



CERTIFICATION REPORT

**The certification of the gold mass fraction in
Al-0.1%Au alloy: ERM®-EB530A, B and C**

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The certification of the gold mass fraction in Al-0.1%Au alloy: ERM®-EB530A, B and C

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Summary

This report describes the production of ERM®-EB530A, B and C, aluminium gold alloy material certified for the mass fraction of gold. The material was produced following ISO Guide 34:2009 [1].

Pure aluminium and pure gold were arc melted together to obtain a master alloy Al-5%Au (mass percent). The master alloy was melted with pure aluminium in a resistance furnace, casted in ingot and heat treated. The ingot was processed mechanically (wire drawing or rolling) to obtain thin wire (diameter 0.5 mm and 1.0 mm) and thin foil (thickness 0.1 mm).

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with 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 estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4] and include uncertainties related to possible inhomogeneity, and instability and to characterisation.

The material is intended for the calibration of methods (k_0 -neutron activation analysis). As any reference material, it can also be used for control charts or validation studies. The CRM is packed in plastic boxes and available in three different versions:

ERM-EB530A: foil of 50 cm², thickness: 0.100 mm

ERM-EB530B: 1 meter of wire diameter 0.500 mm

ERM-EB530C: 1 meter of wire diameter 1.000 mm

The minimum amount of sample to be used is 0.55 mg.

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

The following value was assigned:

	Gold mass fraction	
	Certified value ¹⁾ [mg/kg]	Uncertainty ²⁾ [mg/kg]
Au	1005	7

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

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
CRM	Certified reference material
EC	European Commission
EN	European norm (standard)
ERM [®]	Trademark of European Reference Materials
GUM	Guide to the Expression of Uncertainty in Measurements [4]
IAEA	International Atomic Energy Agency
ICP	Inductively coupled plasma
(I)NAA	(Instrumental) neutron activation analysis
IRMM	Institute for Reference Materials and Measurements of the JRC
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0 -NAA	k_0 -Neutron activation analysis
MS_{between}	Mean of squares between-unit from an ANOVA
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
RM Unit	Reference Materials Unit of the IRMM
RSD	Relative standard deviation
r^2	Coefficient of determination of the linear regression
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
$t_{\alpha, \text{df}}$	Critical t -value for a t -test, with a level of confidence of $1-\alpha$ 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_{rec}	Standard uncertainty related to possible between-unit inhomogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate
\bar{x}	Arithmetic mean
\bar{x}_{ref}	Arithmetic mean of results of reference samples
α	significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s, \text{meas}}$	Degrees of freedom for the determination of the standard deviation s_{meas}
ν_{MSwithin}	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

Due to its selectivity, sensitivity and its ability to analyse solid samples without specific sample preparation, instrumental neutron activation analysis (INAA) occupies an important place among the various analytical methods for elements [5]. It is a powerful analytical technique without specific sample preparation for concentrations at or below the $\mu\text{g/g}$ range, while up to 60 elements can be determined performing two irradiations and several gamma-spectrum measurements after different decay periods [6].

Neutron activation analysis is applied in environmental sciences, nutritional studies, health related studies, geological and geochemical sciences, material sciences, archaeological studies, forensic studies and nuclear data measurements [5; 7]. In addition to these applications, INAA has an important role in the quality assurance of chemical analysis.

The analytical characteristics of neutron activation analysis are optimal for the analysis of three major categories of materials:

- Refractory materials (soils, rocks, minerals, ores, etc...);
- Solid materials that are easy to contaminate during analysis (Si semiconductor material, air particulate matter and biological tissues and fluids);
- Solid materials that are unique and should keep their integrity (materials from forensic studies and archaeological, cultural and art objects).

Moreover, its accuracy, the virtual absence of matrix effects, wide dynamic range and the completely different analytical principles when compared to other analytical techniques, makes it particularly suitable for the certification of candidate reference materials (RMs) [8].

