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CERTIFICATION REPORT

The certification of trace elements mass fraction in electrolytic copper: ERM®-EB074A, B and C

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Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)

Contact information
Reference materials sales
Address: Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium
E-mail: jrc-irmm-rm-sales@ec.europa.eu
Tel.: +32 (0)14 571 705

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Abstract
This report describes the production of ERM®-EB074A, B and C, a pure copper material with low level of added impurities certified for the mass fractions of Ag, As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb Sb, Se, Te, Ti and Zn. The material was produced following ISO Guide 34:2009 .
A melt is consisting of pure copper and alloy to obtain a copper material with added impurities. After casting, the material was processed by hot extrusion and cold machining to produce discs of 39 mm diameter (ERM-EB074A), cylinders of 8 mm diameter (ERM-EB074B) and chips of 250 mg (ERM-EB074C).
Between unit-homogeneity was quantified and stability during dispatch and storage were assessed following ISO Guide 35:2006. Within-unit homogeneity was quantified to determine the minimum sample intake.
The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically, invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM); the estimated total uncertainty includes uncertainties related to possible inhomogeneity, instability and characterisation.
The material is intended for use in the quality control and assessment of method performance. As any reference material, it can also be used for control charts or validation studies. The certified reference material (CRM) is available in three different formats:
- ERM-EB074A: disc of 39 mm diameter; 30 mm thick; packed in a a box
- ERM-EB074B: cylinder of 8 mm diameter; 100 mm length; sealed in a plastic sachets under vacuum
- ERM-EB074C: bottle of 50 g of chips; chip weight of approximately 250 mg

For ERM-EB074A, B and C, the minimum amount of sample to be used is 10 mg for Ag, As, Be, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, Se, Ti and Zn; 20 mg for Au, In and Te.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials Consortium.

CERTIFICATION REPORT

The certification of trace elements mass fraction in electrolytic copper: ERM®-EB074A, B and C

Thomas BACQUART, Thomas P.J. LINSINGER

European Commission, Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Geel, Belgium

Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM®-EB074A, B and C, a pure copper material with low level of added impurities certified for the mass fractions of Ag, As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb Sb, Se, Te, Ti and Zn. The material was produced following ISO Guide 34:2009 [1].

A melt is consisting of pure copper and alloy to obtain a copper material with added impurities. After casting, the material was processed by hot extrusion and cold machining to produce discs of 39 mm diameter (ERM-EB074A), cylinders of 8 mm diameter (ERM-EB074B) and chips of 250 mg (ERM-EB074C).

Between unit-homogeneity was quantified and stability during dispatch and storage were assessed following ISO Guide 35:2006 [2]. Within-unit homogeneity was quantified to determine the minimum sample intake.

The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025 [3]. Technically, invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4]; the estimated total uncertainty includes uncertainties related to possible inhomogeneity, instability and characterisation.

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For ERM-EB074A, B and C, the minimum amount of sample to be used is 10 mg for Ag, As, Be, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, Se, Ti and Zn; 20 mg for Au, In and Te.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following certified values were assigned for ERM-EB074A, B and C:

	Mass Fraction	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
Ag	1.03	0.07
As	1.23	0.08
Au	0.52	0.06
Be	0.31	0.06
Bi	0.51	0.04
Cd	0.40	0.04
Co	0.83	0.06
Cr	0.37	0.04
Fe	5.8	0.8
In	0.49	0.07
Mg	2.03	0.27
Mn	0.93	0.07
Ni	0.61	0.08
P	1.53	0.25
Pb	2.7	0.4
Sb	0.57	0.04
Se	0.55	0.07
Te	0.50	0.06
Ti	0.97	0.18
Zn	2.2	0.4

1) Unweighted mean value of the means of accepted sets of data each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of Units (SI).

2) The uncertainty of the certified value is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

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Glossary

AC	Alternating current
ASTM International	ASTM International (formerly American Society for Testing and Materials)
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
CEN	European Committee for Standardization
CI	Confidence interval
CRM	Certified reference material
DC	Direct current
EC	European Commission
EN	European norm (standard)
ERM®	Trademark of European Reference Materials
ETV	Electro-thermal vaporisation
EU	European Union
GD	Glow discharge
GUM	Guide to the Expression of Uncertainty in Measurements [4]
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma-mass spectrometry
IGF	Inert gas fusion
INAA	Instrumental neutron activation analysis
IR	Infra-red
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0-NAA	k_0-Neutron activation analysis
LA	Laser ablation
LOD	Limit of Detection
MS	Mass spectrometry
$MS_{between}$	Mean of squares between-unit from an ANOVA
SDS	Safety data sheet
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
n.d.	Not detectable
NIST	National Institute of Standards and Technology (USA)
OES	Optical emission spectrometry
QC	Quality control
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate

SI	International System of Units
s_{meas}	Standard deviation of measurement data; an additional index "rel" is added as appropriate
s_{ns}	Standard deviation of results of normal stock samples
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
$t_{\alpha, df}$	Critical *t*-value for a *t*-test, with a level of confidence of 1-α and df degrees of freedom
u	Standard uncertainty
U	Expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate
u_{Δ}	Combined standard uncertainty of measurement result and certified value
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{rec}	Standard uncertainty related to possible between-unit inhomogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate
u_t	Standard uncertainty of trueness
VIM	Vacuum induction melting
VIDP	Vacuum induction degassing pouring
$\overline{X}$	Arithmetic mean
$\overline{X}_{ns}$	Arithmetic mean of all results of normal stock samples
$\overline{X}_{ref}$	Arithmetic mean of results of reference samples
α	Significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s,meas}$	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

Copper is essential for humans in their daily life and industry. Copper was one of the first metals ever extracted and used by humans (e.g. coins, ornaments) and one of the first alloying metal with zinc (brass), aluminium and tin (bronze) [5]. Copper is important to the development of human civilisation (e.g. Bronze Age).

Currently, copper is present in various sectors and industries: building construction, power generation and transmission, electronic product manufacturing, production of industrial machinery and the transportation sector [6]. Its relevance is due to its physical (ductility) and chemical properties (excellent thermal and electrical conductivity, corrosion resistance) [7] its high antimicrobial activity [8].

Copper is traded internationally; production and transformation of copper (from cathode to semi-finished product and final production) are widespread geographically. The demand for refined copper was estimated to be 0.5 million tons in 1900 and was 20 million tons in 2012 [5]. The copper market is an important globalised market, which drives the need for international standardisation.

Depending on the commodity exchange, the chemical composition of electrolytic copper cathode is defined according to three standards: EN 1978:1998 (Cu-CATH-1) [9], GB/T 467-2010 (Cu-CATH-1) [10] and ASTM B115-10 (cathode Grade 1) [11]. These require the determination of 12 to 18 elements which should, alone or in groups of a few elements, not exceed upper limits of a few mg/kg: Ag, As, Bi, Cd, Co, Cr, Fe, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te and Zn [9-11].

The price of copper is established as a function of the impurity levels, the premium being paid for very low levels and penalties for high levels.

As the analyses of impurities at these very low levels are subject to many possibilities of error, the industry has a strong need for reliable certified reference materials to ensure the quality and the accuracy of their measurements.

To support the industry, two CRMs for trace elements in copper were produced in 1992 within the scope of the European Commission's BCR-programme. The two CRMs (BCR-074 and BCR-075 [12]) are close to exhaustion and need replacement.

In addition to the elements required by the various standards, eleven elements (Al, Au, Be, H, Hg, In, Mg, O, Ti, W and Zr) were found to be of interest for copper industry and quality control laboratories involved in copper trade. These elements were considered relevant for the certification or as indicative values and were included in the scope of the project.

1.2 Choice of the material

ERM-EB074 is produced from pure copper with the addition of low-level impurities. The addition of impurities permits achieving pre-defined levels of trace elements more easily. These levels of trace elements were chosen to below the limits set in the international standards. The levels of trace elements are similar to those of the nearly exhausted CRM for trace elements in electrolytic copper: BCR-074 [12].

The material was produced in three different formats in compliance with the various analytical methods used by industry:

ERM-EB074A: discs of 39 mm diameter were designed for solid sampling techniques (e.g. spark optical emission spectrometry (spark-OES) or glow discharge mass spectrometry (GD-MS)),

ERM-EB074B: cylinders of 8 mm diameter were designed for solid sampling techniques (e.g. GD-MS) and analysis after acid dissolution,

ERM-EB074C: chips of approximately 250 mg were designed for solid sampling techniques (e.g. direct current arc optical emission spectrometry (DC-arc-OES)) and analysis after acid dissolution.

1.3 Design of the project

After processing, homogeneity of the materials was evaluated in a dedicated study of each material format using different techniques. The homogeneity results of the three formats were finally pooled to obtain an overall uncertainty. The stability was assessed using a similar existing material. The certification was performed using an interlaboratory comparison. The results showed no difference between the three formats, so one single value for each element for all three formats could be assigned.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

Luvata Pori Oy, Pori, FI

Wieland-Werke, Ulm, DE

2.3 Homogeneity study

Alfred H Knight International Ltd, St Helens, UK

Evans Analytical Group SAS, Tournefeuille, FR

Umicore Analytical competence center, Olen, BE

Umicore Analytical Competence Center, Hanau-Wolfgang, DE

2.4 Characterisation

Activation Laboratories Ltd., Ancaster, CA
(measurements performed under the scope of ISO/IEC 17025 accreditation, SCC No. 266)

Aurubis AG, Hamburg, DE

Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin, DE
(measurements performed under the scope of ISO/IEC 17025 accreditation, DAkkS No. DP-L-11075-14-00)

CCR affinerie, Montreal, CA

Evans Analytical Group LLC, Liverpool, NY, US

Evans Analytical Group SAS, Tournefeuille, FR

Institut "Jozef Stefan" (IJS), Department of Environmental Sciences, Ljubljana, SI
(measurements performed under the scope of ISO/IEC 17025 accreditation, Slovenska Akreditacija-LP090)

Laboratory Testing Inc., Hatfield, US
(measurements performed under the scope of ISO/IEC 17025 accreditation, A2LA No. 0117.05)

National Research Council Canada, Ottawa, CA
(measurements performed under the scope of ISO/IEC 17025 accreditation, SCC No. 474)

Umicore Analytical Competence Center, Olen, BE

Umicore Analytical Competence Center, Hanau-Wolfgang, DE

Studiecentrum voor Kernenergie, SCK, Mol, BE
(measurements performed under the scope of ISO/IEC 17025 accreditation; BELAC No. 015-TEST)

TU Delft, Delft, NL
(measurements performed under the scope of ISO/IEC 17025 accreditation; Rva L049)

Ultra Traces Analyses Aquitaine (UT2A), Pau, FR

3 Material processing and process control

3.1 Origin/Purity of the starting material

The starting materials were pure copper (purity > 99.999 %) from Luvata Pory Oy (Pori, FI), pure metals (Ag, Al, Au, In, Ni, Pb, Sb, Sn and Zn; purity > 99.7 %) and copper master alloys (CuAs30, CuBe4, CuBi2, CuCd50, CuCo15, CuCr10, CuFe20, CuMg20, CuMn50, CuP10, CuS20, CuSe37, CuSi10, CuTe50, CuTi30, CuZr50; purity > 99.5 %) from Wieland Werke (Ulm, DE). The specifications of the starting material complied with international standards EN 1981: 2003 [13]) and were documented in certificates of analysis from producers.

3.2 Processing

The production of ERM-EB074A, B and C was done in two steps:

- Melting and casting of copper rods with added impurities,

- Extrusion of copper billets and mechanical processing into final dimensions.

Melting and casting of copper with added impurities and the first extrusion into rods was realised by Wieland-Werke (Ulm, DE). The rods were then processed into their final shape by Luvata Pori Oy (Pori, FI). The production scheme is detailed in Figure 1.

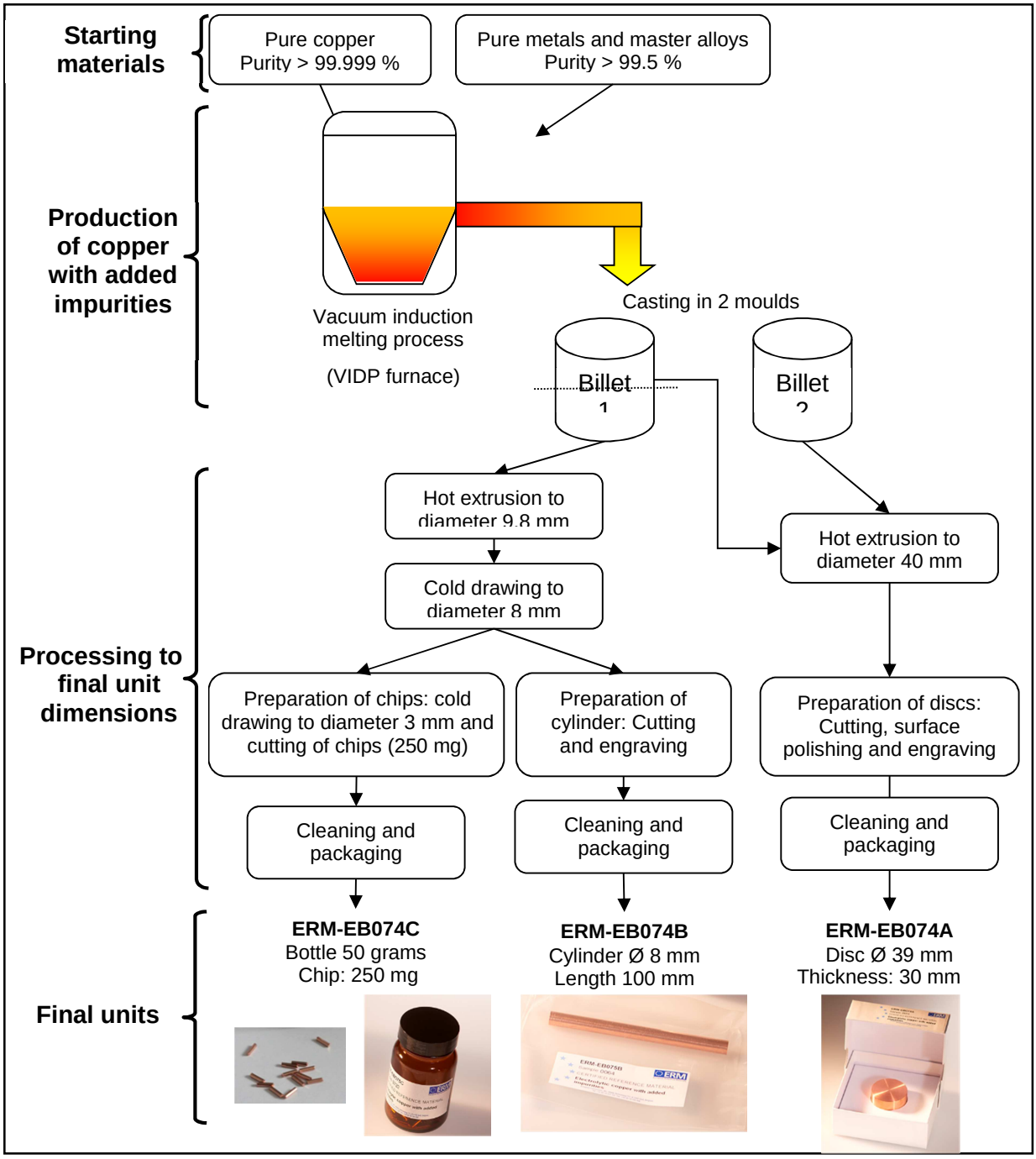

Figure 1: Processing scheme of ERM-EB074A, B and C

3.2.1 Melting and casting of copper billets with added impurities

The first step of the production was obtaining a homogeneous melt of pure copper with the added impurities by Wieland-Werke (Ulm, DE) by vacuum induction melting (VIM), a technique for melting metal via electromagnetic induction under vacuum. An induction furnace containing an electrographite crucible surrounded by an induction coil is located inside a vacuum chamber. The induction furnace is connected to an AC power source at a frequency that is precisely correlating to the furnace size and the material being melted.

The advantages of VIM are:

- Homogeneous distribution of chemical elements in the material due to constant stirring of the molten metal during melting and casting;

- Limitation of non-metallic oxide inclusions. Melting under vacuum helps to limit metal reactivity with atmospheric oxygen;

- Precise adjustment of alloy composition, since the temperature, vacuum, gas atmosphere, pressure and material transport (e.g. through stirring of the bath) can be adjusted independently of one another.

The VIM technique produces a highly homogenous melt and allows casting of materials with controlled composition. The crucible used for melting was a dedicated electrographite crucible, which mitigates the risk of metallic contamination.

Approximately 2.2 tons of copper were charged into the electrographite crucible in the vacuum induction degassing pouring furnace (VIDP furnace) under vacuum (10^{-1} – 10^{-2} mbar). The molten metal composition was then adjusted using the different pure metals and master alloys until the precise melt chemistry was achieved. The manufactuer performed a single analysis to verify the composition before casting. After verification, two copper billets were cast in two different moulds.

3.2.2 Extrusion of copper billets and mechanical processing into final dimensions

The two copper billets were dispatched for the production of ERM-EB074A, B and C by hot extrusion and mechanical machining.

ERM-EB074A: Production of discs

One and a half billets were dedicated to the production of ERM-EB074A (discs with a diameter of 39 mm). Each billet was first cut into two parts, and hot extruded to a final diameter of 40 mm by Wieland-Werke (Ulm, DE). The three last rods had a length of nine meters; they were labelled and cut into three parts for further processing.

From the nine last rods (diameter: 40 mm; length: 3 m), 7 rods were selected for final processing by Luvata Pori Oy (Pori, FI). The rods were cut to 30 mm length and polished (on all surfaces), the final diameter after polishing is 39 mm. The discs were engraved mechanically on the curved surface with “74-XXX”. The code “74-XXX” corresponds to the material ID (74 stands for ERM-EB074) and the unit number (XXX). Then, the discs were degreased, cleaned with deionised water, dropped into 2-propanol / isopropanol and dried. Finally, the discs were visually checked at IRMM and packed in individual cardboard boxes.

ERM-EB074B and C: production of cylinders and chips

A half billet was dedicated to the production of ERM-EB074B and C. The half billet was hot extruded to diameter of 9.8 mm and then processed to 8 mm diameter using cold drawing by Wieland-Werke (Ulm, DE). In total, 61 rods were obtained with a diameter of 8 mm and a length of 3 m.

Thirty-five rods were selected after analysis of Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn and Zr by GD-MS (one GD-MS analysis per rod) and rods with grossly deviating values were excluded from further processing (Section 3.3). Nine rods were randomly selected for the production of ERM-EB074B and 26 rods for the production of ERM-EB074C.

For ERM-EB074B, the nine selected rods were cut into cylinders of 100 mm length and engraved mechanically with the code “74-XXX” by Luvata Pori Oy (Pori, FI). Afterwards, the cylinders were degreased, cleaned with deionised water, dropped into 2-propanol /

isopropanol and dried. The final batch of cylinders was visually checked at IRMM and packed into plastic sachets sealed under vacuum.

For ERM-EB074C, the 26 selected rods were processed to 3 mm diameter using cold drawing by Luvata Pori Oy (Pori, FI). The material obtained was cut into pieces of 250 mg (with a relative tolerance of 3 %). The pieces were grouped per rods (~ 5200 pieces per rod) and followed a cleaning process (degreasing, cleaning with deionised water, rinsing with 2-propanol / isopropanol and drying). Finally, 50 g of chips were placed into cleaned amber glass bottles, flushed with inert gas (Ar) and closed.

The final products were:

ERM-EB074A: 550 units. Each unit is a disc of 39 mm diameter with thickness of 30 mm;

ERM-EB074B: 240 units. Each unit is a cylinder of 8 mm diameter with length of 100 mm;

ERM-EB074C: 675 units. Each unit is a bottle containing 50 g of chips. Each chip has a mass of approximately 250 mg.

3.3 Process control

Several controls of the composition and the homogeneity of trace elements in copper in the semi-finished products were realised by the manufacturer during the melting (one composition analysis by GD-MS) and after casting of the two billets (one GD-MS analysis on the top and bottom of each billet). No major element inhomogeneity was observed by the measurements.

Before processing the 8 mm rods into their final formats ERM-EB074B and C, one GD-MS analysis was performed on every 8 mm rod for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn and Zr by GD-MS (data not shown). The objective was to select the thirty-five 8 mm rods for the production of ERM-EB074B and C and to exclude outlying values and extreme values (highest and lowest values for each element).

Visual control was done for each unit during the packaging. A few units were excluded due to major scratches or unclear engraving.

The segregation between billets is a source of inhomogeneity in metal production; the different processing steps could be another source of difference between the formats A, B and C. It was studied during the process control (data not shown) and it is detailed in Section 4.1.2.

4 Homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value. It is not relevant if the variation between-units is significant compared to the analytical variation. Consequently, ISO Guide 34 requires RM producers to quantify the between-unit variation. This aspect is covered in between-unit homogeneity studies.

Production of metallic CRMs requires extensive homogeneity test since several inhomogeneity sources have to be taken into account:

- Trend or segregation within billet: during the casting some elements are known to segregate within the billet, e.g., lead in copper. The trend or segregation within billet was tested using ERM-EB074A units from one billet (Section 4.1.2). The outcome of the study is considered to be similar for all billets as they were melted and cast under the same conditions.

- Between-billet homogeneity (Section 4.1.3): the final material is composed of two casted billets that may show differences due to the melting or casting process (i.e. inhomogeneity of the melt, delay in casting) for some elements (see Section 3.3.2). Between-billet homogeneity was studied using a large number of ERM-EB074A units from the two billets.

- Between-unit homogeneity (Section 4.1.4).

- Within-unit inhomogeneity is essential for solid sampling techniques (e.g., GD-MD, spark-OES). These techniques use tiny sample intake and are subject to differences due to the aliquot location (radial homogeneity on discs; Section 4.2.1) and to the sample intake (minimum sample intake).

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

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values are valid for all units of the material, within the stated uncertainty.

4.1.1 Study setup

The between-unit homogeneity study was performed for each format independently using an appropriate analytical method (Table 2). This approach allows coherence among the intended use, homogeneity estimation and the minimum sample intake.

The within-billet homogeneity and the between-billet homogeneity were evaluated using results on the ERM-EB074A units (Table 2). The evaluation of these three studies was necessary to select the most appropriate uncertainty estimation (s_{bb}, u^*_{bb} or u_{rec}).

35 units of ERM-EB074A, 27 units of ERM-EB074B and the 29 bottles of ERM-EB074C were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch was divided into 27, 29 or 35 groups (with a similar number of units) and one unit was selected randomly from each group.The number of selected units (35 units for ERM-EB074A, 27 units for ERM-EB074B and 29 bottles for ERM-EB074C) corresponds to more than 3.8 % of the production of each format (more than the cubic root of the total number of the produced units) and is considered sufficient to represent a lot/batch consisting of large number of units for which it is impractical to test 8 % of the units as recommended in ASTM E826 [14].

Four independent aliquots for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr and three independent aliquots for O were taken from each selected unit, and analysed by glow discharge mass spectroscopy and by inert gas fusion with IR detection for ERM-EB074A and B. For ERM-EB074C, four independent aliquots for As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, Sb, Se, Sn, Te, Ti and W and three independent aliquots for O and S were taken from each selected unit, and analysed by ICP-MS, ICP-OES (for Ag, Al, Si, Zn and Zr), by inert gas fusion with IR detection (O) and by combustion with IR detection (S). A summary of the study is given in Table 2.

Table 2: Summary of the homogeneity study.

Material format	Within-billet homogeneity study Number of units selected	Between-unit homogeneity study Number of units selected	Elements	Techniques	Number of replicates / Number of analytical runs
ERM-EB074A	1 billets 15 discs	35 discs (15-20 discs per production billet)	Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr	GD-MS	4 / 4
			O	IGF-IR	3 / 3
ERM-EB074B	n.a.	27 cylinders	As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, W	GD-MS	4 / 4
			O	IGF-IR	3 / 3
ERM-EB074C	n.a.	29 bottles	Ag, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	4 / 4
			Ag, Al, Si, Zn, Zr	ICP-OES	4 / 4
			O	IGF-IR	3 / 3
			S	Combustion-IR	3 / 3

The measurements were performed in a randomised block design because the number of replicates on all units (81 - 140 analyses) could not be included in a single run due to instrumental constraints (drift towards the end of a long run, time of analysis). Improved precision (measured as the within-unit standard deviation) was obtained using several short runs in a randomised block design compared to the one achieved in a single run with 81 to 140 analyses.

The design applied consisted of three to four measurement sequences, each comprising a single measurement on each unit. The order of units in each run was randomised individually for each sequence to separate a potential analytical drift from a trend in the processing sequence.

A two-way analysis of variance without replication was used to estimate the within- and between-unit standard deviations independently any potential analytical sequence effect.

For two elements (Hg and W), the results in all units were reported below the detection limit of the method (0.01 mg/kg). The data treatment was not applied to these two elements.

For Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn, Zr, the data evaluation was performed in the following order:

1 – Trends in analytical run / correction for significant trends

Regression analyses were performed to evaluate potential trends in each analytical run. Some significant (95 % confidence level) trends in the analytical sequence were visible; indicating a signal drift in the analytical system (Tables 3-5). The correction of biases, even if they are statistically not significant, allows the combination of the smallest uncertainty with the highest probability to cover the true value [11]. Correction of trends was therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant at 95 % confidence level were corrected as described in equation 1.

$$x_T(r,i) = x(r,i) - b(r) \cdot i$$ **Equation 1**

i position of the result in the analytical run

r number of the analytical run from 1 to 4

b(r) slope of the linear regression for the analytical run *r*

x(r,i) measurement results on the position *i* in the analytical run *r*

$x_T(r,i)$ corrected results for analytical trend in the position *i* in the analytical run *r*

2 – Evaluation of between-analytical run effect / Normalisation of dataset (if necessary)

The analytical trend-corrected dataset was evaluated for significant differences between analytical runs (95 % confidence level) using one-way ANOVA. Significant differences between analytical runs were observed on the 95 % confidence level for all elements in ERM-EB074A (except O) in ERM-EB074B (except for Cr, Fe, Si and Zr) and for Al, As, Au, Bi, Co, Fe, Mn, Ni, Sb, Se, Si, Zn, Zr in ERM-EB074C (Tables 3-5). As it is assumed that run effects and unit effects are independent, the differences between analytical runs on 95 % confidence level were normalised as described in equation 2.

$$x_R(r,i) = \frac{x_T(r,i)}{\bar{x}_T(r)} \times \bar{x}_T$$ **Equation 2**

i position of the result in the analytical run

r number of the analytical run from 1 to 4

$\bar{x}_T$ mean results of all the analytical runs

$\bar{x}_T(r)$ mean results of the analytical run *r* after correction for the trend in analytical sequence (if necessary)

$x_T(r,i)$ corrected results for analytical trend on the position *i* in the analytical run *r*

$x_R(r,i)$ normalised results on the position *i* in the analytical run *r*

3 – Statistical evaluation of the datasets

The normalised datasets were tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results, and the unit means (Tables 3-5). The unit means for ERM-EB074A, B and C are presented graphically in Annex A.

Table 3: Results of the statistical evaluation of the homogeneity studies of ERM-EB074A; *n* = number of outliers; *T* = number of series with an analytical trend.

ERM-EB074A	Analytical trends	Between analytical run difference Tested with one way ANOVA	Outliers at 99% confidence level		Distribution	
Analyte	Significant at 95% confidence level (*T*)	Significant difference at 95% confidence level (F-test)	Unit means (n)	Individual results (n)	Unit means	Individual results
Ag	Yes (1)	Yes	Yes (1)	No	bimodal	bimodal
Al	No	Yes	No	Yes (1)	unimodal	unimodal
As	Yes (2)	Yes	No	No	unimodal	unimodal
Au	Yes (3)	Yes	No	No	unimodal	unimodal
Be	Yes (1)	Yes	No	No	unimodal	unimodal
Bi	Yes (3)	Yes	No	Yes (1)	unimodal	unimodal
Cd	No	Yes	No	Yes (1)	unimodal	unimodal
Co	Yes (2)	Yes	No	No	bimodal	bimodal
Cr	Yes (4)	Yes	No	No	bimodal	bimodal
Fe	Yes (3)	Yes	No	No	bimodal	bimodal
In	Yes (2)	Yes	No	Yes (1)	unimodal	unimodal
Mg	Yes (3)	Yes	No	No	unimodal	unimodal
Mn	Yes (1)	Yes	No	No	bimodal	bimodal
Ni	Yes (1)	Yes	No	No	bimodal	bimodal
O	No	No	No	Yes (2)	bimodal	bimodal
P	Yes (4)	Yes	No	No	unimodal	unimodal
Pb	Yes (3)	Yes	No	Yes (1)	bimodal	bimodal
S	Yes (1)	Yes	No	No	bimodal	bimodal
Sb	Yes (3)	Yes	No	No	unimodal	unimodal
Se	Yes (2)	Yes	No	No	unimodal	unimodal
Si	Yes (1)	Yes	No	No	bimodal	bimodal
Sn	No	Yes	No	No	bimodal	bimodal
Te	Yes (2)	Yes	No	No	unimodal	unimodal
Ti	Yes (3)	Yes	No	Yes (2)	unimodal	unimodal
Zn	Yes (2)	Yes	No	No	bimodal	bimodal
Zr	Yes (4)	Yes	No	Yes (1)	unimodal	unimodal

Table 4: Results of the statistical evaluation of the homogeneity studies of ERM-EB074B; *n* = number of outliers; *T* = number of series with an analytical trend.

ERM-EB074B	Analytical trends	Between analytical run difference Tested with one way ANOVA	Outliers at 99% confidence level		Distribution	
Analyte	Significant at 95% confidence level (T)	Significant difference at 95% confidence level (F-test)	Unit means (n)	Individual results (n)	Unit means	Individual results
Ag	Yes (1)	Yes	No	No	unimodal	unimodal
Al	No	Yes	No	Yes (1)	unimodal	unimodal
As	Yes (1)	Yes	No	No	unimodal	unimodal
Au	Yes (1)	Yes	No	No	unimodal	unimodal
Be	Yes (1)	Yes	No	No	unimodal	unimodal
Bi	Yes (1)	Yes	No	No	unimodal	unimodal
Cd	No	Yes	No	No	unimodal	unimodal
Co	Yes (4)	Yes	No	No	unimodal	unimodal
Cr	Yes (4)	No	No	No	unimodal	unimodal
Fe	Yes (2)	No	No	Yes (1)	unimodal	unimodal
In	Yes (1)	Yes	No	No	unimodal	unimodal
Mg	Yes (1)	Yes	No	No	unimodal	unimodal
Mn	Yes (3)	Yes	No	No	unimodal	unimodal
Ni	Yes (3)	Yes	No	No	unimodal	unimodal
O	Yes (1)	Yes	No	No	unimodal	unimodal
P	Yes (1)	Yes	No	No	unimodal	unimodal
Pb	Yes (1)	Yes	Yes (1)	No	unimodal	unimodal
S	No	Yes	No	No	unimodal	unimodal
Sb	Yes (3)	Yes	No	No	unimodal	unimodal
Se	Yes (1)	Yes	No	Yes (1)	unimodal	unimodal
Si	No	No	Yes (1)	Yes (1)	unimodal	unimodal
Sn	No	Yes	No	No	unimodal	unimodal
Te	Yes (2)	Yes	No	No	unimodal	unimodal
Ti	Yes (3)	Yes	No	Yes (1)	unimodal	unimodal
Zn	Yes (1)	Yes	No	No	unimodal	unimodal
Zr	Yes (3)	No	No	Yes (1)	unimodal	unimodal

Table 5: Results of the statistical evaluation of the homogeneity studies of ERM-EB074C; *n* = number of outliers; *T* = number of series with an analytical trend.

ERM-EB074C	Analytical trends	Between analytical run difference Tested with one way ANOVA	Outliers at 99% confidence level		Distribution	
Analyte	Significant at 95% confidence level (T)	Significant difference at 95% confidence level (F-test)	Unit means (n)	Individual results (n)	Unit means	Individual results
Ag	No	No	No	No	unimodal	unimodal
Al	Yes (1)	Yes	Yes (1)	Yes (1)	unimodal	unimodal
As	No	Yes	No	No	unimodal	unimodal
Au	Yes (1)	Yes	No	Yes (1)	unimodal	unimodal
Be	Yes (1)	No	No	No	unimodal	unimodal
Bi	Yes (1)	Yes	No	Yes (2)	unimodal	unimodal
Cd	Yes (1)	No	No	No	unimodal	unimodal
Co	No	Yes	No	No	unimodal	unimodal
Cr	No	No	No	Yes (1)	unimodal	unimodal
Fe	No	Yes	Yes (1)	Yes (1)	unimodal	unimodal
In	No	No	No	No	unimodal	unimodal
Mg	No	No	No	Yes (1)	unimodal	unimodal
Mn	No	Yes	No	No	unimodal	unimodal
Ni	No	Yes	No	No	unimodal	unimodal
O	Yes (1)	No	No	No	unimodal	unimodal
P	No	No	No	No	unimodal	unimodal
Pb	No	No	Yes (1)	Yes (1)	unimodal	unimodal
S	No	No	No	No	unimodal	unimodal
Sb	No	Yes	No	No	unimodal	unimodal
Se	No	Yes	No	Yes (1)	unimodal	unimodal
Si	No	Yes	No	No	unimodal	unimodal
Sn	No	No	No	No	unimodal	unimodal
Te	No	No	No	Yes (1)	unimodal	unimodal
Ti	No	No	No	No	unimodal	unimodal
Zn	Yes (1)	Yes	No	No	unimodal	unimodal
Zr	No	Yes	No	Yes (1)	unimodal	unimodal

No outlying means were detected at the 99 % confidence level except for Ag mass fraction in ERM-EB074A, for Pb and Si mass fraction in ERM-EB074B and for Al, Fe and Pb mass fraction in ERM-EB074C. Some outlying individual results were detected. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

4.1.2 Evaluation of the trend or segregation within-billet

The normalised datasets of ERM-EB074A study were used to detect significant trend within-billet. Fifteen units of ERM-EB074A were selected using a random stratified sampling scheme covering half billet for the within-billet homogeneity test. Regression analyses were performed using these 15 units to evaluate potential trends within-billet. No outlying means were detected at the 99 % confidence level in the datasets used for within-billet homogeneity study.

Regression analyses were performed using these nine units to evaluate potential trends within the billet. No trends in the billet were visible on the 95 % confidence level for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, O, P, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr. A significant trend within billet was detected for Pb on the 95 % confidence level.

For Pb , where the trend in the billet (segregation) was significant at the 95 % confidence level, the uncertainty was assessed in a different way. Here, u_{rec} was estimated using a rectangular distribution between the highest and lowest unit mean. The corrected uncertainty in those cases where there was a significant trend in the filling sequence is given in Equation 3.

$$u_{rec,rel} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot \bar{y}} \qquad \textbf{Equation 3}$$

$\bar{y}$ mean of all results of the homogeneity study

This applies for Pb for ERM-EB074A, B and C.

4.1.3 Between-billet inhomogeneity quantification for ERM-EB074A

ERM-EB074A was the only format produced using different billets (two billets). The Significance of the between-billet difference was evaluated using the results of the ERM-EB074A homogeneity study.

In the ERM-EB074A homogeneity study, 15 and 20 units were selected from each of the two billets. Quantification of between billet inhomogeneity was accomplished using the analytical trend corrected dataset by the mean of a two-way ANOVA. A two-way ANOVA can separate the between-run variation (s_R), the between-billet variation ($s_{bb,billet}$) and the within-billet variation ($s_{wb,billet}$). An F-test was used to determine if the variance due to the billets is significant on a 95 % confidence level. For Ag, Co, Cr, Fe, Mn Ni, O, Pb, S, Si, Sn and Zn, the difference between billets was significant. The data do not follow a unimodal distribution for Ag, Co, Cr, Fe, Mn Ni, O, Pb, S, Si, Sn and Zn mass fraction in ERM-EB074A. Therefore, $u_{rec,rel}$ was estimated using a rectangular distribution between the highest and lowest unit mean [12]. The uncertainty in those cases is given as

$$u_{rec,rel} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot \bar{y}} \qquad \textbf{Equation 4}$$

$\bar{y}$ mean of all results of the homogeneity study

The results of these evaluations are listed in Table 6.

4.1.4 Between-unit inhomogeneity quantification

Quantification of between-unit inhomogeneity was accomplished using the analytical trend corrected dataset by two-way ANOVA, which can separate the between-run variation (s_R), the between-unit variation (s_{bb}) and the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative of the whole unit.

Evaluation by ANOVA requires unit means that follow at least a unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations.

Recall that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and, therefore, subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), 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 inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [15]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Analysis of variance applied to a randomised block design with one observation per unit per run leads to a between-run mean square MS_R together with a between-unit mean square $MS_{between}$, and a residual mean square MS_{within}. The residual mean square MS_{within} is an unbiased estimate of the repeatability variance s_r^2. The between-unit standard deviation s_{bb} is calculated as described in equation 5. Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}}$$ **Equation 4**

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}}$$ **Equation 5**

$$u^{*}_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}}$$ **Equation 6**

MS_{within} mean square within a unit from an ANOVA

$MS_{between}$ mean squares between-unit from an ANOVA

$\bar{y}$ mean of all results of the homogeneity study

n number of analytical runs

$v_{MSwithin}$ degrees of freedom of MS_{within}

For ERM-EB074A, the homogeneity study showed unimodal distribution and no outlying unit means or trends within-billet for As, Al, Au, Be, Bi, Cd, In, Mg, P, Sb, Se, Te, Ti and Zr. Therefore, the between-unit standard deviation can be used as estimate of u_{bb}. As u^{*}_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^{*}_{bb} is adopted as the uncertainty contribution to account for potential inhomogeneity.

For ERM-EB074B and C, the homogeneity study showed unimodal distribution, no outlying unit means or trends within-billet for all elements except the Pb and Si mass fraction in ERM-EB074B and the Al, Fe and Pb mass fraction in ERM-EB074C. Therefore, the between-unit standard deviation can be used as estimate of u_{bb}. As u^{*}_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^{*}_{bb} is adopted as the uncertainty contribution to account for potential inhomogeneity.

However, a different approach was adopted for the Ag mass fraction of ERM-EB074A, for the Pb and Si mass fractions of ERM-EB074B and for the Al, Fe and Pb mass fractions of ERM-EB074C for which one outlying unit mean was detected. In these cases between-unit inhomogeneity was modelled as a rectangular distribution limited by the largest outlying unit mean, and the rectangular standard uncertainty of homogeneity was estimated by:

$$u_{rec} = \frac{\left|outlier - \bar{y}\right|}{\sqrt{3} \cdot \bar{y}}$$ **Equation 7**

$\bar{y}$ mean of all results of the homogeneity study

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

The results of the evaluation of the between-unit variation in ERM-EB074A, B and C are summarised in Tables 6-8. The resulting values from the above equations were converted into relative uncertainties.

Table 6: Results of the homogeneity study of ERM-EB074A

ERM-EB074A	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Ag	2.76	0.63	0.52	2.06	2.06
Al	7.43	3.23	1.40	n.a. [2)]	3.23
As	3.83	0.29	0.72	n.a. [2)]	0.72
Au	3.07	0.57	0.58	n.a. [2)]	0.58
Be	11.71	3.60	2.19	n.a. [2)]	3.60
Bi	6.62	n.c. [1)]	1.24	n.a. [2)]	1.24
Cd	5.50	0.95	1.03	n.a. [2)]	1.03
Co	2.54	1.07	0.48	2.21	2.21
Cr	2.92	1.86	0.55	2.46	2.46
Fe	1.69	1.67	0.32	2.15	2.15
In	7.66	n.c. [1)]	1.43	n.a. [2)]	1.43
Mg	6.82	1.74	1.28	n.a. [2)]	1.74
Mn	1.77	1.25	0.33	1.91	1.91
Ni	3.79	6.28	0.71	6.28	6.28
O	12.80	7.23	2.65	13.01	13.01
P	7.68	1.73	1.44	n.a. [2)]	1.73
Pb	6.44	6.78	1.21	7.13	7.13
S	5.25	3.67	0.98	5.09	5.09
Sb	4.69	n.c. [1)]	0.88	n.a. [2)]	0.88
Se	5.04	0.94	0.94	n.a. [2)]	0.94
Si	6.65	5.29	1.25	9.60	9.60
Sn	5.23	12.24	0.98	9.54	12.24
Te	5.54	0.31	1.04	n.a. [2)]	1.04
Ti	5.66	3.03	1.06	n.a. [2)]	3.03
Zn	5.33	5.57	1.00	5.61	5.61
Zr	7.13	2.83	1.33	n.a. [2)]	2.83

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

[2)] n.a.: not applicable

Table 7: Results of the homogeneity study of ERM-EB074B

ERM-EB074B	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Ag	2.70	0.58	0.54	n.a. [2)]	0.58
Al	6.82	2.89	1.37	n.a. [2)]	2.89
As	2.71	0.31	0.54	n.a. [2)]	0.54
Au	3.85	n.c. [1)]	0.77	n.a. [2)]	0.77
Be	8.78	n.c. [1)]	1.76	n.a. [2)]	1.76
Bi	7.13	n.c. [1)]	1.43	n.a. [2)]	1.43
Cd	5.15	1.08	1.03	n.a. [2)]	1.08
Co	2.42	0.75	0.48	n.a. [2)]	0.75
Cr	3.25	0.54	0.65	n.a. [2)]	0.65
Fe	2.25	0.64	0.45	n.a. [2)]	0.64
In	6.73	1.95	1.35	n.a. [2)]	1.95
Mg	5.66	n.c. [1)]	1.13	n.a. [2)]	1.13
Mn	1.71	n.c. [1)]	0.34	n.a. [2)]	0.34
Ni	4.13	2.91	0.83	n.a. [2)]	2.91
O	13.39	7.78	3.42	n.a. [2)]	7.78
P	6.09	2.17	1.22	n.a. [2)]	2.17
Pb	6.53	1.90	1.31	4.48	4.48
S	5.18	1.73	1.04	n.a. [2)]	1.73
Sb	5.17	0.52	1.03	n.a. [2)]	1.03
Se	5.37	1.41	1.07	n.a. [2)]	1.41
Si	16.23	5.02	3.29	12.74	12.74
Sn	4.99	1.45	1.00	n.a. [2)]	1.45
Te	5.58	1.70	1.12	n.a. [2)]	1.70
Ti	4.36	1.90	0.87	n.a. [2)]	1.90
Zn	3.77	1.49	0.75	n.a. [2)]	1.49
Zr	6.60	2.97	1.33	n.a. [2)]	2.97

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

[2)] n.a.: not applicable

Table 8: Results of the homogeneity study of ERM-EB074C

ERM-EB074C	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,rel}$ [%]	$u_{bb,rel}$ [%]
Ag	5.68	1.46	1.12	n.a. [2)]	1.46
Al	24.01	n.c. [1)]	4.73	17.56	17.56
As	6.74	n.c. [1)]	1.32	n.a. [2)]	1.32
Au	14.53	n.c. [1)]	2.85	n.a. [2)]	2.85
Be	30.53	n.c. [1)]	6.00	n.a. [2)]	6.00
Bi	18.66	n.c. [1)]	3.68	n.a. [2)]	3.68
Cd	6.99	n.c. [1)]	1.37	n.a. [2)]	1.37
Co	10.70	n.c. [1)]	2.11	n.a. [2)]	2.11
Cr	12.29	n.c. [1)]	2.41	n.a. [2)]	2.41
Fe	5.67	1.77	1.12	5.21	5.21
In	6.69	n.c. [1)]	1.31	n.a. [2)]	1.31
Mg	12.92	n.c. [1)]	2.54	n.a. [2)]	2.54
Mn	8.35	n.c. [1)]	1.66	n.a. [2)]	1.66
Ni	13.75	n.c. [1)]	2.70	n.a. [2)]	2.70
O	9.88	5.01	1.60	n.a. [2)]	5.01
P	23.57	5.44	4.63	n.a. [2)]	5.44
Pb	3.60	0.70	0.71	3.05	3.05
S	19.87	5.69	3.22	n.a. [2)]	5.69
Sb	9.55	n.c. [1)]	1.88	n.a. [2)]	1.88
Se	19.62	n.c. [1)]	3.85	n.a. [2)]	3.85
Si	13.19	n.c. [1)]	2.59	n.a. [2)]	2.59
Sn	8.41	n.c. [1)]	1.65	n.a. [2)]	1.65
Te	14.11	4.10	2.77	n.a. [2)]	4.10
Ti	11.93	6.58	2.34	n.a. [2)]	6.58
Zn	15.04	1.22	2.96	n.a. [2)]	2.96
Zr	10.31	2.39	2.03	n.a. [2)]	2.39

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

[2)] n.a.: not applicable

The three formats were produced from the same melt; it was decided to assign one uncertainty contribution to ERM-EB074. It is detailed in Section 4.3.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative of the whole unit and thus can be used in an analysis. Sample sizes greater than or equal to the minimum sample intake guarantee the certified value within its stated uncertainty.

