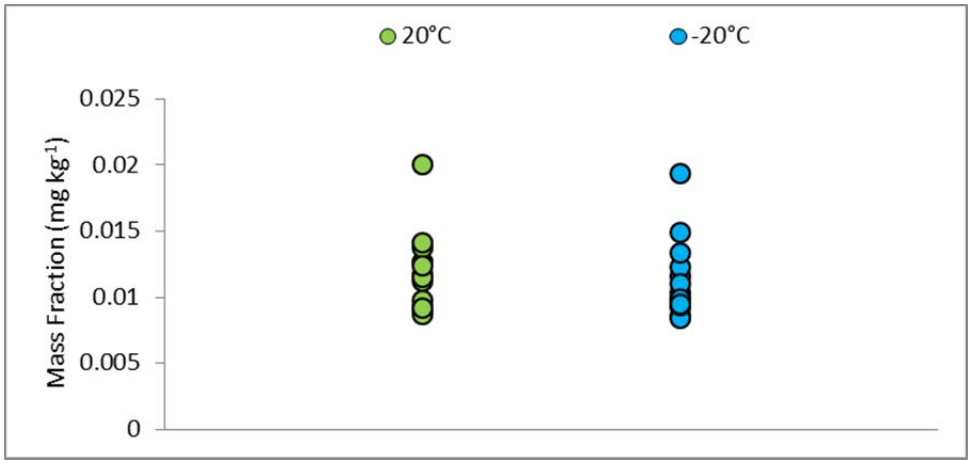

FIG. 15. Results of long term stability study for lead.

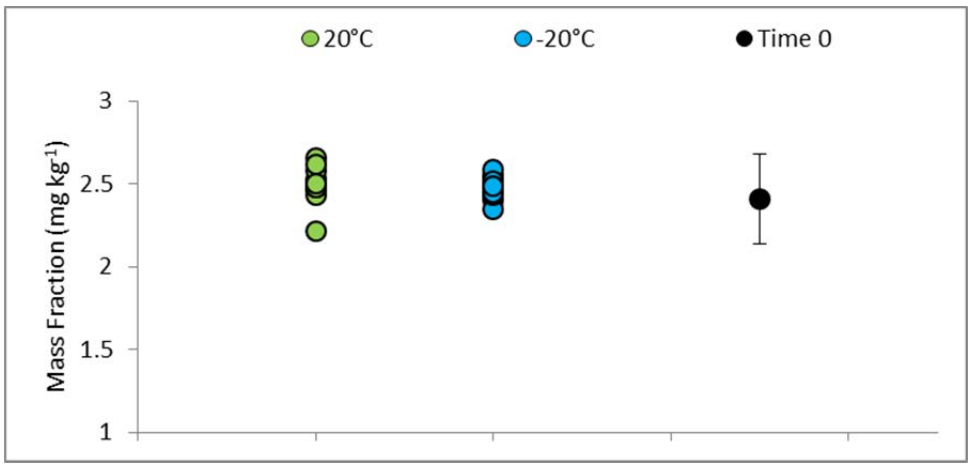

FIG. 16. Results of long term stability study for rubidium.

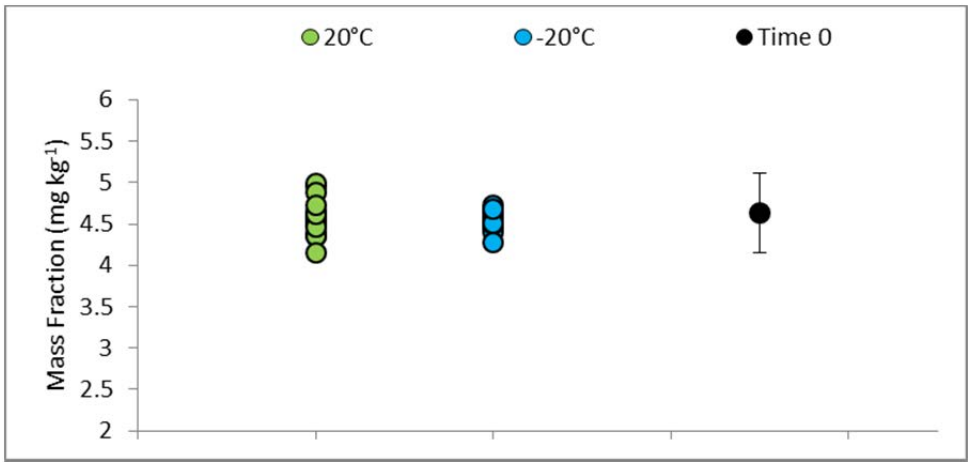

FIG. 17. Results of long term stability study for selenium.

\

.

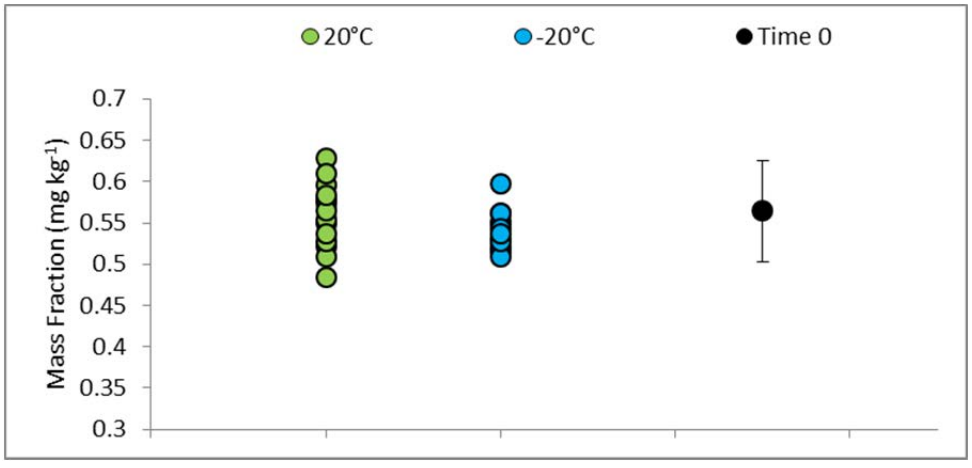

FIG. 18. Results of long term stability study for strontium.

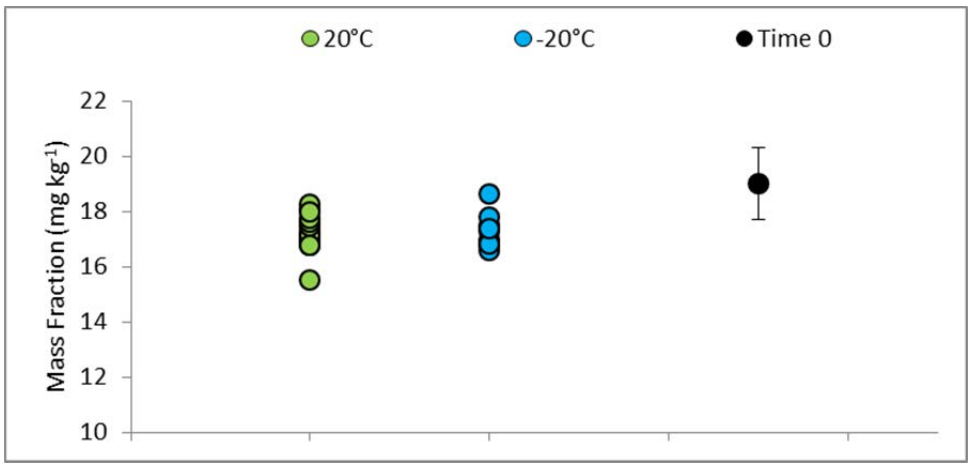

FIG. 19. Results of long term stability study for zinc.

APPENDIX II
RESULTS OF THE CHARACTERIZATION MEASUREMENTS

The reported by the participating results, their expended uncertainty, measurement techniques and CRMs used for quality assurance purposes are presented in Tables 7-18. Figures 20 – 31 provide graphical presentation of the individual results and their expanded uncertainties (k=2) as well as the reference value for the respective trace element and its expanded uncertainty (k=2).

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
10	1.93	0.09	NIST 1566B	Graphite Furnace AAS
13A	2.09	0.21	DORM-2	HR-ICP-MS
5B	1.87	0.43	NIST 1566B	HR-ICP-MS
1	1.95	0.14	IAEA-407	ICP-MS
12	1.98	0.09	DORM-3	ICP-MS
14	1.94	0.28	DORM-3	ICP-MS
15	2.13	0.32	DORM2	ICP-MS
13B	2.05	0.21	IAEA-436	ICP-MS
5A	2.00	0.48	NIST 1566B	ICP-MS
4	1.84	0.10	NIST 1566B	Neutron Activation
8A	1.97	0.14	NIST 1547	Neutron Activation