INAA can be performed using 3 different methods: the relative method, the absolute method and the k_0 standardisation method. The relative method of INAA relies on standards for each element to be determined. It limits its application to the availability of reliable standards. The absolute method does not rely on standards but on theoretical calculations. It suffers from inaccuracies in published values of (n, γ) cross sections, gamma intensities and isotopic abundances. However, the k_0 standardisation method can be interpreted as an absolute standardisation with substitution of the absolute nuclear data for experimentally determined k_0 -factors, which leads to the elimination of systematic errors due to unreliability and uncertainty of nuclear data, on the condition that the experimental k_0 -factors are accurate [5]. Gold is a good "comparator" material for k_0 -standardisation of neutron activation analysis [9; 10]. Measurements of the activity of the targeted element are made relative to ^{198}Au . The mass fractions of the unknown element can be calculated using published $k_{0,\text{Au}}$ data, available for many radionuclides [11].

The IRMM-produced k_0 comparator, an Al-0.1%Au alloy named IRMM-530 [9], was replaced by IRMM-530R [12] after exhaustion. These reference materials were successfully used as k_0 -NAA calibrant material during the last 25 years. IRMM-530R is now close to exhaustion and needs to be replaced.

1.2 Choice of the material

Gold is an excellent comparator material for the k_0 -standardisation of INAA because of its well-defined nuclear properties. The most suitable form for a reference material is a dilute aluminium-gold alloy (Al-0.1 % Au, mass %), for which the self-shielding effect for neutrons is small.

Gold can be used for reactor neutron flux rate measurements primarily for neutrons in the thermal or intermediate energy regions [13; 14] making use of the reaction $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$. The activated gold decays to stable ^{198}Hg with emission of a 411.8 keV γ -ray and $T_{1/2} = 2.695$ days [11].

Gold is monoisotopic, with an appropriate half-life, is very well characterised with respect to its cross section [11; 15] and gamma intensity [16].

The cross section for gold is relatively large and significant neutron self-shielding can occur in the pure metal. An appropriate solution is to use a dilute Al-Au alloy [17].

It was decided to make ERM-EB530 available in three different formats identical to those offered for IRMM-530R:

- ERM-EB530A: thin foil
- ERM-EB530B: thin wire
- ERM-EB530C: wire

1.3 Design of the project

ERM-EB530A, B and C was characterised as one material for gold mass fraction using an inter-laboratory comparison approach.

Additional material information is given for molybdenum (potential spectral interference in gamma ray spectroscopy) and for the physical properties (thickness of foil and wire diameter).

The material is intended to replace IRMM-530R for the calibration of methods (k_0 -NAA).

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
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

Montanuniversität Leoben, Leoben, AT

Fransor Industrie, Colombes, FR

2.3 Homogeneity study

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)

2.4 Stability study

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)

2.5 Characterisation

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)

Activation Laboratories Ltd., Ancaster, CA

(measurements performed under the scope of ISO/IEC 17025 accreditation; SCC No. 266)

AngloAmerican Research, Johannesburg, ZA

Australian Nuclear Science and Technology Organisation, Lucas Heights, AU

Comisión Nacional de Energía Atómica (CNEA), Laboratorio de Análisis por Activación Neutrónica, Bariloche, AR

Constellium Centre de Recherches Voreppe, Voreppe, FR

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)

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Nuclear Physics Institute ASCR, Rez, CZ

Österreichisches Gießerei-Institut (ÖGI), Leoben, AT

Umicore Analytical Competence Center, Olen, BE

Umicore Analytical Competence Center, Hanau-Wolfgang, DE

Umicore PMR, Hoboken, BE

SLOWPOKE NAA Laboratory Ecole Polytechnique Montreal, Montreal, CA

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)

3 Material processing and process control

3.1 Origin/Purity of the starting material

The starting materials were Al metal with purity 99.999 % (AluSuisse Super Raffinal, CH) and gold foil 0.5 mm thick quality premion® (purity: 99.9985 %) from Alfa Aesar (Karlsruhe, DE).

3.2 Processing

The production of ERM-EB530A, B and C was divided into 3 steps:

- 1) Production of master alloy Al-5%Au (mass percent),
- 2) Production of one ingot Al-0.1%Au (mass percent),
- 3) Transformation of the ingot into foils and wires.