4.2.1 Radial within-unit homogeneity for ERM-EB074A

For ERM-EB074A which was suspected of being inhomogeneous across the face of a disk, perhaps due to the migration of certain elements during cooling of casting, face homogeneity was tested using solid sampling techniques that consume microgram quantities of material. A mapping technique was applied in which analytical spots were selected across the face of the discs.

For the radial within unit homogeneity study, one unit of ERM-EB074A was selected randomly and cut into four thinner discs to test four different faces for the radial within-unit homogeneity test.

For the radial within unit homogeneity study, one unit of ERM-EB074A was selected randomly and cut into four thinner discs (~10 mm thick) to test four different faces for the radial within-unit homogeneity test. The discs were prepared according to the instructions for use, including mechanical cleaning of the surface.

The disc face was divided into three areas: central, intermediate and external (Figure 2B). Three, four and six independent locations were analysed from the central, intermediate and external areas respectively. Analyses were performed by spark-OES for Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Ti, Zn, Zr mass fraction.

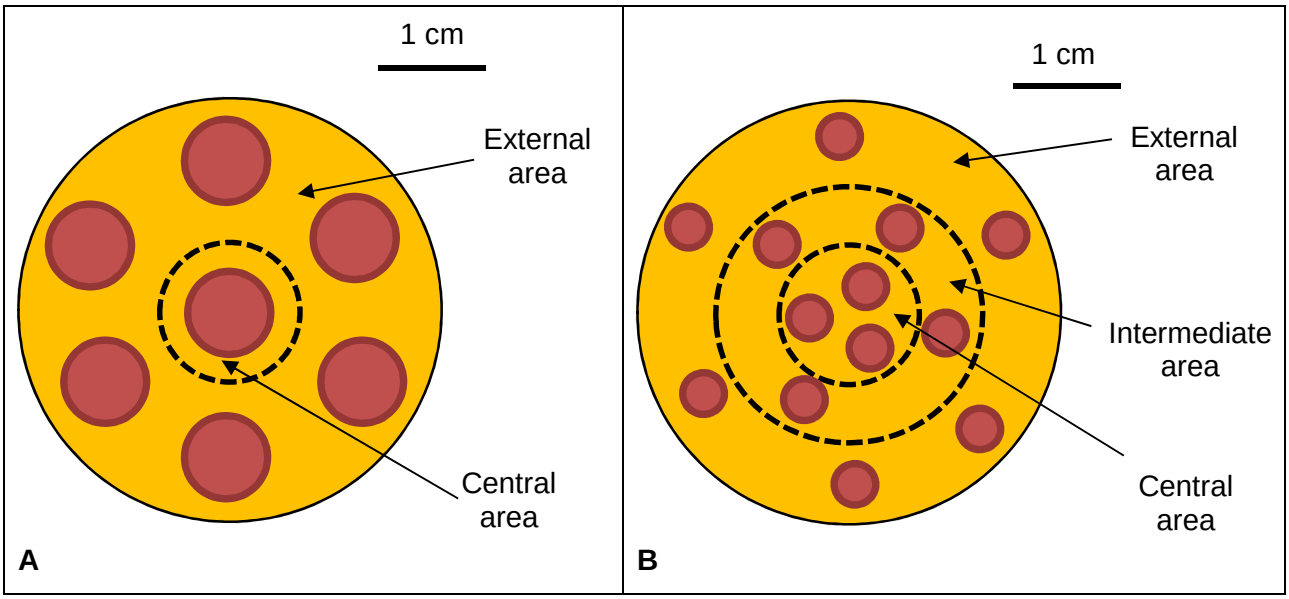

Figure 2: Figure 2A: Localisation of the two different areas for the radial within-unit homogeneity study by GD-MS; Figure 2B: localisation of the three different areas for radial within-unit homogeneity study by spark-OES. The red points represent the number of spot analysis per area.

For Au, In and Te, the within-unit homogeneity study was performed by GD-MS. The analysis area is larger for GD-MS than for spark-OES. Therefore, it was only possible to perform one analysis in the central area and six analyses in the external area. No analyses were made in

the intermediate area (Figure 2A). One and six independent locations from central and external areas were analysed by GD-MS for Au, In and Te.

The measurements were performed in a randomised block design because the number of replicates on all units (52 analyses) could not be included in a single run due to instrumental constraints (drift towards the end of a long run). Improved precision (measured as the within-unit standard deviation) was obtained using several short runs in a randomised block design.

In the randomised block design for 13 independent analyses on each of four faces of ERM-EB074A, four measurement sequences (one measurement sequence per face) were planned, with each spot measured once in random order. Runs were randomised individually in a manner to be able to separate a potential analytical drift from any radial trend in the disc.

Regression analysis and F-test (or T-test for Au, In and Te) were used to estimate the radial within-unit homogeneity independently of the analytical sequence effect.

The data evaluation was performed in the following order:

1 – Trends in analytical run / correction for significant trends

Regression analyses were done to evaluate potential trends in each analytical run. Some significant (95 % confidence level) trends in the analytical sequence were visible, pointing at a signal drift in the analytical system (Table 9). As the analytical sequence and the unit numbers were not correlated, trends significant on a 95 % confidence level were corrected as explained in equation 1.

2 – Evaluation of between analytical run effect / Normalisation of dataset (if necessary)

The analytical trend-corrected dataset was evaluated for significant differences between analytical runs (95 % confidence level) using one-way ANOVA. Significant differences between analytical runs were observed on the 95 % confidence level for all elements in ERM-EB074A except As, Be, Co, Mn, Ni, Se, Sn, Zn and Zr (Table 9). As it is assumed that run effects and unit effects were independent, differences between analytical runs on 95 % confidence level were corrected as explained in equation 2.

3 – Statistical evaluation of the datasets

The normalised datasets were tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means (Table 9).

No outlying means were detected on the 99 % confidence level except for In. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Table 9: Results of the statistical evaluation of the radial within-unit homogeneity study of ERM-EB074A; *T* = number of series with analytical trend

ERM-EB074A	Analytical trends	Between analytical run difference	Outliers at 99% confidence level		Trend / inhomogeneity		Inhomogeneity uncertainty
Analyte	Significant at 95% confidence level (*T*)	Significant difference at 95% confidence level	Unit means	Individual results	Radial linear trend at 95% confidence level	Between area difference at 95% confidence level	$u_{rec,rel}$ [%]
Ag	Yes (1)	Yes	None	None	No	Yes (F-test)	1.23
Al	No	Yes	None	None	Yes	No (F-test)	0.52
As	Yes (1)	No	None	None	No	No (F-test)	n.a. [2]
Au[1]	No	Yes	None	None	n.a. [2]	Yes (T-test)	1.85
Be	No	No	None	None	No	Yes (F-test)	1.03
Bi	Yes (1)	Yes	None	None	No	No (F-test)	n.a. [2]
Cd	Yes (2)	Yes	None	None	No	No (F-test)	n.a. [2]
Co	Yes (1)	No	None	None	No	No (F-test)	n.a. [2]
Cr	Yes (1)	Yes	None	None	No	No (F-test)	n.a. [2]
Fe	Yes (1)	Yes	None	None	No	Yes (F-test)	2.12
In[1]	No	Yes	Yes (1)	Yes (1)	n.a. [2]	Yes (T-test)	6.35
Mg	Yes (1)	Yes	None	Yes (1)	No	Yes (F-test)	0.87
Mn	Yes (2)	No	None	None	Yes	No (F-test)	0.27
Ni	No	No	None	Yes (2)	No	No (F-test)	n.a. [2]
P	Yes (2)	Yes	None	None	No	No (F-test)	n.a. [2]
Pb	Yes (1)	Yes	None	None	No	No (F-test)	n.a. [2]
S	No	Yes	None	None	No	No (F-test)	n.a. [2]
Sb	No	Yes	None	None	No	No (F-test)	n.a. [2]
Se	Yes (1)	No	None	None	No	No (F-test)	n.a. [2]
Si	Yes (1)	Yes	None	None	No	No (F-test)	n.a. [2]
Sn	Yes (2)	No	None	None	No	No (F-test)	n.a. [2]
Te[1]	No	Yes	No	Yes (1)	n.a. [2]	Yes (T-test)	5.11
Ti	No	Yes	No	None	No	No (F-test)	n.a. [2]
Zn	No	No	None	None	No	No (F-test)	n.a. [2]
Zr	No	No	None	None	Yes	Yes (F-test)	1.85

[1] Au, In and Te were tested using GD-MS and only on central and external area
[2] n.a.: not applicable

Regression analyses were performed to evaluate potential radial trends within-unit. No trends within the unit face were visible on a 95 % confidence level for all elements except Al, Mn and Zr, where significant radial trends within unit (decrease or increase from centre to external area) were detected (95 % confidence level).

An F-test was used to determine if a significant difference is observed between the three areas on the 95 % confidence level. For Be Fe, Mg and Zr, the difference between face areas was significant on a 95% confidence level.

For Au, In and Te, a T-test was used to determine if a significant difference is observed between the central and external areas on a 95 % confidence level. For Au, In and Te, the difference between central and external area was significant on a 95 % confidence level.

For Al, Au, Be, Fe, In, Mg, Mn, Te and Zr, inhomogeneity was observed along the radial axis of ERM-EB074A face. Therefore, u_{rec} was estimated using a rectangular distribution between the highest and lowest face area mean [12]. The uncertainty in those cases is given in:

$$u_{rec,rel} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot \bar{y}} \qquad \textbf{Equation 3}$$

$\bar{y}$ mean of all results of the homogeneity study

The results of the study are summarised in Table 9. Central, intermediate and external area mean values are given in Annex B.

The radial inhomogeneity was tested and found not significant for As, Bi, Cd, Co, Cr, Ni, P, Pb, S, Sb, Se, Si, Ti and Zn. Significant radial inhomogeneity was observed for Ag, Al, Au,

Be, Fe, In, Mg, Mn, Sn, Te and Zr and estimated using rectangular distribution. The uncertainty contribution from radial within-unit uncertainty is below 2.5% for all elements (except In and Te) which is considered sufficiently small to make the material useful.

For In and Te, the central area of ERM-EB074A showed significantly lower results than the external area. The radial within-unit uncertainty is estimated to 5.1 % and 6.4 %. The within-unit contribution is not negligible and it will be included in the final uncertainty budget of ERM-EB074A, B and C.

4.2.2 Minimum sample intake estimation

Homogeneity/stability experiments were performed using GD-MS and spark-OES technique for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr. The sample intake of these methods gives acceptable repeatability, demonstrating that the within-unit inhomogeneity does not contribute to analytical variation at this sample intake.

Quantification of the sample intake for GD-MS and spark-OES is difficult, as both are direct surface sampling and analysis methods. In contrast, the minimum sample intake required for ICP-MS is significantly larger and quantifiable. Based on the acceptable repeatability of the direct surface sampling and analysis methods, the sample intake of those methods meets the minimum sample intake requirements for ERM-EB074A, B and C.

A rough estimation was done for each technique to estimate the sample intake used for GD-MS and spark-OES.. For spark-OES, a spot analysis of 4 mm diameter, a depth of 0.1 mm and the copper density of 8.96 g/cm^3 was assumed. For GD-MS, a spot analysis of 8 mm diameter, a depth of 0.05 mm and the copper density of 8.96 g/cm^3 was assumed. Therefore, the sample intake of spark-OES was estimated to approximately 11 mg and 20 mg for GD-MS. Using the rough estimation of GD-MS and spark-OES sample intake, the following minimum sample intakes are derived:

- Sample intake of 10 mg for Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Ti, W, Zn, Zr

- Sample intake of 20 mg for Au, In and Te.

Results by laser ablation (data not shown) indicate that the material is not homogeneous on the micrometre scale. Results from several points need to be pooled when using laser ablation

4.3 Uncertainty of homogeneity of ERM-EB074A, B and C

The three formats are produced from the same melt; it was decided to assign the same uncertainty contribution to all three formats.

For ERM-EB074A, the final homogeneity uncertainty is the combination of the $u_{bb,rel}$ and the $u_{within\text{-}rad,rel}$.

The largest $u_{bb,rel}$ of ERM-EB074A, B and C is adopted as the uncertainty of inhomogeneity of ERM-EB074 except when the uncertainty contribution of ERM-EB074C corresponds to $u^*_{bb,rel}$ for the following reason:

The methods used to assess homogeneity (Table 2) were different for ERM-EB074A, B (GD-MS) and ERM-EB074C (ICP-MS / ICP-OES). The GD-MS method used for ERM-EB074A and B provided better repeatability and lower $u^*_{bb,rel}$ than the method used for ERM-EB074C. It should be noticed that in all cases except for Ag, Fe, O, P, Pb, S, Te, Ti and Zr, the homogeneity uncertainty assigned to ERM-EB074C corresponds to $u^*_{bb,rel}$, i.e. only an upper limit of potential inhomogeneity could be calculated. In order to avoid overestimation of the uncertainty of homogeneity due to the method repeatability, $u^*_{bb,rel}$ of ERM-EB074C was not used for the estimation of $u_{bb,rel}$ of ERM-EB074. The combined homogeneity uncertainties are given in Table 10.

The uncertainty of homogeneity of the Ag, Al, As, Au, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Sb, Sn, Te, Ti, W and Zn mass fractions in ERM-EB074A, B and C is sufficient small to make the material useful. The homogeneity study showed significant inhomogeneity for the Al, O and Si and Sn mass fractions, which limits the use of the materials as reference materials for these elements.

Table 10: Summary of the homogeneity study for ERM-EB074. The data shown in the right column were used as estimate of the uncertainty of homogeneity for all three formats.

Analyte	ERM-EB074A				ERM-EB074B		ERM-EB074C		ERM-EB074
	$u_{bb,rel}$ [%]		$u_{within-rad,,rel}$ [%]	Combined $u_{bb,rel}$ [%]	$u_{bb,rel}$ [%]		$u_{bb,rel}$ [%]		$u_{bb,rel}$ [%]
Ag	$u_{rec,rel}$	2.06	1.23	2.40	$s_{bb,rel}$	0.58	$s_{bb,rel}$	1.46	2.40
Al	$s_{bb,rel}$	3.23	0.52	3.27	$s_{bb,rel}$	2.89	$u_{rec,rel}$	17.56	17.56
As	$u^*_{bb,rel}$	0.72	n.a. [1)]	0.72	$u^*_{bb,rel}$	0.54	$u^*_{bb,rel}$	1.32	0.72
Au	$u^*_{bb,rel}$	0.58	1.85	1.94	$u^*_{bb,rel}$	0.77	$u^*_{bb,rel}$	2.85	1.94
Be	$s_{bb,rel}$	3.60	1.03	3.75	$u^*_{bb,rel}$	1.76	$u^*_{bb,rel}$	6.00	3.75
Bi	$u^*_{bb,rel}$	1.24	n.a. [1)]	1.24	$u^*_{bb,rel}$	1.43	$u^*_{bb,rel}$	3.68	1.43
Cd	$u^*_{bb,rel}$	1.03	n.a. [1)]	1.03	$s_{bb,rel}$	1.08	$u^*_{bb,rel}$	1.37	1.08
Co	$u_{rec,rel}$	2.21	n.a. [1)]	2.21	$s_{bb,rel}$	0.75	$u^*_{bb,rel}$	2.11	2.21
Cr	$u_{rec,rel}$	2.46	n.a. [1)]	2.46	$u^*_{bb,rel}$	0.65	$u^*_{bb,rel}$	2.41	2.46
Fe	$u_{rec,rel}$	2.15	2.12	3.02	$s_{bb,rel}$	0.64	$u_{rec,rel}$	5.21	5.21
In	$u^*_{bb,rel}$	1.43	6.35	6.51	$s_{bb,rel}$	1.95	$u^*_{bb,rel}$	1.31	6.51
Mg	$s_{bb,rel}$	1.74	0.87	1.94	$u^*_{bb,rel}$	1.13	$u^*_{bb,rel}$	2.54	1.94
Mn	$s_{bb,rel}$	1.91	0.27	1.93	$u^*_{bb,rel}$	0.34	$u^*_{bb,rel}$	1.66	1.93
Ni	$s_{bb,rel}$	6.28	n.a. [1)]	6.28	$s_{bb,rel}$	2.91	$u^*_{bb,rel}$	2.70	6.28
O	$u_{rec,rel}$	13.01	n.a. [1)]	13.01	$s_{bb,rel}$	7.78	$s_{bb,rel}$	5.01	13.01
P	$s_{bb,rel}$	1.73	n.a. [1)]	1.73	$s_{bb,rel}$	2.17	$s_{bb,rel}$	5.44	5.44
Pb	$u_{rec,rel}$	7.13	n.a. [1)]	7.13	$u_{rec,rel}$	4.48	$u_{rec,rel}$	3.05	7.13
S	$s_{bb,rel}$	5.09	n.a. [1)]	5.09	$s_{bb,rel}$	1.73	$s_{bb,rel}$	5.69	5.69
Sb	$u^*_{bb,rel}$	0.88	n.a. [1)]	0.88	$u^*_{bb,rel}$	1.03	$u^*_{bb,rel}$	1.88	1.03
Se	$u^*_{bb,rel}$	0.94	n.a. [1)]	0.94	$s_{bb,rel}$	1.41	$u^*_{bb,rel}$	3.85	1.41
Si	$u_{rec,rel}$	9.60	n.a. [1)]	9.60	$u_{rec,rel}$	12.74	$u^*_{bb,rel}$	2.59	12.74
Sn	$u_{rec,rel}$	12.24	5.11	12.24	$s_{bb,rel}$	1.45	$u^*_{bb,rel}$	1.65	12.24
Te	$u^*_{bb,rel}$	1.04	n.a. [1)]	5.22	$s_{bb,rel}$	1.70	$s_{bb,rel}$	4.10	5.22
Ti	$s_{bb,rel}$	3.03	n.a. [1)]	3.03	$s_{bb,rel}$	1.90	$s_{bb,rel}$	6.58	6.58
Zn	$u_{rec,rel}$	5.61	n.a. [1)]	5.61	$s_{bb,rel}$	1.49	$u^*_{bb,rel}$	2.96	5.61
Zr	$s_{bb,rel}$	2.83	1.23	3.38	$s_{bb,rel}$	2.97	$s_{bb,rel}$	2.39	3.38

[1)] n.a.: not applicable

5 Stability

Stability assessment is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in the summer, temperatures up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature is to be applied.

Metallic copper is stable over time and temperature as archaeological artefacts and antique copper cooking ware demonstrate: they remain unchanged without special precautions for hondreds and tousands of years.

Copper has good chemical resistance to degradation under normal storage and handling conditions. However, copper is subject to surface oxidation over time. Before using ERM-EB074A, B and C, it is mandatory to remove the oxide layer that may appear on the surface of the material as explained in section 9.3 Instructions for use.

The stability of trace elements in electrolytic copper was studied using data from BCR-075 [12]. BCR-075 was produced and certified in 1992 and used in this investigation as a quality

control material for evaluation of the characterisation results. The BCR-075 results reported in this study confirmed the certified values, taking into consideration the measurement uncertainty and substantiated the stability of trace elements in copper.

The trace element mass fractions in ERM-EB074A, B and C are therefore considered stable under normal dispatch conditions (up to 60 °C).

Based on previous experience, a validity period of the certificate for ERM-EB074A, B and C of 10 years is set.

Recommended storage and transport conditions:

The material can be transported under ambient conditions without special precautions and stored at a temperature not exceeding 18 ± 5 °C. Uncertainties due to storage and shipment conditions are considered negligible regarding the material property.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

6 Characterisation

The material characterisation is the process of determining the property values of a reference material. The material characterisation was based on an intercomparison of expert laboratories. The Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, H, Hg, In, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn and Zr mass fractions of the ERM-EB074A, B and C were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias. The intercomparison of laboratories seeks to reduce the combined uncertainty.

6.1 Selection of participants

Eighteen laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices by submitting results for intercomparison exercises or method validation reports. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where the scope of accreditation covers measurement,, the accreditation number is stated in the list of participants (Section 0).

6.2 Study setup

Each laboratory received two units of ERM-EB074A, B and C and was requested to provide at least three independent results per unit. Several analytical techniques (i.e. GD-MS, spark-OES, DC-arc-OES) were not able to analyse trace elements in all three formats due to instrument constraints (sample size). Each laboratory was required to provide the results of at least three independent results on each of the two units for one format analysed for the following elements: Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, H, Hg, In, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn and Zr.

The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations and measurements had to be spread over at least two days to ensure intermediate precision conditions. An independent calibration was performed for each result.

Each participant received a sample of BCR-075 as a blind quality control (QC) sample except for L13, which used BCR-075 for calibration. In this case, the calibration results were used to support the evaluation of the characterisation results.

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures. These uncertainties were used to evaluate the dispersion of the laboratory results (Annex E).

6.3 Methods used

A variety of acid digestion (HCl, HNO_3, HF), extraction methods (co-precipitation with yttrium) with different quantification steps (ICP-MS, ICP-OES) as well as methods without sample preparation (combustion with IR quantification, GD-MS, LA-ICP-MS, IGF-IR, INAA or spark-OES) were used to characterise the material. The combination of results from methods based on entirely different principles mitigates undetected method bias.

All methods used during the characterisation study are summarised in Annex C. The laboratory code (e.g. L1) is a random number and does not correspond to the order of laboratories in Section 0. The lab-method code consists of a number assigned to each laboratory (e.g. L01) and abbreviation of the measurement method used (e.g. ICP-MS).

6.4 Evaluation of results

The characterisation campaign resulted in 3-15 datasets per element. All individual results of the participants, grouped per element are displayed in a tabular and/or graphical form in Annex E.

ERM-EB074A, B and C were considered homogeneous. Therefore, the results were pooled per laboratory independently of the format analysed by each laboratory. In support of this assumption, the characterisation study was performed for each format using the accepted datasets. The mean of laboratory means and the standard deviation of the mean are presented in each format in Annex D, demonstrating the equivalence of the three formats.

6.4.1 Technical evaluation

The data obtained were first checked for compliance with the requested analysis protocol and their validity based on technical reasons. The following criteria were considered during the evaluation:

- appropriate validation of the measurement procedure,
- compliance with the analysis protocol: sample preparations and measurements performed on two days, and the analytical sequence,
- absence of values given as the below limit of detection or below limit of quantification,
- absence of technical problems (i.e. contamination, RSD > 50 %),
- method performance, i.e. agreement of the measurement results with the assigned value of the QC sample. As this test is performed using the respective uncertainties of the certified values and the measurement uncertainties estimated by the laboratory, it should be borne in mind that even national metrology institutes tend to underestimate their measurement uncertainties [16].

Most technical problems were inherent in one laboratory only, except data for Zr: Laboratories not using HF for digestion found considerable lower values for Zr than laboratories using HF. This can be explained by the fact that Zr precipitates in the absence of HF [17]. Laboratory 9 repeated the analysis using HF and obtained results between 4.3 and 6.4 mg/kg, confirming that this is not a laboratory-dependent effect. Therefore, results from digestions without HF were excluded for Zr.

For Hg and W, most of the laboratories provided results below their reported LOD. In these specific cases, all data were retained to assign indicative values (Table 15).

Based on the above criteria, the following datasets were rejected as not technically valid (Table 11).

Table 11: Datasets that showed non-compliances with the analysis protocol and technical specifications, and action taken

Analyte	Lab code	Description of problem	Action taken
Ag	L1, L12 L6, L21	Deviating result on QC sample Report results below LOD	not used for evaluation
Al	L1, L4 L9 L18	Technical problem (RSD > 50%) Report results below LOD Technical problem (contamination)	not used for evaluation
As	L8, L18 L21	Deviating result on QC sample Report results below LOD	not used for evaluation
Au	L9	Laboratory did not use aqua regia for digestion.	not used for evaluation
Bi	L3, L4, L5, L18 L2, L21	Deviating result on QC sample Report results below LOD	not used for evaluation
Cd	L6, L21 L18	Report results below LOD Deviating result on QC sample	not used for evaluation
Co	L6, L21 L10, L15 L18	Report results below LOD Deviating result on QC sample	not used for evaluation
Cr	L14, L15, L18 L20, L21	Deviating result on QC sample Report results below LOD	not used for evaluation
Fe	L1 L7, L8, L9, L15, L21 L10	Technical problem (contamination) Deviating result on QC sample Report results below LOD	not used for evaluation
Mg	L1 L20	Report results below LOD Technical problem (blank)	not used for evaluation
Mn	L5, L8, L11 and L18 L21	Deviating result on QC sample Report results below LOD	not used for evaluation
Ni	L4 L1, L6, L8, L21 L8, L18	Technical problem Report results below LOD Deviating result on QC sample	not used for evaluation
O	L17	Not compliant with analysis protocol	not used for evaluation
P	L1, L2, L6, L9	Report results below LOD	not used for evaluation
Pb	L1, L2, L8, L18, L20, L21	Deviating result on QC sample	not used for evaluation
S	L4 L9	Technical problem (RSD > 50%) Report results below LOD	not used for evaluation
Sb	L2, L21 L5	Report results below LOD Deviating result on QC sample	not used for evaluation
Se	L2, L7, L21 L1, L4, L8, L11, L20	Report results below LOD Deviating result on QC sample	not used for evaluation
Si	L1, L6, L9	Report results below LOD	not used for evaluation
Sn	L21	Report results below LOD	not used for evaluation
Te	L9, L11 L2, L7	Deviating result on QC sample Report results below LOD	not used for evaluation
Zn	L6, L21 L1, L8, L9	Report results below LOD Deviating result on QC sample	not used for evaluation
Zr	L1, L8, L9, L11, L16 L18	Technical problem in digestion (HF not used for digestion)	not used for evaluation

6.4.2 Statistical evaluation

The datasets accepted based on technical reasons were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots. Datasets were further evaluated for outlying means using the Grubbs test and the Cochran test for outlying standard deviations, (both at a 99 % confidence level). Standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 12.

Table 12: Statistical evaluation of the technically accepted datasets for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn and Zr. *p*: number of technically valid datasets

Analyte	*p*	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean of the laboratory mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
Ag	15	No	Yes (L9)	Yes	1.027	0.073	0.073	0.095
Al	8	No	Yes (L5)	Yes	0.851	0.382	0.409	0.129
As	15	No	Yes (L1)	Yes	1.234	0.144	0.122	0.092
Au	10	No	Yes (L16)	Yes	0.520	0.087	0.081	0.031
Be	12	No	Yes (L5)	Yes	0.311	0.091	0.080	0.038
Bi	11	No	Yes (L16)	Yes	0.507	0.055	0.056	0.053
Cd	12	No	Yes (L9)	Yes	0.402	0.057	0.059	0.037
Co	13	No	Yes (L2)	Yes	0.830	0.063	0.063	0.072
Cr	12	No	Yes (L9)	Yes	0.373	0.045	0.034	0.117
Fe	11	No	Yes (L2)	Yes	5.777	0.680	0.604	1.007
In	14	No	Yes (L5)	Yes	0.494	0.053	0.051	0.055
Mg	10	No	Yes (L4)	Yes	2.025	0.397	0.394	0.280
Mn	9	No	No	Yes	0.931	0.076	0.075	0.070
Ni	11	No	Yes (L7)	Yes	0.607	0.037	0.031	0.079
O	3	No	No	Yes	8.411	1.529	1.435	1.232
P	9	No	Yes (L4)	Yes	1.529	0.275	0.265	0.221
Pb	11	No	Yes (L5)	No	2.675	0.218	0.220	0.208
S	7	No	Yes (L7)	Yes	3.270	1.147	1.105	0.651
Sb	16	No	Yes (L9)	Yes	0.567	0.068	0.064	0.042
Se	11	No	Yes (L9)	Yes	0.555	0.108	0.105	0.075
Si	5	No	No	Yes	1.240	0.407	0.368	0.122
Sn	15	No	Yes (L1)	Yes	1.492	0.159	0.151	0.195
Te	14	No	Yes (L3)	Yes	0.505	0.055	0.051	0.066
Ti	12	No	Yes (L5)	Yes	0.973	0.211	0.199	0.123
Zn	14	Yes (L18)	Yes (L4)	No	2.189	0.369	0.396	0.326
Zr	7	No	Yes (L15)	Yes	8.843	2.017	2.060	1.612

The laboratory means follow a normal distribution. None of the data contained outlying means except Bi, Pb and Zn. The statistical evaluation flagged at least one laboratory as having an outlying variance for each analyte except for O and Si (Table 12). This reflects the fact that different methods have distinctive intrinsic variability. As all the measurement methods were found to be technically sound, all the results were retained. The datasets are therefore consistent, and the mean of laboratory means is a good estimate of the true value.

The statistical evaluation flagged laboratory L18 as an outlier for Zn mass fraction, although outlier tests do not take uncertainty information into consideration. A closer investigation revealed that the difference between the mean value of laboratory L18 and the other results is covered by the measurement uncertainty of laboratory L18. There is, therefore, no evidence that the results of laboratory L18 deviate from the other results, and the result was retained.

The statistical evaluation flagged laboratory L18 as an outlier for Bi and Pb mass fraction. As the difference between the mean value of laboratory L18 and the other results is not covered by the measurement uncertainty of laboratory L18, there is evidence of a significant disagreement of results. As the technical evaluation of results did not indicate any technical flaws in any method, there is no reason for discarding any of the results. As there is the possibility that the results of laboratory L18 are the only correct ones, no value is assigned to Bi and Pb mass fraction.

For the As, Ti mass fractions, a closer investigation revealed that the measurement uncertainty did not cover a difference between the assigned value and the L20 mean value.. However, the measurement uncertainty reported by L20 is considered underestimated (two times the standard deviation). Standard deviations among laboratories are larger than the standard deviation within laboratories, showing that two times the standard deviation of replicate measurements is unsuitable as an estimate of measurement uncertainty. Moreover, L20 mean value was not flagged as an outlier by the statistical test. Therefore, it was decided to retain the uncertainties of As and Ti as calculated in Table 13.

For the Au mass fraction, a closer investigation revealed that a difference between the assigned value and the L8 and L20 mean value was not covered by the measurement uncertainty. However, the measurement uncertainty reported by L8 and L20 most likely underestimated, as it is based only on the experimental standard deviation. Moreover, the mean values of L8 and L20 were not flagged as outliers by the statistical test. Therefore, it was decided to keep the Au uncertainty as calculated in Table 13.

For the Be mass fraction, a closer investigation revealed that a difference between the assigned value and respectively, the L8 mean value was not covered by the measurement uncertainty. However, the measurement uncertainty reported by L8 and L16 is considered underestimated compared to other uncertainties for the ICP-MS method. Moreover, L8 mean value was not flagged as an outlier by the statistical test. Therefore, it was decided to keep the Be uncertainty as calculated in Table 13.

For the Mg and Ti mass fraction, a closer investigation revealed that the measurement uncertainty did not cover a difference between the assigned value and L16 mean value.. However, the measurement uncertainty reported by L16 is considered underestimated compared to other uncertainties for the ICP-MS method. Moreover, the L16 mean value was not flagged as an outlier by the statistical test. Therefore, it was decided to keep the Mg and Ti uncertainty as calculated in Table 13.

The datasets were, therefore, consistent, and the mean of laboratory means is considered to be a good estimate of the true value. The uncertainty related to the characterisation (u_{char}) is estimated as the standard error of the mean of laboratory means (Table 13).

Table 13: Uncertainty of characterisation for Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn and Zr.

Analyte	*p*	Mean [mg/kg]	*s* [mg/kg]	u_{char} [mg/kg]	$u_{char,rel}$ [%]
Ag	15	1.027	0.073	0.019	1.82
Al	8	0.851	0.382	0.135	15.87
As	15	1.234	0.144	0.037	3.02
Au	10	0.520	0.087	0.027	5.28
Be	12	0.311	0.091	0.026	8.42
Bi	11	0.507	0.055	0.017	3.27
Cd	12	0.402	0.057	0.016	4.06
Co	13	0.830	0.063	0.017	2.09
Cr	12	0.373	0.045	0.013	3.47
Fe	11	5.777	0.680	0.205	3.55
In	14	0.494	0.053	0.014	2.89
Mg	10	2.025	0.397	0.126	6.20
Mn	9	0.931	0.076	0.025	2.71
Ni	11	0.607	0.037	0.011	1.83
O	3	8.411	1.529	0.883	10.50
P	9	1.529	0.275	0.092	5.99
Pb	11	2.675	0.218	0.066	2.45
S	7	3.270	1.147	0.434	13.26
Sb	16	0.567	0.068	0.017	3.01
Se	11	0.555	0.108	0.032	5.85
Si	5	1.240	0.407	0.182	14.68
Sn	15	1.492	0.159	0.041	2.74
Te	14	0.505	0.055	0.015	2.90
Ti	12	0.973	0.211	0.061	6.26
Zn	14	2.189	0.369	0.099	4.51
Zr	7	8.843	2.017	0.762	8.62

7 Value Assignment

Certified, indicative and informative values were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require pooling of not less than 6 datasets to assigned certified values. Full uncertainty budgets following the 'Guide to the Expression of Uncertainty in Measurement' [4] were established.

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. Uncertainties are evaluated according to the same rules as for certified values.

Additional material information refers to values that were obtained in the course of the study. For example, results reported from only one or two laboratories or in cases where individual measurement uncertainty is high falls under this category.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets, as shown in Table 12 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 0), potential between-unit inhomogeneity, u_{bb} (Section 4.1), radial within unit inhomogeneity, $u_{within\text{-}rad,rel}$ (Section 4.3). The uncertainty related to stability during transport/long-term storage was estimated to be negligible. These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,\,rel}$) with a coverage factor k as:

$$U_{CRM,rel} = k \cdot \sqrt{u_{char,rel}^2 + u_{bb,rel}^2} \quad \textbf{Equation 2}$$

- $u_{char,rel}$ was estimated as described in Section 6,
- $u_{bb,rel}$ was estimated as described in Section 4.1,

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor k of 2 was applied, to obtain the expanded uncertainties.

The certified values and their uncertainties are summarised in Table 14.

Table 14: Certified values and their uncertainties for ERM-EB074A, B and C

Analyte	Certified value [mg/kg] [1)]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [3)]
Ag	1.03	1.82	2.40	6.02	0.07
As	1.23	3.02	0.72	6.21	0.08
Au	0.52	5.28	1.94	11.24	0.06
Be	0.31	8.42	3.75	18.44	0.06
Bi	0.51	3.27	1.43	7.14	0.04
Cd	0.40	4.06	1.08	8.41	0.04
Co	0.83	2.09	2.21	6.08	0.06
Cr	0.37	3.47	2.46	8.51	0.04
Fe	5.8	3.55	5.21	12.61	0.8
In	0.49	2.89	6.51	14.24	0.07
Mg	2.03	6.20	1.94	13.00	0.27
Mn	0.93	2.72	1.93	6.67	0.07
Ni	0.61	1.83	6.28	13.09	0.08
P	1.53	5.99	5.44	16.18	0.25
Pb	2.7	2.46	7.13	15.08	0.4
Sb	0.57	3.01	1.03	6.37	0.04
Se	0.55	5.85	1.41	12.02	0.07
Te	0.50	2.90	5.22	11.94	0.06
Ti	0.97	6.26	6.58	18.17	0.18
Zn	2.2	4.51	5.61	14.39	0.4

[1)] rounded certified value

[2)] n.a.: not applicable

[3)] Expanded (k = 2) and rounded uncertainty.

7.2 Indicative values and their uncertainties

Indicative values were assigned for Hg, S, Sn and W and Zr.

For Sn, the inhomogeneity observed between units leads to a high uncertainty for the Sn mass fraction in ERM-EB074A, B and C. However, the results were viewed as sufficiently trustworthy to assign indicative values.

For the Hg and W mass fractions, all laboratories reported values below detection limits. Therefore, ERM-EB074 has been considered to contain less than the highest LOD reported by participating laboratories. With 95 % confidence, the Hg and W mass fraction of the material is below 0.1 mg/kg and 0.25 mg/kg, respectively. The highest LOD reported by participating laboratories is, therefore, a conservative estimate of the indicative value.

For Zr, the fact that all neutron activation results are clustered on the high side of the population indicates that significant method differences might have been found if more datasets had been obtained. For this reason, only indicative values were assigned.

Indicative values may not be used as certified values. The uncertainty budgets were set up as for the certified values and are listed together with the assigned values in Table 15.

Table 15: Indicative values and their uncertainties for ERM-EB074A, B and C

Analyte	Indicative value [1] [mg/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [3]
Hg	< 0.1 [2]				
S	3.3	13.26	5.69	28.86	1.0
Sn	1.5	2.74	12.24	25.08	0.4
W	< 0.25 [2]				
Zr	8.8	8.62	3.38	18.52	1.7

[1] rounded value

[2] With a 95 % probability, the indicative value is below this level.

[3] Expanded (k = 2) and rounded uncertainty.

7.3 Additional material information

The data provided in this section should be regarded as informative only on the general composition of the material and cannot be, in any case, used as certified or indicative value.

For Al, the inhomogeneity observed between unit and the high uncertainty between laboratories lead to a high expanded uncertainty for Al mass fraction in ERM-EB074A, B and C. For these reasons, the Al mass fraction and its uncertainties were reported as additional material information.

Two laboratories (L9 and L11) performed hydrogen analysis by fusion followed by thermal conductivity detection on 2 units of ERM-EB074A, B and C. The results are given as a range between the lowest unit mean and the highest unit mean.

For O, the inhomogeneity observed between unit and the small number of laboratories involved in the intercomparison (p: 3 and 5) lead to a high uncertainty for O mass fraction in ERM-EB074A, B and C. Two of the three laboratories had recently successfully participated in the characterisation of O in titanium alloy [18]. The results were regarded as sufficiently trustworthy to be reported in the additional material information section.

Table 16: Summary of the additional material information. The range given reflects the range of individual results.p: The number of laboratories

Analyte	Mass fraction [mg/kg]	p	Number of measurements	Method
Al	0.3-1.9	8	120 individual analyses	See Annex C
H	0.7 - 2.5	2	18 independent analysis / laboratory	IGF-conductivity
O	7-11	3	48 individual results	See Annex C

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr are clearly defined analytes. The participants used different methods for the sample preparation, as well as for the final determination, demonstrating the absence of measurement bias. The measurand is therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. Different calibrants/calibrants of (known purity and), specified traceability of their assigned values were used, and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

For Hg and W, the absence of the analyte at the level of the indicative value stated in Section 7.2 was reported using validated methods that report results traceable to SI, so the reported LOD are therefore traceable to SI.

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific (or specific groups of) analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not entirely known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CSLI Guideline C-53A [19] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

It should be borne in mind that the methods used in the characterisation are methods routinely applied for measuring trace elements in electrolytic copper. The agreement of results from different methods demonstrates that the processing did not affect any properties relevant for these methods and that ERM-EB074A, B and C behave like a real sample.

ERM-EB074A, B and C were produced from pure copper with added impurities. The analytical behaviour will be the same as for a routine sample of electrolytic copper. For samples other than electrolytic copper, the commutability has to be assessed.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials will be stored at 18 °C ± 5 °C in the dark. Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened units/bottles.

9.3 Preparation and use of the material

For ERM-EB074A and B, the usual mechanical cleaning should be applied prior to the measurement (the CRM and the user's samples should be treated in the same way).

For ERM-EB074C, it is recommended to clean the chips chemically before use to remove any traces of oxidation.

9.4 Minimum sample intake

For ERM-EB074A, B and C, the minimum amount of sample to be used is 10 mg for Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, Se, Si, Ti and Zn; 20 mg for Au, In and Te.

9.5 Use of the certified value

The main purpose of these materials is to assess method performance, i.e. for checking the accuracy of analytical results/calibration. As any reference material, they can also be used for control charts or validation studies.