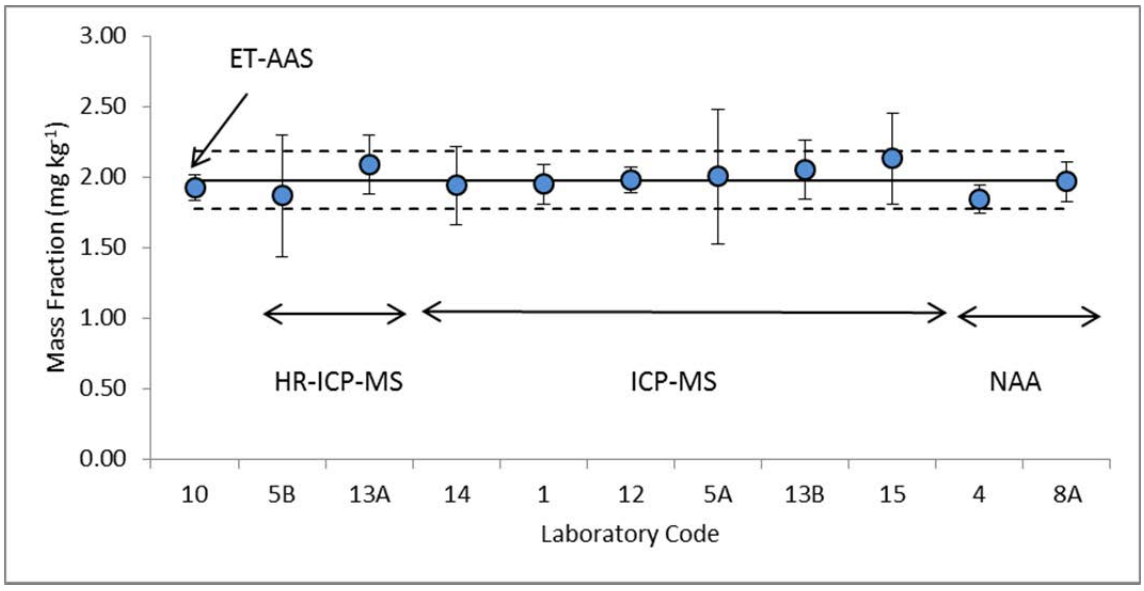

FIG. 20. Laboratory results for arsenic mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	119	30	NIST 1566B	HR-ICP-MS
5A	122	24	NIST 1566B	ICP-MS
12	126	35	LFB	ICP-MS
1	137	16	IAEA-407	ICP-MS
13B	150	24	IAEA-436	ICP-MS
14	120	21	DORM-3	ICP-OES
4	129	10	NIST 1566B	Neutron Activation

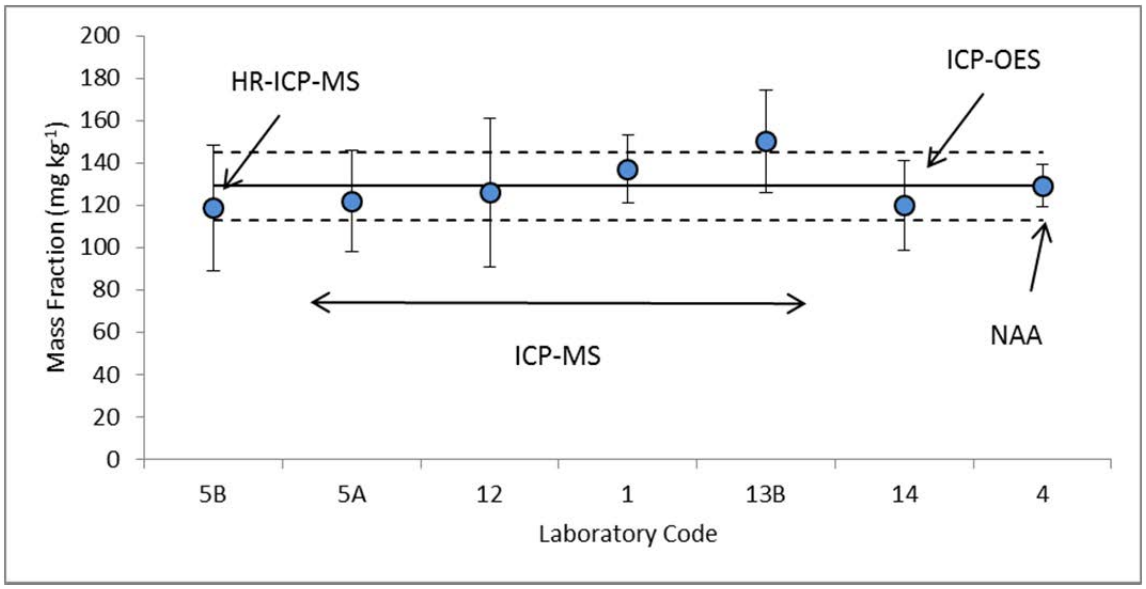

FIG. 21. Laboratory results for calcium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
10	0.045	0.002	DORM-4	Graphite Furnace AAS
13C	0.050	0.006	DORM-2	Graphite Furnace AAS
13A	0.052	0.005	DORM-2	HR-ICP-MS
5B	0.050	0.014	NIST 1566B	HR-ICP-MS
1	0.053	0.010	IAEA-407	ICP-MS
12	0.046	0.011	TORT-3	ICP-MS
14	0.040	0.006	DORM-3	ICP-MS
15	0.052	0.016	DORM2	ICP-MS
13B	0.054	0.005	IAEA-436	ICP-MS
5A	0.050	0.010	NIST 1566B	ICP-MS

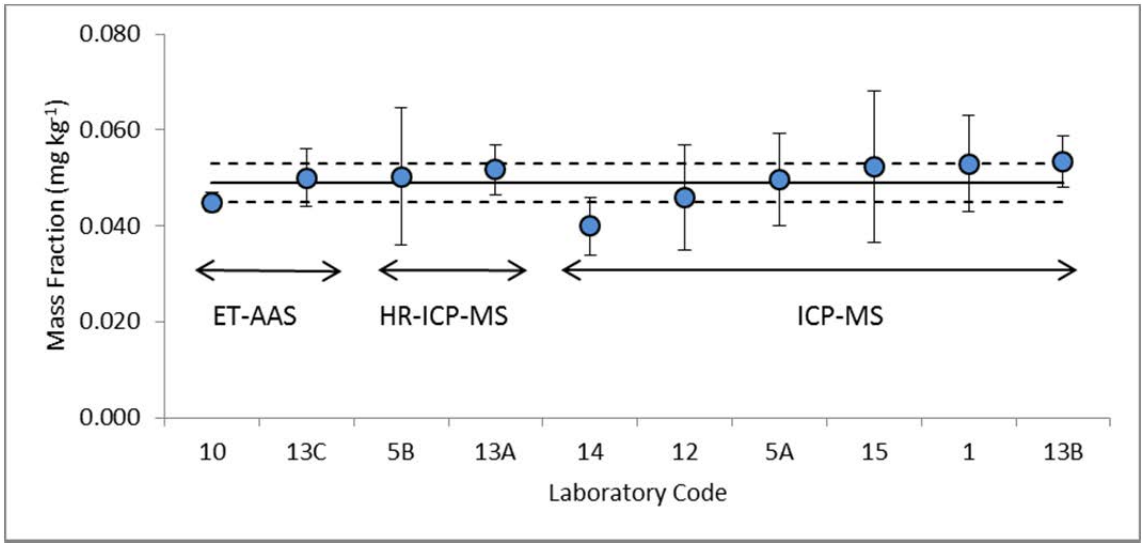

FIG. 22. Laboratory results for cadmium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
10	1.97	0.22	NIST 1566B	Flame AAS
13C	1.74	0.21	DORM-2	Graphite Furnace AAS
5B	1.57	0.39	NIST 1566B	HR-ICP-MS
13A	1.94	0.23	DORM-2	HR-ICP-MS
5A	1.51	0.33	NIST 1566B	ICP-MS
12	1.66	0.12	DORM-3	ICP-MS
1	1.72	0.39	IAEA-407	ICP-MS
13B	1.76	0.18	IAEA-436	ICP-MS
15	1.78	0.53	DORM-2	ICP-MS

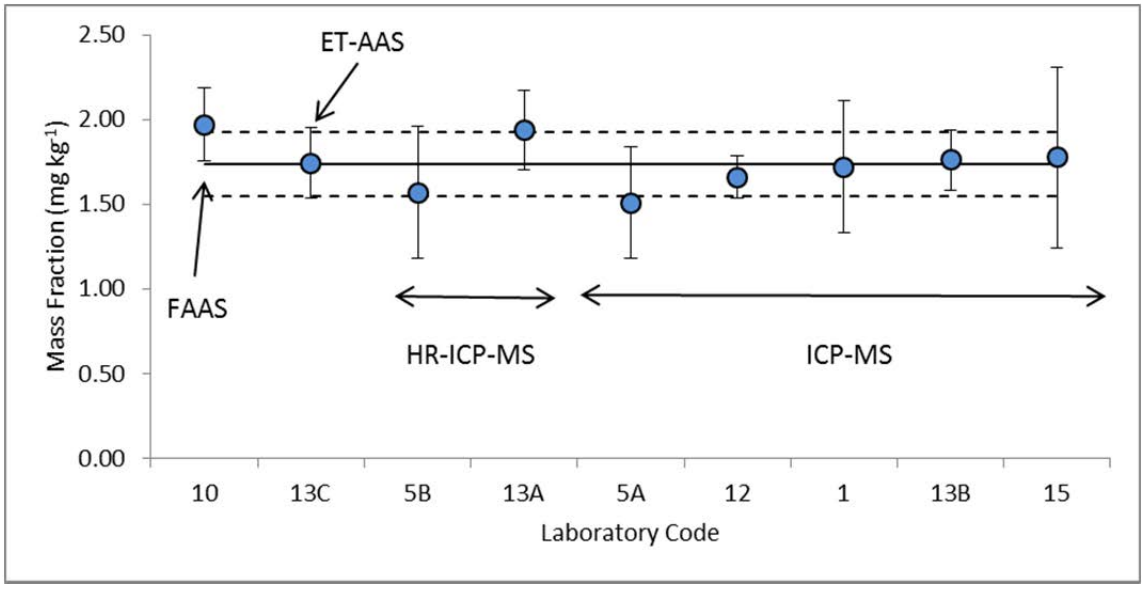

FIG. 23. Laboratory results for copper mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13C	86.7	10.4	IAEA-407	Flame AAS
10	88.9	8.3	DORM-4	Flame AAS
5B	83.7	15.9	NIST 1566B	HR-ICP-MS
5A	84.8	10.0	NIST 1566B	ICP-MS
12	87.6	2.8	DORM-3	ICP-MS
15	88.6	8.9	TORT-2	ICP-MS
13B	92.3	9.2	IAEA-436	ICP-MS
14	94.5	9.8	DORM-3	ICP-OES
4	84.0	6.0	NIST 1566B	Neutron Activation
8A	89.0	6.4	NIST 1547	Neutron Activation