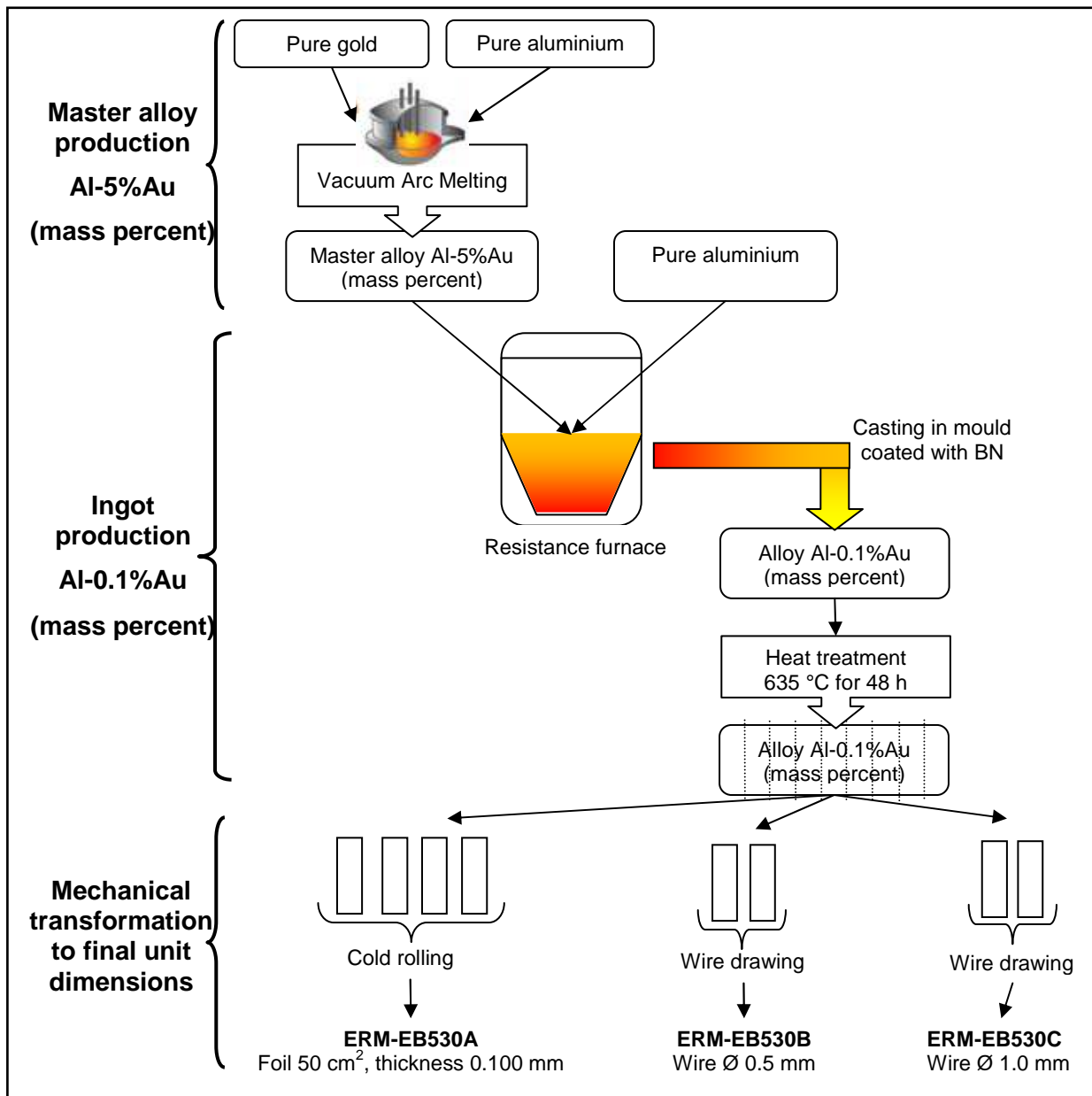


Figure 1. Scheme of the complete production of ERM-EB530A, B and C units.

The first and second steps of production were realised by the Montanuniversität Leoben (Leoben, AT). The third step was realised by Fransor Industrie (Colombes, FR).

Master alloy production

The master alloy with a composition Al-5%Au (mass percent) was prepared in an arc melting furnace using pure aluminium and pure gold as described in Section 3.1.