Use as a calibrant

It is not recommended to use this matrix material as calibrant. If used, nevertheless, the uncertainty of the certified value will be taken into account in the estimation of the measurement uncertainty.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [20]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty (u_{Δ}) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use of quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as inhomogeneity was included in the uncertainties of the certified values.

10 Acknowledgments

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11 References

1 ISO Guide 34, General requirements for the competence of reference materials producers, International Organization for Standardization, Geneva, Switzerland, 2009

2 ISO Guide 35, Reference materials – General and statistical principles for certification, International Organization for Standardization, Geneva, Switzerland, 2006

3 ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories, International Organization for Standardization, Geneva, Switzerland, 2005

4 ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement, (GUM 1995), International Organization for Standardization, Geneva, Switzerland, 2008

5 International Copper Study Group. The World Copper Factbook 2013. Lisbon, Portugal: International Copper Study Group, 2013

6 M. Radetzki, Seven thousand years in the service of humanity—the history of copper, the red metal, Resources Policy 34 (2009) 176-184

7 G. Joseph, Copper: Its Trade, Manufacture, Use, and Environmental Status, G. Joseph K. Konrad (Eds), ASM International, Materials Park, USA, 1999

8 U. Bogdanović, V. Lazić, V. Vodnik, M. Budimir, Z. Marković, S. Dimitrijević, Copper nanoparticles with high antimicrobial activity, Materials Letters 128 (2014) 75-78

9 EN 1978:1998, Copper and copper alloys. Copper cathodes, European Committee for standardisation, Brussels, Belgium, 1998

10 GB/T 467-2010, Copper cathode, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ), Beijing, China, 2010

11 ASTM Standard B115, 2010, "Standard Specification for Electrolytic Copper Cathode" ASTM International, West Conshohocken, PA, USA, 2010

12 S. Vandendriessche, B. Griepink, K. Strijckmans, The certification of impurities (Ag, As, Bi, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sb, Se, Sn, Te and Zn) in copper, CRM 074: Electrolytic copper, CRM 075: copper with added impurities. Commission of the European Communities , Luxembourg, Luxembourg, 1992

13 EN1981, 2003, “Copper and copper alloys - Master alloys”, European Committee for standardisation, Brussels, Belgium, 2003

14 ASTM E826, 2008 " Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry" ASTM International, West Conshohocken, PA, 2008

15 T.P.J. Linsinger, J. Pauwels, A.M.H. van der Veen, H. Schimmel, A. Lamberty, Homogeneity and stability of reference materials, Accred. Qual. Assur. 6 (2001) 20-25

16 M Cox (2007) The evaluation of key comparison data: Determining the largest consistent subset, Metrologia 44:187–200

17 A. Makashima, R. Tanaka, E. Nakamura (2009) Precise elemental and isotopic analyses in silicate samples employing ICP-MS: Application of hydrofluoric acid solution and analytical techniques, Analyt. Scie. 25:1181-1187

18 T. Bacquart, T. Linsinger, The certification of the minor elements and trace elements mass fraction in TiAl6V4: BCR®-089. EUR Report 26831– European Community, Luxembourg – 2014 ISBN ????

19 H. Vesper, H. Emons, M. Gnezda, C. P. Jain, W. G. Miller, R. Rej, G. Schumann, J. Tate, L. Thienpont, J. E. Vaks, Characterization and Qualification of Commutable Reference Materials for Laboratory Medicine; Approved Guideline, CLSI document EP30-A, Clinical and Laboratory Standards Institute, Wayne, PA, USA, 2010

20 T.P.J. Linsinger, ERM Application Note 1: Comparison of a measurement result with the certified value, www.erm-crm.org (last accessed on 17/09/2014)

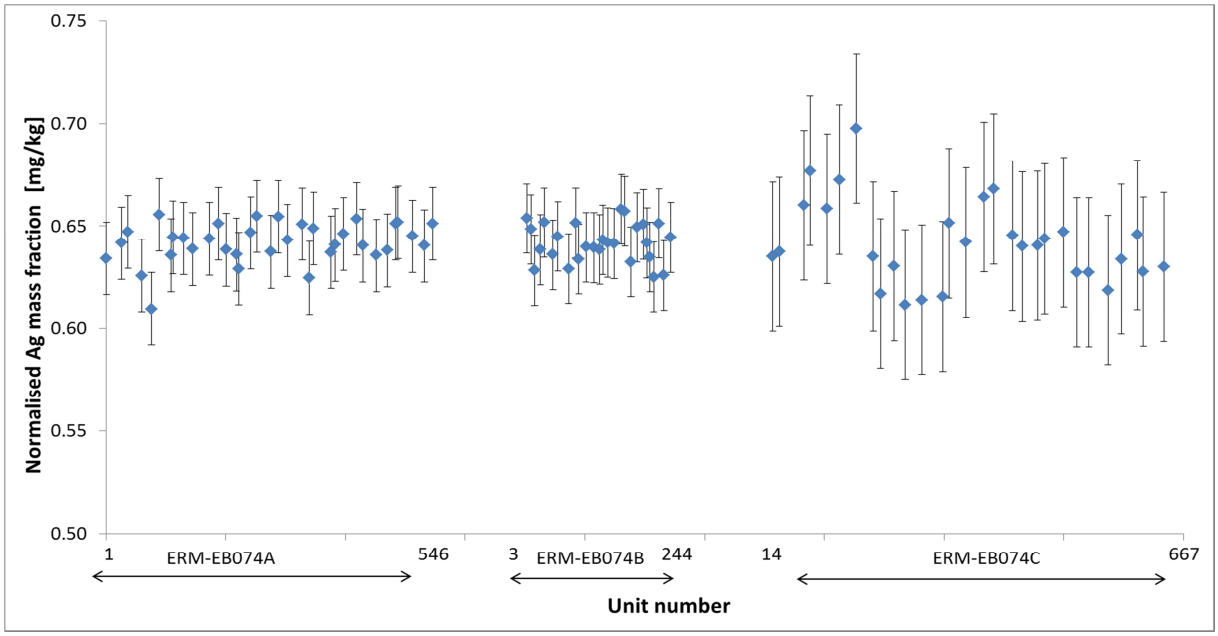
Annexes

Annex A: Results of the between-unit homogeneity measurements

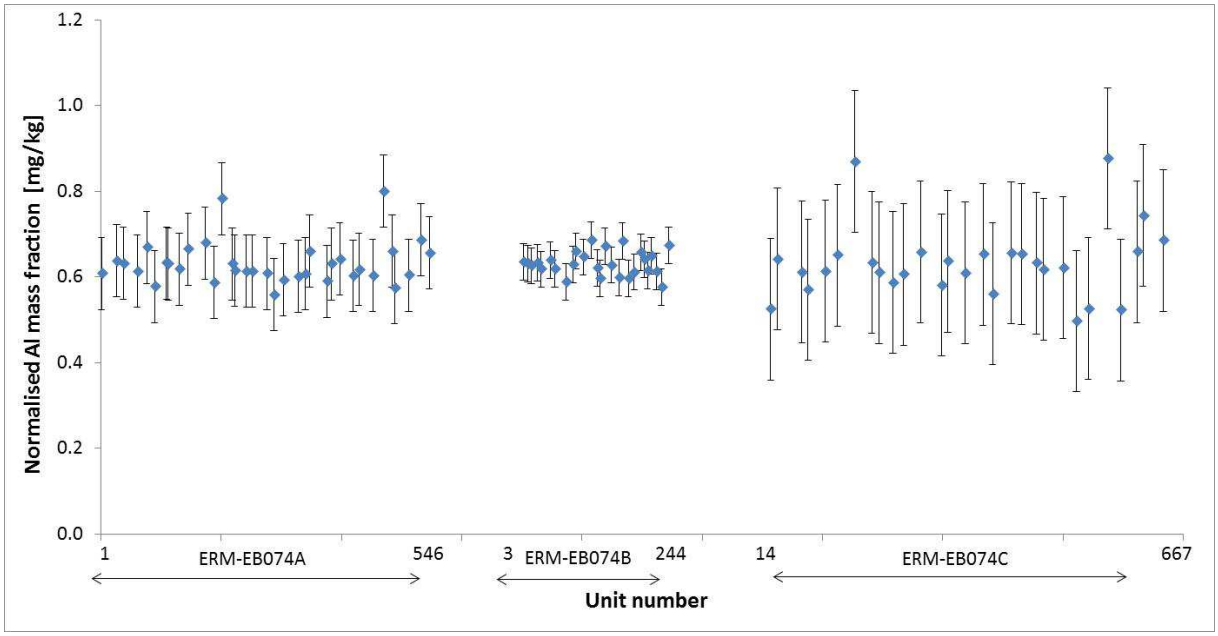
Results of the homogeneity studies for the three formats ERM-EB074A, B and C. The studies were not performed using the same technique (Table 2) which may explain the difference in results between the three formats. The unit means are presented after correction for analytical trend and normalisation to the mean of the three formats' means. The associated uncertainty equals to s_{wb} from ANOVA for all units of each study. The distance between tick marks is 200 units.

The within-billet homogeneity study was performed using the first nine units of ERM-EB074A.

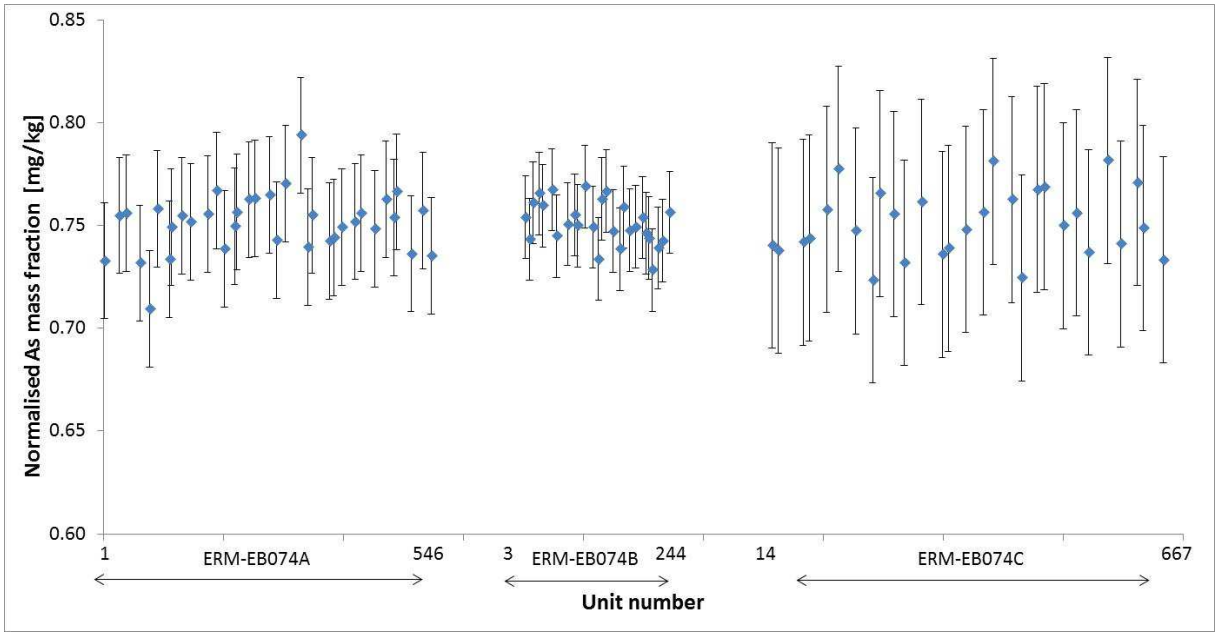
Ag (Silver)



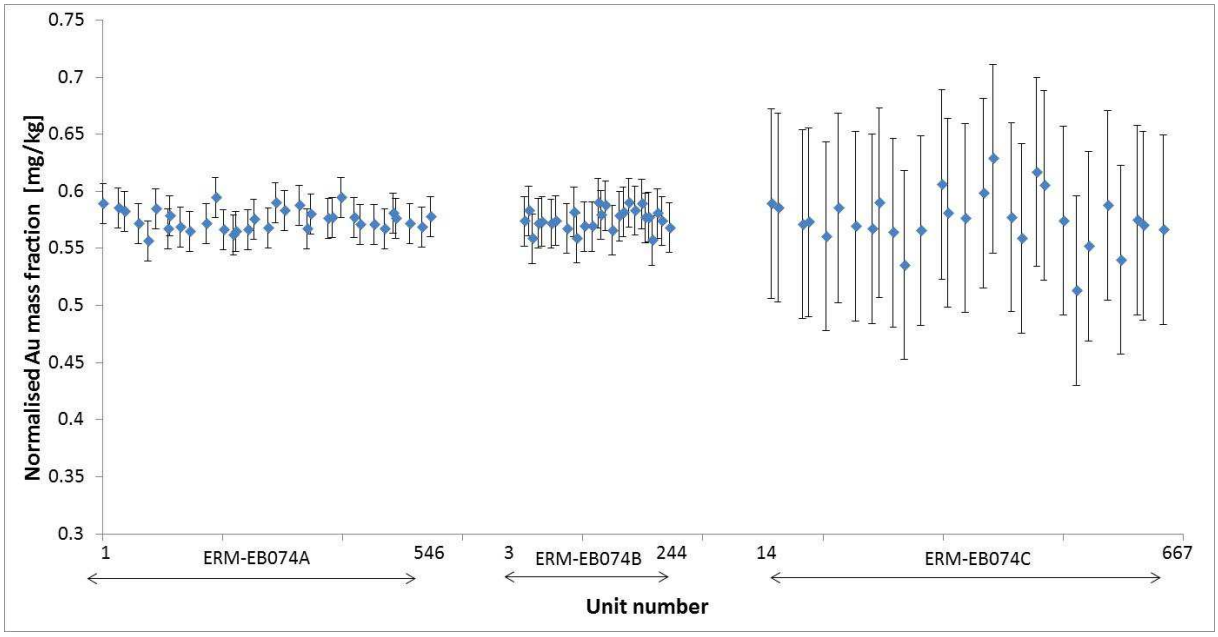
Al (Aluminium)



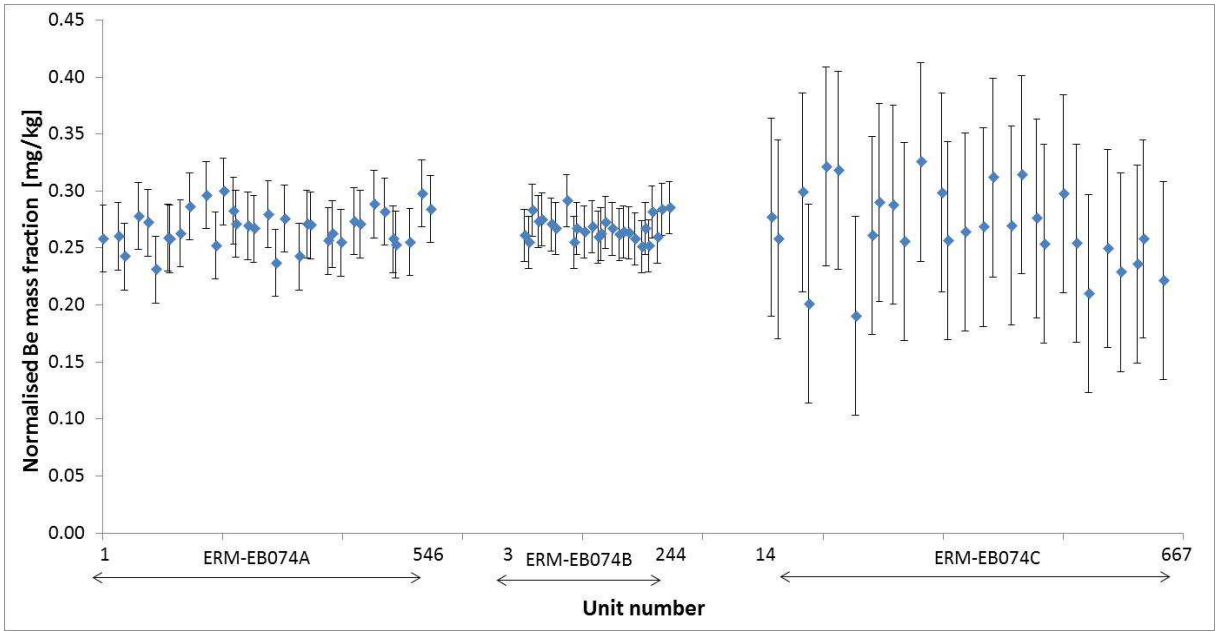
As (Arsenic)



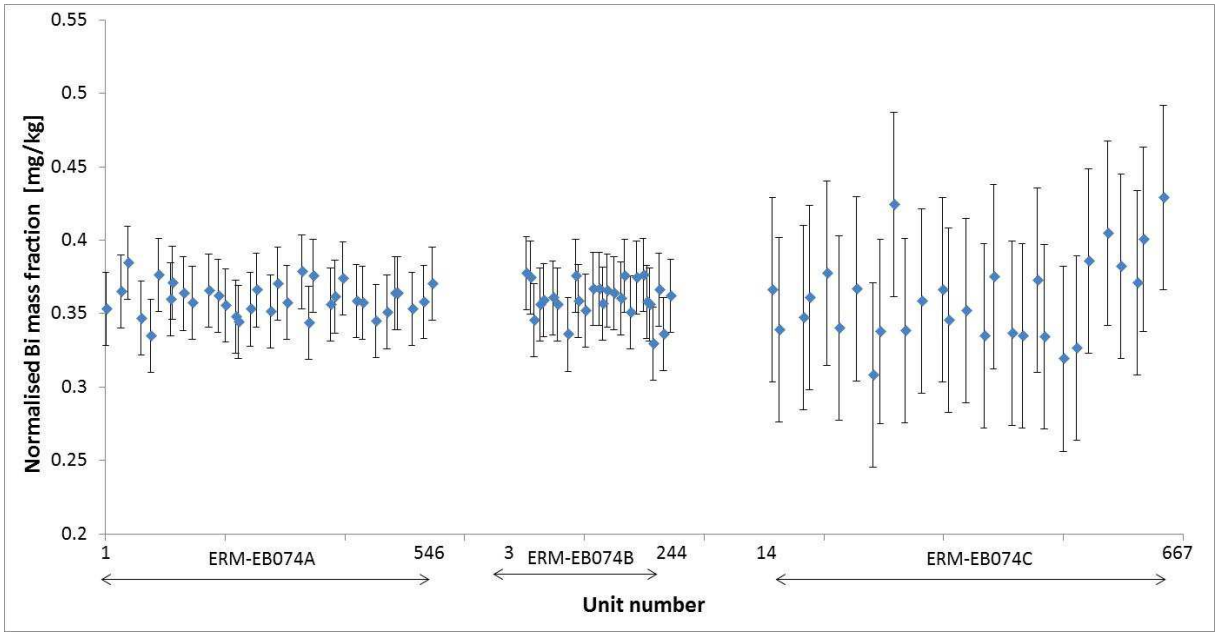
Au (Gold)



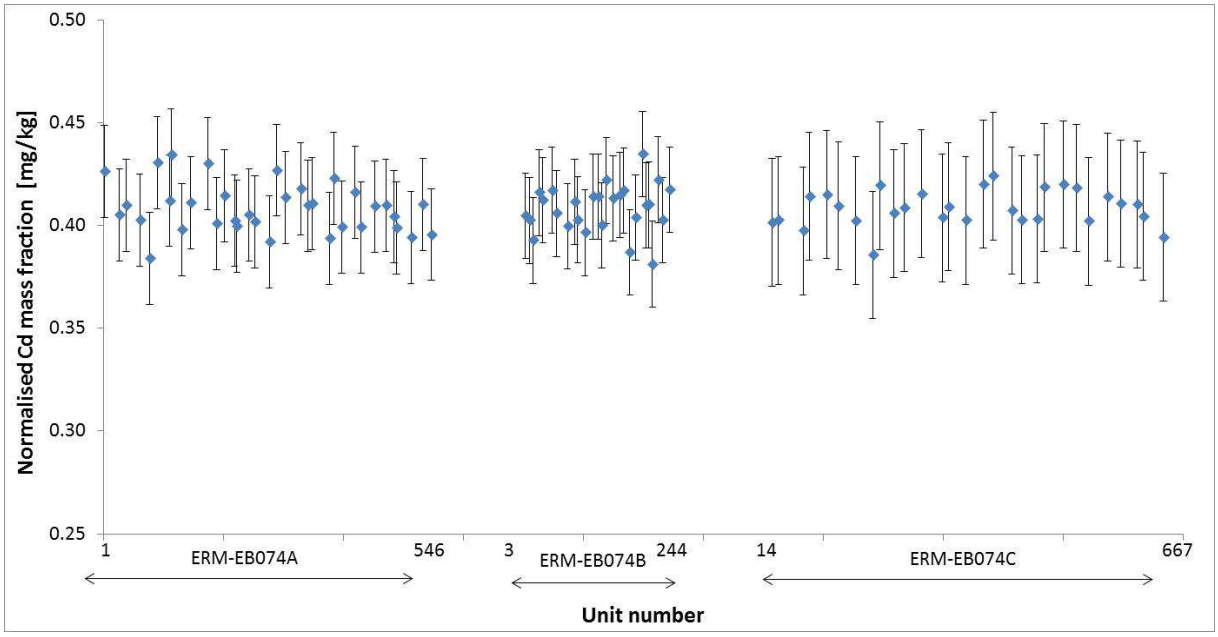
Be (Beryllium)



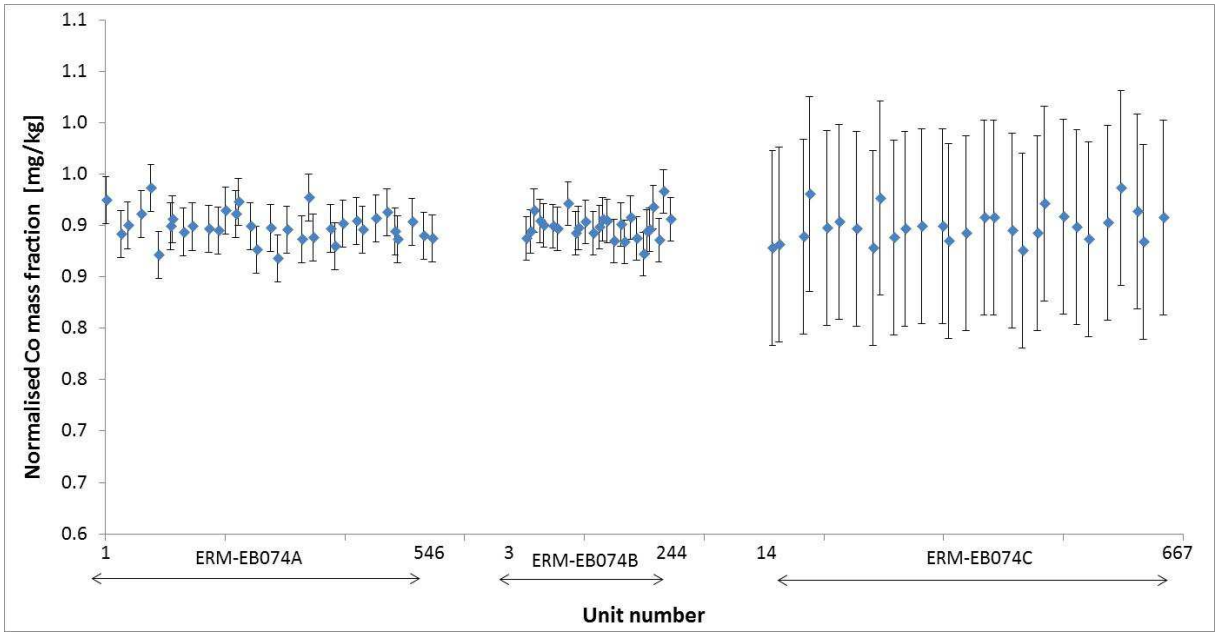
Bi (Bismuth)



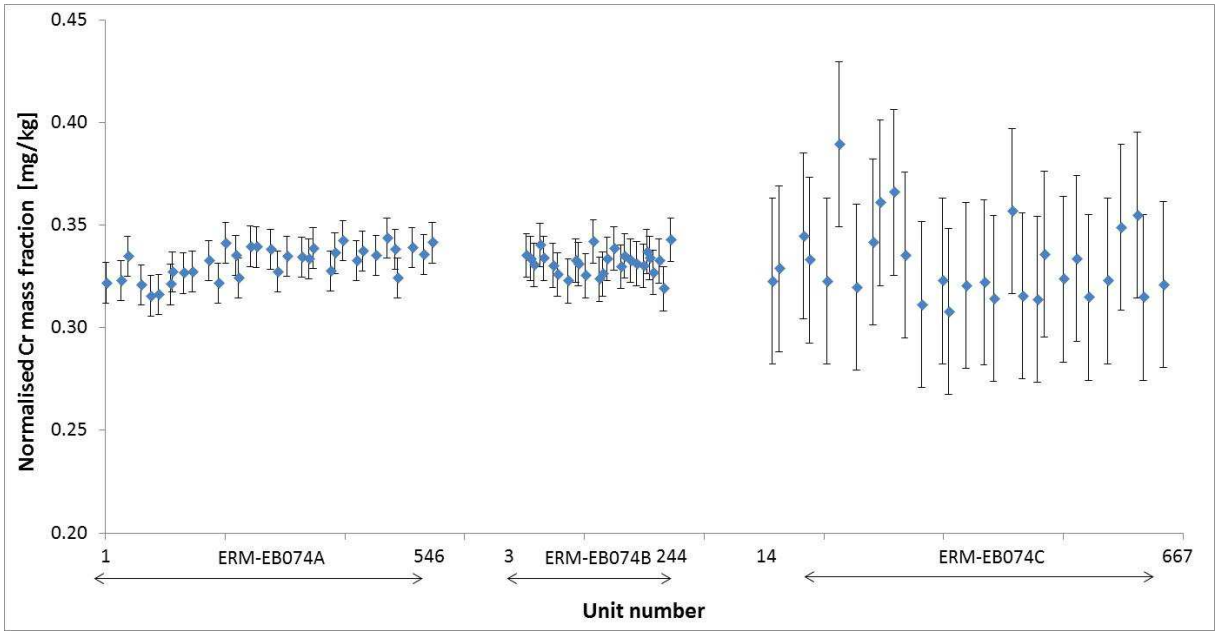
Cd (Cadmium)



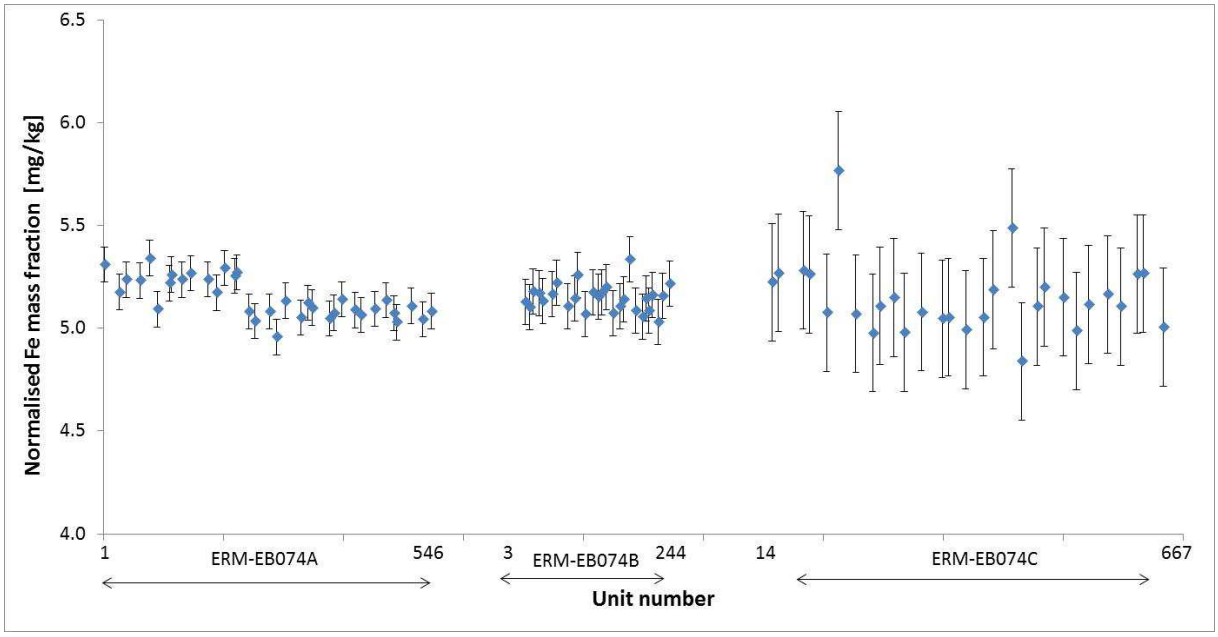
Co (Cobalt)



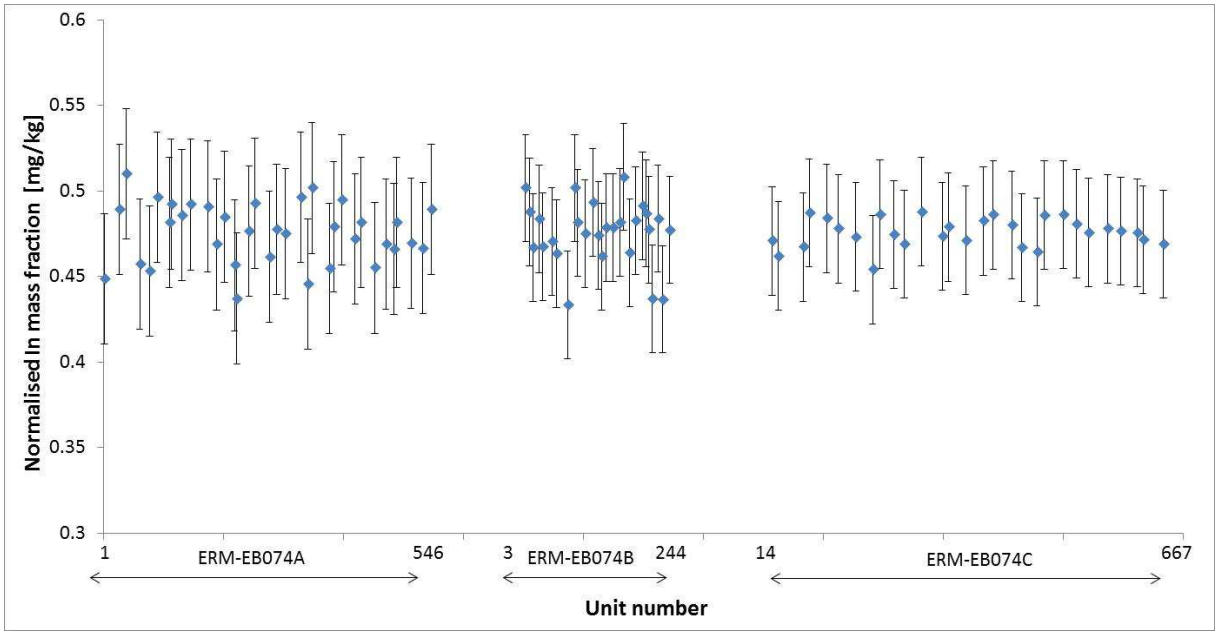
Cr (Chromium)



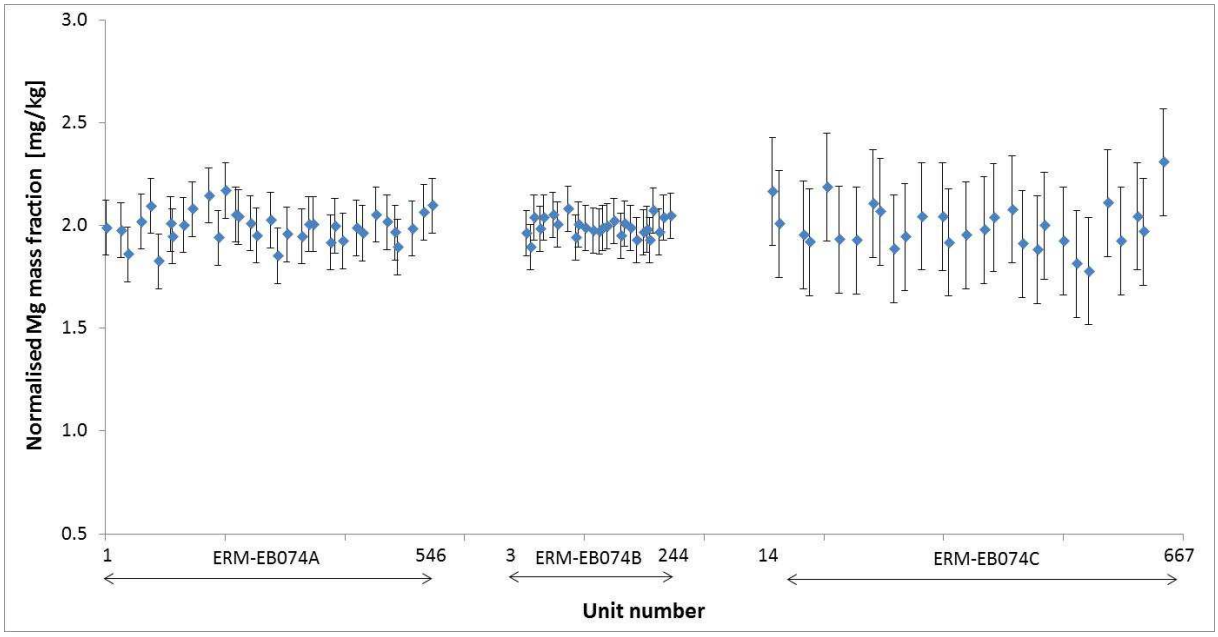
Fe (Iron)



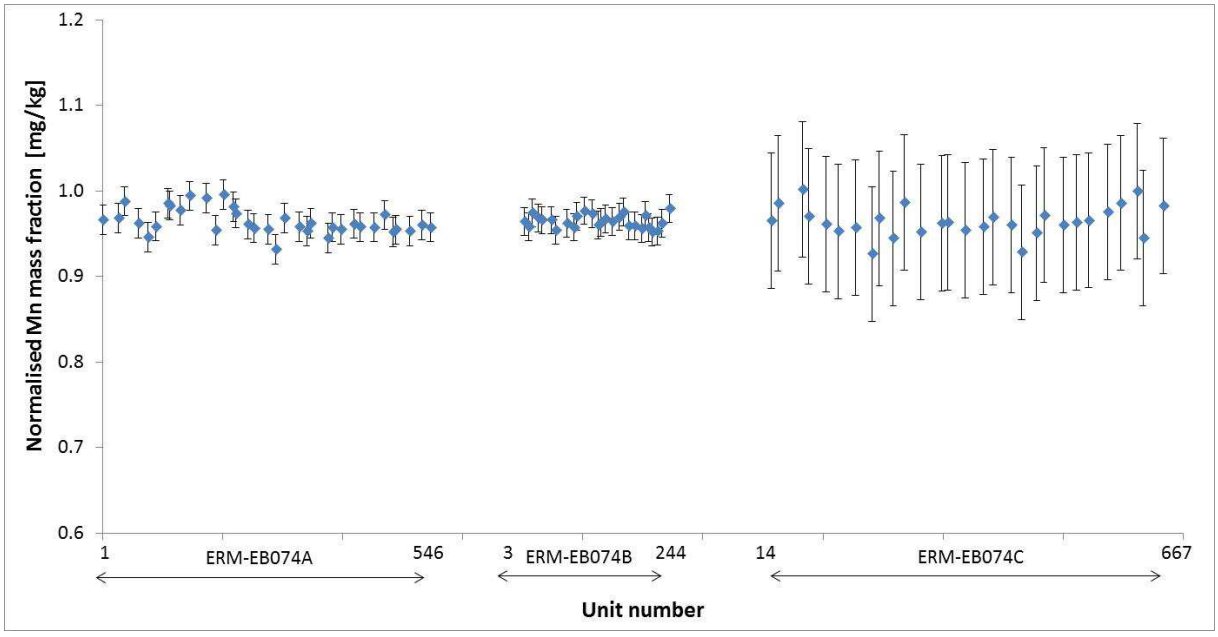
In (Indium)



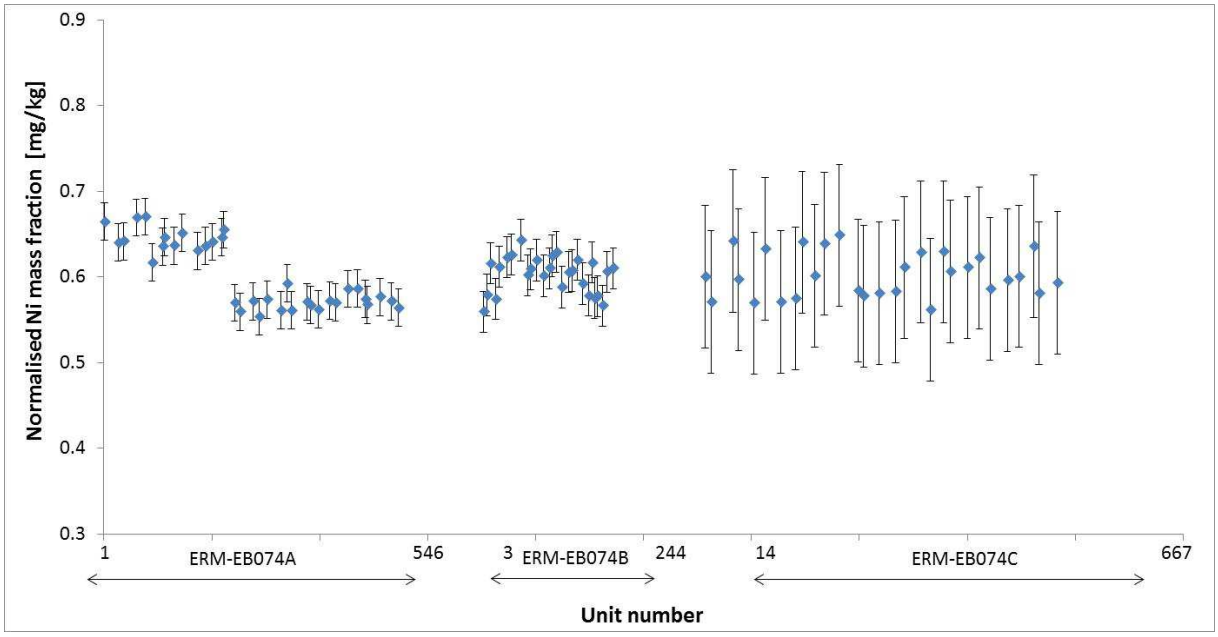
Mg (Magnesium)



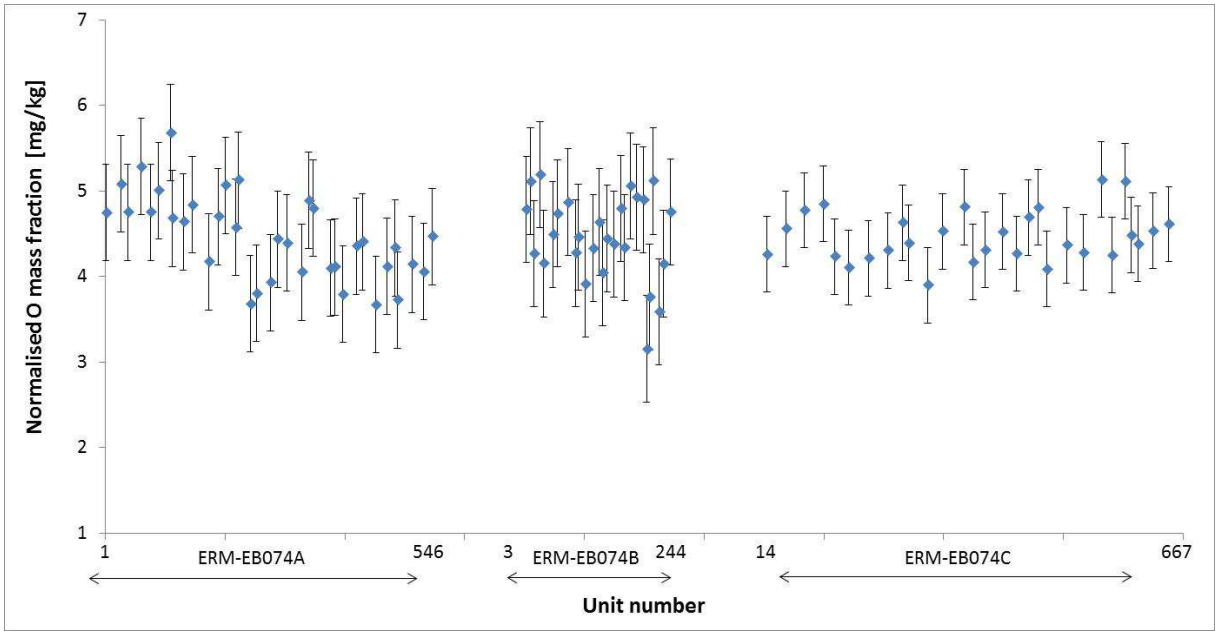
Mn (Manganese)