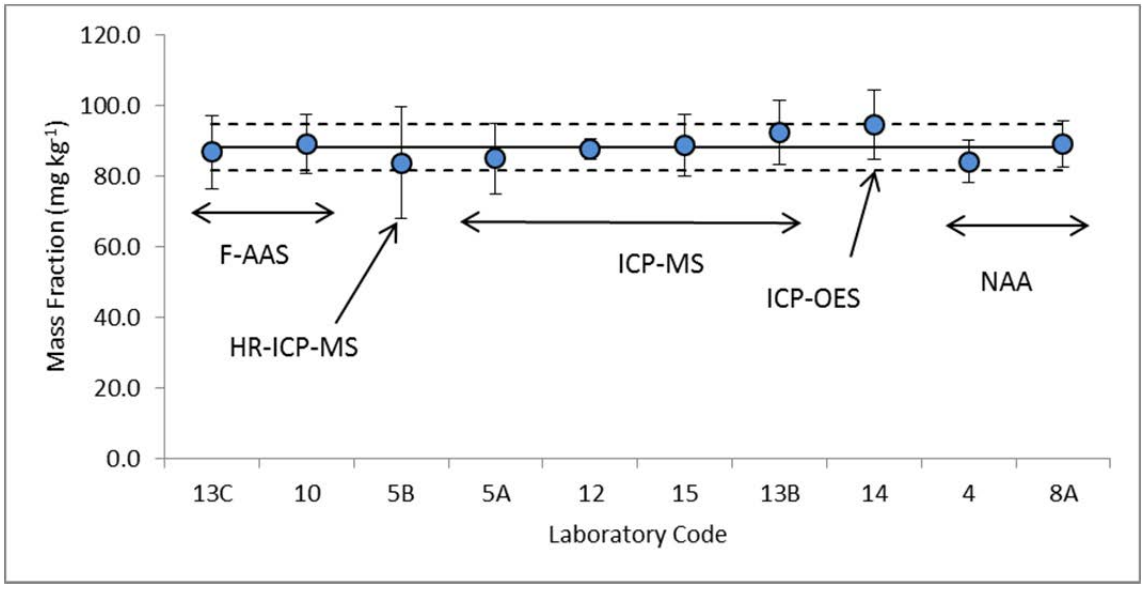

FIG. 24. Laboratory results for iron mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
8A	4.16	0.30	DORM4	Cold Vapor AAS
5A	4.32	0.63	NIST 1566B	Cold Vapor AAS
10	3.98	0.17	Dorm-4	Cold Vapor AFS
12	4.36	0.43	DORM-4	Cold Vapor AFS
13A	4.33	0.43	DORM-2	Cold Vapor AFS
5B	4.26	0.78	NIST 1566B	Cold Vapor AFS
9B	4.27	0.98	DORM-4	Cold Vapor AFS
1	4.05	0.20	IAEA-407	ICP-MS
13B	4.60	0.46	DORM-2	Solid AAS
9A	4.23	0.72	DORM-4	Solid AAS

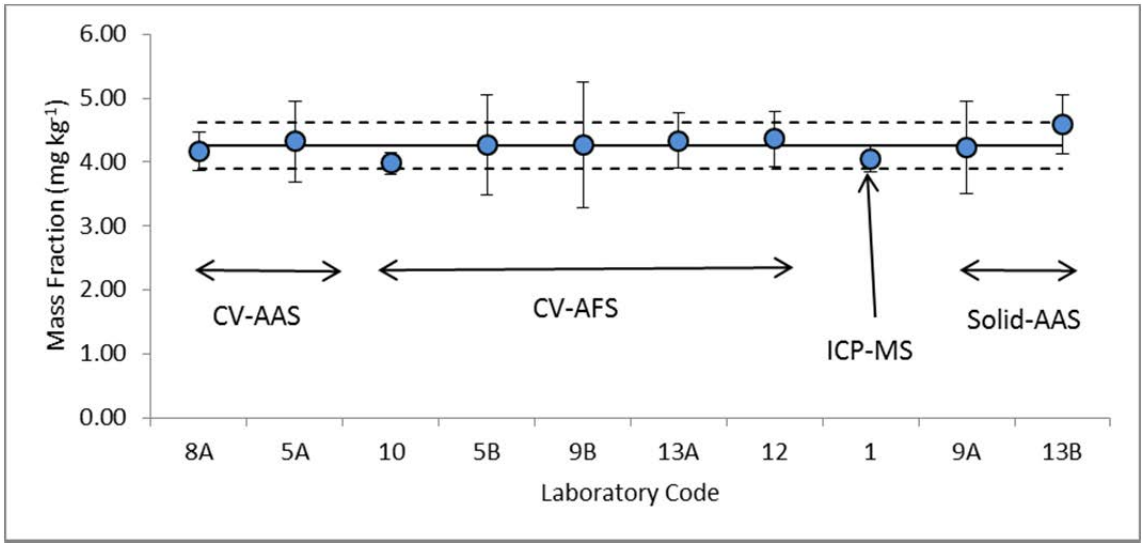

FIG. 25. Laboratory results for mercury mass fraction (mg kg^{-1}) in IAEA-436A.

TABLE 13. METHYL MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1} as Hg)

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
8B	3.67	0.18	ERMCE 464	Cold Vapor AAS
10	3.51	0.31	NIST 1566B	Cold Vapor AFS
8A	3.61	0.20	ERMCE 464	GC-AFS
9A	3.77	0.49	DORM-3	GC-AFS
12	3.67	0.57	DORM-4	GC-AFS
13B	3.39	0.41	IAEA-436	GC-AFS
5A	4.04	0.82	NRC DORM4	GC-AFS
13A	3.33	0.50	DOLT-2	Solid AAS

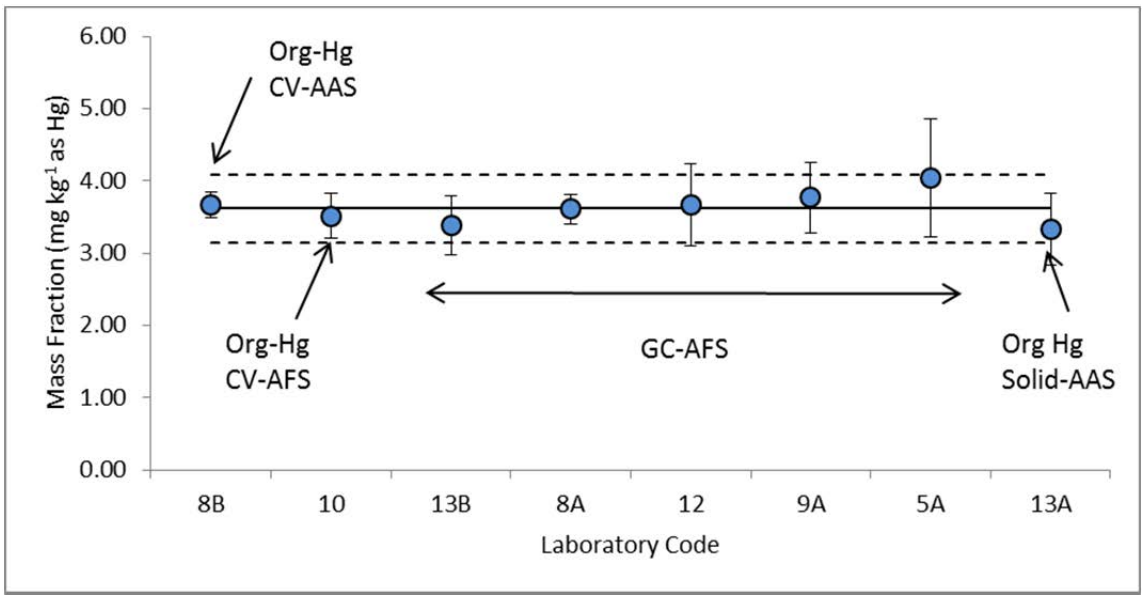

FIG. 26. Laboratory results for methyl mercury mass fraction (mg kg^{-1} as Hg) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13C	0.225	0.027	DORM-2	Graphite Furnace AAS
5B	0.212	0.053	NIST 1566B	HR-ICP-MS
5A	0.208	0.060	NIST 1566B	ICP-MS
12	0.208	0.013	TORT-3	ICP-MS
14	0.213	0.020	DORM-3	ICP-MS
13B	0.248	0.025	IAEA-436	ICP-MS
15	0.251	0.038	TORT-2	ICP-MS
4	0.212	0.040	NIST 1566B	Neutron Activation