The master alloy was produced in a rod shape through several melting steps in order to enhance the homogeneity of gold in the aluminium matrix. To homogenise the gold mass fraction in the master alloy, each rod was re-melted from the top, turned by an internal gripper and melted from the bottom. The melting procedure was repeated four times for homogenization. Between each melting step, the rod was cut in the centre, and the outside ends put to face each other before re-melting.

After achieving a vacuum below 2×10^{-6} mbar, arc melting was performed under 800 mbar of argon (argon purity: 99.999 %).

Three Al-5%Au master alloys (mass percent) were produced to obtain the mass needed for the production of the alloy Al-0.1%Au (mass percent).

Al-0.1%Au (mass percent) production

For the production Al-0.1%Au (mass percent) alloy, pure aluminium (see Section 3.1) and Al-5%Au master alloy (mass percent) were melted under an argon atmosphere (argon purity 99.999%) in a resistance furnace.

The melting temperature was 750 °C. The melting time was 1 hour in the resistance furnace, after addition of the Al-5%Au master alloy into pure Al (see Section 3.1).

The melt was manually stirred every 15 minutes, four times in total during the hold-time.

A mould was coated with boron nitride to avoid Fe-pick up. The mould was preheated to 300 °C for casting.

After careful stirring and cleaning, the alloy was cast at 750 °C in the shape of an ingot.

To enhance gold homogeneity in the material and to produce a refined microstructure, the ingot was heated to 635 °C for 48 h, and quenched in cold water.

Wire and foil production

The production of the three ERM-EB530 formats was made by Fransor Industrie (Colombes, FR) from the Al-0.1%Au ingot produced by Montanuniversität Leoben (Leoben, AT).

The ingot was cut into nine sections (Figure 2). Each section was processed in the same way (orientation and direction of the work). Four sections were further processed by cold rolling to approximately 0.100 mm foil (Figure 2, blocks P1, P2, P6 and P7). Two sections were processed by swaging and then drawing through diamond dies to obtain approximately 0.500 mm diameter wire (Figure 2, blocks P3 and P4). Three sections were processed to approximately 1.000 mm diameter wire by swaging and then drawing through diamond dies (Figure 2, blocks P5, P8 and P9). Information was gathered throughout the whole process to establish an exact link between the final units and its original position in the ingots before processing. This information is essential to determine if segregation or inhomogeneity occur within the ingots.

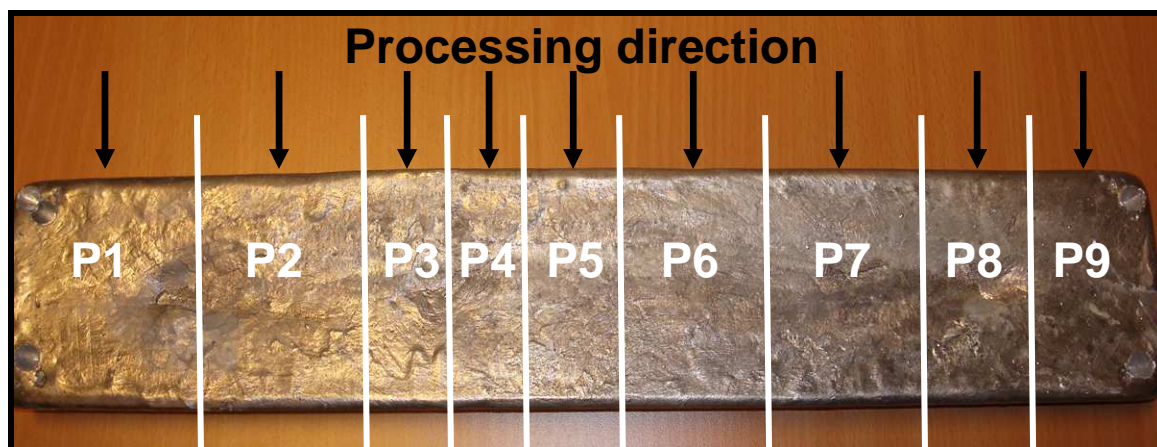


Figure 2. Organisation of the production of wire and foil from the ingot casted. The white lines delimitate the block sampled from the casted ingot. The references are given from P1 to P9. The black arrows represent the starting point of each production.