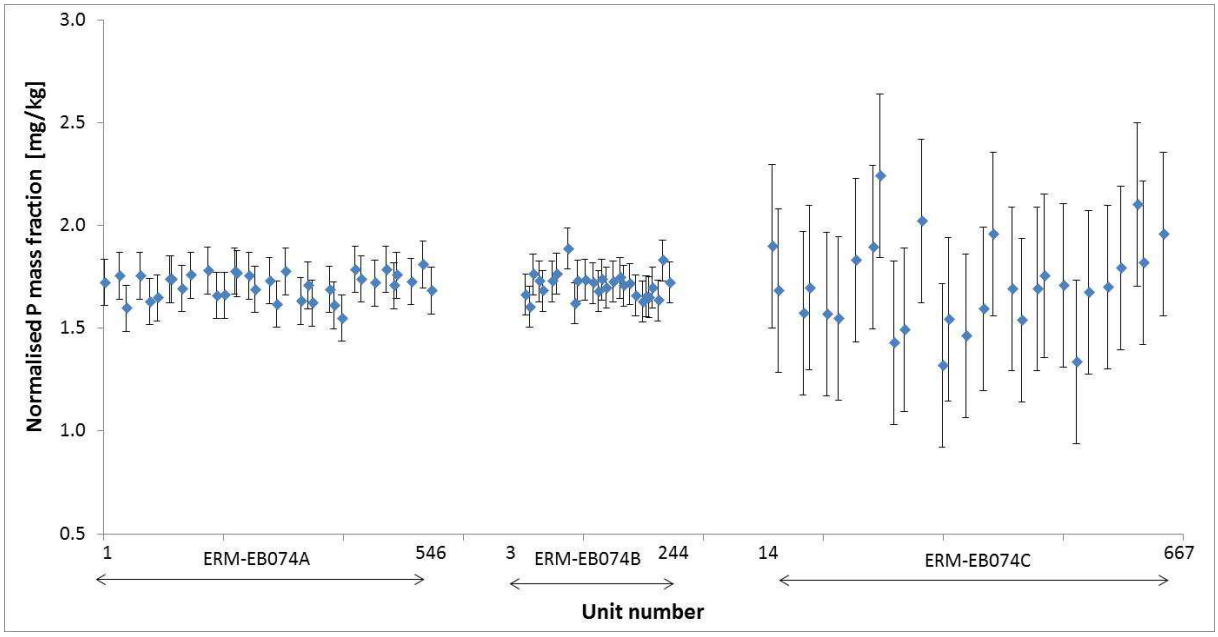
Ni (Nickel)



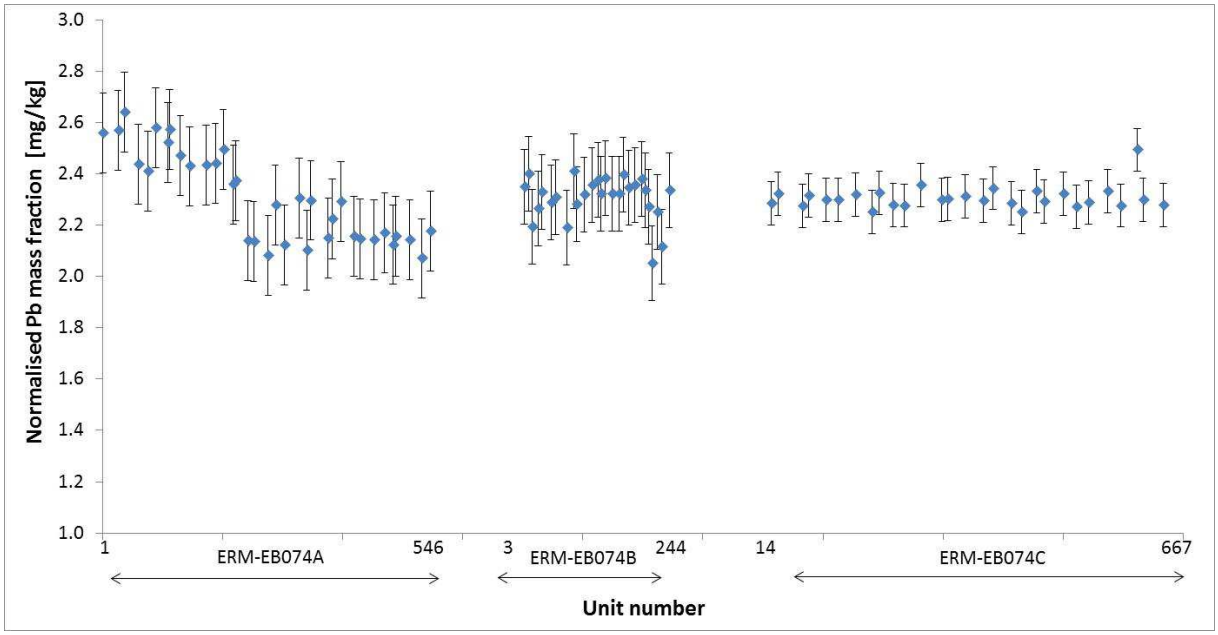
O (Oxygen)



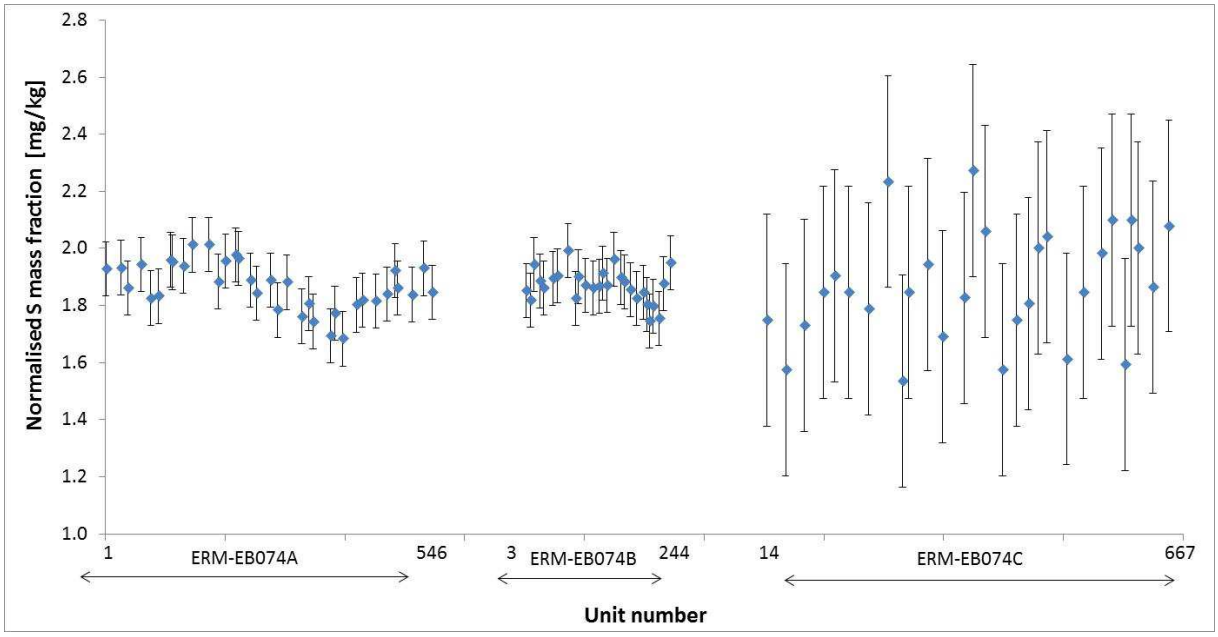
P (Phosphorus)



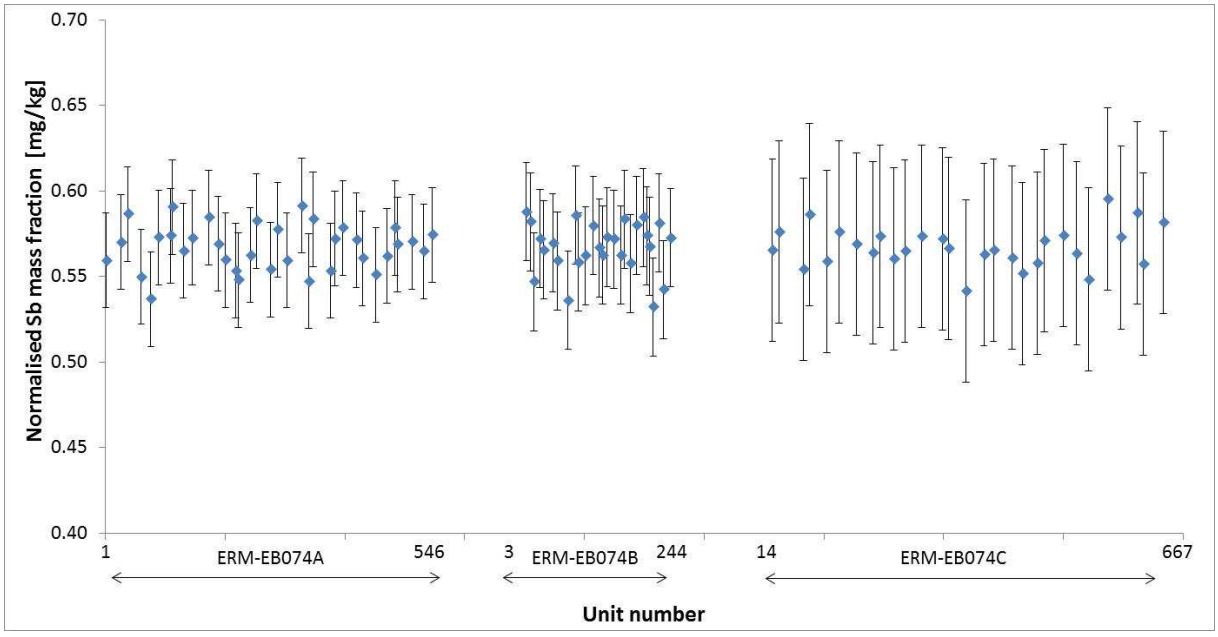
Pb (Lead)



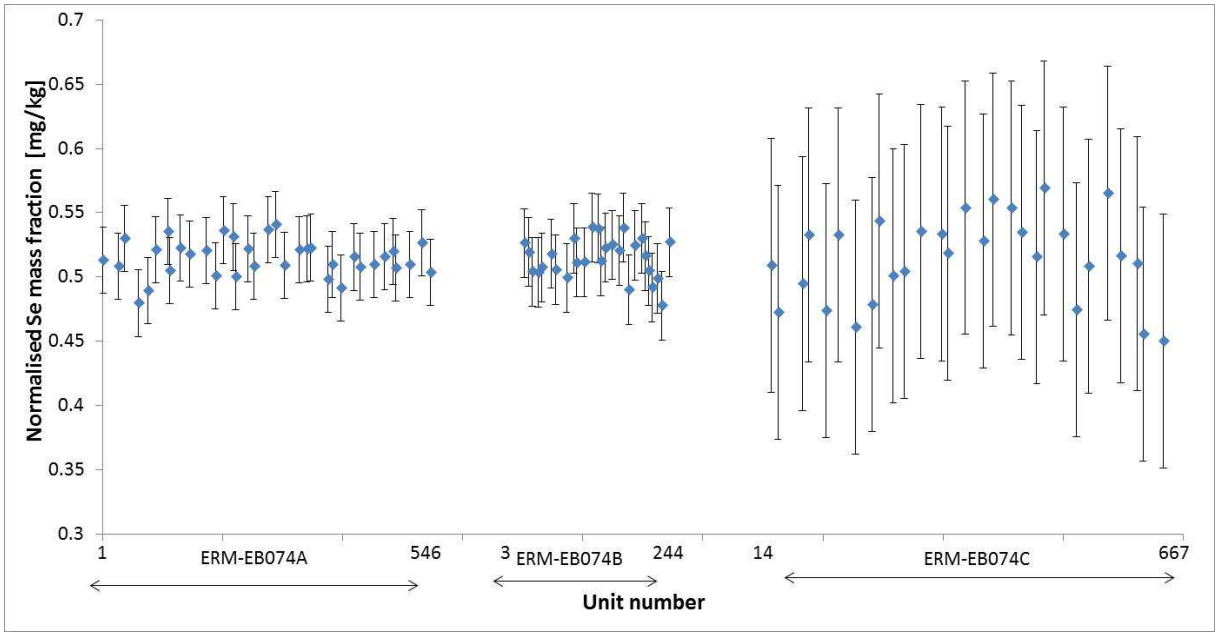
S (Sulfur)



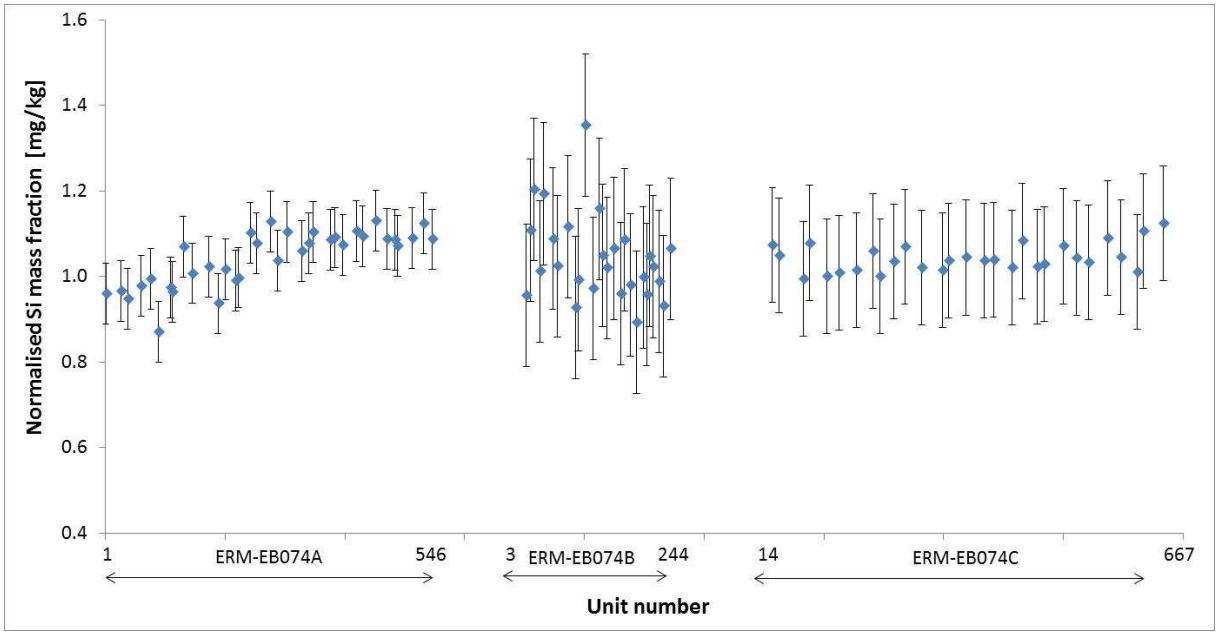
Sb (Antimony)



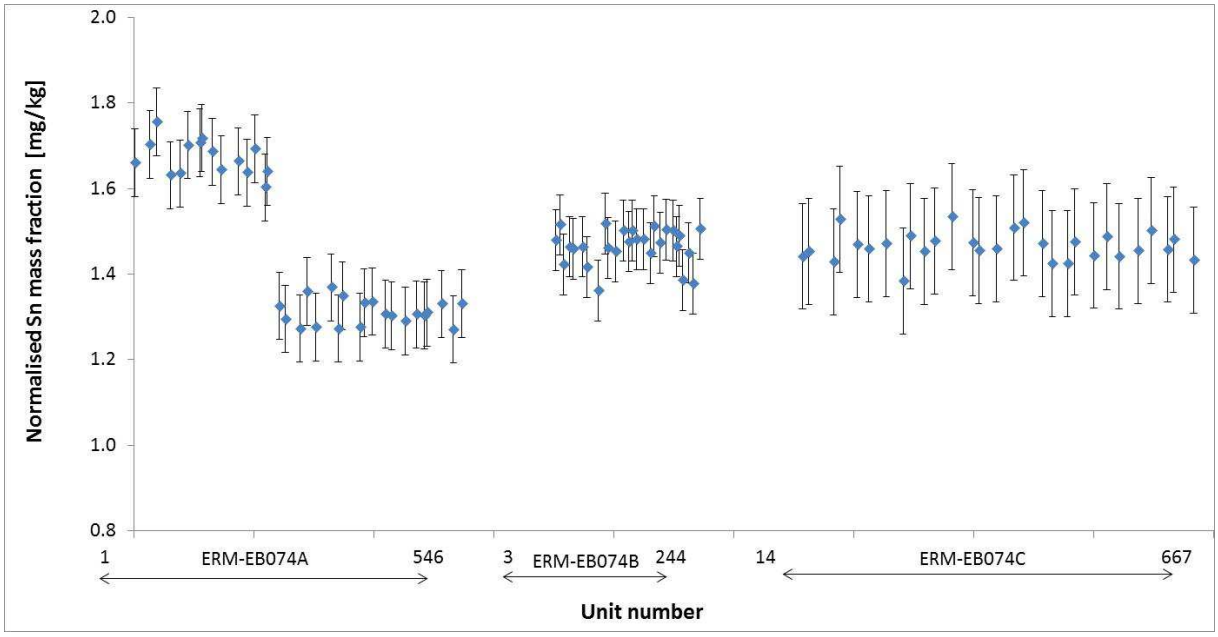
Se (Selenium)



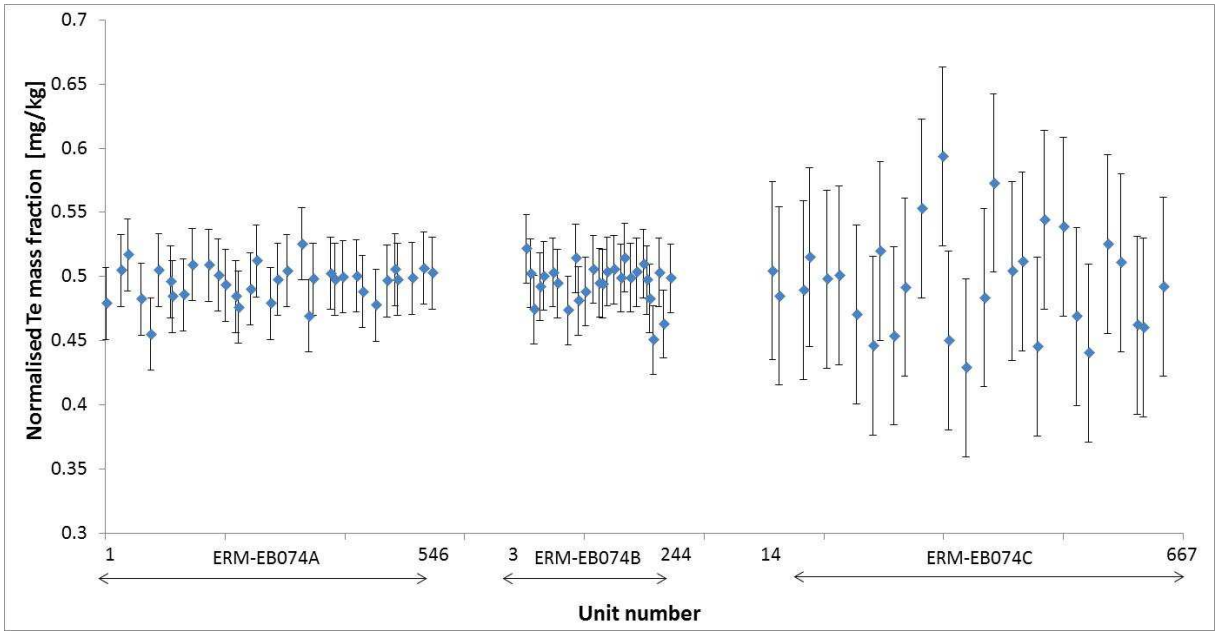
Si (Silicon)



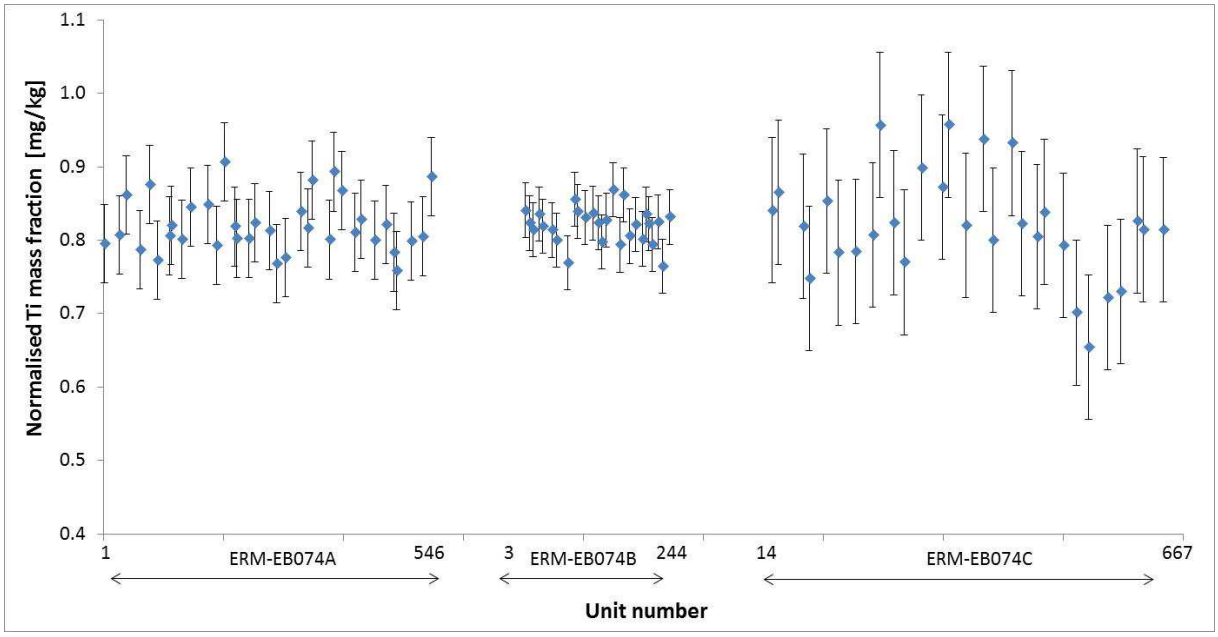
Sn (Tin)



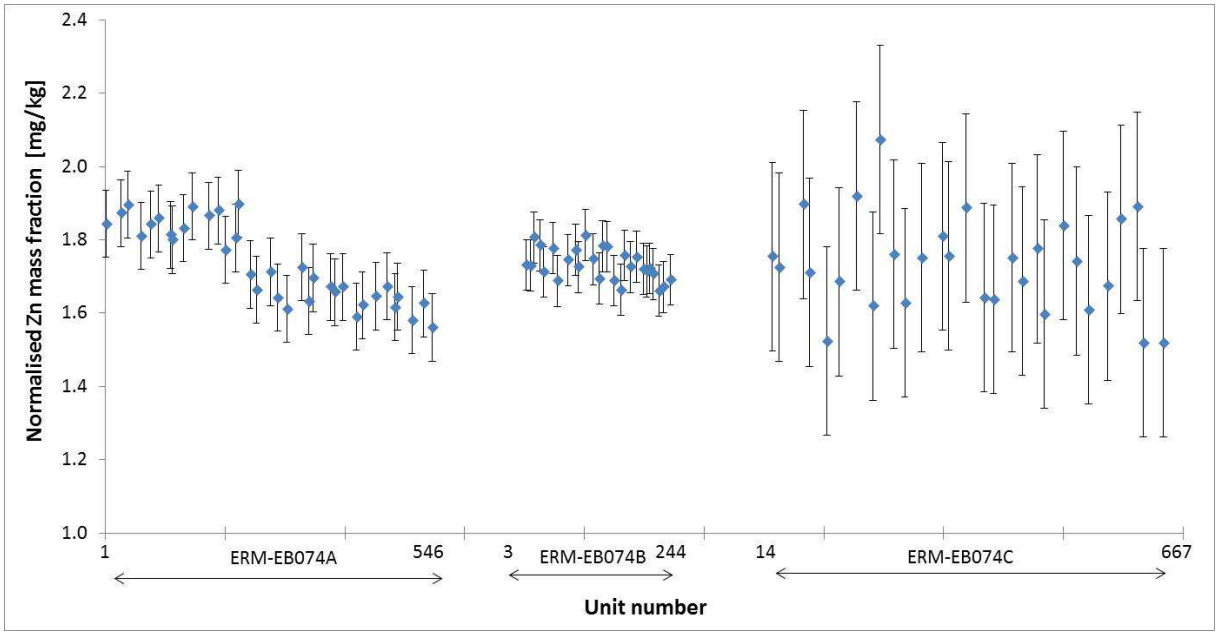
Te (Tellurium)



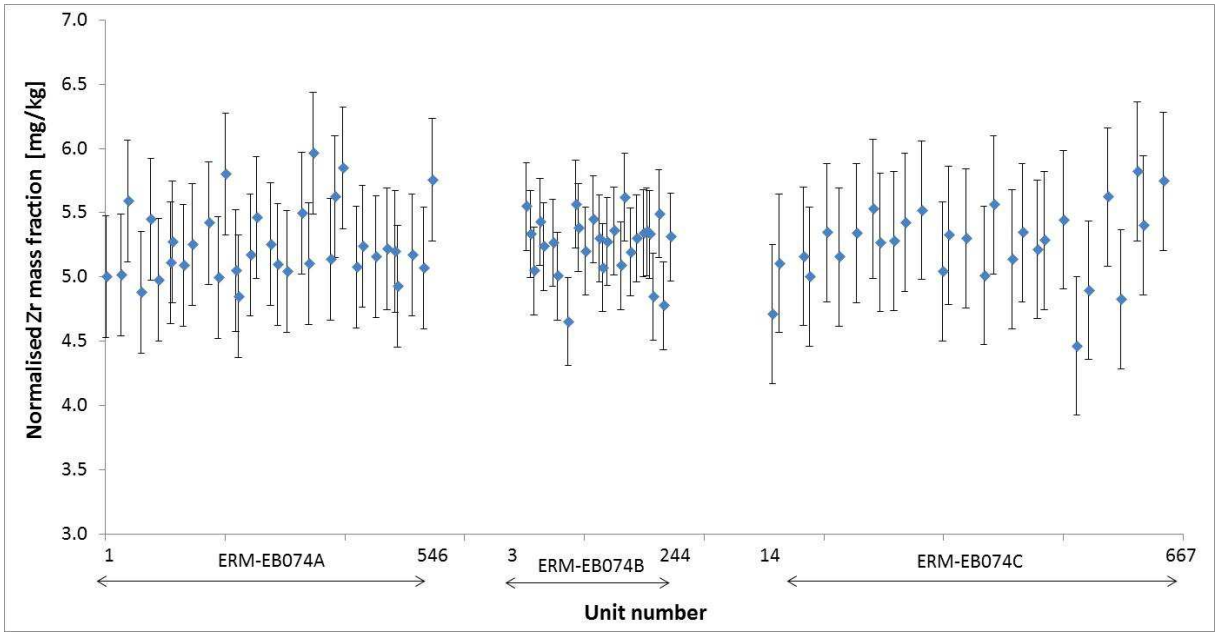
Ti (Titanium)



Zn (Zinc)



Zr (Zirconium)



Annex B: Results of the minimum sample intake measurements

The results presented in the Table correspond to the mean of each area on the four different disc faces analysed of ERM-EB074A. The standard deviation reported is the standard deviation between the results of the four disc faces. The measurements were performed by spark-OES except for Au, In and Te which were tested by GD-MS.

	Central area		Intermediate area		External area	
Analyte	Corrected / Normalised results [mg/kg]	Standard deviation of the measurements [mg/kg]	Corrected / Normalised results [mg/kg]	Standard deviation of the measurements [mg/kg]	Corrected / Normalised results [mg/kg]	Standard deviation of the measurements [mg/kg]
Ag	1.023	0.030	1.064	0.020	1.068	0.009
Al	1.447	0.050	1.458	0.072	1.473	0.044
As	1.457	0.100	1.588	0.084	1.559	0.118
Au [1)]	0.946	0.021	n.a.	n.a.	1.009	0.011
Be	0.603	0.006	0.627	0.006	0.625	0.009
Bi	0.382	0.072	0.358	0.099	0.347	0.076
Cd	0.563	0.025	0.558	0.024	0.527	0.021
Co	0.426	0.055	0.461	0.107	0.404	0.087
Cr	0.986	0.073	0.937	0.073	0.920	0.035
Fe	5.657	0.119	5.426	0.242	5.257	0.173
In [1)]	0.825	0.069	n.a.	n.a.	1.029	0.025
Mg	2.073	0.043	2.131	0.019	2.137	0.010
Mn	0.926	0.054	0.930	0.036	0.934	0.039
Ni	0.562	0.073	0.509	0.031	0.490	0.031
P	1.768	0.150	1.781	0.036	1.841	0.073
Pb	2.777	0.162	3.034	0.260	3.135	0.111
S	4.159	0.261	4.155	0.166	4.315	0.117
Sb	1.438	0.220	1.184	0.248	1.206	0.197
Se	0.802	0.096	0.795	0.071	0.771	0.035
Si	1.717	0.180	1.629	0.092	1.732	0.047
Sn	2.280	0.363	2.192	0.353	2.310	0.313
Te [1)]	0.857	0.070	n.a.	n.a.	1.024	0.030
Ti	1.351	0.018	1.345	0.013	1.347	0.010
Zn	2.241	0.079	2.164	0.169	2.230	0.077
Zr	6.104	0.096	6.289	0.146	6.507	0.085

[1)] element analysed by GD-MS, the analysis area did not allow to perform measurements in the intermediate area.

Annex C: Summary of methods used in the characterisation study

Laboratory code: L1

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, In, Mg, Mn, Ni, Pb, Sn, Te, Ti, Zn, Zr	ICP-MS	1	Hot acid digestion in HNO_3	external calibration, prepared from certified standard solutions Inorganic Venture	ELAN and Agilent 7700x
Cu	Titration	0.5 - 1	n.a.	Pure Cu shot from Alfa Aesar	Metrohm
Fe, P, Sb	ICP-OES	1	Hot acid digestion in HNO_3	external calibration, prepared from certified standard solutions Inorganic Venture	Agilent 735-ES
Au and Se	INAA	1	n.a.	external calibration, prepared from certified standard solutions Inorganic Venture	Canberra Ge Detector GC1318
Hg	CV-AAS	1	n.a.	external calibration, prepared from certified standard solutions ISOSpec	CETAC M-7600
O, H	IGF-IR	1	n.a.	RM from LECO and Alfa Aesar	Eltra ONH-2000
S	C-IR	1	n.a.	using metal RM from Alpha	Leco CS-200

Laboratory code: L2

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb, Sb, Se, Sn, Te, Ti, Zn, Zr	ICP-OES	4	Hot acid digestion in HNO_3 and HF	external calibration, prepared from certified standard solutions	Spectro (Arcos) and Perkin Elmer (5300DV)
Cu	electrogravimetry	2	Dissolution in HNO_3		
S	spark-OES	n.a.	n.a.	23 copper RMs and CRMs including BAM-M-381-386 and BCR-074 and BCR-075	Spectro Lab M9

Laboratory code: L3

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
As, Bi, Ni, Pb, Sb, Se, Sn, Te	ETV-ICP-OES	0.02	n.a.	4 copper RMs and CRMs including BCR-074 and BCR-075	Spectro Arcos-EOP

Laboratory code: L4

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	1	Hot acid digestion in HNO_3 and HF	external calibration, prepared from certified standard solutions from Merck, Alfa Aesar and Bernd Kraft	Thermo Element XR

Laboratory code: L5

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, W, Zn, Zr	GD-MS	n.a.	n.a.	Solid calibrants prepared from certified standard solutions from Merck, Alfa Aesar and Bernd Kraft	Thermo Element GD

Laboratory code: L6

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
As, Be, Bi, Fe, Pb, Sb, Se, Sn, Te	ICP-MS	2.5	Acid digestion/Yttrium collection to remove Cu matrix	High Purity certified stds	Perkin-Elmer Elan DRCII
Ag, Cd, Co, Cr, Mn, Ni, P, Si, Zn	ICP-OES	2.5	Acid digestion	SCP PlasmaCal certified stds	Varian 735-ES

Laboratory code: L7

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, As, Bi, Fe, Ni, Pb, S, Sb, Se, Sn, Te, Zn	DC-arc-OES	0.3	n.a.	NIST and Leco for sulfur Copper Spec for all others	Teledyne Leeman Prodigy

Laboratory code: L8

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	0.1	Acid digestion with HNO_3	external calibration, prepared from certified standard solutions from Inorganic Venture	Perkin Elmer DRC II

Laboratory code: L9

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, P, Pb, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	0.1	Acid digestion with HNO_3	external calibration, prepared from certified standards solution from Inorganic Venture	Perkin Elmer Elan 9000
O	IGF-IR	1	n.a.	external calibration with RMs from Alpha Resources and LECO	LECO TC-436
H	IGF-conductivity	1	n.a.	external calibration with RMs from Alpha Resources and LECO	LECO TC-436
S	C-IR	1	n.a.	external calibration with RMs from Alpha Resources and LECO	Analyseur C/S Horiba EMIA 820V

Laboratory code: L10

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, As, Au, Co, Cr, Cu, Fe, Hg, In, Sb, Se, Te, Zn	k_0 neutron activation analysis	0.2	n.a.	IRMM-530R	250 kW TRIGA Mark II reactor (GA), HPGe detector with 40 % relative efficiency (Canberra)

Laboratory code: L11

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Be, Bi, Cd, Co, Cr, Hg, In, Mg, Mn, Ni, Pb, S, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	0.1	Acid digestion with HNO_3	external calibration, prepared from certified standard solutions from VHG	THERMO iCAP QC
Fe, Mn, P, Si	ICP-OES	0.5	Acid digestion with HNO_3	external calibration, prepared from certified standard solutions from VHG	SPECTRO ARCOS
Au	ICP-MS	0.1	Acid digestion with HNO_3 and HCl	external calibration, prepared from certified standard solutions from VHG	THERMO iCAP QC
O, S, H	E1019	1	n.a.	external calibration with RM from Alpha Resources and LECO	LECO

Laboratory code: L12

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Bi, Cd, Co, In, Pb	ICP-MS	0.25	Acid digestion with HNO_3	external calibration, prepared from pure metal, KRISS CRM and from certified standard solutions from Perkin Elmer	Perkin-Elmer NEXION 300
Cr, Fe, Ni, P, Zn	ICP-MS	0.05	Acid digestion with HNO_3	external calibration, prepared from pure metal, KRISS CRM and from certified standard solutions from Perkin Elmer	Thermo Fisher ELEMENT XR magnetic sector field ICP mass spectrometer

Laboratory code: L13

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, O, P, Pb, S, Sb, Se, Sn, Te, Ti, Zn	GD-MS	n.a.	n.a.	external calibration using certified reference materials (BCR-075, BCR-022, SRM-494, BAM M382 and BAM M386)	VG9000

Laboratory code: L14

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, As, Au, Co, Cr, Cu, Fe, In, Sb, Se, Te, Zn, Zr	k_0 neutron activation analysis	0.2	n.a.	IRMM-530R	Samples irradiated in reactor and measured with HPGe detectors

Laboratory code: L15

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Au, Co, Cr, Fe, Sb, Se, Zn, Zr	Instrumental neutron activation analysis	0.2	n.a.	Calibration using SRMs from NIST	Samples irradiated in nuclear reactor Detector: 2 HPGe coaxial

Laboratory code: L16

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
As, Au, Bi, Cd, Cr, Hg, In, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, W, Zn	ICP - MS	2	Digestion with HCl and HNO_3	external calibration, prepared from certified standard solutions from Merck	Thermo iCAP Q
Ag, Al, Be, Co, Fe, Mg, Mn, Si, Zr	ICP-OES	2	Digestion with HCl and HNO_3	external calibration, prepared from certified standard solutions from Merck	Varian 725ES

Laboratory code: L17

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP - MS	2	Digestion with HCl and HNO_3	external calibration, prepared from certified standard solutions from Merck	Agilent 7500cx
Ag	ICP - MS	0.5	Digestion with HNO_3	external calibration, prepared from certified standard solutions from Merck	Agilent 7500cx
Al, P, S, Si	ICP-OES	5	Digestion with HCl and HNO_3	external calibration, prepared from certified standard solutions from Merck and Alfa Aesar	Varian 730-ES
O	C-IR	1	n.a.	LECO RM	Leco TC600

Laboratory code: L18

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, Al, As, Au, Be, Bi, Cd, Co, Cr, Fe, Hg, In, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Ti, W, Zn, Zr	ICP-MS	0.2	Hot acid digestion with HNO_3	external calibration, prepared from certified standard solutions from Inorganic Ventures	Agilent technologies AT 7500 CCT

Laboratory code: L20

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
As, Au, Be, Bi, Cd, Co, Cr, Fe, In, Mg, Mn, Ni, Pb, Se, Te, Ti, Zr, W	ICP-MS	0.25 g	Dissolution in closed vessel with acid and HBF4	external calibration, prepared from certified standard solutions for ICP	Agilent ICP-MS 7700
Ag, Al, Sb, Sn, Zn	ICP-MS	0.25 g	Open vessel dissolution with acid	external calibration, prepared from certified standard solutions for ICP	Agilent ICP-MS 7700

Laboratory code: L21

Elements	Technique	Sample mass [g]	Sample preparation	Calibration	Instrumentation
Ag, As, Bi, Cd, Co, Cr, Fe, Mn, Ni, P, Pb, S, Sb, Se, Sn, Te, Zn	Spark-OES	n.a.	Sample cleaned with diluted HNO_3 and ethanol	external calibration using CRMs	Spectrolab M8

Annex D: Results of the characterisation measurements for ERM-EB074A, B and C (data not pooled).

The results reported correspond to the mean of the mean of the laboratory for each format (ERM-EB074A, B and C).

	ERM-EB074A		ERM-EB074B		ERM-EB074C	
Analyte	Mean of laboratory mean [mg/kg]	standard deviation of mean [mg/kg]	Mean of laboratory mean [mg/kg]	standard deviation of mean [mg/kg]	Mean of laboratory mean [mg/kg]	standard deviation of mean [mg/kg]
Ag	1.007	0.022	1.041	0.033	1.032	0.023
Al	0.741	0.142	0.755	0.164	0.747	0.172
As	1.209	0.030	1.230	0.034	1.262	0.042
Au	0.499	0.026	0.500	0.028	0.530	0.026
Be	0.294	0.021	0.291	0.025	0.310	0.027
Bi	0.478	0.034	0.475	0.033	0.486	0.023
Cd	0.402	0.018	0.395	0.020	0.410	0.018
Co	0.807	0.040	0.794	0.040	0.782	0.040
Cr	0.372	0.014	0.378	0.020	0.370	0.015
Fe	6.065	0.457	5.640	0.169	5.644	0.238
In	0.482	0.015	0.490	0.015	0.502	0.017
Mg	2.018	0.140	2.056	0.130	2.040	0.130
Mn	0.924	0.025	0.894	0.031	0.928	0.024
Ni	0.612	0.023	0.604	0.014	0.608	0.013
O	7.497	1.001	8.942	0.826	8.206	1.294
P	1.522	0.091	1.597	0.107	1.566	0.127
Pb	2.670	0.074	2.668	0.084	2.398	0.286
S	3.178	0.359	3.449	0.713	3.187	0.622
Sb	0.572	0.020	0.565	0.019	0.566	0.018
Se	0.551	0.039	0.551	0.025	0.550	0.063
Si	1.235	0.185	1.289	0.200	1.356	0.070
Sn	1.455	0.051	1.520	0.068	1.522	0.028
Te	0.529	0.027	0.519	0.022	0.525	0.044
Ti	0.970	0.061	0.915	0.063	0.975	0.072
Zn	2.201	0.132	2.158	0.122	2.243	0.121
Zr	6.175	1.429	6.002	1.320	6.215	1.324

Annex E: Results of the characterisation measurements

The characterisation study was performed using the results with the number of significant digits provided by each laboratory. In the Figures of Annex E, the results are reported with two significant digits after the coma for formatting reason.