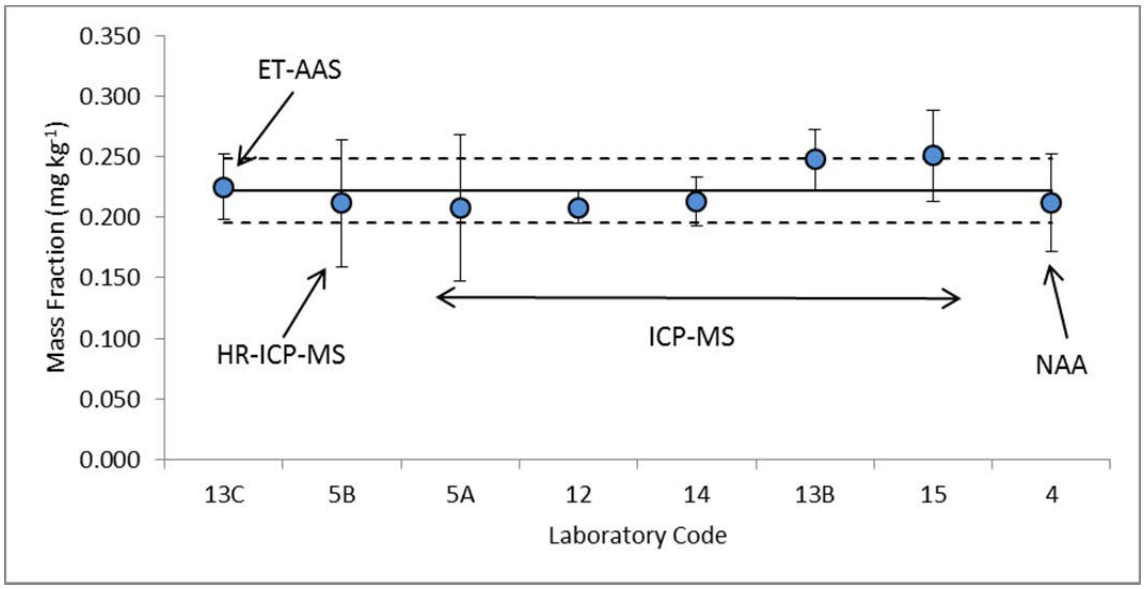

FIG. 27. Laboratory results for manganese mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	2.03	0.50	NIST 1566B	HR-ICP-MS
1	2.39	0.15	IAEA-407	ICP-MS
5A	2.40	0.40	NIST 1566B	ICP-MS
13B	2.43	0.29	IAEA-436	ICP-MS
8A	2.34	0.18	NIST 1547	Neutron Activation

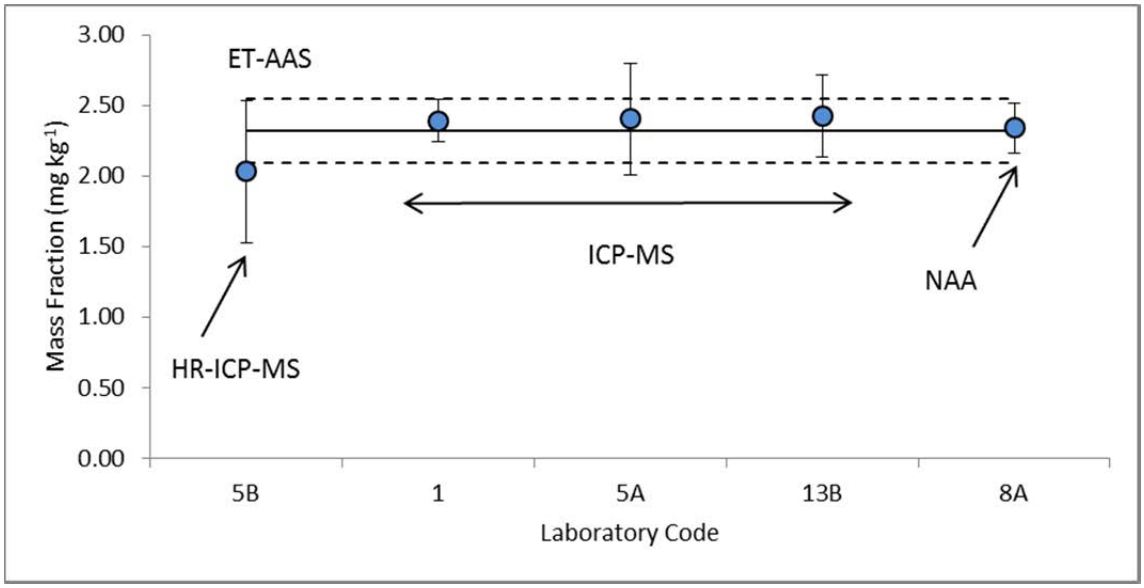

FIG. 28. Laboratory results for rubidium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	4.25	0.80	NIST 1566B	HR-ICP-MS
12	4.06	0.15	TORT-3	ICP-MS
5A	4.38	0.67	NIST 1566B	ICP-MS
1	4.40	0.80	IAEA-407	ICP-MS
15	4.59	0.69	DORM-2	ICP-MS
13B	4.71	0.47	IAEA-436	ICP-MS
14	4.74	0.50	DORM-3	ICP-MS
4	4.20	0.21	NIST 1566B	Neutron Activation
8A	4.51	0.38	NIST 1547	Neutron Activation

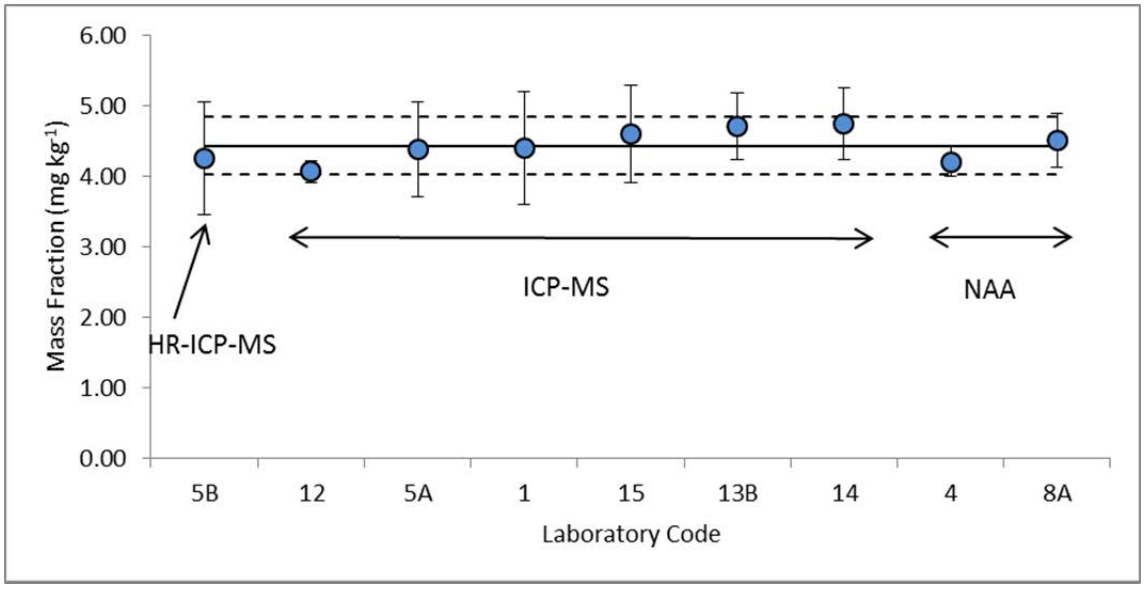

FIG. 29. Laboratory results for selenium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	0.500	0.122	NIST 1566B	HR-ICP-MS
5A	0.498	0.096	NIST 1566B	ICP-MS
1	0.500	0.040	IAEA-407	ICP-MS
12	0.572	0.154	TORT-3	ICP-MS
13B	0.581	0.070	IAEA-436	ICP-MS

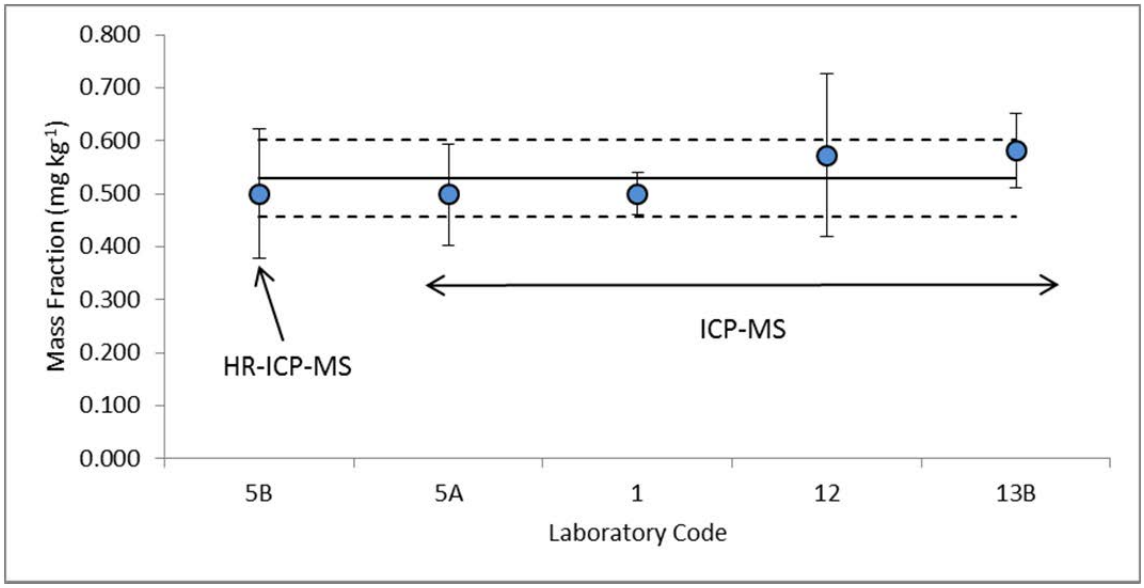

FIG. 30. Laboratory results for strontium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
10	18.1	0.5	DORM-4	Flame AAS
13C	18.5	2.2	DORM-2	Flame AAS
5B	17.1	4.9	NIST 1566B	HR-ICP-MS
12	17.5	0.8	DORM-3	ICP-MS
1	17.8	1.1	IAEA-407	ICP-MS
5A	17.9	3.2	NIST 1566B	ICP-MS
13B	19.1	1.9	IAEA-436	ICP-MS
15	20.4	3.1	DORM-2	ICP-MS
14	17.9	1.6	DORM-3	ICP-OES
4	15.6	0.8	NIST 1566B	Neutron Activation
8A	18.3	1.2	NIST 1547	Neutron Activation