The final production was:

ERM-EB530A: 451 units. Each unit is a foil of 50 cm² with thickness of 0.100 mm foil;

ERM-EB530B: 510 units. Each unit is a wire of 1 meter with diameter of 0.500 mm;

ERM-EB530C: 221 units. Each unit is a wire of 1 meter with diameter of 1.00 mm.

The individual units of the CRM were packed in plastic boxes.

3.3 Process control

Control of the raw material was performed by ICP-OES and neutron activation analysis. After the different production steps, analysis of gold mass fraction was performed by ICP-OES. Impurities pick up (Fe, Cu and Mo) was checked by ICP-OES through the whole process. No contamination on Fe, Cu and Mo mass fraction was observed between the raw materials and the casted material. Final sample thickness (foil) and diameter were checked by FRANSOR Industrie (Colombes, FR) and by IRMM using a calibrated micrometer. The results are given in the additional information Section 7.2.

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. In contrast to that it is not relevant if this 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.

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 of the CRM are valid for all units of the material, within the stated uncertainty.

The number of selected units (30 units in total) is higher than the cubic root of the total number of the produced units (1182 units in total). Ten units of ERM-EB530A, 10 units of ERM-EB530B and 10 units of ERM-EB530C were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the material batches were divided into 10 groups (with a similar number of units) and one unit was selected randomly from each group. Four independent samples (sample intake of three mg) were taken from each selected unit, and analysed by ICP-OES.

The measurements were performed in a randomised block design because the number of replicates on all units (120 analyses) cannot be included in a single run due to instrumental constraints (drift towards the end of a long run). In that circumstance better precision (measured as the within-unit standard deviation) can be obtained using several short runs in a randomised block design than the one obtained in a single run with 120 analyses.

In a randomised block design for four replicates on each of 30 units of ERM-EB530, the simplest randomised block design involves four measurement runs and each unit is measured once in random order. Runs were randomised individually in a manner to be able to separate a potential analytical drift from a trend in the production sequence.

Two-way analysis of variance without replication was used to estimate the within- and between-unit standard deviations independently of the run effect.

The data evaluation was performed in the following order:

- 1) Regression analyses to evaluate potential trends in each analytical run. Some significant (95 % confidence level) trends in the analytical sequence were visible in run 1 and 3, pointing at a signal drift in the analytical system.

- 2) Correction of dataset for significant analytical trend (95% confidence level). The correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [18]. Correction of trends is 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 on at least a 95 % confidence level were corrected as shown below:

$$x_T(r, i) = x(r, i) - b(r) \cdot i \quad \text{Equation 1}$$

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 on the position i in the analytical run r

3) The analytical trend-corrected dataset was evaluated for significant difference between analytical runs (95 % confidence level) using one way ANOVA. A significant difference between analytical runs was observed on 95 % confidence level.

4) Normalisation of data showing significant difference between analytical run (95 % confidence level). As it is assumed that run effects and unit effects are independent, difference between analytical runs on at least a 95 % confidence level was corrected as shown below:

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

i	position of the result in the analytical run
r	number of the analytical run from 1 to 4
$\bar{x}_T(r)$	mean results of the analytical run r after correction for 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

5) The normalised dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. The trend-corrected dataset was used to evaluate significant trend in the production sequence using three approaches:

- One way ANOVA between the three sample types: ERM-EB530A, ERM-EB530B and ERM-EB530C to evaluate if the process of wire drawing and cold drawing caused a significant difference between the materials.
- Significant trend along the production block (Figure 2, blocks P1 to P9) to evaluate if there is a trend over the length of the ingots.
- Significant trend along the production (at 95 % confidence level). The units were organised in function of the mass of material processed and in function of the block position in the original ingots. This design takes into account the units discarded during production for non-compliance to technical specifications (thickness, damaged or scratched units). The results are plotted in Annex A.

No significant difference (95 % confidence level) was observed between ERM-EB530A, ERM-EB530B and ERM-EB530C. The three materials are considered homogeneous and equivalent among each other.

No trends in the production sequence were detected at the 95 % confidence level. The gold mass fraction is homogeneously distributed in the materials.

No outlying individual results and no outlying means were detected at the 99 % confidence level.

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 which follow at least a uni-modal distribution and results for each unit that follow uni-modal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Minor deviations from uni-modality 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.* [19]. 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 analysis of variance table also includes associated degrees of freedom for each term. 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 exactly as in equation 4. The results of two way ANOVA are given in Table 1.