Ag (Silver)

Table E1. Individual results for Ag mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	1.00	1.00	1.00	1.00	1.20	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.10	1.50	1.00	1.00	1.00	1.00	1.04	0.25
L4-ICP-MS	0.99	1.15	1.12	1.00	1.15	1.00	1.16	1.02	1.03	1.18	1.14	1.03	1.03	1.03	1.18	1.19	1.04	0.72	1.06	0.09
L5-GD-MS	0.96	0.97	0.91	1.05	0.91	0.93	1.05	0.99	0.89	1.03	0.96	0.93							0.97	0.10
L7-DC-arc-OES													1	1	1	1	1	1	1	n.a.
L8-ICP-MS	0.95	0.95	0.96	0.94	0.96	0.97	0.97	0.96	0.95	0.95	0.95	0.96	0.95	0.97	0.96	0.95	0.96	0.97	0.96	0.10
L9-ICP-MS	1.30	0.99	1.25	1.19	0.99	0.98	1.25	1.31	1.27	1.29	0.99	1.27	1.24	1.03	0.99	1.00	0.99	0.99	1.13	0.23
L10-INAA	1.08	1.12	1.10	1.09	1.12	1.12	1.12	1.10	1.11	1.12	1.11	1.10	1.10	1.16	1.13	1.17	1.12	1.14	1.12	0.05
L11-ICP-MS	0.93	0.91	0.97	0.92	0.91	0.90	0.92	0.94	0.90	0.92	1.03	1.04	1.00	0.95	0.95	0.93	0.94	0.93	0.94	0.24
L13-GD-MS	1.00	1.06	1.05	1.01	1.08	1.03	1.11	1.03	1.07	1.08	1.08	1.03							1.05	0.05
L14-INAA	0.99	1.03	0.94	1.03	1.01	1.04	0.99	1.03	0.94	1.03	1.01	1.04	1.02	1.06	1.09	1.10	1.04	1.09	1.03	0.05
L15-INAA	1.06	1.10	1.00	1.19	1.17	1.02	1.05	1.09	1.14	1.08	1.05	1.15	1.16	1.10	1.17	1.19	1.27	1.25	1.12	0.05
L16-ICP-OES	0.86	0.93	0.90	0.89	0.89	0.95	0.93	0.67	0.86	0.87	0.67	0.71	0.92	0.98	0.76	1.32	0.77	0.78	0.87	0.14
L17-ICP-MS	0.99	1.02	1.03	1.06	1.01	1.05	1.00	1.04	1.04	1.06	1.04	1.05	1.05	1.07	1.02	1.06	1.06	1.07	1.04	0.14
L18-ICP-MS	0.85	0.88	0.87	0.87	0.92	0.87	1.23	1.26	1.30	1.25	1.09	1.23	0.87	0.90	0.90	0.90	0.95	0.90	1.00	0.34
L20-ICP-MS													1.10	1.00	1.10	1.30	1.00	0.90	1.07	0.27
Results not used for certification																				
L1-ICP-MS	0.34	0.26	0.23	0.35	0.19	0.29	0.14	0.18	0.23	0.23	0.26	0.38	0.22	0.28	0.17	0.27	0.24	0.23	0.25	0.13
L12-ICP-MS	0.92	0.84	0.83	0.93	0.86	0.98	0.84	0.95	0.94	0.84	0.84	0.98	0.92	0.94	0.84	0.87	0.93	0.92	0.90	0.20
L6-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1		
L21-Spark-OES	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2								

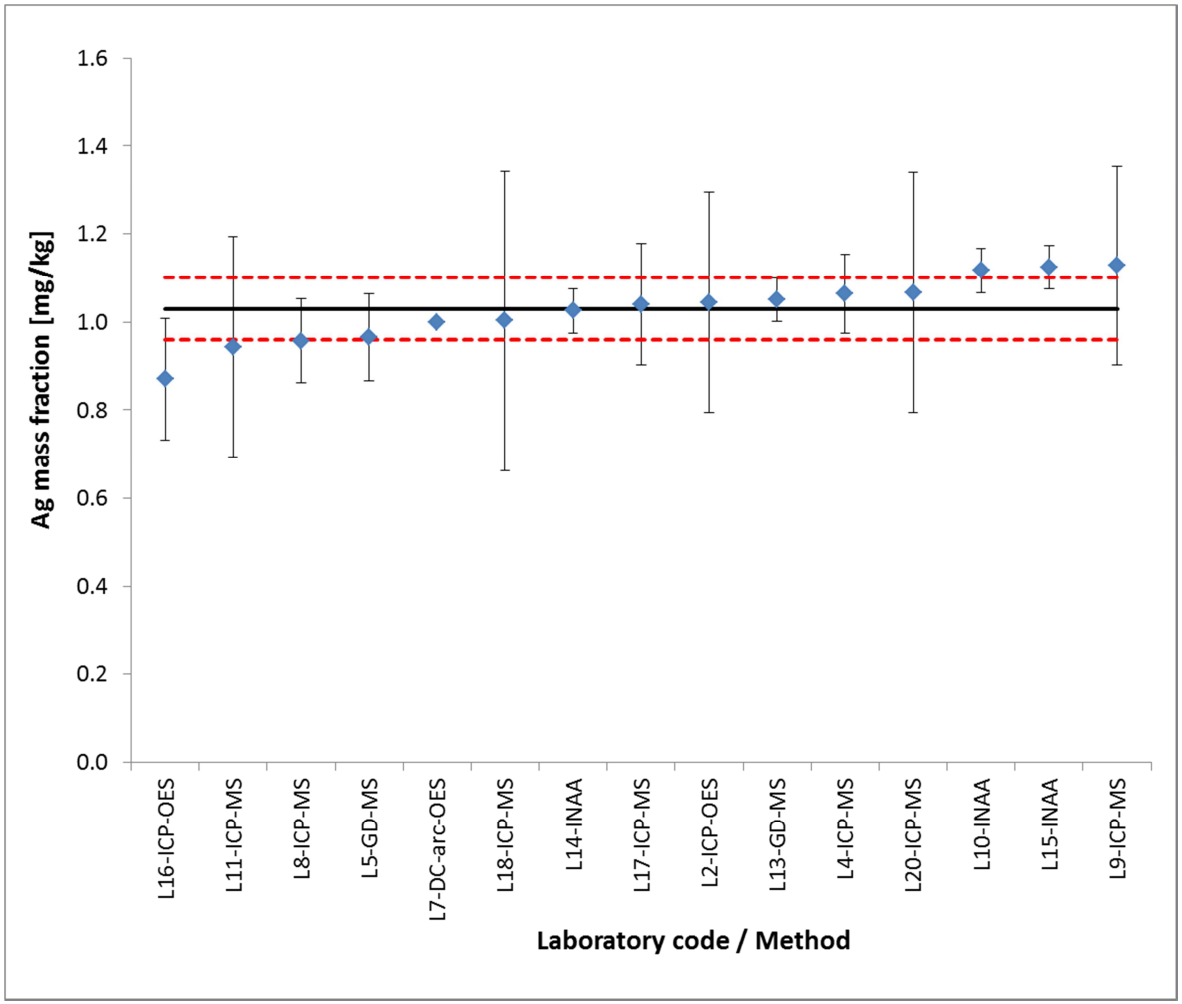


Figure E1. Mean Ag mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Al (Aluminium)

Table E2. Individual results for Al mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	1.20	1.20	1.50	1.30	1.60	1.20	1.20	1.30	1.40	1.30	1.90	1.30	1.20	1.30	1.30	1.40	1.40	1.20			1.34	0.36
L5-GD-MS	0.55	0.36	0.39	0.71	0.62	0.37	0.93	0.96	0.32	0.95	0.54	0.40									0.59	0.43
L8-ICP-MS	0.45	0.45	0.45	0.46	0.46	0.45	0.45	0.46	0.46	0.44	0.45	0.45	0.47	0.44	0.46	0.46	0.47	0.45			0.45	0.05
L11-ICP-MS	1.33	1.26	1.35	1.40	1.42	1.12	1.41	1.21	1.42	1.39	1.42	1.46	1.45	1.31	1.41	1.41	1.34	1.38			1.36	0.34
L13-GD-MS	0.98	1.00	1.05	1.07	0.91	0.98	1.10	1.02	1.13	1.05	1.05	1.14									1.04	0.12
L16-ICP-MS	0.65	0.51	0.27	0.73	0.51	0.79	0.30	0.30	0.38	0.50	0.49	0.44	0.44	0.40	0.33	0.33	0.61	0.53			0.47	0.16
L17-ICP-OES	0.67	0.55	0.49	0.61	0.63	0.56	0.52	0.50	0.51	0.56	0.48	0.51	0.44	0.55	0.51	0.61	0.57	0.56			0.55	0.11
L20-ICP-MS													1.00	1.00	1.10	0.90	0.90	1.10			1.00	0.18
Results not used for certification																						
L1-ICP-MS	1.41	4.70	2.88	3.60	1.80	2.50	5.30	1.01	1.34	1.86	2.19	1.85	2.18	2.93	3.32	2.70	1.91	3.96			2.64	2.35
L4-ICP-MS	0.78	0.99	1.11	0.51	1.95	0.21	2.16	1.45	0.35	3.08	0.93	0.43	0.40	1.43	1.34	1.66	0.37	1.25			1.13	0.17
L9-ICP-MS	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	<1				
L18-ICP-MS	14.26	5.82	17.11	14.77	13.41	12.80	11.74	13.13	20.56	15.59	10.80	10.79	12.64	14.91	15.41	16.28	15.33	11.95			13.74	6.24

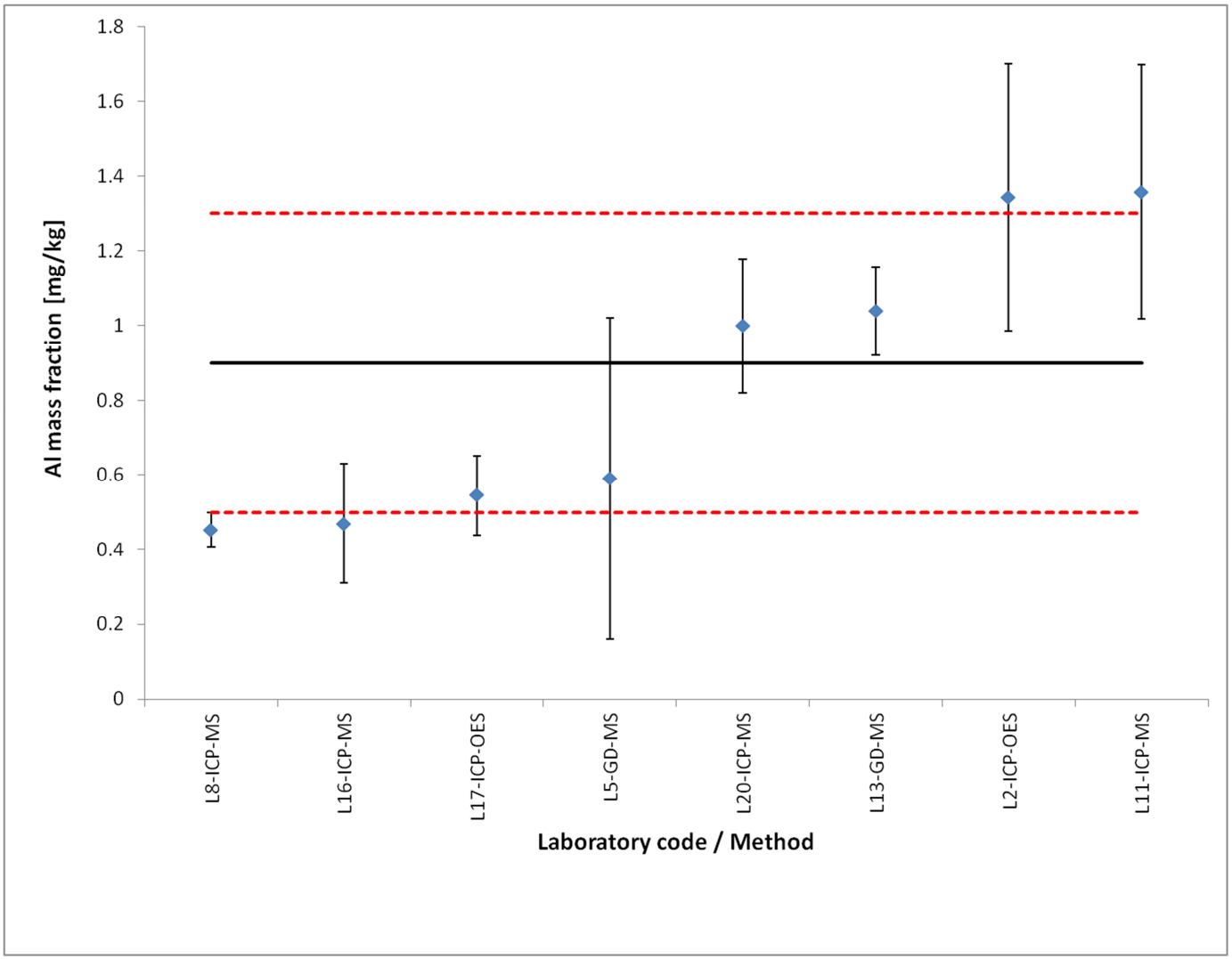


Figure E2. Mean Al mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the mean of laboratory means, while the broken lines represent the expanded uncertainty of the mean of laboratory means. Each laboratory is represented by its code.

As (Arsenic)

Table E3. Individual results for As mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	1.30	1.38	1.09	1.31	1.20	1.07	1.28	0.89	1.29	1.49	1.18	1.18	1.36	1.19	1.15	1.39	1.25	1.37			1.24	0.28
L2-ICP-OES	1.20	1.10	1.40	1.10	1.10	1.10	1.10	1.10	1.00	1.20	1.00	1.30	1.30	1.00	1.20	1.10	1.10	1.20			1.14	0.22
L3-ETV-ICP-OES	1.17	1.16	1.14	1.14	1.16	1.10	1.10	1.10	1.15	1.11	1.15	1.15	1.16	1.15	1.16	1.15	1.13	1.12	1.13	1.11	1.14	0.07
L4-ICP-MS	1.08	1.09	1.14	1.05	1.05	1.03	1.15	1.05	1.05	1.10	1.09	1.05	1.08	1.03	1.11	1.08	1.05	1.16			1.08	0.07
L5-GD-MS	1.13	1.13	1.01	1.13	1.01	1.07	1.15	1.07	1.06	1.12	1.04	1.12									1.09	0.09
L6-ICP-MS	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.30	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20			1.21	0.05
L7-DC-arc-OES													1.20	1.10	1.00	1.10	1.10	1.00			1.08	0.15
L9-ICP-MS	1.30	1.22	1.32	1.27	1.27	1.25	1.30	1.25	1.30	1.31	1.26	1.28	1.35	1.26	1.24	1.24	1.25	1.25			1.27	0.25
L10-INAA	1.28	1.09	1.20	1.12	1.20	1.20	1.41	1.29	1.44	1.26	1.18	1.22	1.16	1.42	1.19	1.35	1.43	1.30			1.26	0.15
L11-ICP-MS	1.18	1.18	1.23	1.24	1.21	1.22	1.19	1.18	1.21	1.19	1.21	1.23	1.23	1.14	1.20	1.19	1.21	1.19			1.20	0.30
L13-GD-MS	1.07	1.18	1.14	1.17	1.10	1.17	1.24	1.11	1.18	1.20	1.16	1.19									1.16	0.13
L14-INAA	1.22	1.20	1.25	1.21	1.24	1.13	1.31	1.20	1.26	1.18	1.30	1.20	1.35	1.12	1.31	1.24	1.27	1.29			1.24	0.18
L16-ICP-MS	1.29	1.87	1.59	1.22	1.43	1.31	1.76	1.16	1.33	1.72	1.69	1.49	1.40	1.31	1.67	1.67	1.35	1.69			1.50	0.33
L17-ICP-MS	1.24	1.31	1.39	1.26	1.38	1.25	1.29	1.30	1.24	1.37	1.38	1.25	1.25	1.26	1.38	1.47	1.23	1.49			1.32	0.28
L20-ICP-MS													1.50	1.58	1.65	1.60	1.55	1.60			1.58	0.10
Results not used for certification																						
L8-ICP-MS	0.42	0.40	0.34	0.39	0.41	0.38	0.41	0.41	0.38	0.41	0.39	0.39	0.36	0.35	0.38	0.38	0.39	0.41			0.39	0.04
L18-ICP-MS	1.79	1.82	1.77	1.71	1.88	1.71	1.55	1.46	1.56	1.27	1.04	1.28	1.70	1.79	1.83	1.74	1.75	1.68			1.63	0.46
L21-Spark-OES	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5										

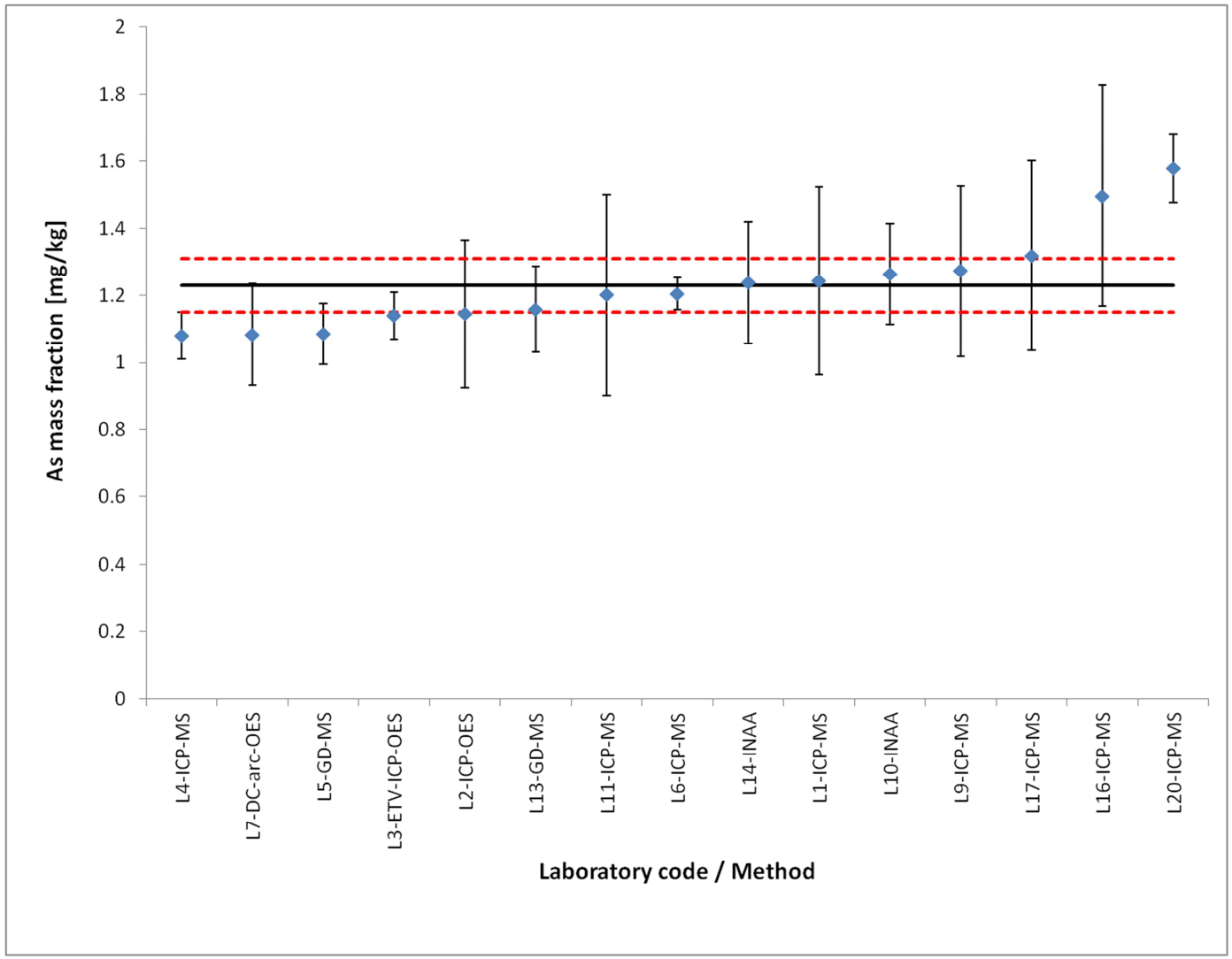


Figure E3. Mean As mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Au (Gold)

Table E4. Individual results for Au mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-INAA	0.48	0.44	0.41	0.45	0.50	0.43	0.45	0.48	0.43	0.44	0.42	0.40	0.50	0.50	0.46	0.53	0.46	0.47			0.46	0.07
L8-ICP-MS	0.66	0.66	0.64	0.65	0.61	0.65	0.70	0.62	0.65	0.68	0.63	0.66	0.67	0.64	0.67	0.65	0.67	0.64			0.65	0.07
L10-INAA	0.52	0.53	0.51	0.51	0.52	0.52	0.52	0.52	0.51	0.53	0.52	0.52	0.52	0.53	0.52	0.54	0.52	0.53			0.52	0.02
L11-ICP-MS	0.57	0.57	0.59	0.59	0.59	0.58	0.56	0.57	0.57	0.58	0.57	0.56	0.56	0.58	0.58	0.58	0.59	0.59			0.58	0.08
L14-INAA	0.50	0.50	0.51	0.50	0.51	0.50	0.51	0.49	0.51	0.49	0.52	0.50	0.54	0.51	0.51	0.51	0.53	0.52			0.51	0.02
L15-INAA	0.52	0.49	0.50	0.52	0.53	0.51	0.50	0.53	0.52	0.50	0.50	0.51	0.52	0.53	0.52	0.53	0.53	0.53			0.52	0.01
L16-ICP-MS	0.44	0.41	0.41	0.37	0.43	0.35	0.40	0.21	0.31	0.46	0.37	0.34	0.36	0.35	0.40	0.40	0.38	0.50			0.38	0.22
L17-ICP-MS	0.40	0.45	0.46	0.42	0.45	0.39	0.52	0.44	0.46	0.51	0.48	0.45	0.47	0.48	0.48	0.47	0.42	0.46			0.46	0.10
L18-ICP-MS	0.42	0.43	0.43	0.48	0.49	0.48	0.52	0.45	0.49	0.49	0.43	0.49	0.43	0.47	0.48	0.49	0.51	0.53			0.47	0.07
L20-ICP-MS													0.67	0.68	0.63	0.62	0.67	0.65			0.65	0.05
Results not used for certification																						
L9-ICP-MS	0.34	0.40	0.41	0.26	0.31	0.39	0.37	0.33	0.36	0.31	0.34	0.39	0.30	0.29	0.28	0.27	0.27	0.34			0.33	0.07

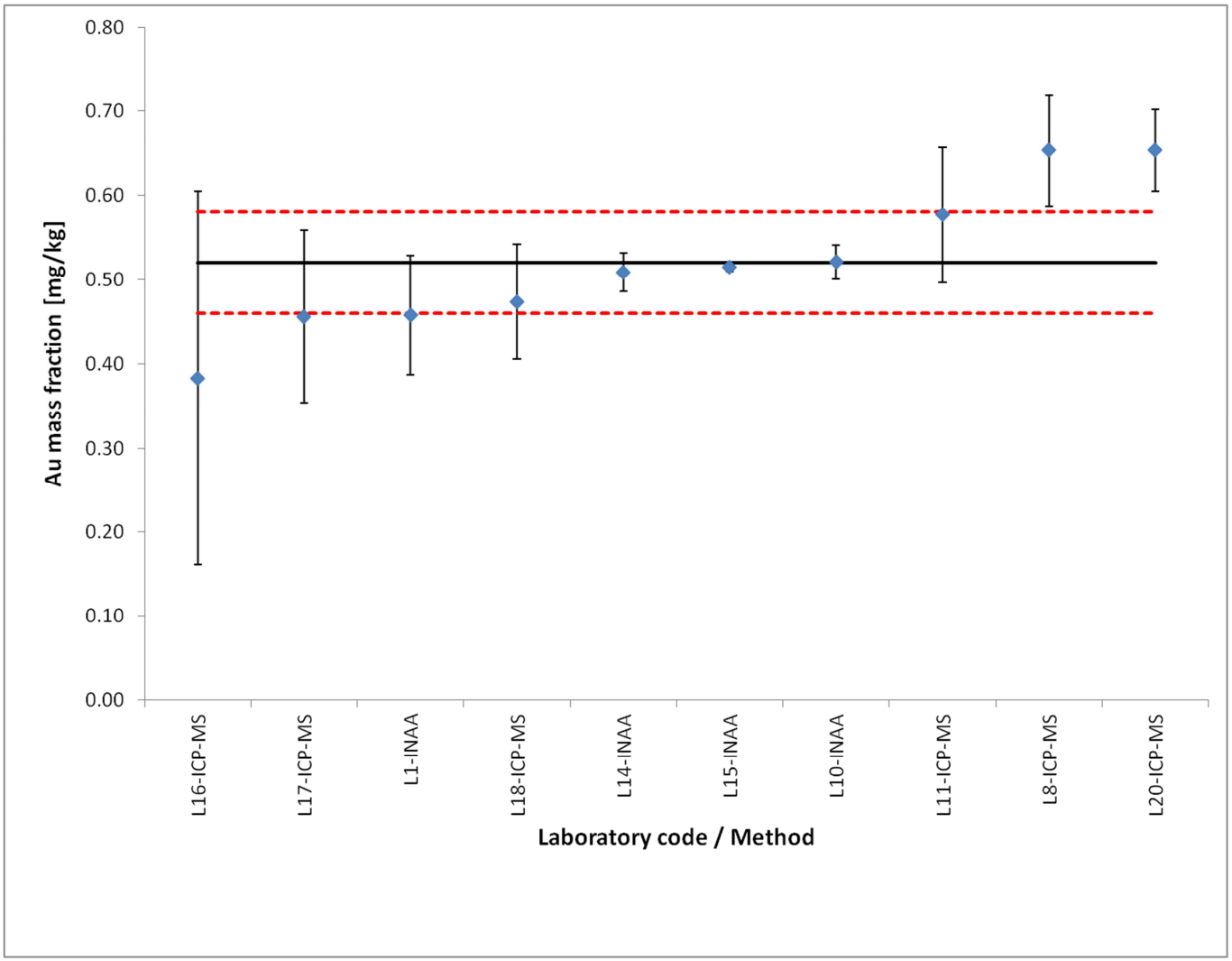


Figure E4. Mean Au mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Be (Beryllium)

Table E5. Individual results for Be mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.31	0.29	0.34	0.32	0.34	0.32	0.29	0.26	0.33	0.33	0.29	0.26	0.27	0.26	0.29	0.30	0.32	0.30			0.30	0.06
L2-ICP-OES	0.39	0.37	0.38	0.37	0.38	0.36	0.37	0.39	0.38	0.38	0.38	0.39	0.39	0.38	0.38	0.39	0.38	0.39			0.38	0.02
L4-ICP-MS	0.31	0.36	0.36	0.29	0.35	0.29	0.36	0.32	0.33	0.35	0.34	0.32	0.30	0.30	0.31	0.35	0.31	0.35			0.33	0.04
L5-GD-MS	0.47	0.33	0.22	0.26	0.28	0.26	0.37	0.37	0.50	0.32	0.33	0.39									0.34	0.13
L6-ICP-MS	0.37	0.32	0.32	0.38	0.36	0.41	0.34	0.40	0.38	0.33	0.34	0.41	0.40	0.34	0.34	0.34	0.37	0.34			0.36	0.06
L8-ICP-MS	0.19	0.20	0.19	0.21	0.21	0.20	0.20	0.22	0.21	0.19	0.19	0.20	0.21	0.19	0.19	0.19	0.20	0.20			0.20	0.02
L9-ICP-MS	0.36	0.26	0.29	0.35	0.35	0.26	0.30	0.25	0.32	0.24	0.26	0.27	0.31	0.36	0.28	0.33	0.34	0.34			0.30	0.06
L11-ICP-MS	0.40	0.30	0.33	0.29	0.32	0.33	0.32	0.40	0.40	0.36	0.34	0.38	0.35	0.35	0.30	0.36	0.38	0.34			0.35	0.09
L16-ICP-MS	0.19	0.15	0.15	0.12	0.16	0.14	0.11	0.08	0.14	0.15	0.16	0.11	0.18	0.15	0.22	0.22	0.16	0.17			0.15	0.11
L17-ICP-MS	0.22	0.22	0.28	0.21	0.23	0.21	0.23	0.22	0.20	0.28	0.22	0.20	0.20	0.21	0.22	0.28	0.22	0.27			0.23	0.06
L18-ICP-MS	0.34	0.31	0.33	0.33	0.34	0.30	0.28	0.26	0.29	0.23	0.20	0.24	0.27	0.27	0.29	0.28	0.29	0.27			0.28	0.08
L20-ICP-MS													0.50	0.50	0.40	0.60	0.40	0.60			0.50	0.18
L1-ICP-MS	0.31	0.29	0.34	0.32	0.34	0.32	0.29	0.26	0.33	0.33	0.29	0.26	0.27	0.26	0.29	0.30	0.32	0.30			0.30	0.06

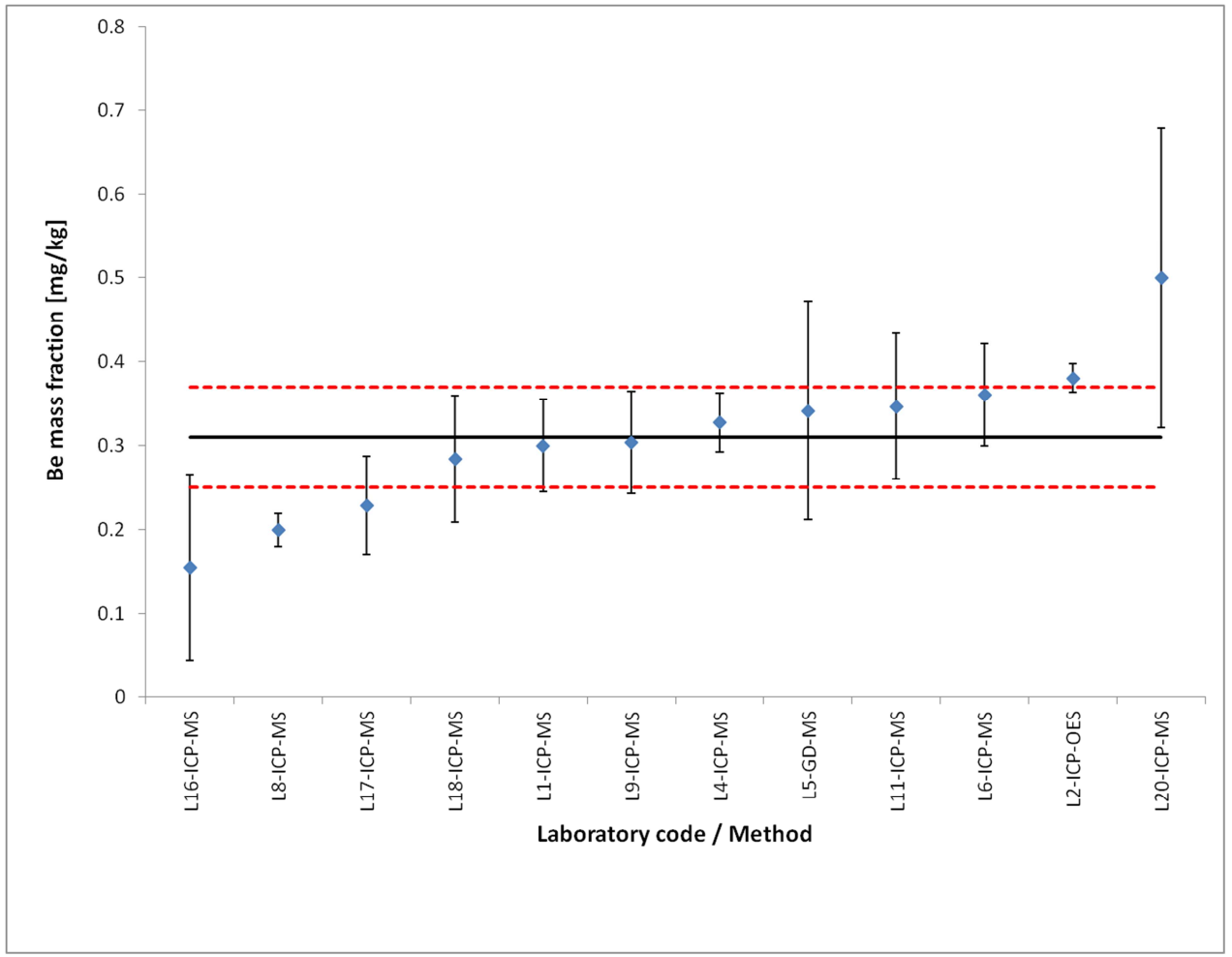


Figure E5. Mean Be mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Bi (bismuth)

Table E6. Individual results for Bi mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.47	0.45	0.45	0.49	0.45	0.50	0.45	0.35	0.50	0.49	0.41	0.51	0.53	0.54	0.49	0.45	0.49	0.45			0.47	0.09
L6-ICP-MS	0.52	0.47	0.48	0.52	0.48	0.53	0.49	0.51	0.51	0.48	0.47	0.51	0.51	0.47	0.46	0.46	0.52	0.47			0.49	0.05
L7-DC-arc-OES													0.50	0.48	0.50	0.49	0.48	0.47			0.49	0.02
L8-ICP-MS	0.59	0.56	0.59	0.58	0.58	0.60	0.59	0.57	0.57	0.59	0.60	0.58	0.58	0.57	0.57	0.57	0.58	0.58			0.58	0.06
L9-ICP-MS	0.50	0.54	0.57	0.47	0.62	0.57	0.52	0.53	0.52	0.52	0.60	0.50	0.49	0.48	0.51	0.48	0.49	0.50			0.52	0.10
L11-ICP-MS	0.57	0.56	0.56	0.63	0.56	0.55	0.54	0.54	0.55	0.60	0.55	0.57	0.58	0.55	0.56	0.58	0.55	0.55			0.56	0.14
L12-ICP-MS	0.48	0.50	0.48	0.50	0.47	0.50	0.47	0.47	0.48	0.48	0.47	0.49	0.50	0.48	0.48	0.47	0.49	0.53			0.48	0.04
L13-GD-MS	0.49	0.57	0.56	0.53	0.57	0.55	0.55	0.53	0.55	0.55	0.59	0.50									0.55	0.06
L16-ICP-MS	0.21	0.27	0.24	0.43	0.35	0.51	0.17	0.46	0.44	0.46	0.40	0.40	0.23	0.26	0.47	0.69	0.59	0.31			0.38	0.21
L17-ICP-MS	0.46	0.50	0.51	0.50	0.50	0.50	0.49	0.48	0.49	0.52	0.51	0.48	0.49	0.49	0.50	0.52	0.49	0.52			0.50	0.02
L20-ICP-MS													0.53	0.55	0.56	0.57	0.56	0.54			0.55	0.03
Results not used for certification																						
L2-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
L3-ETV-ICP-OES	0.43	0.42	0.40	0.41	0.41	0.40	0.39	0.40	0.42	0.40	0.42	0.42	0.41	0.42	0.42	0.42	0.40	0.40	0.41	0.41	0.41	0.04
L4-ICP-MS	0.45	0.45	0.45	0.44	0.44	0.44	0.45	0.44	0.44	0.45	0.44	0.44	0.44	0.44	0.45	0.45	0.45	0.45			0.45	0.01
L5-GD-MS	0.33	0.41	0.44	0.52	0.42	0.42	0.52	0.48	0.32	0.56	0.49	0.42									0.44	0.11
L18-ICP-MS	0.21	0.23	0.24	0.27	0.27	0.26	0.25	0.21	0.24	0.23	0.21	0.23	0.26	0.28	0.30	0.29	0.31	0.31			0.26	0.07
L21-Spark-OES	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5										

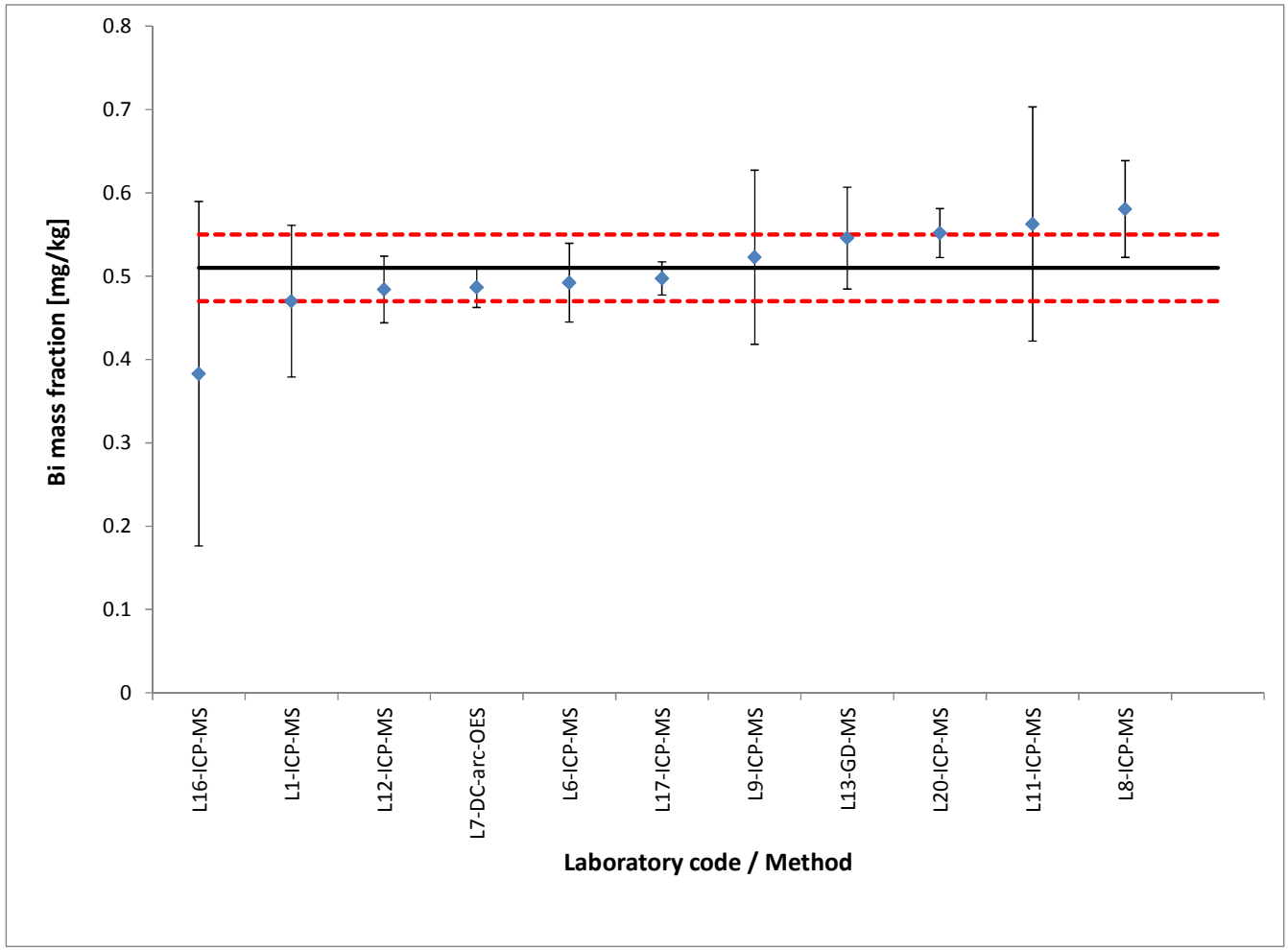


Figure E6. Mean Bi mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Cd (Cadmium)

Table E7. Individual results for Cd mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.39	0.37	0.38	0.36	0.39	0.40	0.35	0.26	0.38	0.40	0.34	0.35	0.40	0.41	0.37	0.37	0.42	0.37			0.37	0.07
L2-ICP-OES	0.34	0.31	0.33	0.31	0.34	0.28	0.32	0.34	0.33	0.32	0.34	0.33	0.32	0.31	0.32	0.34	0.28	0.34			0.32	0.04
L4-ICP-MS	0.40	0.43	0.41	0.39	0.41	0.38	0.41	0.39	0.40	0.40	0.42	0.40	0.40	0.40	0.42	0.41	0.40	0.41			0.40	0.02
L5-GD-MS	0.34	0.39	0.39	0.39	0.34	0.38	0.42	0.39	0.34	0.41	0.41	0.39									0.38	0.06
L8-ICP-MS	0.41	0.43	0.42	0.40	0.39	0.38	0.41	0.40	0.40	0.41	0.41	0.41	0.40	0.42	0.41	0.39	0.40	0.42			0.41	0.04
L9-ICP-MS	0.39	0.29	0.28	0.37	0.38	0.28	0.26	0.26	0.26	0.28	0.26	0.27	0.38	0.39	0.30	0.37	0.37	0.38			0.32	0.06
L11-ICP-MS	0.44	0.42	0.41	0.41	0.43	0.41	0.41	0.41	0.42	0.42	0.43	0.43	0.43	0.41	0.41	0.41	0.40	0.41			0.42	0.10
L12-ICP-MS	0.48	0.37	0.38	0.43	0.35	0.42	0.36	0.45	0.44	0.37	0.35	0.44	0.45	0.44	0.37	0.36	0.45	0.36			0.40	0.14
L13-GD-MS	0.36	0.44	0.42	0.40	0.44	0.44	0.41	0.41	0.42	0.42	0.40	0.37									0.41	0.06
L16-ICP-MS	0.50	0.64	0.61	0.45	0.55	0.48	0.67	0.39	0.48	0.58	0.59	0.51	0.48	0.51	0.60	0.60	0.46	0.64			0.54	0.13
L17-ICP-MS	0.41	0.45	0.44	0.45	0.42	0.45	0.43	0.43	0.44	0.44	0.44	0.43	0.43	0.43	0.44	0.46	0.44	0.45			0.44	0.05
L20-ICP-MS													0.42	0.41	0.37	0.40	0.43	0.42			0.41	0.04
Results not used for certification																						
L6-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
L21-Spark-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1										
L18-ICP-MS	0.37	0.38	0.39	0.34	0.37	0.35	0.34	0.31	0.34	0.30	0.26	0.30	0.37	0.38	0.38	0.38	0.39	0.38			0.35	0.07

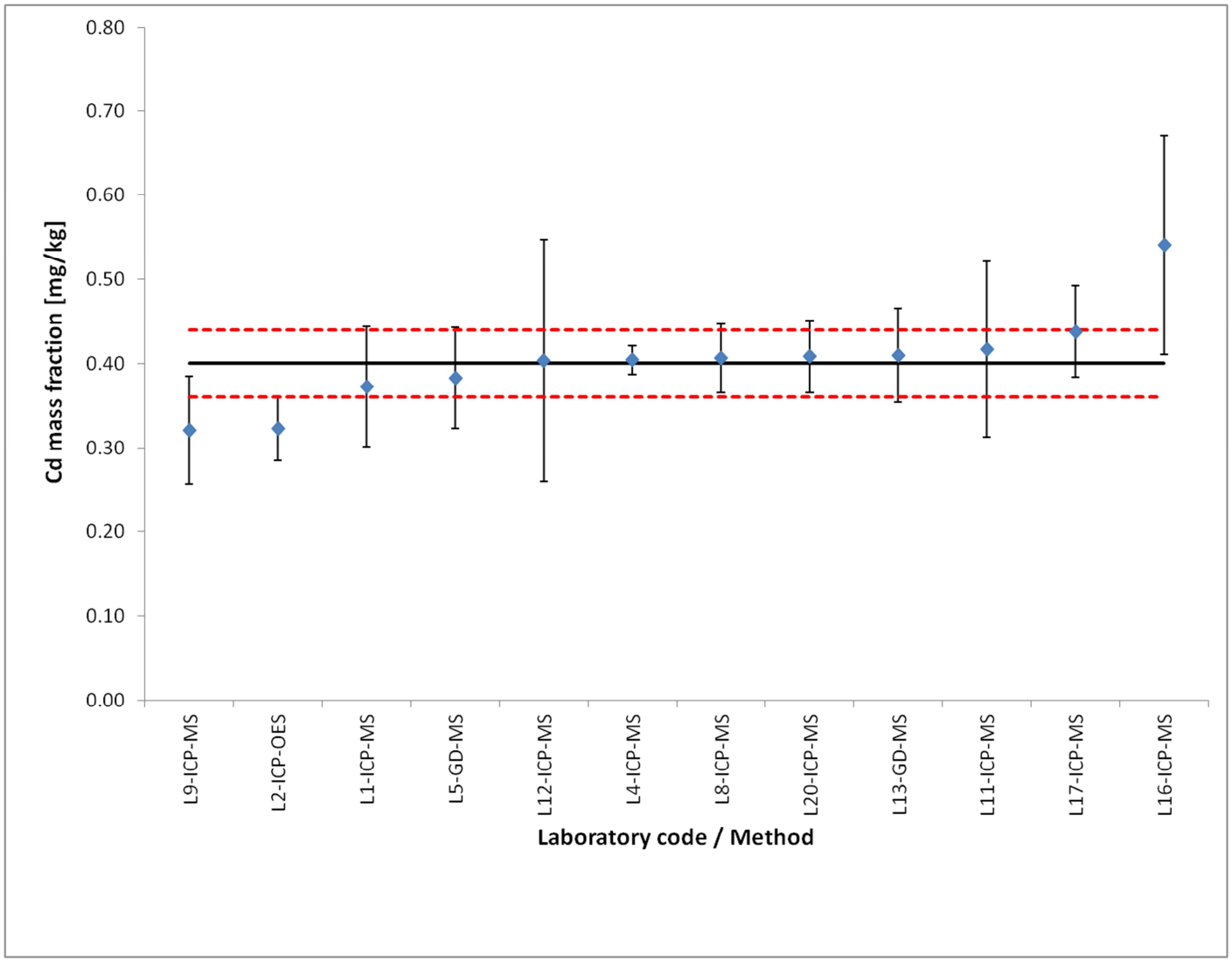


Figure E7. Mean Cd mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Co (cobalt)