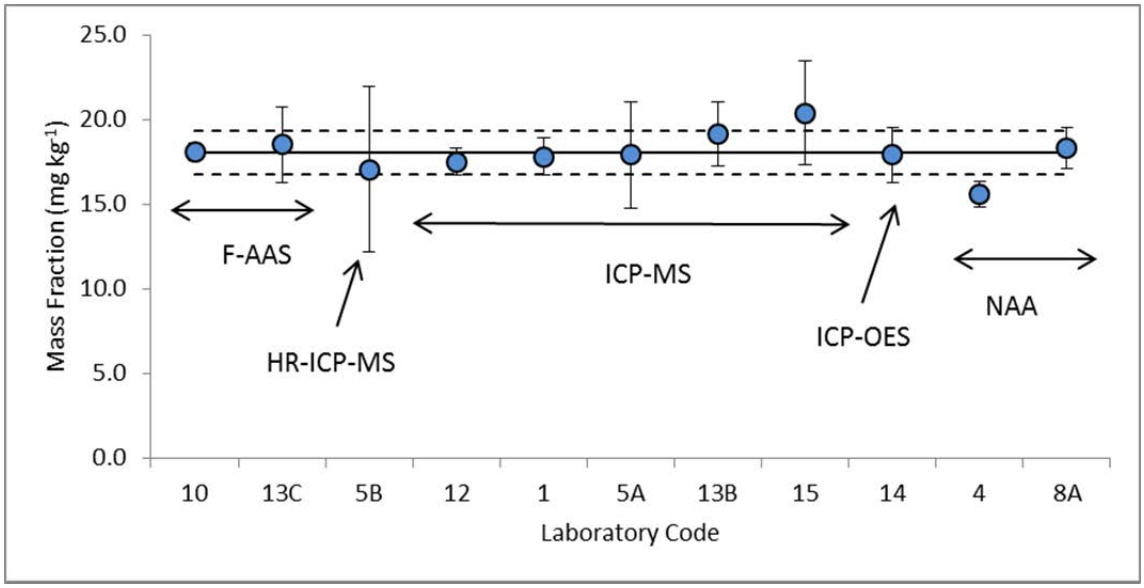

FIG. 31. Laboratory results for zinc mass fraction (mg kg^{-1}) in IAEA-436A.

APPENDIX III

RESULTS OF THE CHARACTERIZATION MEASUREMENTS FOR ELEMENTS WITH INFORMATION VALUES

The reported by the participating results, their expended uncertainty, measurement techniques and CRMs used for quality assurance purposes are presented in Tables 19-29. Figures 32 – 42 provide graphical presentation of the individual results and their expanded uncertainties (k=2) as well as the information value for the respective trace element and its expanded uncertainty (k=2).

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13A	0.004	0.001	DORM-2	HR-ICP-MS
13B	0.004	0.001	IAEA-436	ICP-MS
1	0.008	0.004	IAEA-407	ICP-MS

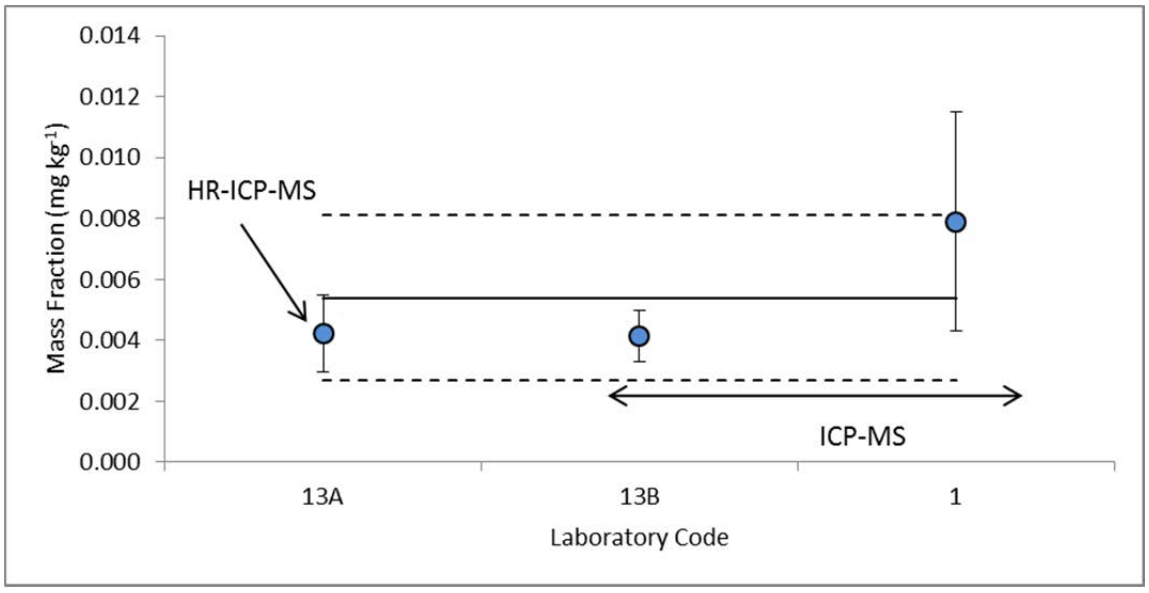

FIG. 32. Laboratory results for silver mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13C	3.20	0.51	DORM-2	Graphite Furnace AAS
5A	2.53	1.00	NIST 1566B	ICP-MS
13B	2.86	0.34	IAEA-436	ICP-MS
1	2.98	0.48	IAEA-407	ICP-MS
12	3.32	1.38	DORM-3	ICP-MS
4	8.60	0.50	NIST 1566B	Neutron Activation

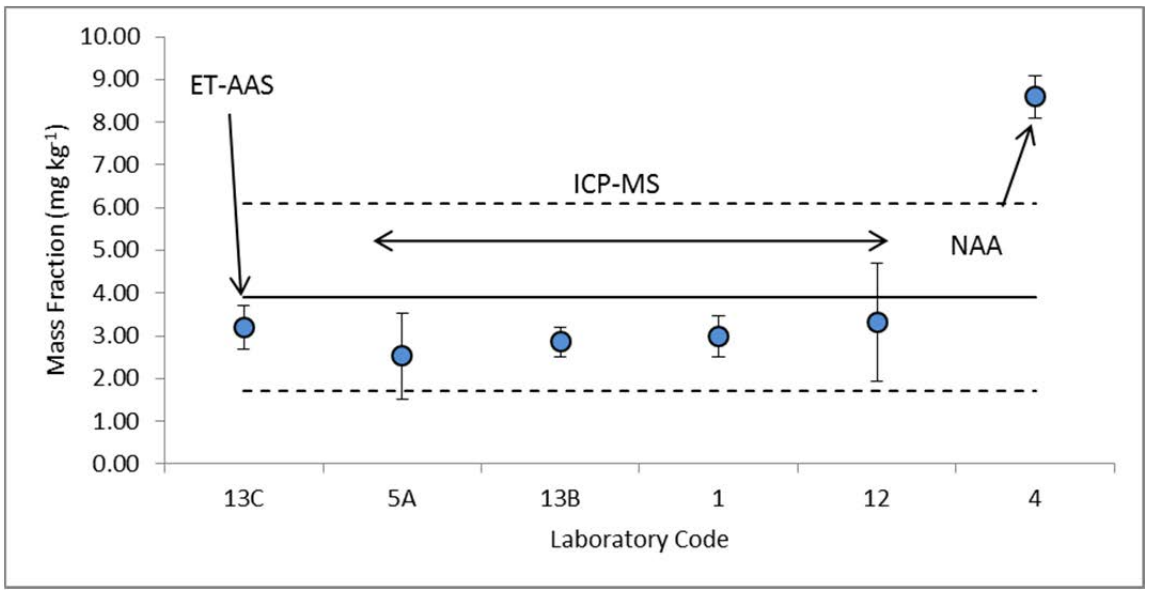

FIG. 33. Laboratory results for aluminum mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	0.056	0.014	NIST 1566B	HR-ICP-MS
5A	0.054	0.014	NIST 1566B	ICP-MS

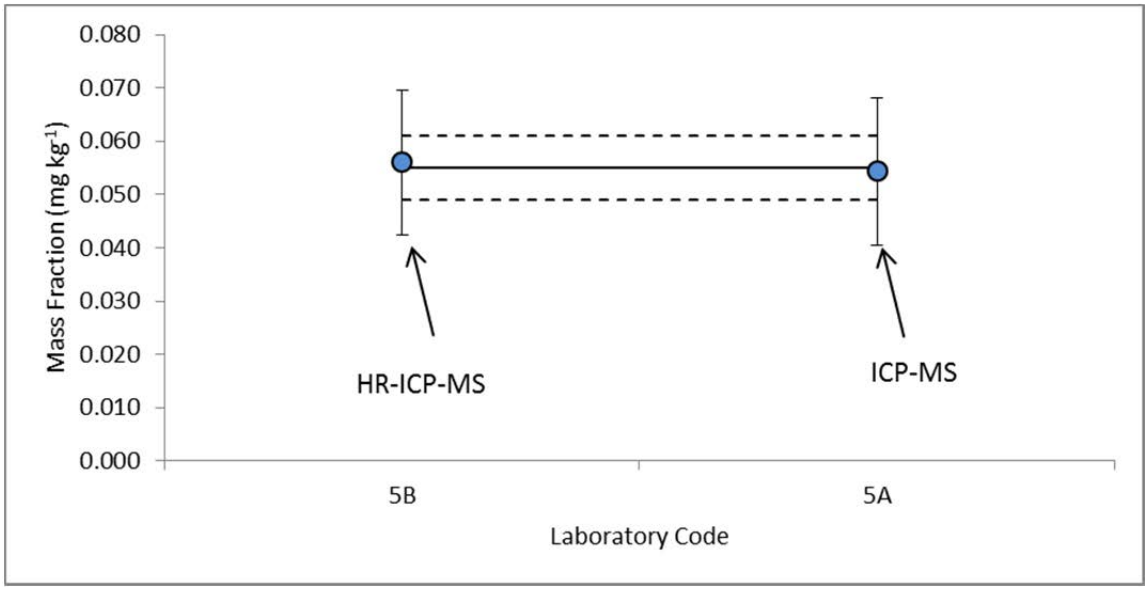

FIG. 34. Laboratory results for barium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13C	0.036	0.007	DORM-2	Graphite Furnace AAS
5B	0.040	0.013	NIST 1566B	HR-ICP-MS
13A	0.042	0.006	DORM-2	HR-ICP-MS
5A	0.040	0.006	NIST 1566B	ICP-MS
15	0.046	0.014	DORM-2	ICP-MS
1	0.047	0.007	IAEA-407	ICP-MS
12	0.049	0.010	LFB	ICP-MS
13B	0.052	0.005	IAEA-436	ICP-MS
4	0.034	0.002	NIST 1566B	Neutron Activation
8A	0.039	0.004	NIST 1547	Neutron Activation