Table 1. Two way ANOVA results. The two way ANOVA was performed on the results corrected only for analytical trends.

	Degrees of freedom	Mean square [(mg/kg) ²]	Standard deviation [mg/ kg]
Between run variation	3	$MS_R = 1120$	5.54
Between unit variation	29	$MS_{Between} = 235$	2.95
Within unit variation	87	$MS_{within} = 200$	14.14

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u_{bb,rel}^*$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \quad \text{Equation 3}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \quad \text{Equation 4}$$

$$u_{bb,rel}^* = \frac{\sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{v_{MS_{within}}}}}{\bar{y}} \quad \text{Equation 5}$$

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
$\nu_{MS_{within}}$	degrees of freedom of MS_{within}

The results of the evaluation of the between-unit variation are summarised in Table 2. The resulting values from the above equations were converted into relative uncertainties.

Table 2: Results of the homogeneity study

ERM-EB530A, B and C	$S_{wb,rel}$ [%]	$S_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$U_{bb,rel}$ [%]
Au	1.444	0.302	0.281	0.302

The homogeneity study showed no outlying unit means or trends in the production sequence. 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 uncertainty contribution to account for potential inhomogeneity.

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 for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

To estimate the minimum sample intake, a series of measurements with decreasing amounts of sample for one randomly selected unit of ERM-EB530B were performed. The following sample intakes were tested: 3.1 mg, 1.1 mg and 0.55 mg. For sample intakes 3.1 mg, 1.1 mg and 0.55 mg, 20 samples, 20 samples and 19 samples, respectively, were measured by ICP-OES under intermediate precision conditions, and in a randomised manner. The measurements were split into two analytical runs performed on the same day. The measurement method was robust over the whole range of the sample intake tested and its repeatability was in the same range or better than the repeatability achieved during the material characterisation (Section 6) and the material homogeneity (Section 4).

The obtained data sets of all sample intakes taken together were first tested for normal or unimodal distribution. In the absence of at least a uni-modal distribution, the calculation of standard deviations is doubtful or impossible. The test was done by visual inspection of normal probability plots and histograms. All results were normally and uni-modally distributed, therefore no correction for significant difference between the two analytical runs was necessary.

Furthermore, the results (all sample intakes taken together) were scrutinised for outliers using the single Grubbs-test. No outliers were observed at the 95 % and 99 % confidence levels.

The minimum sample intake was established by comparison of variances obtained for 0.55 mg and 1.1 mg sample intakes with the variance obtained from the 3.1 mg sample intake. The 3.1 mg sample intake also corresponds to the sample intake used in the homogeneity study. The minimum sample intake was established using the F-test for equality of two samples for variances with 19 degrees of freedom for the 3.1 mg and 1.1 mg sample intakes,

and 19 and 18 degrees of freedom for the 3.1 mg and 0.55 mg sample intakes, respectively. All results are reported at the 95 % confidence level.

The variances were not significantly different at the 95 % confidence level between the 0.55 mg and 3.1 mg sample intakes. Between the 3.1 mg and 1.1 mg sample intakes, the variances were significantly different at the 95% confidence level. No difference was observed at the 99 % confidence level, and the smallest variance was obtained for the 1.1 mg sample intake. The within-unit variation did not increase while lowering the sample intake, and in the case of 3.1 mg and 1.1 mg intakes the within-unit variation was significantly lower for 1.1 mg intake.

The results are presented in Annex B and the minimum sample intakes are summarised in Table 3.

Table 3: Results of the minimum sample intake determination

	Sample intake [mg]	Au Mean value [mg/kg]	Au Variance [mg/kg] ²
ERM-EB530	3.1	990.8	432
ERM-EB530	1.1	999.9	198
ERM-EB530	0.55	991.8	683

As shown above, the demonstrated minimum sample intake representative for gold mass fraction in ERM-EB530 is 0.55 mg.

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 summer time, temperatures up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature will be applied.