Table E8. Individual results for Co mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.87	0.86	0.88	0.80	0.85	0.84	0.85	0.62	0.83			0.79	0.81	0.79	0.84	0.89	0.81	0.88			0.83	0.13
L2-ICP-OES	1.00	1.00	1.30	0.80	0.80	0.90	1.10	1.10	1.10	0.80	1.00	0.90	0.70	0.70	0.80	0.80	0.70	0.80			0.91	0.34
L4-ICP-MS	0.87	0.86	0.86	0.85	0.87	0.85	0.86	0.84	0.84	0.84	0.82	0.82	0.80	0.99	0.81	0.82	0.81	0.82			0.85	0.02
L5-GD-MS	0.90	0.88	0.90	0.90	0.94	0.84	0.91	0.87	0.88	0.91	0.86	0.91									0.89	0.07
L8-ICP-MS	0.86	0.83	0.82	0.84	0.83	0.83	0.81	0.81	0.85	0.81	0.82	0.80	0.81	0.82	0.81	0.80	0.83	0.81			0.82	0.08
L9-ICP-MS	0.86	0.71	0.71	0.82	0.84	0.72	0.74	0.70	0.70	0.87	0.72	0.71	0.75	0.87	0.76	0.80	0.83	0.82			0.77	0.18
L11-ICP-MS	0.72	0.71	0.73	0.70	0.69	0.69	0.73	0.74	0.71	0.71	0.74	0.74	0.71	0.69	0.74	0.67	0.70	0.70			0.71	0.25
L12-ICP-MS	0.71	0.80	0.88	0.65	0.87	0.67	0.75	0.68	0.69	0.78	0.85	0.66	0.68	0.68	0.83	0.86	0.67	0.88			0.76	0.30
L13-GD-MS	0.82	0.81	0.82	0.81	0.81	0.83	0.81	0.82	0.83	0.83	0.79	0.82									0.82	0.07
L14-INAA	0.95	0.98	0.81	0.95	0.94	0.97	0.93	0.88	0.96	0.89	0.94	0.94	0.93	0.98	0.95	0.99	0.96	0.99			0.94	0.05
L16-ICP-MS	0.90	0.93	0.91	0.76	0.82	0.82	0.97	0.60	0.81	0.88	0.90	0.82	0.87	0.89	0.88	0.88	0.77	0.94			0.85	0.17
L17-ICP-MS	0.82	0.84	0.92	0.80	0.86	0.82	0.79	0.85	0.81	0.87	0.89	0.82	0.82	0.81	0.86	0.96	0.81	0.97			0.85	0.05
L20-ICP-MS													0.80	0.80	0.80	0.80	0.80	0.80			0.80	0.00
Results not used for certification																						
L10-INAA	1.56	1.60	1.54	1.55	1.54	1.55	1.56	1.56	1.56	1.57	1.55	1.57	1.56	1.59	1.54	1.60	1.54	1.58			1.56	0.06
L15-INAA	0.69	0.62	0.63	0.61	0.66	0.59	0.62	0.65	0.62	0.57	0.64	0.62	0.64	0.69	0.69	0.65	0.66	0.65			0.64	0.03
L18-ICP-MS	0.88	0.84	0.81	0.73	0.79	0.73	0.71	0.66	0.69	0.56	0.50	0.58	0.73	0.73	0.73	0.73	0.72	0.69			0.71	0.19
L6-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
L21-Spark-OES	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5										

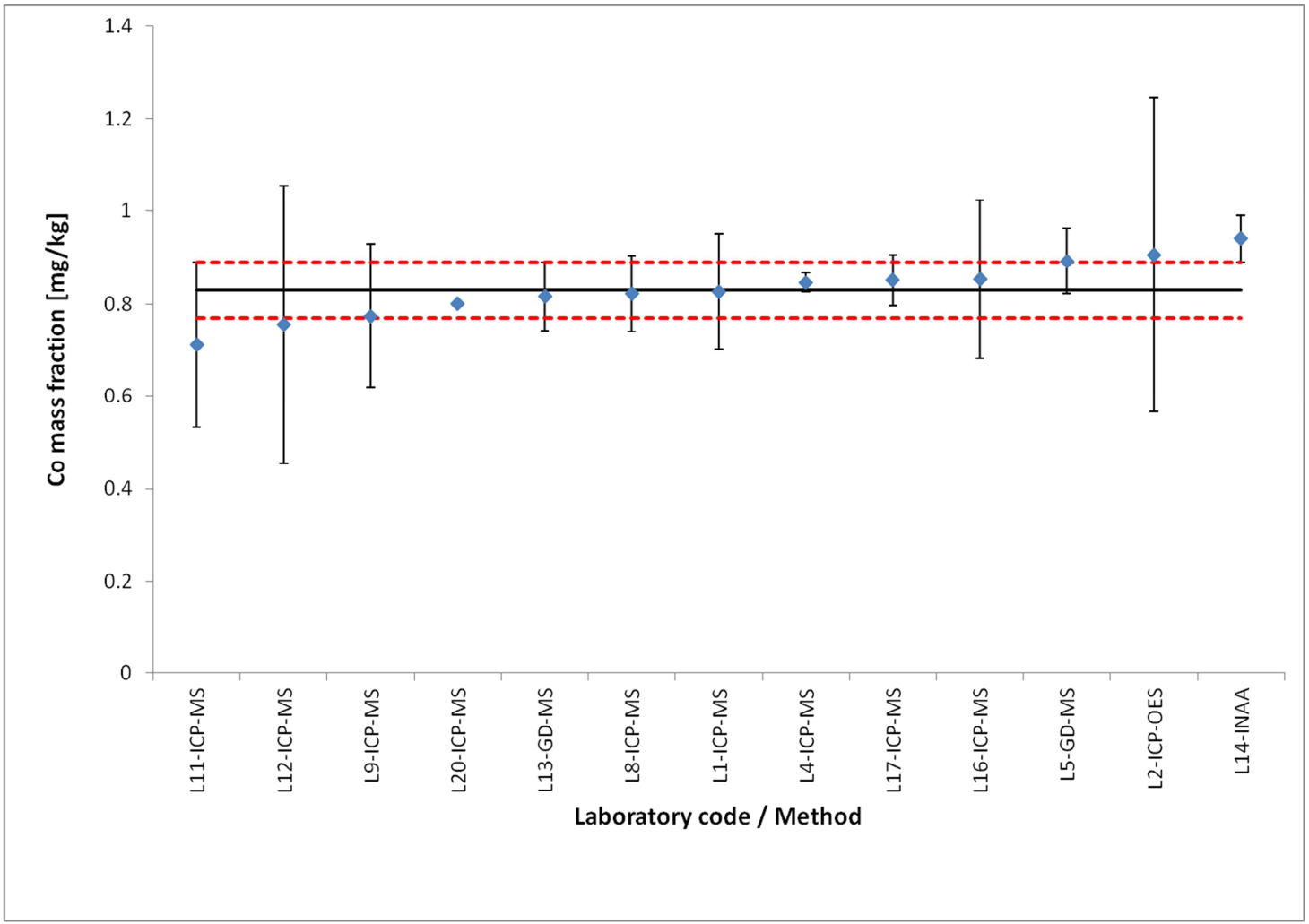


Figure E8. Mean Co mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Cr (Chromium)

Table E9. Individual results for Cr mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.37	0.44	0.37	0.49	0.35	0.42	0.42	0.33	0.39	0.39	0.32	0.39	0.45	0.56	0.53	0.38	0.42	0.50			0.42	0.14
L2-ICP-OES	0.40	0.40	0.50	0.40	0.40	0.30	0.40	0.30	0.40	0.40	0.50	0.40	0.40	0.30	0.50	0.40	0.40	0.40			0.40	0.12
L4-ICP-MS	0.34	0.35	0.33	0.32	0.34	0.33	0.37	0.32	0.50	0.00	0.40	0.34	0.33	0.41	0.44	0.36	0.31	0.33			0.34	0.09
L5-GD-MS	0.44	0.31	0.35	0.39	0.44	0.39	0.40	0.42	0.43	0.42	0.36	0.33									0.39	0.08
L8-ICP-MS	0.42	0.41	0.42	0.42	0.41	0.40	0.42	0.43	0.41	0.39	0.40	0.42	0.42	0.42	0.41	0.39	0.40	0.39			0.41	0.04
L9-ICP-MS	0.23	0.72	0.32	0.27	0.46	0.86	0.25	0.23	0.24	0.18	0.73	1.67	0.26	0.30	0.58	0.34	0.35	0.35			0.46	0.09
L10-INAA	0.35	0.36	0.39	0.35	0.34	0.33	0.38	0.36	0.34	0.40	0.40	0.43	0.34	0.36	0.39	0.33	0.35	0.45			0.37	0.06
L11-ICP-MS	0.35	0.38	0.36	0.35	0.34	0.40	0.33	0.34	0.35	0.34	0.38	0.36	0.36	0.39	0.37	0.35	0.38	0.36			0.36	0.09
L12-ICP-MS	0.35	0.44	0.37	0.35	0.37	0.38	0.35	0.34	0.38	0.34	0.41	0.33	0.32	0.33	0.34	0.35	0.33	0.33			0.36	0.05
L13-GD-MS	0.30	0.30	0.30	0.30	0.32	0.32	0.30	0.31	0.30	0.31	0.30	0.30									0.30	0.03
L16-ICP-MS	0.33	0.33	0.32	0.31	0.32	0.35	0.34	0.24	0.32	0.31	0.32	0.32	0.33	0.34	0.32	0.32	0.31	0.34			0.32	0.03
L17-ICP-MS	0.31	0.39	0.33	0.36	0.42	0.39	0.38	0.30	0.30	0.35	0.37	0.37	0.33	0.34	0.40	0.30	0.33	0.28			0.35	0.08
Results not used for certification																						
L14-INAA							0.37	0.34	0.38	0.33	0.35	0.37	0.30	0.37	0.36	0.38	0.33	0.34			0.35	0.06
L15-INAA	0.38	0.33	0.43	0.42	0.35	0.84	0.42	0.90	0.28	0.68	0.33	0.52	0.48	0.43	0.41	0.36	0.40	0.41			0.46	0.03
L18-ICP-MS	0.39	0.40	0.42	0.41	0.40	0.39	0.40	0.56	0.38	0.27	0.25	0.31	0.32	0.31	0.32	0.30	0.30	0.29			0.36	0.15
L20-ICP-MS													< 1	< 1	< 1	< 1	< 1	< 1				
L21-Spark-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1										

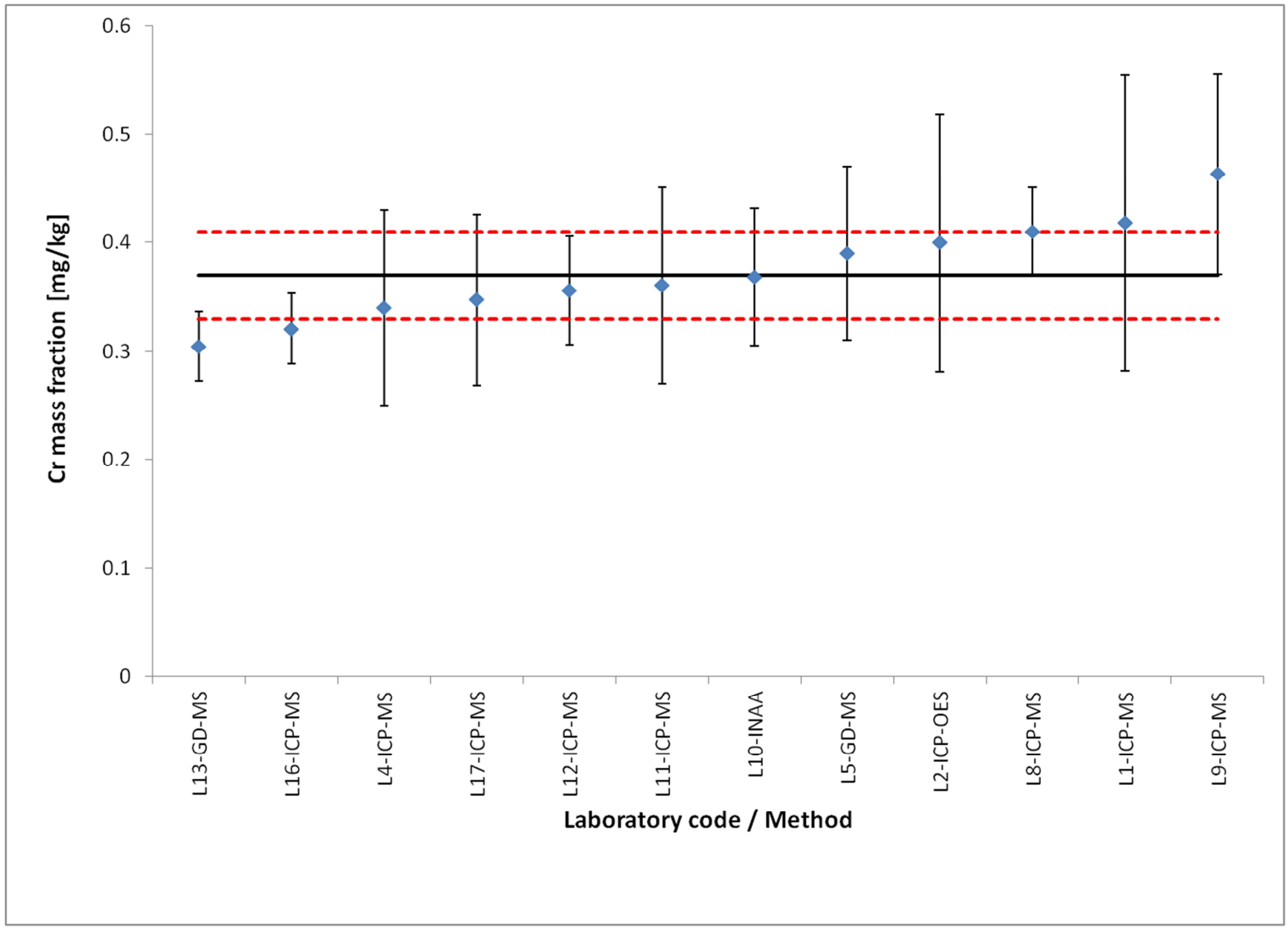


Figure E9. Mean Cr mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Fe (Iron)

Table E10. Individual results for Fe mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	10.40	6.40	7.70	11.30	11.90	7.80	4.60	5.20	6.20	4.60	11.10	7.10	4.70	4.40	5.20	4.80	5.40	4.50			6.85	5.23
L5-GD-MS	5.44	5.77	6.09	5.61	5.63	5.55	5.76	5.59	5.50	5.71	5.85	5.76									5.69	0.70
L6-ICP-MS	6.40	5.90	6.00	6.00	5.90	6.00	5.70	5.60	6.00	6.10	5.50	5.50	5.50	5.40	5.30	5.30	5.70	5.50			5.74	0.62
L11-ICP-OES	4.80	5.30	5.00	4.90	4.90	4.90	4.90	4.90	4.90	4.80	4.80	4.80	4.70	4.90	4.70	5.10	5.30	5.00			4.92	1.23
L12-ICP-MS	6.40	6.20	7.30	5.30	5.40	4.50	5.70	6.20	5.10	6.40	6.40	7.80	6.40	7.30	5.20	7.00	7.50	5.10			6.18	1.30
L13-GD-MS	5.08	5.10	5.29	5.00	5.15	5.11	5.21	5.23	5.26	5.25	5.23	5.12									5.17	0.23
L14-INAA							5.39	5.34	5.73	5.44	5.93	5.58	5.35	6.41	5.59	6.00	5.28	7.19			5.77	2.40
L16-ICP-OES	5.93	5.94	5.55	5.49	4.77	5.95	6.35	5.09	6.54	6.41	5.69	6.58	5.83	6.14	5.28	5.28	5.93	5.47			5.79	0.81
L17-ICP-MS	4.82	5.18	5.45	4.60	5.22	4.42	4.95	4.97	4.67	5.26	5.29	4.78	4.77	4.66	5.23	5.66	4.59	5.63			5.01	0.79
L18-ICP-MS													6.03	5.41	5.44	5.24	5.43	5.02			5.43	1.99
L20-ICP-MS													7.00	7.00	8.00	6.00	7.00	7.00			7.00	1.26
Results not used for certification																						
L1-ICP-OES	5.88	5.57	5.71	6.72	5.39	6.38	5.74	3.94	6.66	7.77	6.04	13.83	14.51	11.53	16.62	5.71	6.13	5.74			7.77	7.36
L8-ICP-MS	5.80	5.30	5.90	5.70	5.80	5.50	5.90	5.60	5.80	5.80	5.80	5.70	5.90	5.50	5.60	5.90	5.50	5.40			5.69	0.57
L7-DC-arc-OES													8.00	11.00	15.00	9.00	9.00	8.00			10.00	5.37
L9-ICP-MS	5.85	4.07	4.02	6.90	4.50	6.32	4.23	3.54	7.04	12.00	6.67	4.55	5.74	5.41	3.98	6.59	6.77	8.89				
L10-INAA	< 7	< 4	< 6	< 6	< 6	< 6	12.6	< 6	< 6	10.0	< 7	< 4	< 7	< 8	< 4	< 8	< 7	< 8				
L15-INAA	6.72	ND	15.60	12.10	5.51	119	29.20	143	4.66	98.30	ND	37.90	6.84	5.09	6.22	4.06	5.81	7.56			31.72	2.00
L21-Spark-OES	4.40	4.40	4.60	4.30	4.30	4.30	4.20	4.70	4.70	4.60	5.00	4.60									4.51	0.46

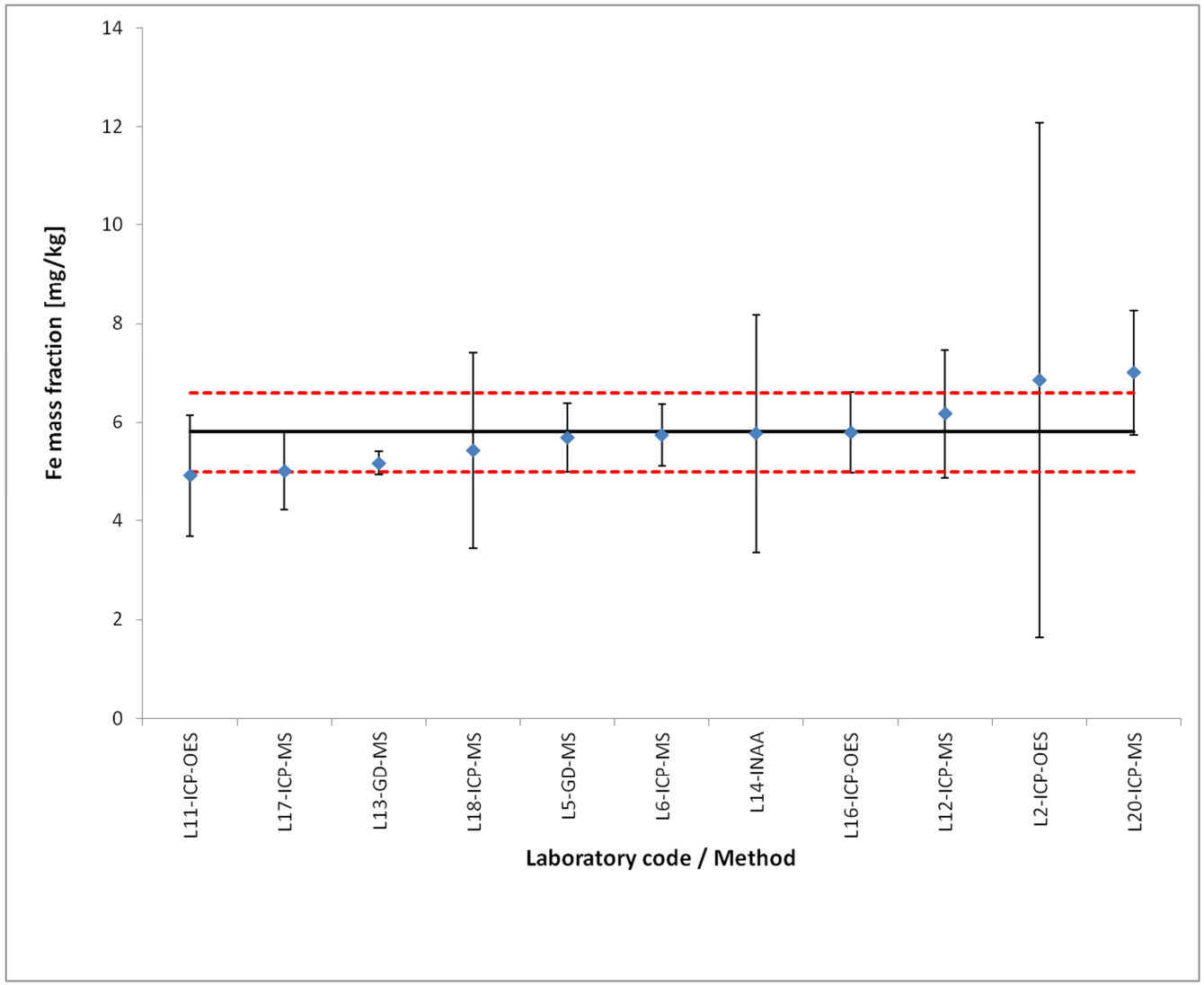


Figure E10. Mean Fe mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

In (Indium)

Table E11. Individual results for In mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.50	0.50	0.50	0.49	0.49	0.50	0.49	0.36	0.50	0.53	0.44	0.48	0.49	0.50	0.50	0.50	0.51	0.49			0.49	0.07
L2-ICP-OES	0.40	0.50	0.40	0.30	0.50	0.40	0.50	0.50	0.50	0.50	0.50	0.40	0.50	0.50	0.50	0.50	0.40	0.50			0.46	0.12
L4-ICP-MS	0.47	0.50	0.49	0.46	0.49	0.46	0.51	0.46	0.46	0.51	0.50	0.46	0.46	0.46	0.49	0.50	0.47	0.49			0.48	0.03
L5-GD-MS	0.29	0.39	0.48	0.53	0.40	0.46	0.54	0.53	0.28	0.61	0.56	0.40									0.46	0.17
L8-ICP-MS	0.52	0.52	0.50	0.56	0.53	0.55	0.50	0.51	0.54	0.56	0.56	0.56	0.54	0.53	0.53	0.58	0.57	0.59			0.54	0.05
L9-ICP-MS	0.31	0.52	0.52	0.31	0.32	0.53	0.50	0.52	0.52	0.30	0.53	0.53	0.35	0.34	0.50	0.34	0.34	0.34			0.42	0.08
L10-INAA	0.55	0.55	0.56	0.50	0.52	0.54	0.59	0.51	0.51	0.61	0.51	0.50	0.57	0.53	0.54	0.53	0.56	0.57			0.54	0.06
L11-ICP-MS	0.52	0.52	0.52	0.53	0.53	0.53	0.53	0.52	0.53	0.52	0.53	0.52	0.55	0.52	0.53	0.55	0.52	0.53			0.53	0.13
L12-ICP-MS	0.45	0.39	0.40	0.46	0.42	0.45	0.39	0.45	0.45	0.40	0.41	0.45	0.46	0.46	0.40	0.43	0.46	0.44			0.43	0.09
L14-INAA	0.51	0.47	0.40	0.54	0.54	0.51	0.49	0.45	0.48	0.43	0.52	0.54	0.48	0.46	0.51	0.50	0.53	0.46			0.49	0.07
L16-ICP-MS	0.52	0.66	0.65	0.45	0.58	0.50	0.75	0.36	0.48	0.61	0.61	0.49	0.50	0.53	0.60	0.60	0.45	0.66			0.56	0.26
L17-ICP-MS	0.49	0.56	0.56	0.54	0.55	0.56	0.53	0.52	0.53	0.58	0.58	0.54	0.55	0.53	0.55	0.58	0.55	0.58			0.55	0.07
L18-ICP-MS	0.39	0.42	0.42	0.41	0.44	0.41	0.41	0.37	0.40	0.34	0.30	0.35	0.42	0.44	0.45	0.44	0.45	0.45			0.41	0.08
L20-ICP-MS													0.50	0.60	0.60	0.60	0.60	0.50			0.57	0.10

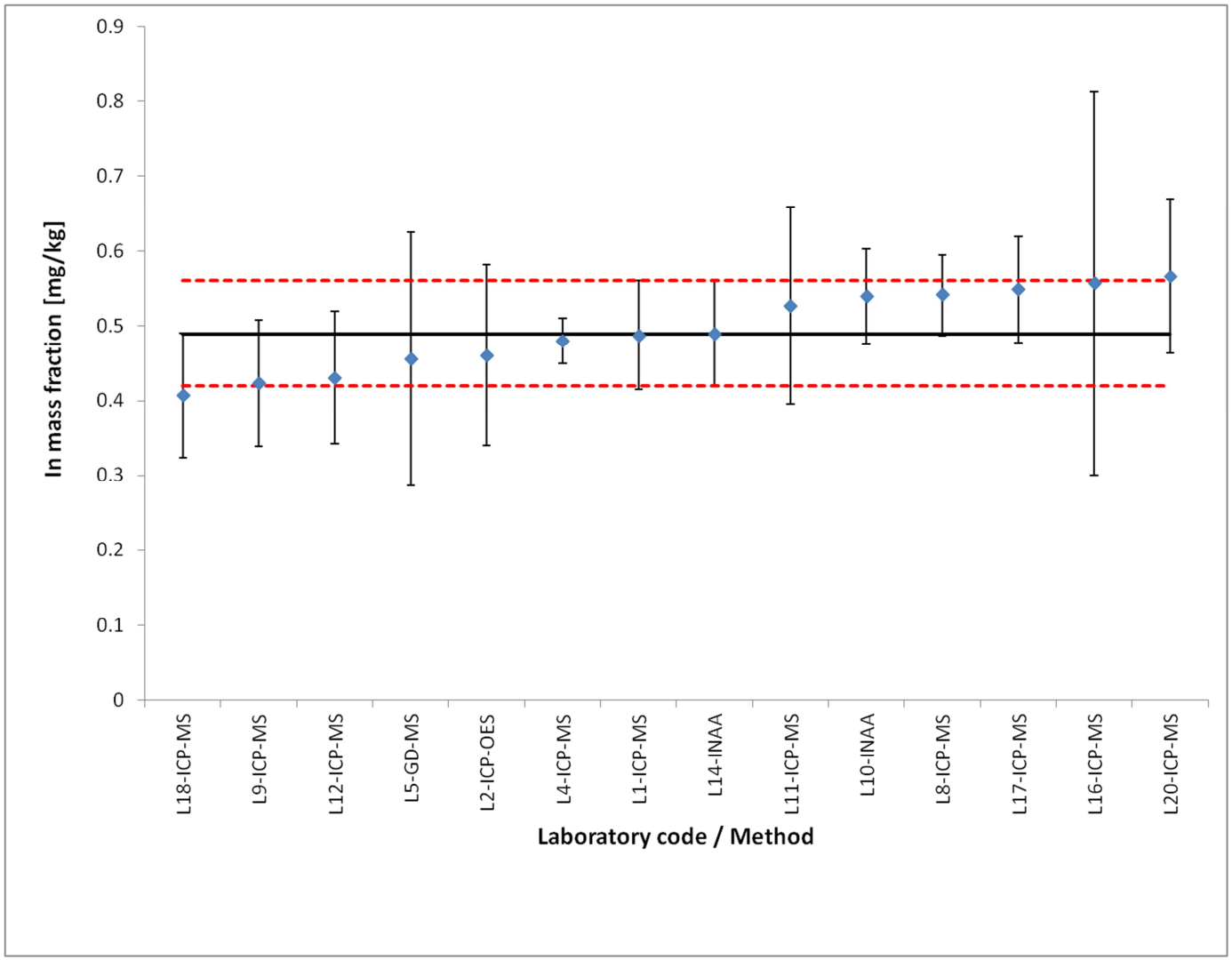


Figure E11. Mean ln mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Mg (Magnesium)

Table E12. Individual results for Mg mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	2.10	1.80	1.90	1.80	2.00	1.70	1.90	2.10	1.90	1.80	2.00	2.00	1.90	1.90	1.90	2.10	1.90	2.10			1.93	0.24
L4-ICP-MS	2.05	1.99	2.12	2.69	3.29	1.66	2.01	1.96	1.76	4.13	2.07	1.86	2.03	1.81	2.19	2.08	1.84	2.26			2.21	1.25
L5-GD-MS	1.65	1.62	1.33	1.26	1.24	1.29	1.66	1.60	1.97	1.47	1.67	1.81									1.55	0.22
L8-ICP-MS	1.70	1.80	1.80	1.60	1.70	1.70	1.60	1.50	1.60	1.60	1.70	1.80	1.70	1.60	1.70	1.70	1.60	1.60			1.67	0.17
L9-ICP-MS	2.18	2.32	2.60	2.28	2.15	2.55	2.46	2.47	2.39	2.36	3.03	2.67	2.42	2.01	2.24	2.23	2.11	2.24			2.37	0.47
L11-ICP-MS	1.89	2.11	2.07	1.93	1.93	1.96	2.13	2.03	2.19	2.05	2.06	2.16	1.88	2.01	2.03	2.13	1.96	1.92			2.03	0.51
L13-GD-MS	2.07	2.15	2.13	2.05	2.17	2.14	2.19	2.17	2.17	2.23	2.15	2.24									2.16	0.11
L16-ICP-MS	1.77	1.44	1.46	1.48	1.49	1.54	1.50	1.02	1.46	1.53	1.49	1.43	1.60	1.64	1.51	1.51	1.61	1.82			1.52	0.21
L17-ICP-MS	1.81	1.89	2.04	1.94	2.24	1.93	1.99	2.06	1.91	2.09	2.06	1.93	1.97	1.86	1.97	2.31	1.87	2.30			2.01	0.39
L18-ICP-MS	3.69	2.20	2.99	3.05	2.91	2.73	2.85	3.22	3.29	2.81	2.04	2.08	2.75	2.53	3.25	2.88	2.88	2.53			2.82	0.86
Results not used for certification																						
L1-ICP-MS	2.86	3.10	3.32	< 2.9	< 2.9	4.29	3.84	< 2.9	2.97	2.94	< 2.9	4.06	3.39	4.37	3.71	3.55	2.88	3.75			3.50	1.04
L20-ICP-MS													3.70	3.80	3.50	3.60	3.80	4.20			3.77	0.48

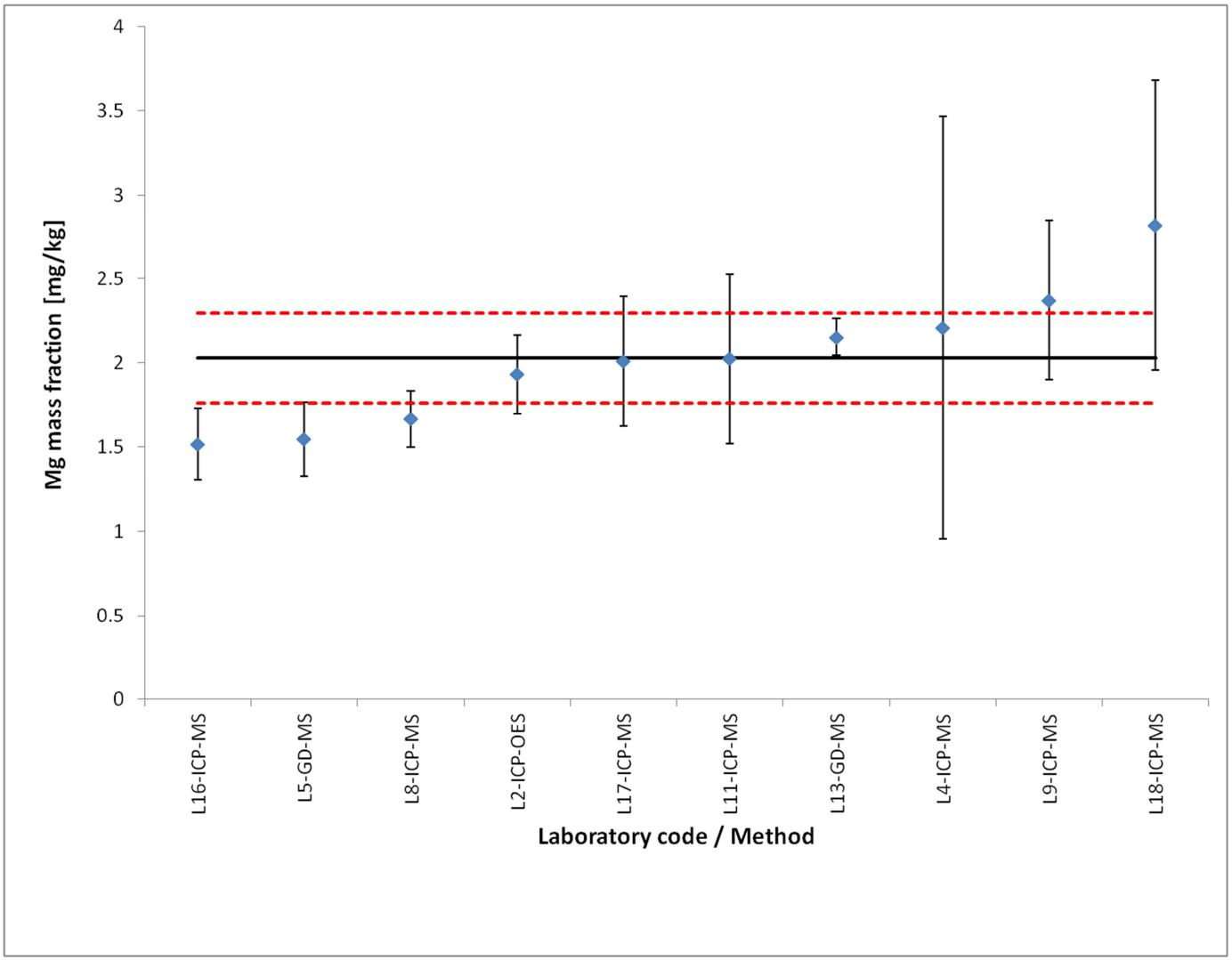


Figure E12. Mean Mg mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Mn (Manganese)

Table E13. Individual results for Mn mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.95	0.90	0.89	0.83	0.86	0.86	0.91	0.64	0.87	0.98	0.82	0.89	0.90	0.88	0.93	0.90	0.88	0.93			0.88	0.14
L2-ICP-OES	0.94	0.89	0.90	0.92	0.96	0.90	0.92	0.93	0.92	0.88	0.94	0.92	0.92	0.91	0.88	0.90	0.91	0.89			0.91	0.04
L4-ICP-MS	0.78	0.90	0.93	0.78	0.92	0.73	0.94	0.75	0.74	0.95	0.92	0.74	0.77	0.75	1.03	0.92	0.76	0.94			0.85	0.12
L9-ICP-MS	0.91	0.83	0.84	0.83	0.87	0.82	0.81	0.70	0.70	0.92	0.88	0.86	0.82	0.93	0.84	0.83	0.87	0.87			0.84	0.17
L11-ICP-MS	1.10	1.10	1.10	1.10	1.10	1.10	1.00	1.10	1.10	1.10	1.10	1.00	1.10	1.10	1.10	1.00	1.10	1.00			1.08	0.27
L13-GD-MS	0.90	0.94	0.95	0.91	0.98	0.94	0.91	0.95	0.95	0.92	0.93	0.91									0.93	0.05
L16-ICP-OES	0.99	0.99	0.99	0.86	0.88	0.92	1.05	0.67	0.92	0.96	0.99	0.93	0.96	0.99	0.96	0.96	0.90	1.03			0.94	0.06
L17-ICP-MS	1.08	0.92	0.98	0.85	0.93	0.82		1.21	0.85	0.93	0.96	0.88	0.89	0.86	0.94	1.02	0.84	1.02			0.94	0.12
L20-ICP-MS													1.00	1.10	1.00	1.00	1.00	0.95			1.01	0.10
Results not used for certification																						
L5-GD-MS	0.78	0.82	0.85	0.83	0.80	0.79	0.85	0.82	0.74	0.86	0.84	0.79									0.81	0.10
L8-ICP-MS	0.76	0.76	0.78	0.77	0.75	0.76	0.75	0.77	0.74	0.78	0.75	0.76	0.75	0.79	0.75	0.77	0.77	0.78			0.76	0.08
L18-ICP-MS	0.98	0.97	0.96	0.85	0.92	0.87	0.86	0.79	0.83	0.68	0.61	0.71	0.89	0.87	0.88	0.84	0.85	0.81			0.84	0.20
L21-Spark-OES	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5										

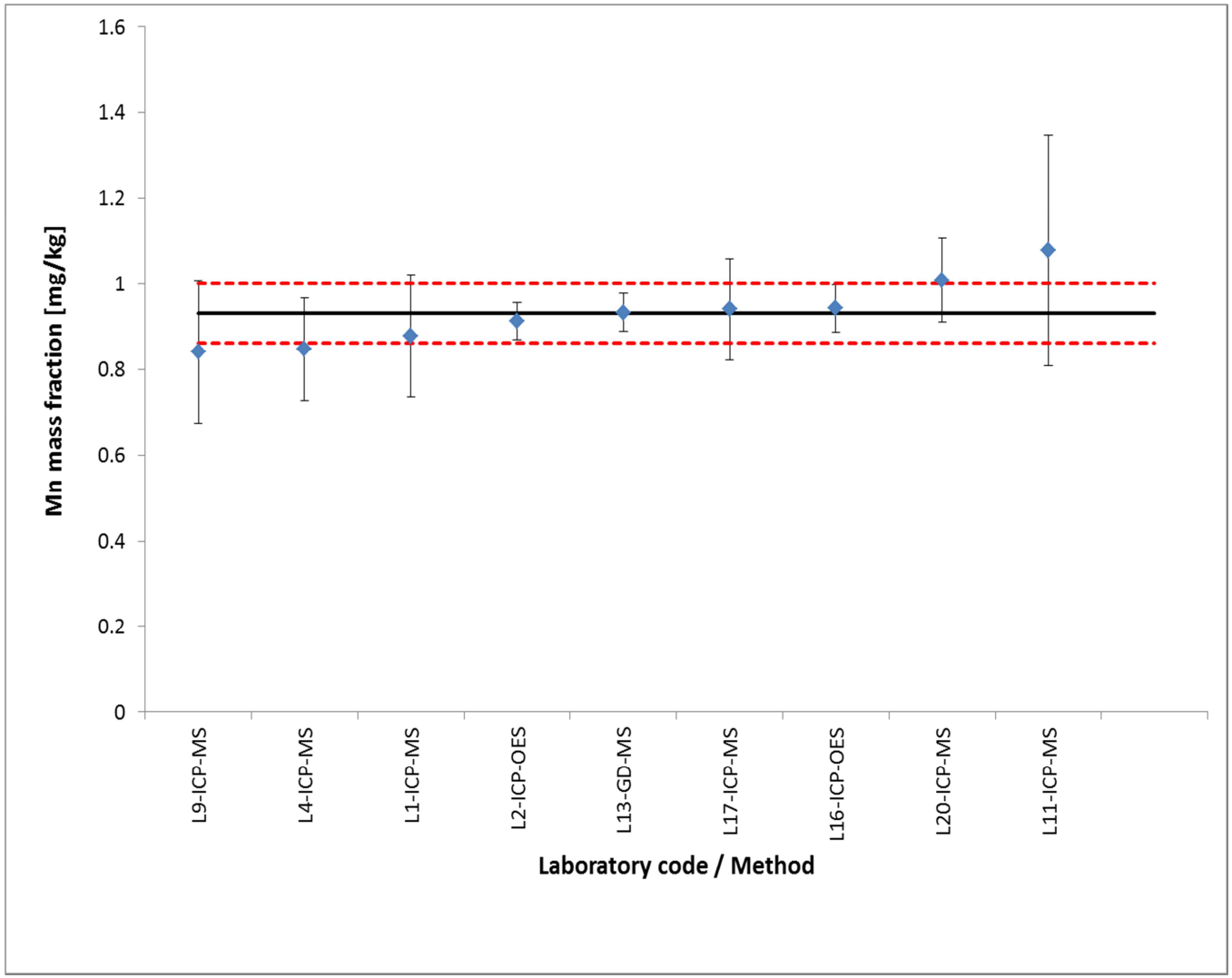


Figure E13. Mean Mn mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Ni (Nickel)