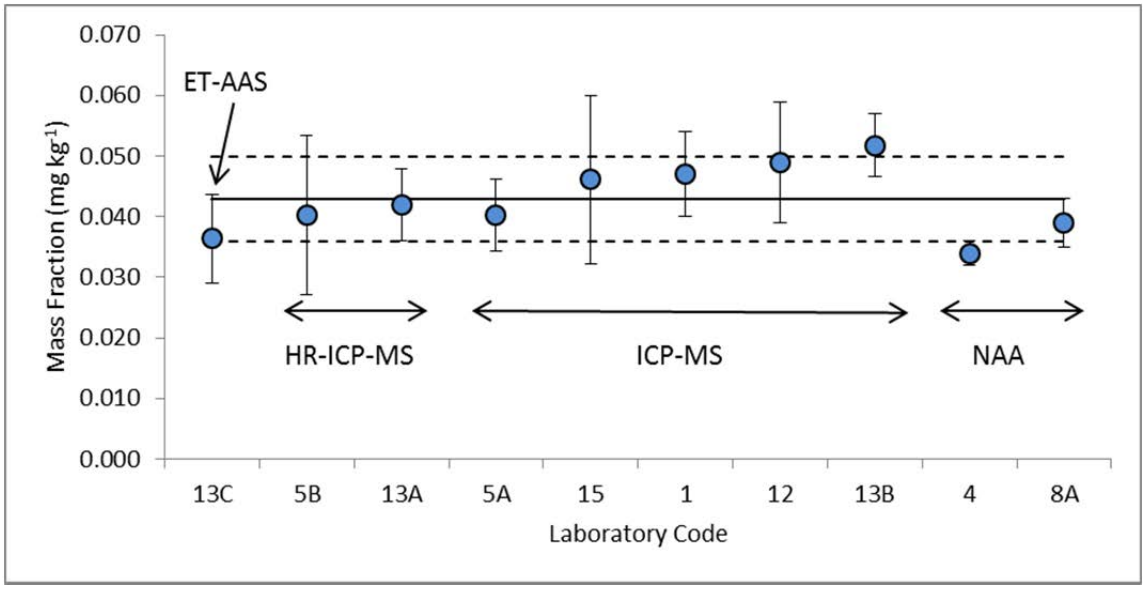

FIG. 35. Laboratory results for cobalt mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13A	0.120	0.036	IAEA-436	Graphite Furnace AAS
5A	0.124	0.043	NIST 1566B	ICP-MS
14	0.130	0.041	DORM-3	ICP-MS
12	0.135	0.054	DORM-3	ICP-MS
15	0.160	0.048	DORM-2	ICP-MS

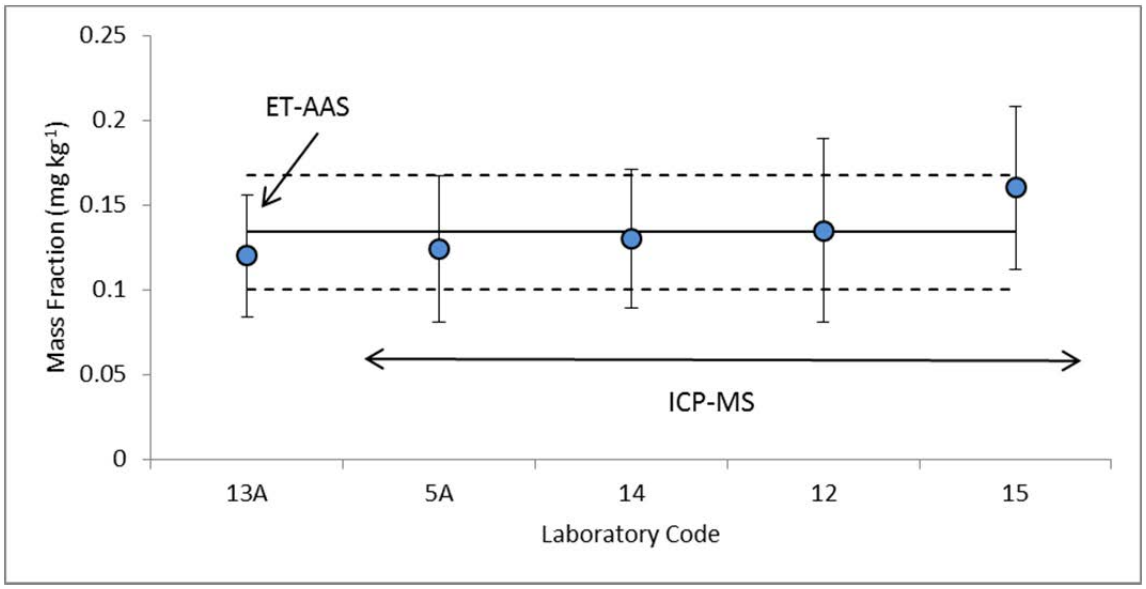

FIG. 36. Laboratory results for chromium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	0.190	0.041	LCS	HR-ICP-MS
5A	0.175	0.026	LCS	ICP-MS
8A	0.183	0.014	NIST 1547	Neutron Activation
4	0.204	0.010	NIST 1566B	Neutron Activation

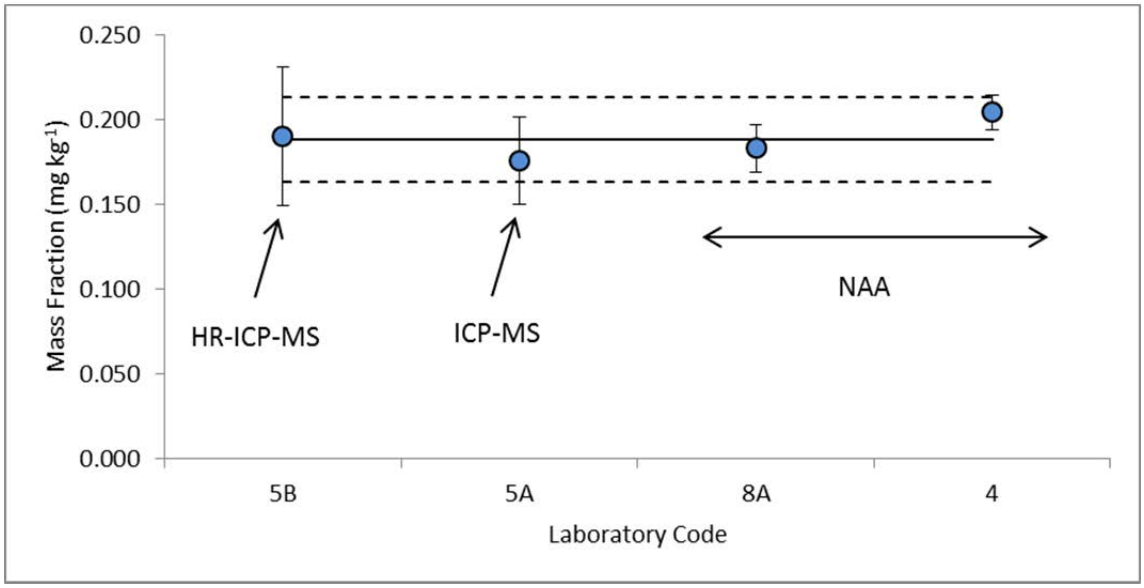

FIG. 37. Laboratory results for cesium mass fraction (mg kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	11.5	1.9	NIST 1566B	HR-ICP-MS
1	12.3	1.0	IAEA-407	ICP-MS
12	12.8	0.3	LFB	ICP-MS
5A	13.0	1.4	NIST 1566B	ICP-MS
4	11.7	0.8	NIST 1566B	Neutron Activation
8A	12.7	0.9	NIST 1547	Neutron Activation

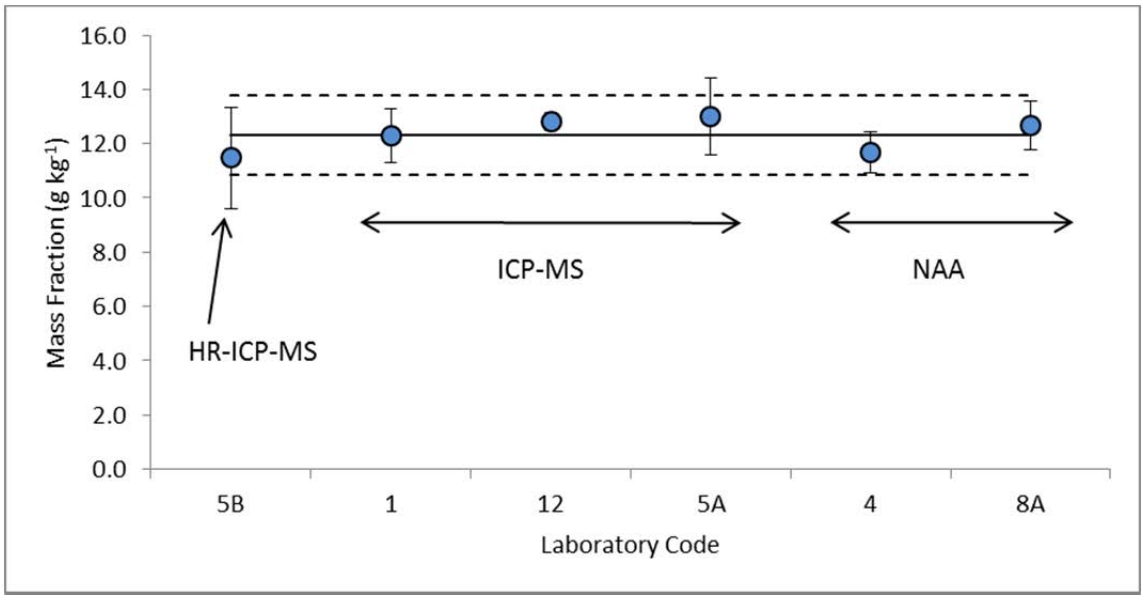

FIG. 38. Laboratory results for potassium mass fraction (g kg^{-1}) in IAEA-436A.

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

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	1.03	0.18	NIST 1566B	HR-ICP-MS
12	1.02	0.04	LFB	ICP-MS
1	1.04	0.08	IAEA-407	ICP-MS
5A	1.08	0.14	NIST 1566B	ICP-MS
14	1.10	0.11	DORM-3	ICP-OES
4	1.11	0.06	NIST 1566B	Neutron Activation

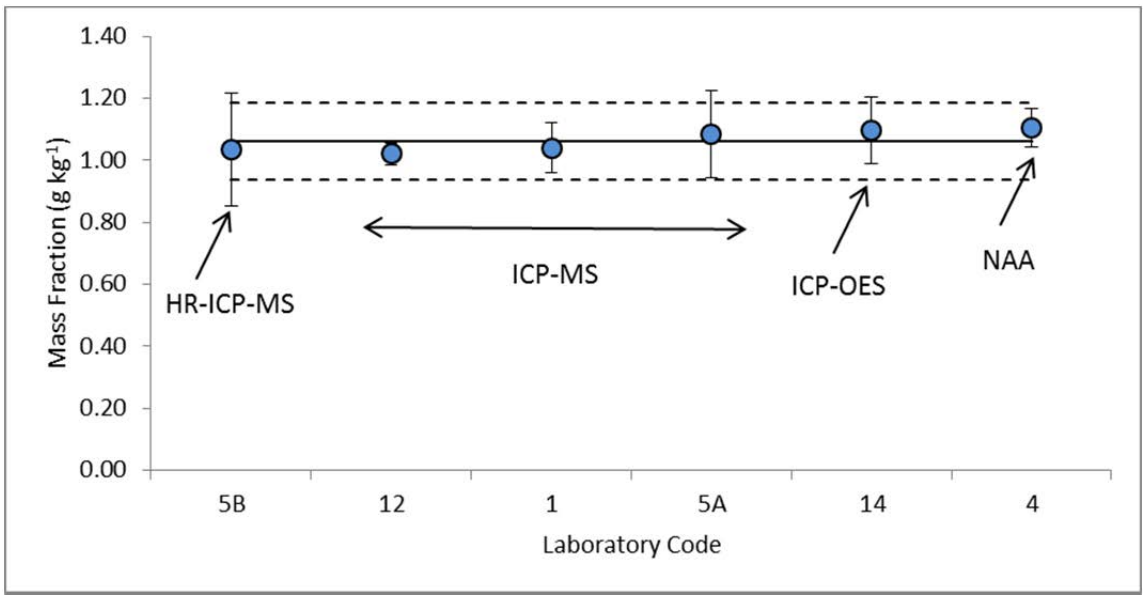

FIG. 39. Laboratory results for magnesium mass fraction (g kg^{-1}) in IAEA-436A.

TABLE 27. SODIUM: RESULTS AS REPORTED BY PARTICIPANTS (g kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
5B	1.37	0.50	NIST 1566B	HR-ICP-MS
1	1.42	0.14	IAEA-407	ICP-MS
12	1.50	0.04	LFB	ICP-MS
5A	1.53	0.30	NIST 1566B	ICP-MS
4	1.36	0.07	NIST 1566B	Neutron Activation
8A	1.56	0.11	NIST 1547	Neutron Activation

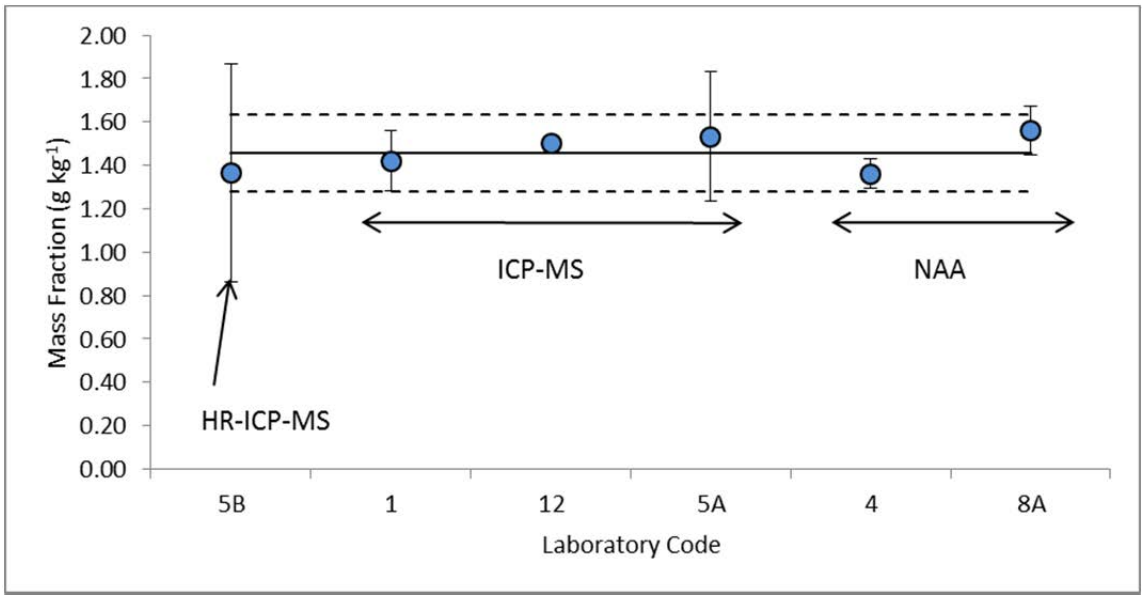

FIG. 40. Laboratory results for sodium mass fraction (g kg^{-1}) in IAEA-436A.

TABLE 28. NICKEL: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
12	0.058	0.032	DORM-3	ICP-MS
13B	0.075	0.015	IAEA-436	ICP-MS
15	0.078	0.023	TORT-2	ICP-MS

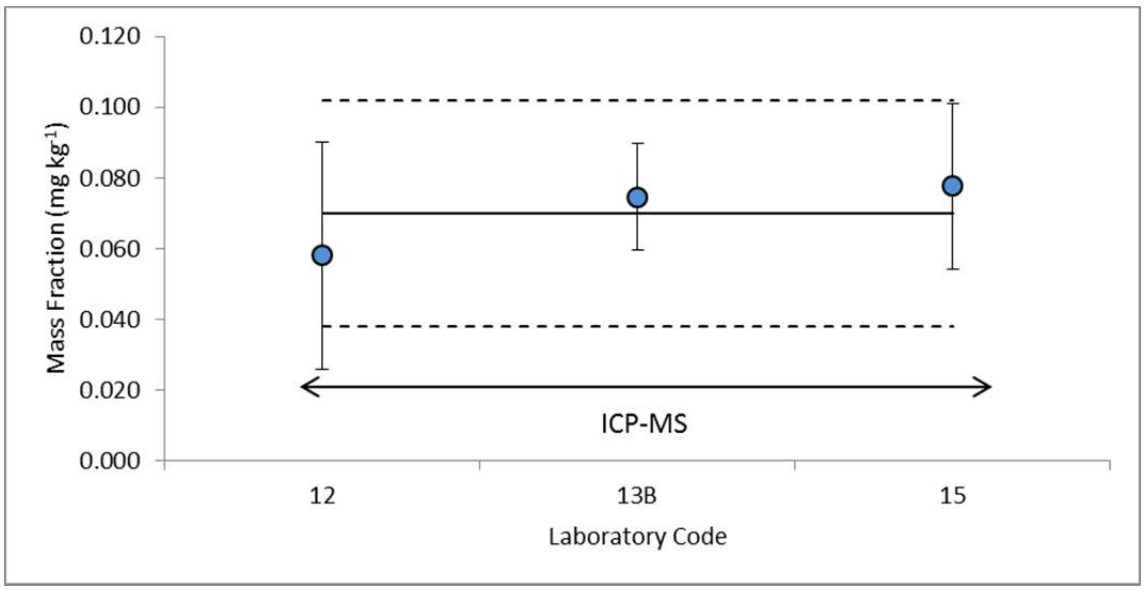

FIG. 41. Laboratory results for nickel mass fraction (mg kg^{-1}) in IAEA-436A.