Table E14. Individual results for Ni mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	0.70	0.80	0.90	0.60	0.70	0.60	0.70	0.50	0.60	0.70	0.80	0.60	0.60	0.60	0.70	0.70	0.70	0.60			0.67	0.19
L3-ETV-ICP-OES	0.68	0.70	0.65	0.68	0.65	0.56	0.55	0.57	0.60	0.56	0.67	0.67	0.65	0.66	0.74	0.61	0.59	0.58	0.59	0.60	0.63	0.15
L5-GD-MS	0.77	0.68	0.64	0.58	0.63	0.53	0.64	0.61	0.70	0.63	0.58	0.65									0.64	0.10
L7-DC-arc-OES													0.50	0.50	0.90	0.50	0.50	0.50			0.57	0.33
L9-ICP-MS	0.65	0.60	0.68	0.51	0.55	0.50	0.61	0.55	0.65	0.58	0.54	0.75	0.58	0.50	0.50	0.54	0.54	0.54			0.58	0.12
L11-ICP-MS	0.59	0.59	0.61	0.60	0.51	0.60	0.64	0.66	0.63	0.64	0.65	0.62	0.64	0.58	0.70	0.56	0.55	0.56			0.61	0.15
L12-ICP-MS	0.58	0.47	0.70	0.56	0.40	0.52	0.48	0.65	0.59	0.55	0.50	0.47	0.62	0.63	0.66	0.51	0.68	0.68			0.57	0.11
L13-GD-MS	0.59	0.60	0.58	0.51	0.53	0.53	0.52	0.61	0.58	0.55	0.58	0.57									0.56	0.05
L16-ICP-MS	0.71	0.77	0.68	0.50	0.54	1.00	0.68	0.44	0.59	0.65	0.66	0.59	0.75	0.62	0.62	0.62	0.59	0.65			0.65	0.10
L17-ICP-MS	0.60	0.58	0.70	0.51	0.56	0.52	0.56	0.59	0.55	0.60	0.62	0.57	0.60	0.55	0.64	0.66	0.54	0.66			0.59	0.10
L20-ICP-MS													0.60	0.70	0.70	0.60	0.60	0.50			0.62	0.15
L2-ICP-OES	0.70	0.80	0.90	0.60	0.70	0.60	0.70	0.50	0.60	0.70	0.80	0.60	0.60	0.60	0.70	0.70	0.70	0.60			0.67	0.19
L3-ETV-ICP-OES	0.68	0.70	0.65	0.68	0.65	0.56	0.55	0.57	0.60	0.56	0.67	0.67	0.65	0.66	0.74	0.61	0.59	0.58	0.59	0.60	0.63	0.15
L5-GD-MS	0.77	0.68	0.64	0.58	0.63	0.53	0.64	0.61	0.70	0.63	0.58	0.65									0.64	0.10
Results not used for certification																						
L4-ICP-MS		0.83	0.78		0.75		4.27		7.95	0.56	0.64		0.41	0.74				0.57			1.75	2.60
L8-ICP-MS	0.62	0.64	0.61	0.63	0.61	0.62	0.64	0.62	0.62	0.61	0.62	0.61	0.62	0.63	0.63	0.62	0.62	0.61			0.62	0.06
L18-ICP-MS	0.68	0.63	0.60	0.51	0.51	0.48	0.56	0.56	0.55	0.44	0.44	0.49	0.55	0.56	0.53	0.50	0.50	0.46			0.53	0.13
L1-ICP-MS	0.88	< 0.69	0.69	0.77	< 0.69	< 0.69	0.70	< 0.69	< 0.69	0.71	< 0.69	< 0.69	< 0.69	< 0.69	< 0.69	< 0.69	0.69	< 0.69			0.74	0.15
L6-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.00	< 1	< 1	< 1	< 1	< 1	< 1	1.00			1.00	0.00
L21-Spark-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1										

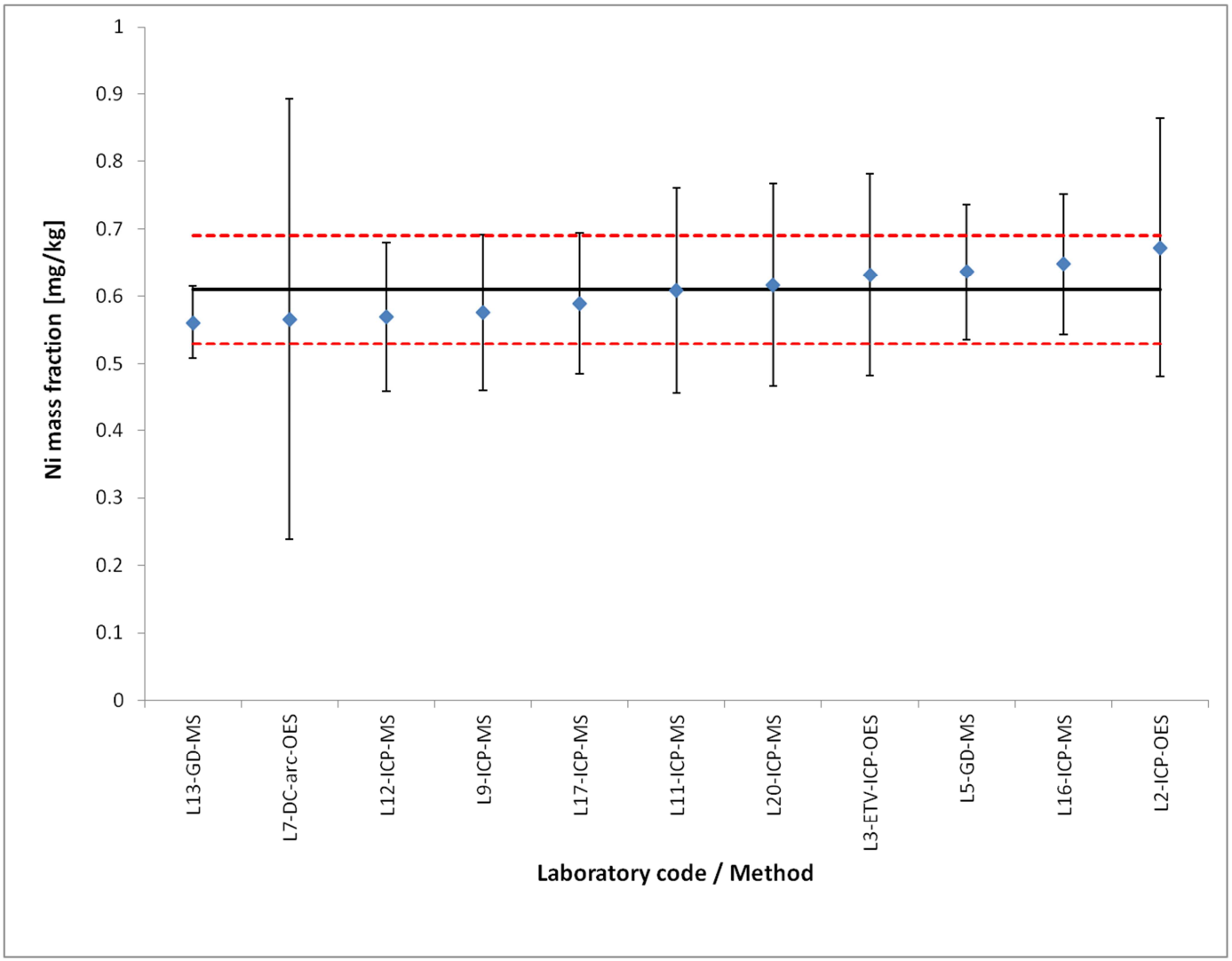


Figure E14. Mean Ni mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

O (Oxygen)

Table E15. Individual results for O mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L9-IGF-IR	7.70	6.50	6.50	6.90	7.90	5.60	9.20	10.00	9.20	8.90	8.70	6.40	11.00	11.00	9.70	11.00	6.50	7.80			8.36	1.67
L11-IGF-IR	6.48	5.94	6.39	6.19	6.22	5.86	8.46	8.09	8.29	6.86	7.09	6.98	7.32	7.33	7.08	6.52	6.65	6.57			6.91	1.73
L13-GD-MS	10.74	9.53	9.78	9.05	8.70	8.97	10.24	10.84	10.24	10.21	10.44	10.83									9.96	1.25
Results not used for certification																						
L1-IGF-IR	< 10	< 10	11.00	12.00	< 10	14.00	27.00	24.00	124	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10			35.33	87.87
L17-IGF-IR				5.00		6.20		7.80	6.50			6.30	8.60	6.40			4.40				6.40	

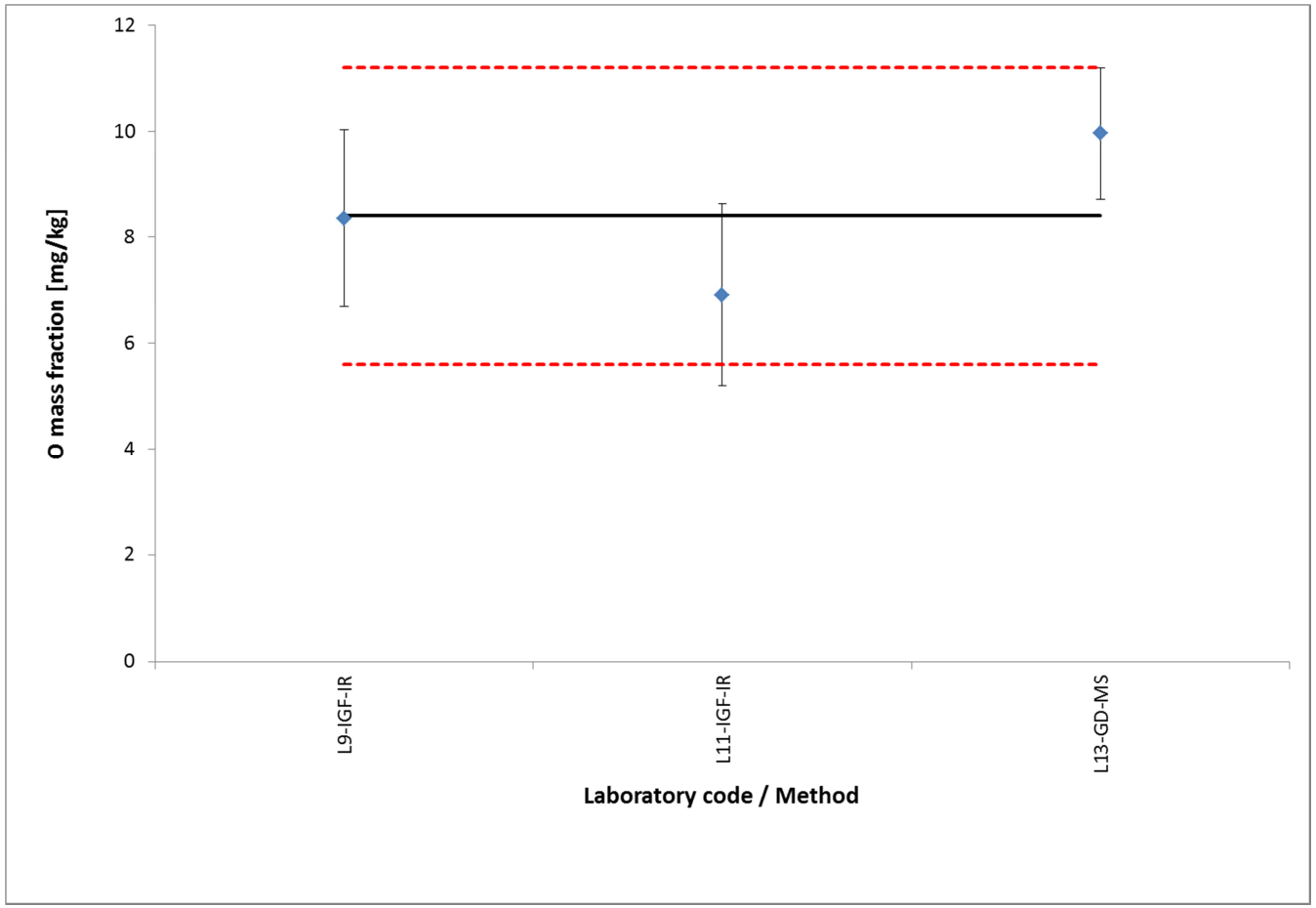


Figure E15. Mean O mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the mean of laboratory means, while the broken lines represent the expanded uncertainty of the mean of laboratory means. Each laboratory is represented by its code.

P (Phosphorus)

Table E16. Individual results for P mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L4-ICP-MS	1.03	2.16	1.85		1.84		1.72	1.22		2.39	2.05	1.21	0.93		1.81	2.03		1.58			1.68	0.80
L5-GD-MS	1.75	1.57	1.02	1.11	1.08	1.27	1.14	1.01	1.82	0.95	1.07	1.50									1.27	0.48
L8-ICP-MS	1.30	1.40	1.30	1.30	1.40	1.30	1.40	1.30	1.40	1.50	1.20	1.30	1.30	1.40	1.20	1.20	1.30	1.40			1.33	0.13
L11-ICP-MS	1.70	1.90	1.50	1.60	1.60	1.60	1.70	1.70	1.70	1.70	1.80	1.70	1.70	1.90	1.70	1.90	1.70	1.70			1.71	0.43
L12-ICP-MS	1.80	1.90	1.90	1.60	1.70	1.40	1.80	1.90	1.80	2.00	2.00	1.60	1.60	1.90	1.90	2.00	1.90	1.60			1.79	0.20
L13-GD-MS	1.11	1.35	1.26	1.37	1.11	1.31	1.41	1.15	1.35	1.43	1.31	1.29									1.29	0.22
L16-ICP-MS	1.34	0.94	1.33	0.91	0.95	1.31	1.12	1.57	1.07	1.17	1.41	1.23	0.88	1.11	1.13	0.91	1.42	1.11			1.16	0.35
L17-ICP-OES	1.58	1.58	1.59	1.76	1.46	1.60	1.34	1.58	1.66	1.80	1.47	1.58	1.35	1.57	1.49	1.72	1.68				1.58	0.21
L21-Spark-OES	1.80	1.70	2.20	1.50	1.60	2.10	1.70	2.00	2.20	2.20	2.40	2.00									1.95	0.57
L4-ICP-MS	1.03	2.16	1.85		1.84		1.72	1.22		2.39	2.05	1.21	0.93		1.81	2.03		1.58			1.68	0.80
L5-GD-MS	1.75	1.57	1.02	1.11	1.08	1.27	1.14	1.01	1.82	0.95	1.07	1.50									1.27	0.48
Results not used for certification																						
L1-ICP-OES	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10				
L2-ICP-OES	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2				
L6-ICP-OES	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5				
L9-ICP-MS	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10				
L1-ICP-OES	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10				

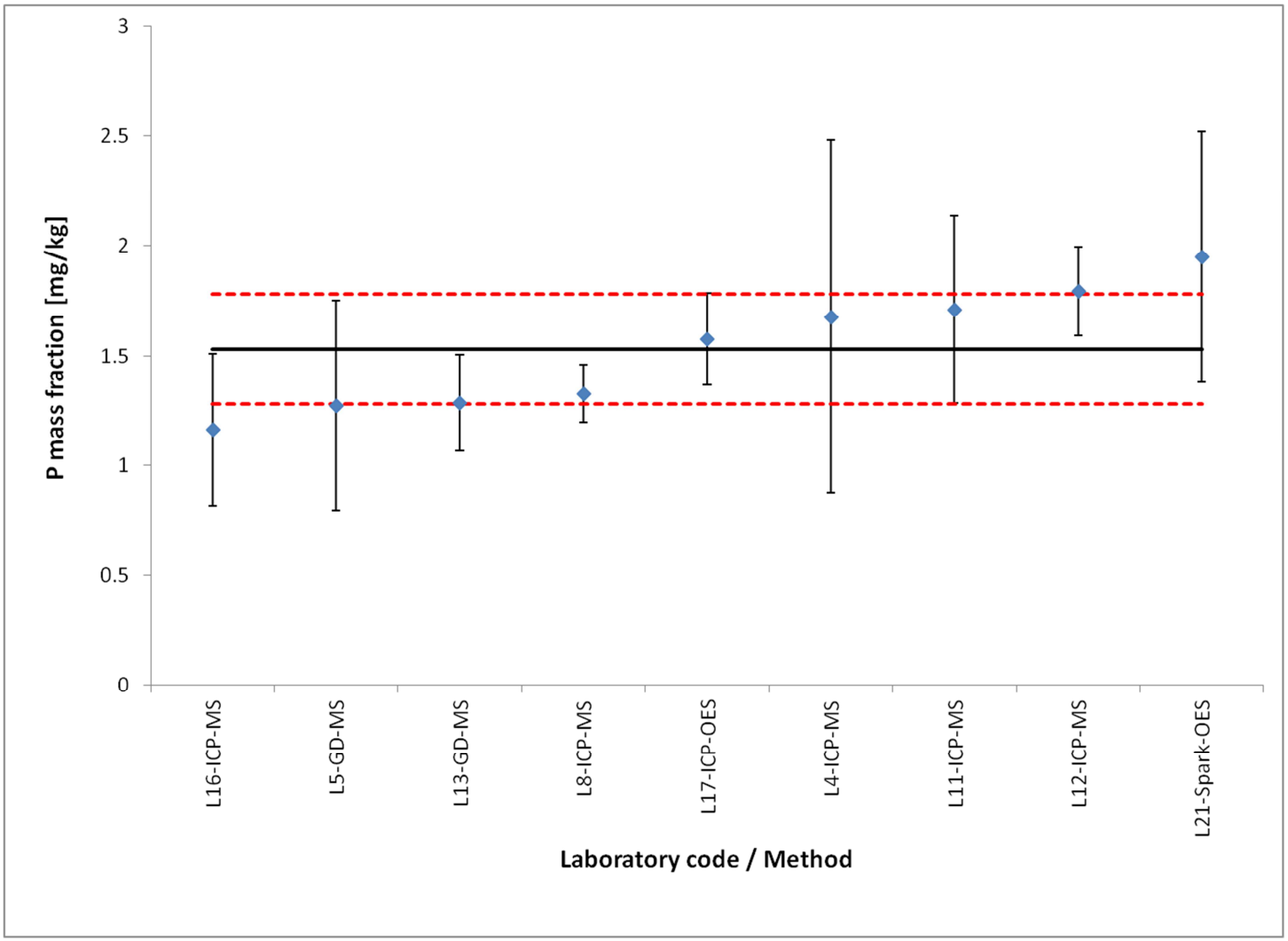


Figure E16. Mean P mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Pb (Lead)

Table E17. Individual results for Pb mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L3-ETV-ICP-OES	2.88	2.81	2.79	2.80	2.90	2.64	2.67	2.67	2.84	2.76	2.84	2.82	2.83	2.80	2.85	2.77	2.74	2.71	2.74	2.70	2.78	0.19
L4-ICP-MS	2.70	2.65	2.68	2.38	2.39	2.37	2.54	2.45	2.45	2.55	2.52	2.52	2.65	2.68	2.77	2.57	2.57	2.61			2.56	0.08
L5-GD-MS	1.84	2.37	2.84	2.74	2.19	2.17	2.97	2.78	1.64	3.31	2.88	2.33									2.51	0.76
L6-ICP-MS	3.40	3.40	3.30	2.90	2.90	2.90	3.20	3.10	3.10	3.20	3.00	3.10	3.10	3.10	3.00	3.00	3.20	3.10			3.11	0.31
L7-DC-arc-OES													2.70	2.40	2.80	2.80	2.60	2.70			2.67	0.30
L9-ICP-MS	2.90	3.03	2.87	2.44	2.38	2.38	2.59	2.55	2.59	2.67	2.64	2.51	2.54	2.21	2.51	2.31	2.35	2.43			2.55	0.51
L11-ICP-MS	2.81	2.78	2.71	2.43	2.41	2.42	2.58	2.58	2.58	2.47	2.54	2.56	2.75	2.84	2.73	2.74	2.67	2.73			2.63	0.66
L12-ICP-MS	2.71	2.45	2.80	2.07	2.23	2.10	2.23	2.16	2.15	2.21	2.27	2.18	2.33	2.34	2.40	2.46	2.35	2.53			2.33	0.45
L13-GD-MS	2.71	3.03	3.21	2.63	2.66	2.59	3.08	2.93	2.93	2.93	3.04	2.77									2.88	0.20
L16-ICP-MS	2.91	2.86	2.82	2.25	2.24	2.41	2.66	1.91	2.47	2.56	2.63	2.56	2.51	2.64	2.61	2.61	2.53	2.66			2.55	0.10
L17-ICP-MS	2.92	3.14	3.17	2.65	2.62	2.68	2.84	2.79	2.82	3.02	2.94	2.84	2.81	2.82	2.81	2.99	2.86	2.96			2.87	0.30
Results not used for certification																						
L1-ICP-MS	3.16	2.90	2.80	2.50	2.25	2.64	2.64	2.00	2.74	2.71	2.26	2.74	2.91	3.00	2.79	2.54	2.80	2.58			2.66	0.57
L2-ICP-OES	2.00	1.90	2.00	1.50	1.40	1.50	1.60	1.70	0.80	1.50	1.70	1.90	1.90	1.80	1.70	1.90	1.70	1.70			1.68	0.57
L8-ICP-MS	2.70	2.60	2.80	2.80	2.70	2.60	2.90	2.50	2.60	2.50	2.60	2.70	2.80	2.60	2.70	2.50	2.60	2.70			2.66	0.27
L18-ICP-MS	1.34	1.48	1.53	1.47	1.46	1.43	1.75	1.48	1.63	1.46	1.33	1.45	1.53	1.67	1.74	1.73	1.82	1.85			1.56	0.32
L20-ICP-MS													4.80	3.70	3.50	4.00	4.20	3.70			3.98	0.94
L21-Spark-OES	4.30	3.90	4.40	3.70	3.30	4.30	4.40	5.00	6.00	5.10	7.10	4.80									4.69	2.07

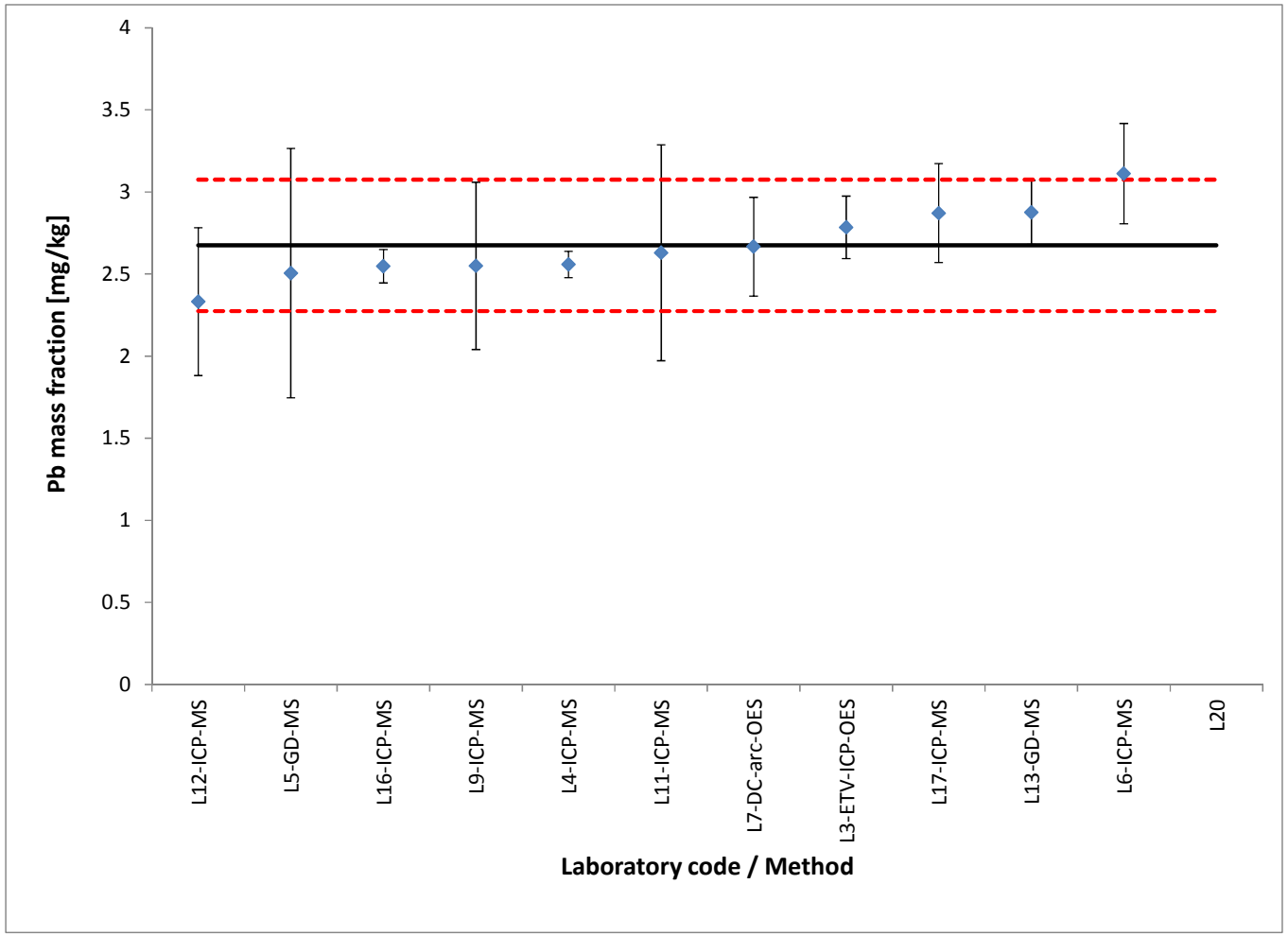


Figure E17. Mean Pb mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

S (Sulphur)

Table E18. Individual results for S mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-spark-OES	2.63	2.77	2.37	2.30	2.87	2.70	2.23	2.30													2.52	0.49
L5-GD-MS	4.02	3.25	2.60	2.57	2.47	2.68	2.79	2.62	3.44	2.40	2.57	2.99									2.87	0.78
L7-DC-arc-OES													4.00	3.00	4.00	6.00	5.00	3.00			4.17	2.34
L9-IGF-IR													2.30	2.00	1.70	2.20	2.00	2.00			2.03	0.41
L11-IGF-IR	3.21	3.32	3.32	3.35	3.24	3.21	3.02	3.02	3.12	3.39	3.32	3.57	2.96	3.24	3.30	3.69	3.42	3.56			3.29	0.82
L13-GD-MS	2.50	2.69	2.59	2.65	2.39	2.53	2.73	2.55	2.71	2.75	2.66	2.84									2.63	0.48
L21-Spark-OES	3.80	5.90	5.50	4.40	3.80	3.70	6.40	5.30	5.60	6.20	6.00	7.90									5.38	2.53
Results not used for certification																						
L1-C-IR	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10				
L4-ICP-MS	10.20	3.23	5.24	5.28	5.78	5.31	2.41	7.55	13.20	4.38	1.03	13.00	11.40	5.69	5.86	9.23		1.82			6.51	7.72

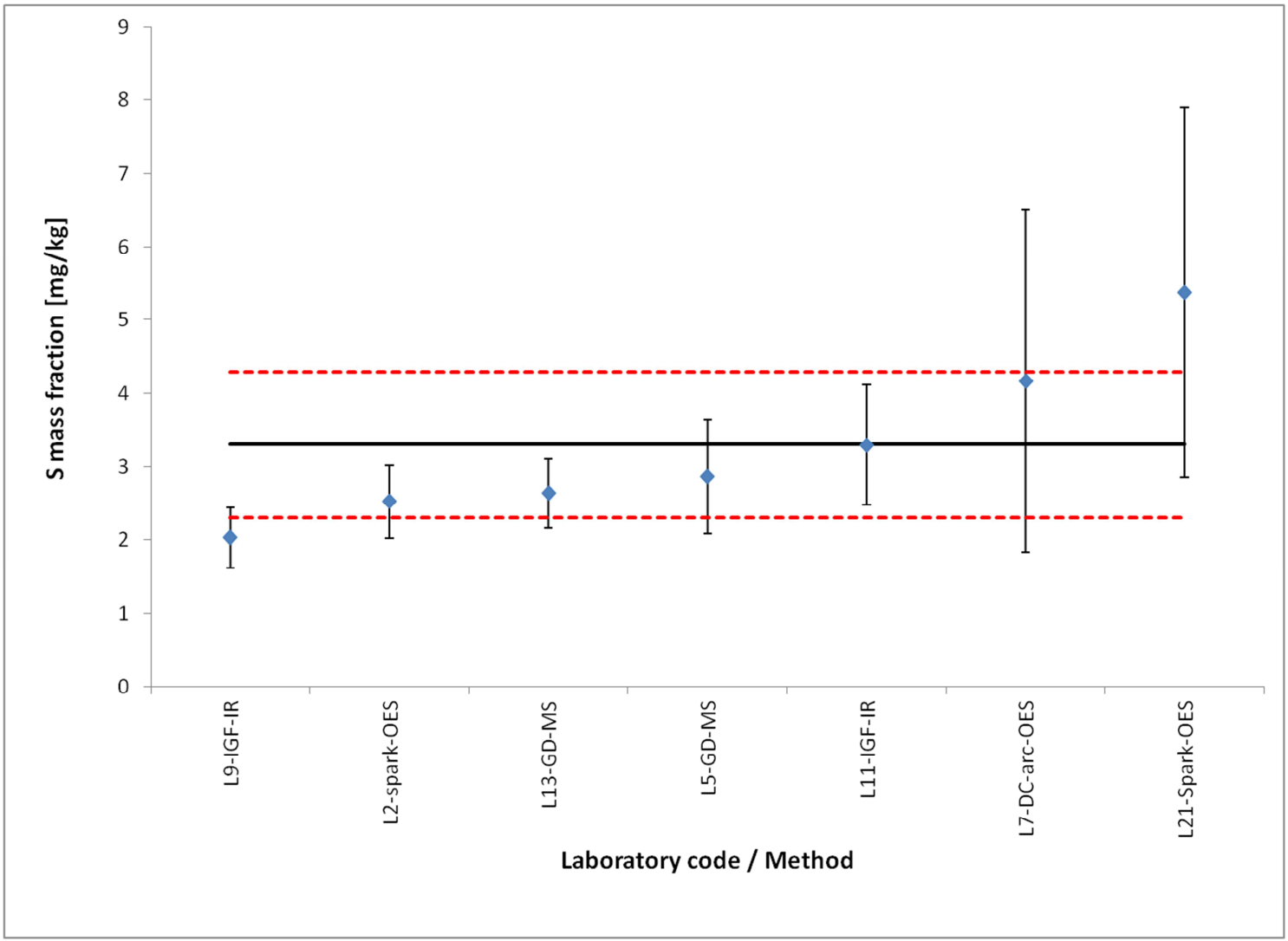


Figure E18. Mean S mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the indicative value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the indicative value. Each laboratory is represented by its code.

Sb (Antimony)

Table E19. Individual results for Sb mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.55	0.57	0.56	0.57	0.56	0.49	0.58	0.40	0.58	0.60	0.53	0.56	0.57	0.63	0.60	0.58	0.58	0.57			0.56	0.10
L3-ETV-ICP-OES	0.58	0.61	0.59	0.60	0.63	0.49	0.53	0.52	0.56	0.53	0.62	0.60	0.61	0.60	0.60	0.56	0.56	0.58	0.56	0.53	0.58	0.11
L4-ICP-MS	0.51	0.54	0.52	0.51	0.54	0.52	0.54	0.51	0.52	0.55	0.53	0.52	0.52	0.51	0.54	0.54	0.52	0.54			0.53	0.03
L6-ICP-MS	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.50	0.50	0.60	0.60			0.59	0.06
L7-DC-arc-OES													0.40	0.50	0.50	0.40	0.50	0.40			0.45	0.11
L8-ICP-MS	0.48	0.51	0.49	0.49	0.47	0.48	0.45	0.48	0.48	0.48	0.48	0.47	0.47	0.47	0.46	0.49	0.48	0.46			0.48	0.05
L9-ICP-MS	0.61	0.45	0.58	0.53	0.52	0.53	0.61	0.60	0.63	0.60	0.55	0.62	0.67	0.41	0.49	0.44	0.45	0.45			0.54	0.11
L10-INAA	0.57	0.58	0.57	0.57	0.58	0.58	0.57	0.57	0.57	0.57	0.57	0.57	0.58	0.57	0.56	0.59	0.57	0.58			0.57	0.02
L11-ICP-MS	0.80	0.76	0.70	0.78	0.73	0.76	0.67	0.66	0.70	0.68	0.67	0.66	0.69	0.59	0.68	0.70	0.69	0.67			0.70	0.18
L13-GD-MS	0.56	0.60	0.61	0.59	0.57	0.57	0.56	0.54	0.58	0.63	0.60	0.57									0.58	0.04
L14-INAA	0.53	0.53	0.46	0.53	0.53	0.53	0.53	0.53	0.46	0.53	0.53	0.53	0.56		0.50	0.54	0.55	0.54			0.52	0.03
L15-INAA	0.58	0.55	0.54	0.60	0.59	0.57	0.58	0.61	0.59	0.57	0.58	0.58	0.60	0.62	0.59	0.60	0.60	0.61			0.59	0.01
L16-ICP-MS	0.65	0.73	0.65	0.56	0.59	0.60	0.74	0.47	0.59	0.66	0.65	0.62	0.69	0.62	0.63	0.63	0.57	0.66			0.63	0.06
L17-ICP-MS	0.57	0.64	0.65	0.63	0.64	0.64	0.63	0.60	0.62	0.68	0.67	0.64	0.62	0.60	0.66	0.66	0.64	0.68			0.64	0.04
L18-ICP-MS	0.46	0.48	0.48	0.48	0.51	0.48	0.46	0.40	0.45	0.40	0.35	0.41	0.49	0.51	0.52	0.51	0.53	0.52			0.47	0.10
L20-ICP-MS													0.70	0.60	0.60	0.70	0.60	0.70			0.65	0.11
Results not used for certification																						
L5-GD-MS	0.40	0.47	0.50	0.55	0.46	0.48	0.55	0.52	0.39	0.59	0.55	0.49									0.50	0.09
L2-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
L21-Spark-OES	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2										

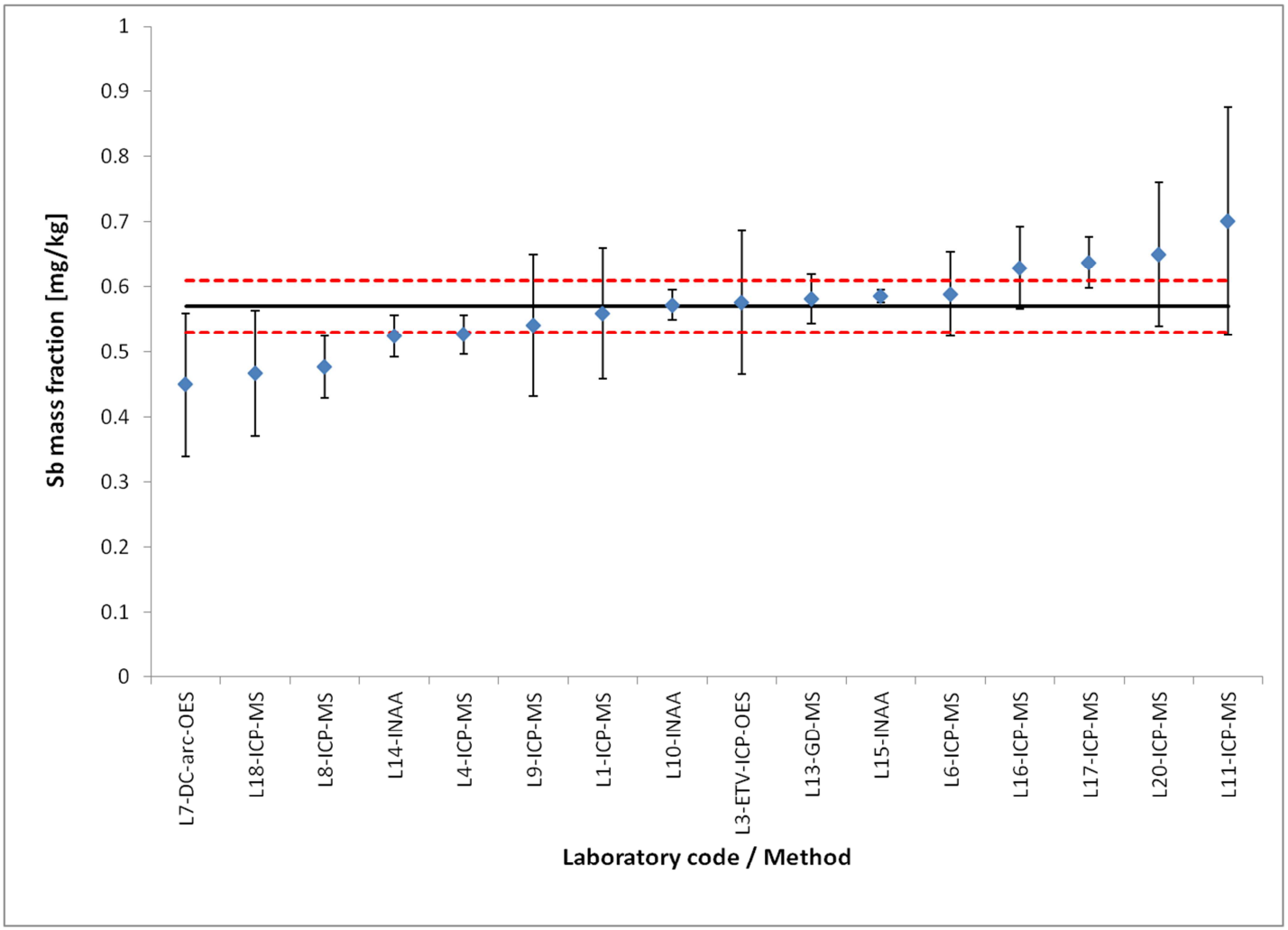


Figure E19. Mean Sb mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Se (Selenium)

Table E20. Individual results for Se mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L3-ETV-ICP-OES	0.40	0.45	0.40	0.44	0.44	0.39	0.53	0.43	0.42	0.40	0.55	0.48	0.48	0.48	0.51	0.72	0.61	0.63	0.59	0.58	0.49	0.24
L5-GD-MS	0.43	0.42	0.45	0.47	0.39	0.44	0.51	0.47	0.41	0.53	0.44	0.44									0.45	0.06
L6-ICP-MS	0.60	0.50	0.50	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.50	0.60	0.50	0.50	0.50	0.50	0.60	0.50			0.56	0.10
L9-ICP-MS	0.59	0.76	0.70	0.86	0.84	0.82	0.60	0.66	0.42	0.69	0.74	0.67	0.58	0.88	0.78	0.86	0.87	0.84			0.73	0.15
L10-INAA	0.52	0.55	0.51	0.52	0.52	0.52	0.52	0.53	0.53	0.54	0.52	0.53	0.56	0.54	0.52	0.46	0.52	0.52			0.52	0.04
L13-GD-MS	0.43	0.46	0.44	0.47	0.42	0.45	0.43	0.40	0.47	0.46	0.45	0.47									0.45	0.04
L14-INAA	0.50	0.51	0.40	0.53	0.51	0.53	0.49	0.49	0.52	0.44	0.49	0.53	0.53	0.50	0.54	0.56	0.50	0.52			0.51	0.04
L15-INAA	0.39	0.40	0.38	0.53	0.55	0.49	0.48	0.75	0.53	0.43	0.46	0.55	0.43	0.64	0.53	0.44	0.57	0.50			0.50	0.04
L16-ICP-MS	0.83	0.75	0.87	0.78	0.81	0.83	0.64	0.67	0.83	1.00	0.65	0.62	0.91	0.91	0.56	0.89	0.83	0.69			0.78	0.38
L17-ICP-MS	0.56	0.60	0.55	0.55	0.58	0.60	0.60	0.55	0.56	0.59	0.60	0.64	0.54	0.54	0.60	0.56	0.59	0.55			0.58	0.16
L18-ICP-MS	0.57	0.58	0.59	0.54	0.60	0.53	0.56	0.51	0.56	0.46	0.37	0.48	0.55	0.59	0.55	0.55	0.56	0.50			0.54	0.11
L3-ETV-ICP-OES	0.40	0.45	0.40	0.44	0.44	0.39	0.53	0.43	0.42	0.40	0.55	0.48	0.48	0.48	0.51	0.72	0.61	0.63	0.59	0.58	0.49	0.24
L5-GD-MS	0.43	0.42	0.45	0.47	0.39	0.44	0.51	0.47	0.41	0.53	0.44	0.44									0.45	0.06
L6-ICP-MS	0.60	0.50	0.50	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.50	0.60	0.50	0.50	0.50	0.50	0.60	0.50			0.56	0.10
Results not used for certification																						
L1-INAA	0.38	0.50	0.52	0.29	0.54	0.51	0.45	0.29	0.45	0.53	0.55	0.55	0.44	0.32	0.51	0.53	0.46	0.48			0.46	0.17
L4-ICP-MS	0.89	0.39	0.67	0.18	0.75	0.31	0.78	0.37	0.41	0.72	0.38	0.26	0.36	0.25	0.49	0.58	0.57	0.65			0.50	0.30
L8-ICP-MS	0.38	0.36	0.38	0.37	0.37	0.38	0.36	0.34	0.38	0.36	0.37	0.36	0.38	0.35	0.37	0.39	0.37	0.36			0.37	0.04
L11-ICP-MS	0.53	0.50	0.46	0.49	0.49	0.42	0.63	0.48	0.49	0.53	0.47	0.40	0.43	0.49	0.55	0.42	0.45	0.46			0.48	0.12
L20-ICP-MS													1.00	1.20	1.10	1.20	1.10	1.00			1.10	0.18
L2-ICP-OES	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
L7-DC-arc-OES													< 1	< 1	< 1	< 1	< 1	< 1				
L21-Spark-OES	< 1	< 1	< 1	< 1	< 1	< 1	1.00	1.00	1.10	1.10	1.00	1.00										