TABLE 29. LEAD: RESULTS AS REPORTED BY PARTICIPANTS (mg kg^{-1})

Laboratory code	Mean	Expanded uncertainty (U)	CRM	Method
13A	0.012	0.001	DORM-2	HR-ICP-MS
13B	0.013	0.001	IAEA-436	ICP-MS

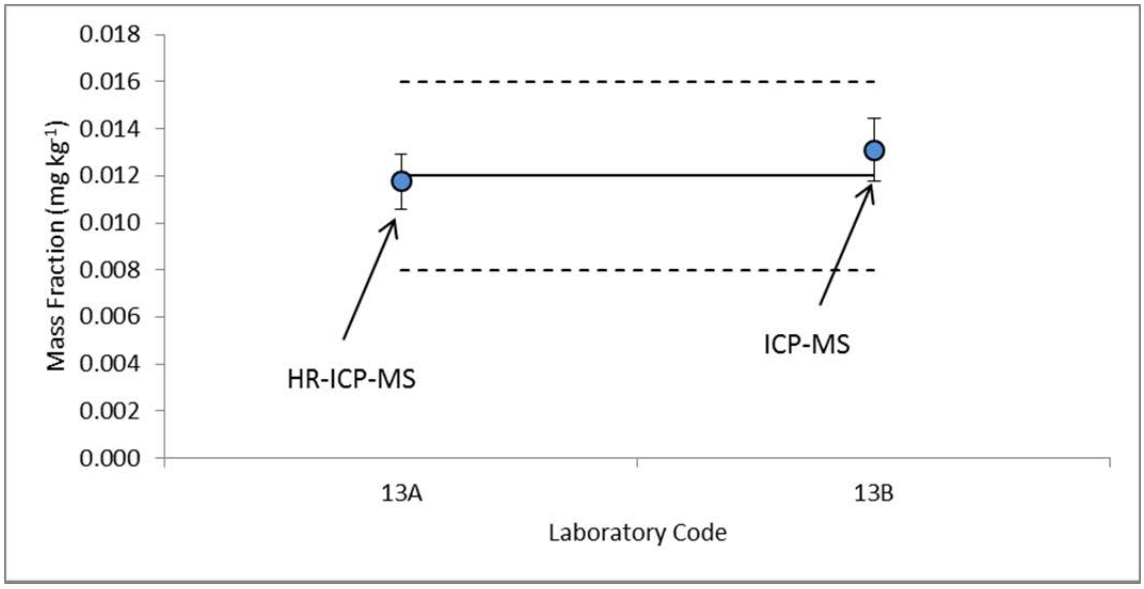

FIG. 42. Laboratory results for lead mass fraction (mg kg^{-1}) in IAEA-436A.

REFERENCES

[1] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO/IEC 17025. General requirements for the competence of testing and calibration laboratories, Geneva, 2005.

[2] INTERNATIONAL ATOMIC ENERGY AGERNCY, World-wide intercomparison exercise for the determination of trace elements and methylmercury in tuna fish flesh homogenate IAEA-436, IAEA, IAEA/AL/157, IAEA, Vienna (2006). https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Trace_Elements_Methylmercury/IAEA-436/IAEA_AL_157.pdf

[3] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Guide 34:2009, General requirements for the competence of reference material producers, ISO, Geneva (2009).

[4] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Guide 35:2006, Reference Materials – General and Statistical Principles for Certification, ISO, Geneva (2006).

[5] LINSINGER T., PAUWELS J., VAN DER VEEN A., SCHIMMEL H., LAMBERTY A., Homogeneity and stability of reference materials, Accredit. Qual. Assur. 6 1 (2001) 20–25.

[6] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO 13528:2005 (E), ISO, Geneva (2005).

[7] JOINT COMMITTEE FOR GUIDES IN METROLOGY (JGCM), Evaluation of measurement data – Guide to the expression of uncertainty in measurement, JGCM 100: 2008 (GUM with minor corrections), (2008).

LIST OF PARTICIPANTS

CANADA

Cram, J.	ALS Environmental (Vancouver) 8081 Lougheed Highway Suite 100 BURNABY BC - V5A 1W9
Flett, R.	Flett Research Ltd. 440 Desalaberry Ave Winnipeg MANITOBA R2L 0Y7
Franco, H.	ALS Environmental (Vancouver) 8081 Lougheed Highway Suite 100 BURNABY BC - V5A 1W9
Gilbert, D.	Flett Research Ltd. 440 Desalaberry Ave Winnipeg MANITOBA R2L 0Y7
Wei, X.	Flett Research Ltd. 440 Desalaberry Ave Winnipeg MANITOBA R2L 0Y7

FINLAND

Sara-Aho, T.	SYKE, Finnish Environment Institute Environmental Chemistry Research Hakuninmaantie 6 FI-00430 HELSINKI

INTERNATIONAL ATOMIC ENERGY AGENCY

Horsky, M.	IAEA Laboratories Seibersdorf Reaktorstrasse 1 A-2444 SEIBERSDORF
Azemard, S.	International Atomic Energy Agency 4 quai Antoine 1er 98000 MONACO
Vasileva, E.	International Atomic Energy Agency 4 quai Antoine 1er 98000 MONACO

ISRAEL

Herut, B.	Israel Oceanographic & Limnological Research, Tel Shikmona, P.O. Box 8030 31080 HAIFA
Kress, N.	Israel Oceanographic & Limnological Research, Tel Shikmona, P.O. Box 8030 31080 HAIFA
Shefer, E.	Israel Oceanographic & Limnological Research, Tel Shikmona, P.O. Box 8030 31080 HAIFA

PERU

Bedregal, P.	Instituto Peruano de Energía Nuclear Laboratorio de Técnicas Analíticas (TEAN) Av. Canadá 1470 SAN BORJA LIMA 41

SLOVENIA

Jacimovic, R.	Jozef Stefan Institute Dept. of Environmental Sciences Jamova cesta 39 1000 LJUBLJANA

UNITED KINGDOM

Fisher, A.	School of Geography, Earth and Environmental Science University of Plymouth Drake Circus PLYMOUTH, DEVON PL4 8AA

UNITED STATES OF AMERICA

Mc Farland, F.	Brooks Applied Labs 18804 North Creek Pkwy, Suit #100 Bothell WASHINGTON 98011

CONTRIBUTORS TO DRAFTING AND REVIEW

The following persons, contributed to the draft and review of this report:

E. Vasileva-Veleva	International Atomic Energy Agency
S. Azemard	International Atomic Energy Agency
L. Barilaro-Hamonic	International Atomic Energy Agency

The following persons, contributed to the review of the report:

A. Fajel	International Atomic Energy Agency
S. Tarjan	International Atomic Energy Agency
M. Horsky	International Atomic Energy Agency

IAEA
International Atomic Energy Agency

No. 25

ORDERING LOCALLY

In the following countries, IAEA priced publications may be purchased from the sources listed below or from major local booksellers.

Orders for unpriced publications should be made directly to the IAEA. The contact details are given at the end of this list.

CANADA

Renouf Publishing Co. Ltd

22-1010 Polytek Street, Ottawa, ON K1J 9J1, CANADA
Telephone: +1 613 745 2665 • Fax: +1 643 745 7660
Email: order@renoufbooks.com • Web site: www.renoufbooks.com

Bernan / Rowman & Littlefield

15200 NBN Way, Blue Ridge Summit, PA 17214, USA
Tel: +1 800 462 6420 • Fax: +1 800 338 4550
Email: orders@rowman.com Web site: www.rowman.com/bernan

CZECH REPUBLIC

Suweco CZ, s.r.o.

Sestupná 153/11, 162 00 Prague 6, CZECH REPUBLIC
Telephone: +420 242 459 205 • Fax: +420 284 821 646
Email: nakup@suweco.cz • Web site: www.suweco.cz

FRANCE

Form-Edit

5 rue Janssen, PO Box 25, 75921 Paris CEDEX, FRANCE
Telephone: +33 1 42 01 49 49 • Fax: +33 1 42 01 90 90
Email: formedit@formedit.fr • Web site: www.form-edit.com

GERMANY

Goethe Buchhandlung Teubig GmbH

Schweitzer Fachinformationen
Willstätterstrasse 15, 40549 Düsseldorf, GERMANY
Telephone: +49 (0) 211 49 874 015 • Fax: +49 (0) 211 49 874 28
Email: kundenbetreuung.goethe@schweitzer-online.de • Web site: www.goethebuch.de

INDIA

Allied Publishers

1st Floor, Dubash House, 15, J.N. Heredi Marg, Ballard Estate, Mumbai 400001, INDIA
Telephone: +91 22 4212 6930/31/69 • Fax: +91 22 2261 7928
Email: alliedpl@vsnl.com • Web site: www.alliedpublishers.com

Bookwell

3/79 Nirankari, Delhi 110009, INDIA
Telephone: +91 11 2760 1283/4536
Email: bkwell@nde.vsnl.net.in • Web site: www.bookwellindia.com

ITALY

Libreria Scientifica "AEIOU"

Via Vincenzo Maria Coronelli 6, 20146 Milan, ITALY
Telephone: +39 02 48 95 45 52 • Fax: +39 02 48 95 45 48
Email: info@libreriaaeiou.eu • Web site: www.libreriaaeiou.eu

JAPAN

Maruzen-Yushodo Co., Ltd

10-10 Yotsuyasakamachi, Shinjuku-ku, Tokyo 160-0002, JAPAN
Telephone: +81 3 4335 9312 • Fax: +81 3 4335 9364
Email: bookimport@maruzen.co.jp • Web site: www.maruzen.co.jp

RUSSIAN FEDERATION

Scientific and Engineering Centre for Nuclear and Radiation Safety

107140, Moscow, Malaya Krasnoselskaya st. 2/8, bld. 5, RUSSIAN FEDERATION
Telephone: +7 499 264 00 03 • Fax: +7 499 264 28 59
Email: secnrs@secnrs.ru • Web site: www.secnrs.ru

UNITED STATES OF AMERICA

Bernan / Rowman & Littlefield

15200 NBN Way, Blue Ridge Summit, PA 17214, USA
Tel: +1 800 462 6420 • Fax: +1 800 338 4550
Email: orders@rowman.com • Web site: www.rowman.com/bernan

Renouf Publishing Co. Ltd

812 Proctor Avenue, Ogdensburg, NY 13669-2205, USA
Telephone: +1 888 551 7470 • Fax: +1 888 551 7471
Email: orders@renoufbooks.com • Web site: www.renoufbooks.com

Orders for both priced and unpriced publications may be addressed directly to:

Marketing and Sales Unit
International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Telephone: +43 1 2600 22529 or 22530 • Fax: +43 1 2600 29302 or +43 1 26007 22529
Email: sales.publications@iaea.org • Web site: www.iaea.org/books

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA
ISSN 2074–7659