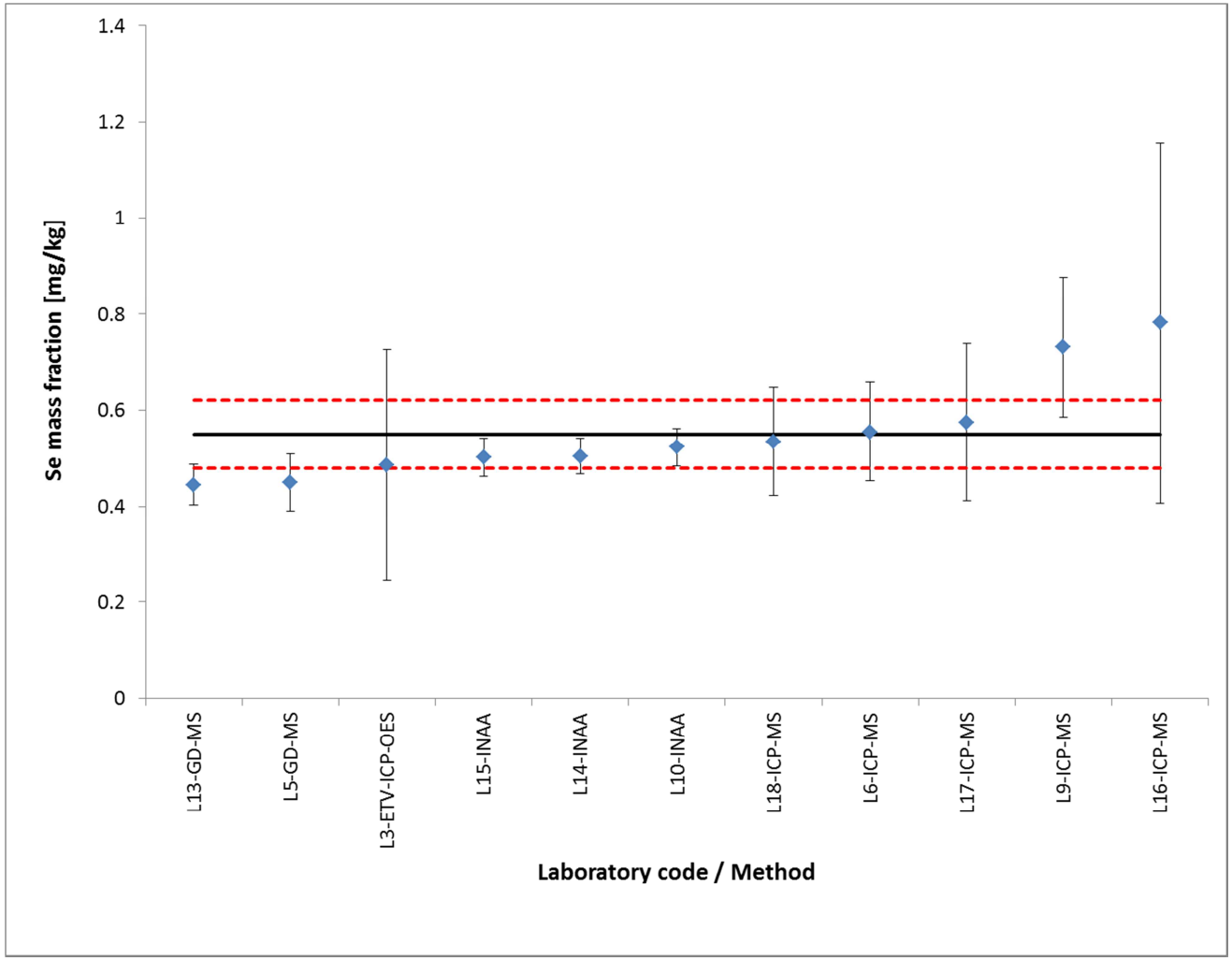


Figure E20. Mean Se mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Si (Silicon)

Table E21. Individual results for Si mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L5-GD-MS	0.62	0.49	0.42	0.61	0.62	0.53	0.63	0.63	0.60	0.57	0.52	0.55									0.57	0.11
L8-ICP-MS	1.60	1.60	1.70	1.70	1.60	1.60	1.60	1.80	1.80	1.50	1.70	1.50	1.40	1.60	1.60	1.50	1.60	1.60			1.61	0.16
L11-ICP-OES	1.40	1.60	1.40	1.40	1.40	1.40	1.70	1.70	1.70	1.70	1.70	1.70	1.40	1.50	1.40	1.30	1.30	1.30			1.50	0.38
L16-ICP-MS	1.46	1.30	1.23	1.61	1.29	1.24	1.12	1.07	1.62	1.14	1.24	1.50	1.29	1.34	1.12	1.12	1.46	1.25			1.30	0.31
L17-ICP-OES	1.21	1.18	1.21	1.21	1.19	1.22	1.22	1.24	1.23	1.23	1.22	1.26	1.24	1.24	1.22	1.24	1.27				1.23	0.12
Results not used for certification																						
L6-ICP-OES	2.20	<2	2.40	3.70	3.80	4.50	< 2	3.40	2.50	< 2	3.10	4.80	4.90	3.40	2.50	2.50	2.50	2.00			3.21	1.92
L1-ICP-OES	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60	< 60				
L9-ICP-MS	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5				

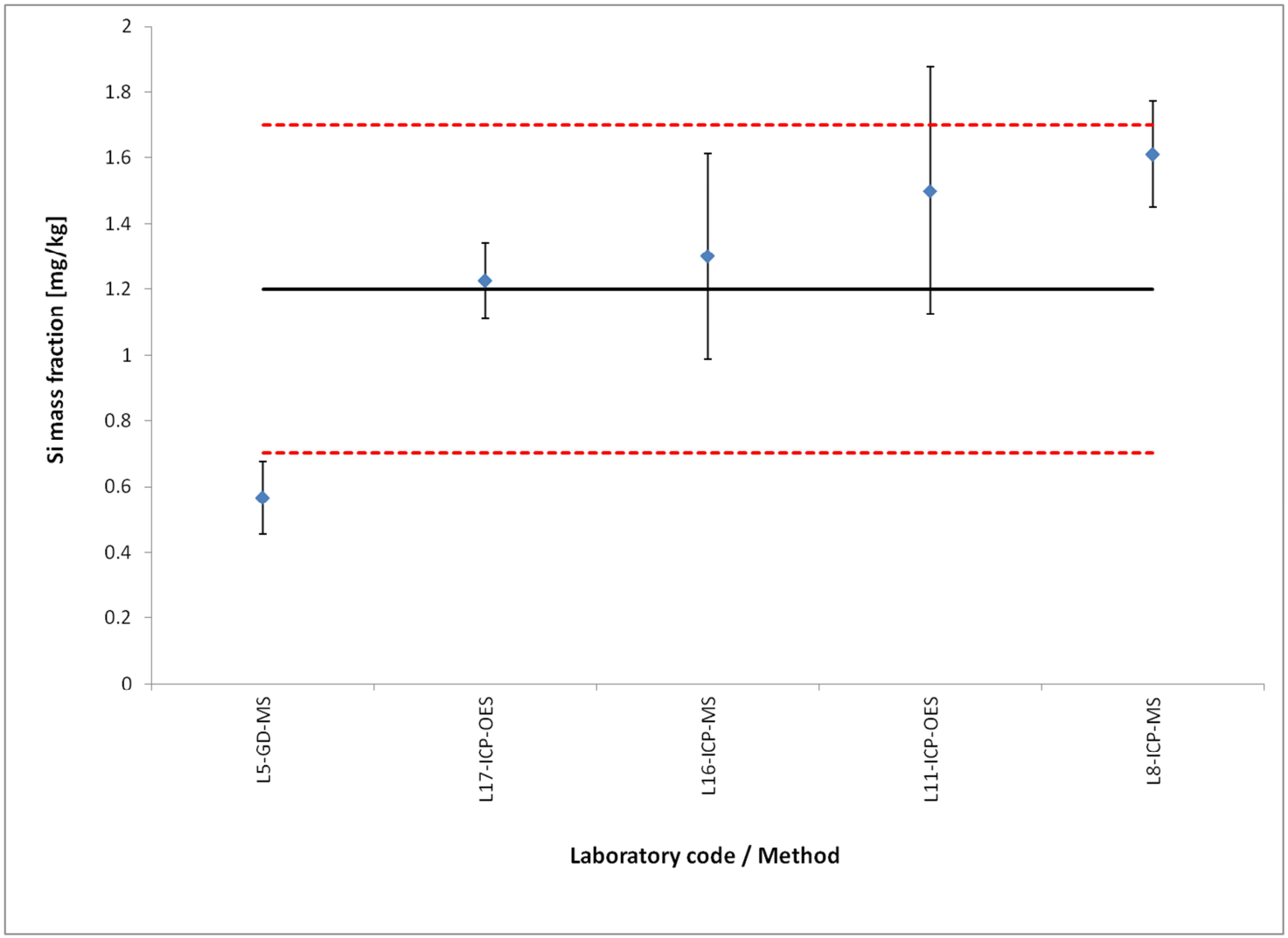


Figure E21. Mean Si mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the mean of laboratory means, while the broken lines represent the expanded uncertainty of the mean of laboratory means. Each laboratory is represented by its code.

Sn (Tin)

Table E22. Individual results for Sn mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	2.24	1.60	1.62	1.70	1.06	2.23	1.38	1.68	2.04			1.80	1.63	2.21	1.64	1.40	1.61	1.31			1.70	0.68
L2-ICP-OES	1.50	1.40	1.70	1.10	1.40	1.00	1.30	1.40	1.40	1.30	1.50	1.40	1.40	1.40	1.50	1.50	1.60	1.50			1.41	0.33
L3-ETV-ICP-OES	1.41	1.38	1.34	1.38	1.37	1.30	1.28	1.31	1.34	1.31	1.39	1.40	1.39	1.39	1.42	1.39	1.35	1.33	1.35	1.34	1.36	0.10
L4-ICP-MS	1.58	1.66	1.67	1.27	1.38	1.18	1.61	1.43	1.47	1.61	1.60	1.49	1.53	1.53	1.68	1.59	1.49	1.62			1.52	0.10
L5-GD-MS	1.01	1.22	1.37	1.07	0.93	0.94	1.35	1.28	0.91	1.46	1.35	1.16									1.17	0.43
L6-ICP-MS	1.80	1.70	1.60	1.40	1.30	1.40	1.60	1.70	1.70	1.50	1.50	1.70	1.70	1.50	1.50	1.50	1.70	1.50			1.57	0.27
L7-DC-arc-OES													1.60	1.60	1.70	1.60	1.50	1.50			1.58	0.15
L8-ICP-MS	1.60	1.30	1.80	1.50	1.60	1.60	1.40	1.50	1.50	1.70	1.80	1.70	1.50	1.60	1.50	1.60	1.70	1.80			1.59	0.16
L9-ICP-MS	2.08	1.98	2.11	1.40	1.25	1.21	1.83	1.73	1.83	1.79	1.43	1.85	1.90	1.47	1.50	1.46	1.50	1.48			1.66	0.33
L11-ICP-MS	1.49	1.52	1.53	1.31	1.20	1.15	1.39	1.39	1.47	1.54	1.42	1.51	1.42	1.50	1.49	1.42	1.40	1.37			1.42	0.35
L13-GD-MS	1.67	1.85	1.79	1.34	1.34	1.33	1.72	1.70	1.71	1.72	1.70	1.62									1.62	0.18
L16-ICP-MS	1.19	1.58	1.42	1.33	1.25	1.44	1.24	2.04	1.66	1.68	1.73	2.04	1.02	1.38	1.87	1.87	1.75	1.70			1.57	0.38
L17-ICP-MS	1.53	1.74	1.75	1.26	1.25	1.30	1.51	1.53	1.53	1.65	1.64	1.51	1.51	1.51	1.53	1.66	1.58	1.65			1.54	0.39
L18-ICP-MS	1.49	1.42	1.63	1.02	1.08	1.07	1.01	0.95	0.99	0.92	0.81	0.95	1.23	1.30	1.32	1.33	1.36	1.34			1.18	0.46
Results not used for certification																						
L21-Spark-OES	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2										

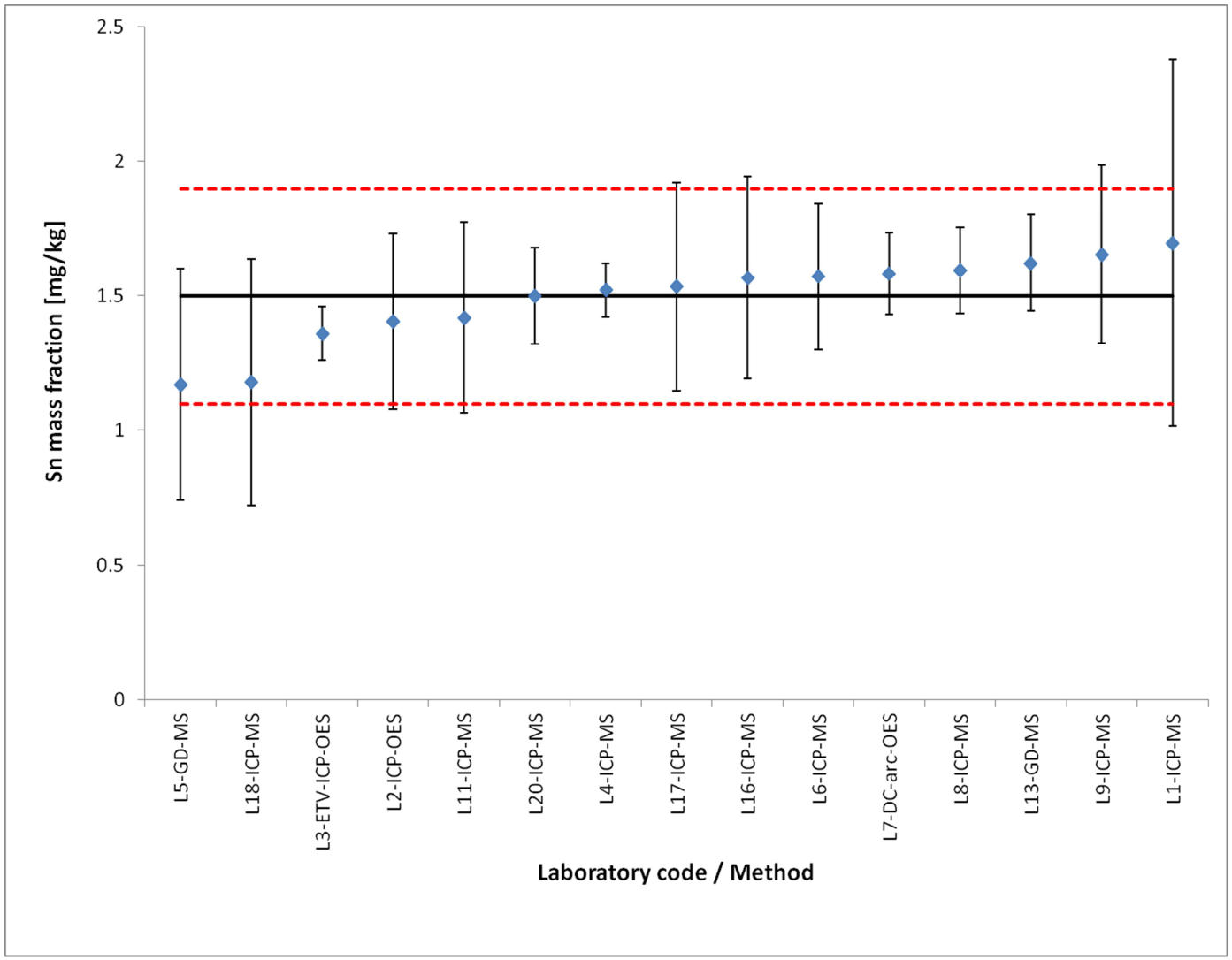


Figure E22. Mean Sn mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the indicative value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the indicative value. Each laboratory is represented by its code.

Te (Tellurium)

Table E23. Individual results for Te mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.57	0.54	0.46	0.46	0.57	0.46	0.48	0.38	0.48	0.52	0.48	0.52	0.45	0.58	0.52	0.58	0.55	0.46			0.50	0.11
L3-ETV-ICP-OES	0.36	0.43	0.38	0.40	0.40	0.42	0.51	0.46	0.46	0.47	0.58	0.43	0.44	0.44	0.45	0.68	0.59	0.60	0.57	0.54	0.47	0.20
L4-ICP-MS	0.47	0.48	0.48	0.42	0.43	0.41	0.48	0.44	0.46	0.45	0.43	0.44	0.47	0.43	0.48	0.48	0.45	0.49			0.46	0.03
L5-GD-MS	0.39	0.44	0.45	0.50	0.38	0.43	0.51	0.49	0.39	0.52	0.49	0.46									0.45	0.07
L6-ICP-MS	0.50	0.50	0.50	0.50	0.50	0.60	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.60	0.50			0.51	0.06
L8-ICP-MS	0.54	0.56	0.58	0.55	0.55	0.56	0.55	0.51	0.56	0.54	0.53	0.54	0.59	0.54	0.52	0.56	0.57	0.58			0.55	0.06
L10-INAA	0.54	0.61	0.67	0.52	0.47	0.53	0.59	0.53	0.59	0.54	0.47	0.53	0.51	0.51	0.48	0.67	0.56	0.40			0.54	0.14
L11-ICP-MS	0.58	0.65	0.65	0.52	0.61	0.51	0.57	0.54	0.57	0.62	0.54	0.60	0.51	0.64	0.60	0.52	0.64	0.61			0.58	0.15
L13-GD-MS	0.41	0.56	0.46	0.54	0.44	0.48	0.53	0.43	0.51	0.53	0.49	0.46									0.49	0.09
L14-INAA	0.60	0.55	0.52	0.56	0.60	0.57	0.54	0.50	0.57	0.53	0.59	0.55									0.55	0.10
L16-ICP-MS	0.23	0.27	0.30	0.46	0.38	0.53	0.21	0.53	0.48	0.45	0.41	0.45	0.23	0.33	0.43	0.36	0.59	0.34			0.39	0.38
L17-ICP-MS	0.46	0.51	0.48	0.51	0.48	0.52	0.50	0.50	0.51	0.52	0.50	0.50	0.50	0.52	0.50	0.50	0.51	0.50			0.50	0.03
L18-ICP-MS	0.49	0.51	0.49	0.46	0.48	0.52	0.42	0.40	0.45	0.37	0.33	0.38	0.53	0.52	0.55	0.54	0.58	0.51			0.47	0.14
L20-ICP-MS													0.60	0.80	0.30	0.80	0.60	0.40			0.58	0.41
Results not used for certification																						
L9-ICP-MS	0.83	0.74	0.99	0.71	0.90	1.09	0.82	0.94	0.98	0.86	0.86	0.90	0.92	0.71	0.71	0.69	0.72	0.70			0.84	0.17
L2-ICP-OES	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2				
L7-DC-arc-OES													< 1	< 1	< 1	< 1	< 1	< 1				
L21-lspark-OES	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3										

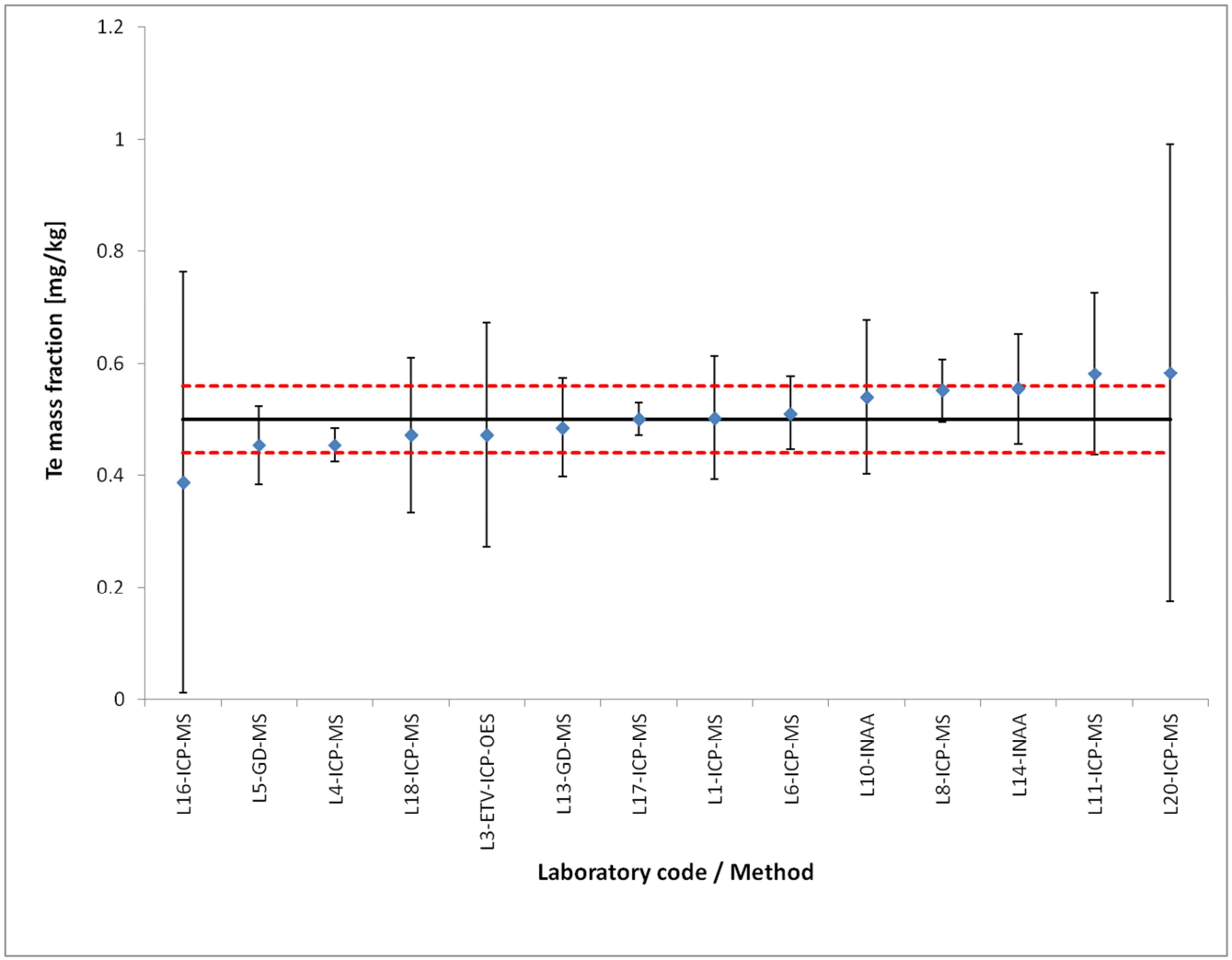


Figure E23. Mean Te mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Ti (Titanium)

Table E24. Individual results for Ti mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	0.83	0.88	0.84	0.91	0.98	1.05	0.77	0.58	0.78	0.79	0.75	0.80	0.77	0.80	0.82	0.80	0.80	0.82			0.82	0.19
L2-ICP-OES	0.80	0.70	0.90	1.00	0.90	1.00	0.70	0.80	0.70	0.80	0.90	0.80	0.70	0.60	0.80	0.90	1.00	0.90			0.83	0.24
L4-ICP-MS	1.12	1.35	1.41	1.22	1.52	1.23	1.25	1.05	1.28	1.42	1.09	1.13	1.13	1.13	1.35	1.24	1.16	1.11			1.23	0.18
L5-GD-MS	0.48	0.69	0.94	0.83	0.69	0.77	1.03	1.08	0.59	1.11	1.21	0.86									0.86	0.28
L8-ICP-MS	1.10	1.20	1.00	1.20	1.10	1.00	1.10	1.10	1.10	1.30	1.30	1.10	1.00	1.20	1.20	1.10	1.10	1.20			1.13	0.11
L9-ICP-MS	0.87	1.00	1.04	1.04	1.03	0.96	0.96	1.04	0.99	1.06	1.01	0.96	0.93	0.95	1.13	0.94	0.89	0.88			0.98	0.20
L11-ICP-MS	1.13	1.00	1.02	1.08	1.08	1.12	0.88	1.06	1.11	1.06	1.04	1.07	0.96	1.07	1.17	1.07	1.21	1.00			1.06	0.27
L13-GD-MS	0.88	1.05	0.99	1.11	0.82	0.93	1.06	0.93	1.12	1.05	1.08	1.13									1.01	0.17
L16-ICP-MS	0.76	0.59	0.54	0.84	0.81	0.82	0.55	0.47	0.62	0.63	0.61	0.57	0.67	0.67	0.67	0.67	0.74	0.74			0.67	0.08
L17-ICP-MS	0.48	0.62	0.71	0.81	0.90	0.81	0.52	0.56	0.58	0.75	0.75	0.62	0.58	0.53	0.63	0.77	0.62	0.77			0.67	0.24
L18-ICP-MS	1.29	1.13	1.28	1.25	1.37	1.20	0.90	1.04	1.08	0.82	0.69	0.76	1.12	1.16	1.15	1.06	1.10	1.03			1.08	0.37
L20-ICP-MS													1.30	1.40	1.30	1.40	1.20	1.40			1.33	0.16

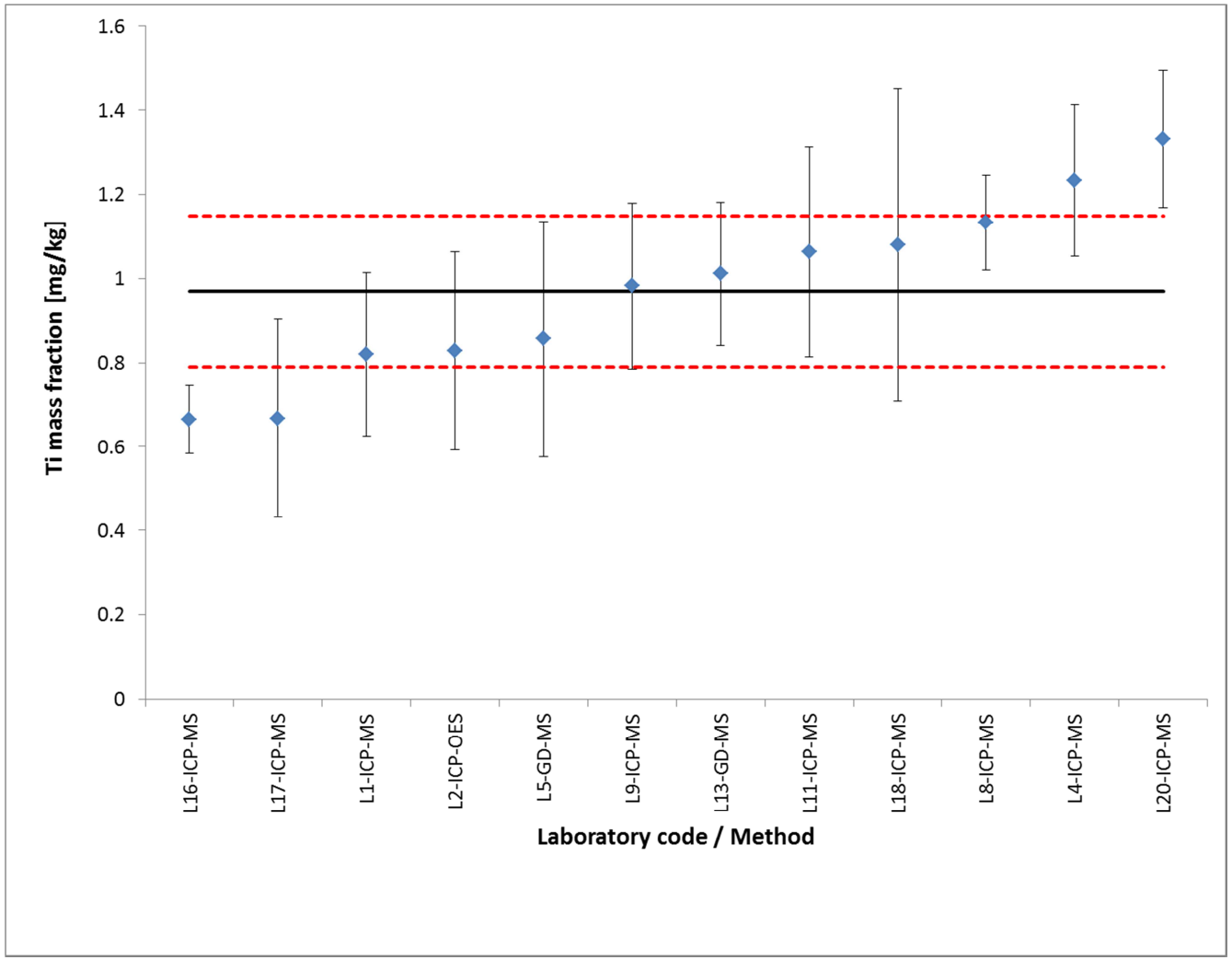


Figure E24. Mean Ti mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Zn (Zinc)

Table E25. Individual results for Zn mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Rep 19	Rep 20	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	3.60	2.30	2.90	2.50	2.70	2.40	2.60	2.40	2.60	2.30	2.80	2.20	2.80	3.10	2.20	2.30	3.00	2.40			2.62	0.74
L4-ICP-MS	1.79	2.48	1.73	4.02		1.10	1.61	1.24	1.34	1.75	2.41	1.24	1.95	1.71	1.94	1.81	1.46	2.25			1.87	1.40
L5-GD-MS	2.51	2.55	2.37	1.95	1.90	2.10	2.27	2.08	2.62	2.01	2.20	2.28									2.24	0.30
L7-DC-arc-OES													2.10	2.10	2.40	2.10	2.00	2.00			2.12	0.29
L10-INAA	2.21	2.39	2.17	1.92	2.02	2.19	2.24	2.12	2.14	2.31	2.05	2.07	2.13	2.30	1.97	2.24	1.94	2.30			2.15	0.21
L11-ICP-MS	1.98	1.96	1.96	2.05	2.06	2.04	1.97	2.00	2.06	2.04	1.98	2.00	2.19	1.96	1.95	2.09	1.97	2.09			2.02	0.51
L12-ICP-MS	2.00	2.70	2.40	1.90	3.10	2.70	2.90	2.10	1.80	2.30	2.30	2.50	1.60	2.70	2.00	2.20	3.00	2.10			2.35	0.60
L13-GD-MS	2.02	1.84	1.84	1.61	1.70	1.74	1.79	1.83	1.82	1.72	1.87	1.84									1.80	0.15
L14-INAA													2.12	2.14	2.13	2.23	2.08	2.19			2.15	0.17
L15-INAA	2.56	2.19	2.04	1.96	1.82	2.61	2.27	2.09	2.60	2.24	2.34	2.35	2.39	2.37	3.42	2.29	2.31	2.03			2.33	0.20
L16-ICP-MS	2.08	1.81	1.69	1.65	1.46	1.80	1.74	1.49	1.94	1.70	1.74	2.04	1.97	1.94	1.76	1.79	1.94	1.75			1.79	0.29
L17-ICP-MS	1.90	1.96	2.03	1.84	1.77	1.71	1.81	1.98	2.03	2.02	1.99	1.89	1.84	1.88	1.91	2.05	1.84	2.08			1.92	0.22
L18-ICP-MS	3.42	2.27	3.93	3.28	3.20	2.90	3.02	2.95	3.82	3.14	2.52	2.98	3.37	3.61	3.80	3.08	3.33	2.95			3.20	0.87
L20-ICP-MS													2.10	2.10	2.20	2.00	2.20	2.00			2.10	0.18
Results not used for certification																						
L1-ICP-MS	3.86	3.02	4.56	4.17	2.61	3.43	5.83	2.29	2.81	3.06	3.27	8.72	7.08	7.72	5.68	6.73	4.21	5.02			4.67	3.81
L8-ICP-MS	3.80	3.60	3.90	3.80	3.70	3.70	3.90	3.90	3.80	3.80	3.90	3.60	3.90	3.80	3.80	3.80	3.70	3.70			3.78	0.38
L9-ICP-MS	3.35	3.76	5.77	2.76	3.92	3.62	3.03	1.52	2.53	2.42	4.06	3.96	2.95	3.24	3.44	3.48	3.41	3.60			3.38	0.68
L6-ICP-MS	< 2	2.00	< 2	2.00	2.00	2.40	< 2	2.10	2.00	< 2	2.00	2.30	2.60	< 2	< 2	< 2	2.20	2.00				
L21-Ispark-OES	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5										

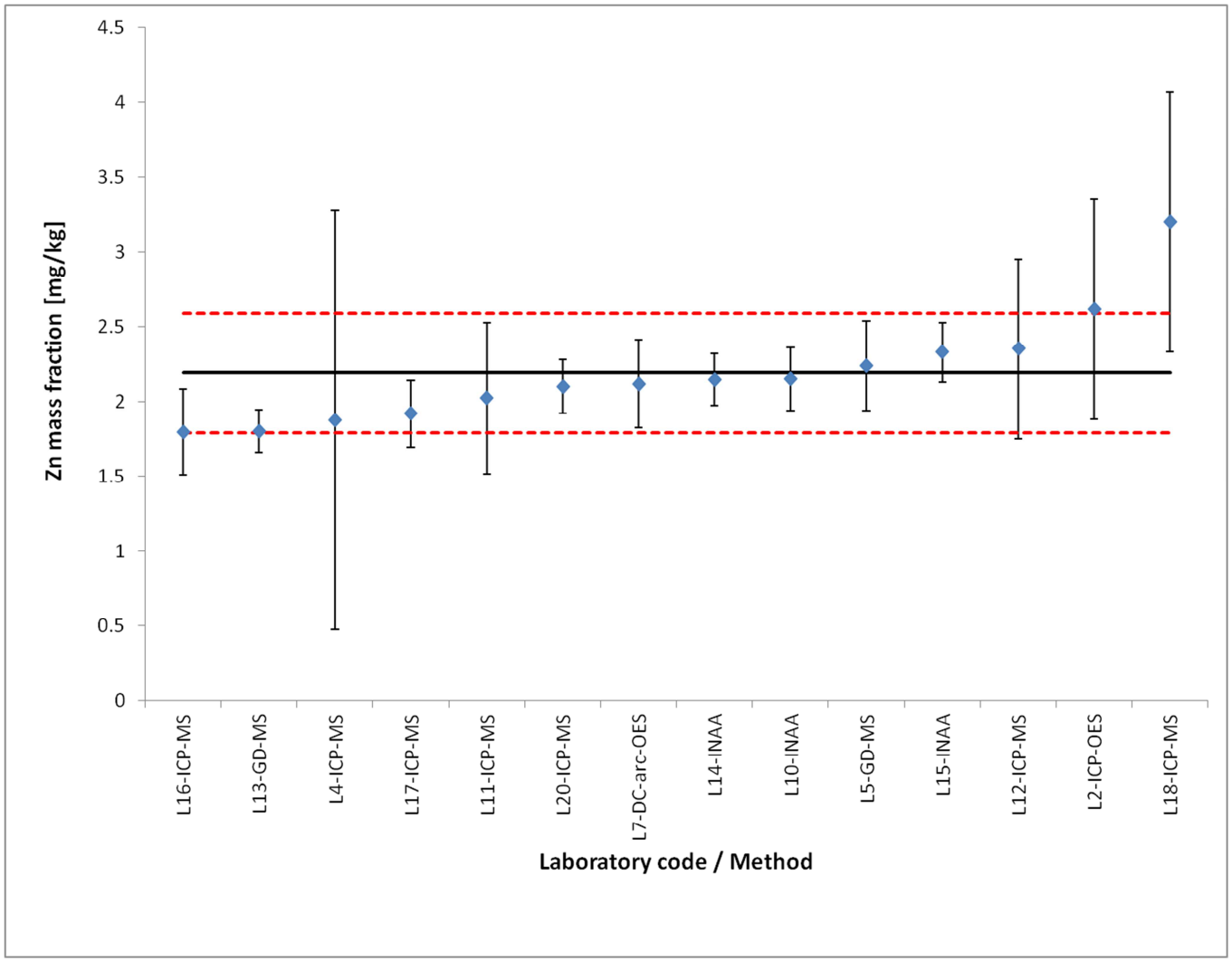


Figure E25. Mean Zn mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the certified value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code.

Zr (Zirconium)

Table E26. Individual results for Zr mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L2-ICP-OES	6.10	6.20	6.10	6.50	6.70	6.30	6.30	6.50	6.70	5.20	5.20	5.20	5.60	5.10	5.50	5.70	5.60	4.90	5.86	1.18
L4-ICP-MS	9.04	9.09	9.11	8.95	9.34	8.89	9.30	8.99	8.85	9.24	9.25	8.93	8.88	8.90	9.28	9.29	8.90	9.34	9.09	0.24
L5-GD-MS	3.18	5.05	8.35	7.75	5.89	6.49	8.68	9.12	3.68	10.24	10.45	6.69							7.13	3.20
L10-INAA	10.20	8.45	8.59	11.30	11.80	11.10	9.33	9.44	9.81	11.50	9.91	10.10	9.29	12.10	10.50	11.30	9.22	9.53	10.19	1.50
L14-INAA	9.81	10.09	8.94	9.22	10.29	10.26	10.59	9.00	10.26	9.26	10.52	9.33	9.28	9.34	10.57	10.80	11.16	10.13	9.94	1.40
L15-INAA	16.30	17.60	7.11	10.10	13.30	16.00	14.40	10.30	12.80	8.02		8.33	9.75	10.30	9.63	10.70	10.50	15.10	11.78	3.00
L20-ICP-MS													7.40	8.50	7.10	7.70	8.00	8.80	7.92	1.30
L1-ICP-MS	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	0.18	< 0.13	< 0.13	0.42	< 0.13	0.34	1.09	< 0.13	< 0.13	< 0.13	0.51	0.81
L8-ICP-MS	1.30	1.30	1.30	1.40	1.20	1.40	1.30	1.30	1.30	1.20	1.40	1.40	1.30	1.40	1.40	1.40	1.10	1.40	1.32	0.13
L9-ICP-MS	2.34	2.35	2.08	2.35	2.63	2.27	2.18	2.11	2.15	2.55	2.77	2.80	2.73	2.63	2.89	2.52	2.15	3.16	2.48	0.50
L11-ICP-MS	4.53	4.50	4.21	4.44	4.24	4.62	4.32	4.60	4.58	4.58	4.47	4.49	4.50	4.42	4.36	4.35	4.52	4.47	4.46	1.11
L16-ICP-MS	5.37	4.40	4.48	4.31	4.53	3.90	4.13	3.00	4.12	4.48	3.69	3.93	5.05	4.98	5.85	5.85	5.52	5.85	4.64	0.74
L18-ICP-MS	0.12	0.17	0.07	0.06	0.07	0.06	0.06	0.05	0.06	0.06	0.09	0.07	0.06	0.06	0.08	0.09	0.08	0.06	0.08	0.06

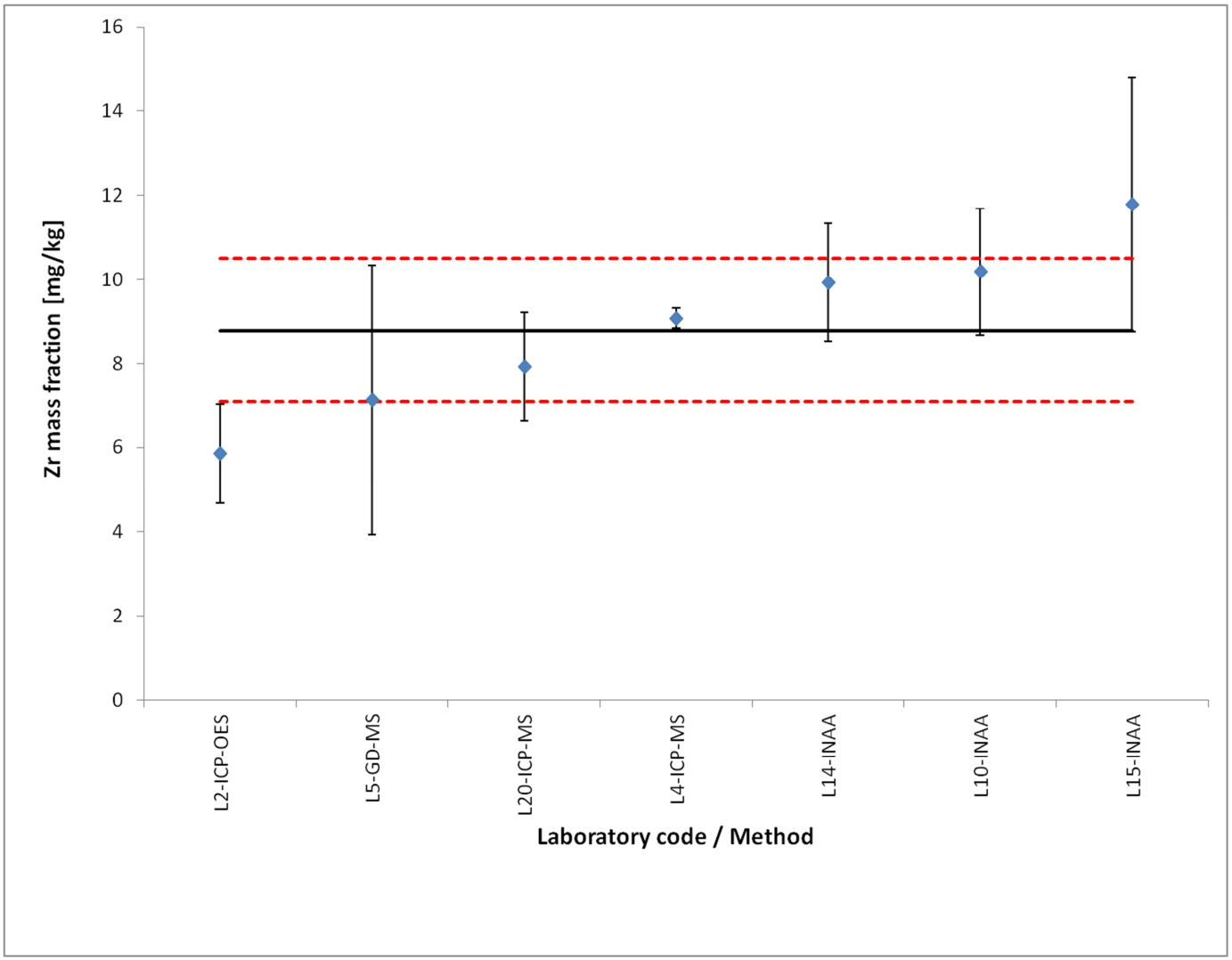


Figure E26. Mean Zr mass fraction in ERM-EB074 reported by particpating laboratories. Error bars represent expanded uncertainties. The solid line represents the indicative value (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the indicative value. Each laboratory is represented by its code.

Hg (Mercury)

Table E27. Individual results for Hg mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-CV-AAS	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
L8-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
L9-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
L10-INAA	< 0.07	< 0.08	< 0.07	< 0.08	< 0.09	< 0.08	< 0.08	< 0.08	< 0.07	< 0.08	< 0.08	< 0.08	< 0.08	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09
L11-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
L16-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
L18-ICP-MS	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04

W (Tungsten)

Table E28. Individual results for W mass fraction in ERM-EB074 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results. The expanded uncertainty budget equals to *k* factor (*k* = 2) multiplied by *u* provided by the laboratory or is estimated as two times the standard deviation of the measurements (if *u* is not provided).

Lab code - Method	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Rep 11	Rep 12	Rep 13	Rep 14	Rep 15	Rep 16	Rep 17	Rep 18	Mean	Uncertainty (k=2)
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
L1-ICP-MS	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	0.08	< 0.08	< 0.08	< 0.08		
L8-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
L4-ICP-MS	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05		0.03	0.03	0.02	0.02	0.014	0.015
L9-ICP-MS	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25		
L11-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
L16-ICP-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
L18-ICP-MS	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04		

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