Aluminium alloy is stable at temperatures below 200 °C. During the production, the material was heat treated at 635 °C for 48 hours in order to improve the chemical homogeneity. The aluminium alloy has good resistance to oxidation or other chemical degradation under normal storage and handling conditions and is highly stable. The gold mass fraction in ERM-EB530A, B and C is therefore considered stable under normal dispatch conditions (up to 60 °C).

As part of the ERM-EB530 characterisation study, five laboratories (L0, L2, L7, L12 and L14) measured the gold mass fraction in IRMM-530 after 21 years of storage. Each laboratory performed 2 independent analyses and their results agreed with the certified value according to ERM application note 1 [21]. Results are reported in Annex C1. The mean of the laboratories mean equals 999 ± 9 mg/kg ($k=2$; uncertainty calculated as 2 times the standard deviation of the mean). The results confirm that the gold mass fraction in IRMM-530 was stable for 21 years.

In the same study, 11 laboratories (L1, L3, L4, L5, L6, L8, L9, L10, L11, L13 and L15) measured gold mass fraction in IRMM-530R after 13 years of storage. Three laboratories (L9, L10 and L11) were excluded of the stability confirmation study for IRMM-530R as they used IRMM-530R as calibrant. For the stability confirmation study, the results of L1, L3, L4, L5, L6, L8, L13 and L15 were taken into consideration. Each laboratory performed two independent analyses and the results of each laboratory agreed with the certified value according to ERM application note 1 [21]. Results are reported in Annex C2. The mean of the laboratories' means equals 1000.4 ± 5.3 mg/kg ($k=2$; uncertainty calculated as two times the standard deviation of the mean). It confirms that gold mass fraction in IRMM-530R was stable for 13 years.

IRMM-530 and IRMM-530R are made from alloy with the same composition as ERM-EB530A, B and C. Data obtained on IRMM-530R and IRMM-530 show that the gold mass fraction in an Al-0.1%Au alloy is stable and the uncertainty due to instability (short term and long term) is considered negligible for a minimum shelf life of 10 years.

Summary of stability:

The material can be transported at ambient conditions without special precautions and stored at a temperature not exceeding 18 ± 5 °C. Uncertainty due to storage conditions and due to shipment conditions were considered negligible regarding the material property and the results reported on IRMM-530R and IRMM-530 following long-term storage.

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 value of a reference material.

The material characterisation was based on an intercomparison of expert laboratories. The gold mass fraction of the material was 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, which reduces the combined uncertainty.

6.1 Selection of participants

Sixteen 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 gold analysis or trace elements analysis in aluminium metal. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 2).

6.2 Study setup

Each laboratory received two units each of ERM-EB530A, ERM-EB530B and ERM-EB530C. It was requested to provide between six to 18 independent results, one to three independent results per unit. The acceptance of six and 10 independent results by labs L14 and L3, respectively was due to the higher sample intake required by their methods of analysis. 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 IRMM-530R or IRMM-530 as a blinded quality control (QC) sample. The results for this sample 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 unit results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 Methods used

A variety of acid digestion using different acid mixture (hydrochloric acid, nitric acid or hydrofluoric acid), gold extraction (lead collection with Ag co-collection) methods with different quantification steps (ICP-OES, weighing) as well as methods without sample preparation (NAA) were used to characterise the material. The combination of results from methods based on completely different principles mitigates undetected method bias.

All methods used during the characterisation study are summarised in Annex D. The laboratory code (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 2. The lab-method code consists of a number assigned to each laboratory (e.g. L1) and abbreviation of the measurement method used, (NAA, ICP-OES).

6.4 Evaluation of results

The characterisation campaign resulted in 17 datasets. All individual results of the participants are displayed in tabular and graphical form in Annex E. The homogeneity study shows no significant difference (95% confidence level) between the different formats ERM-EB530A, ERM-EB530B and ERM-EB530C. So the results of ERM-EB530A, ERM-EB530B and ERM-EB530C were pooled together for each laboratory.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for 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 measurement occasions, and the analytical sequence.
- method performance: agreement of the measurement results with the assigned value of the QC sample (IRMM-530 or IRMM-530R) according to ERM application note 1 [20].

Based on the above criteria, L16 dataset was rejected as not technically valid. It was excluded due to failure to measure the QC sample correctly. The dataset of L16 was therefore not included for the characterisation of the gold mass fraction in ERM-EB530A, B and C.

6.4.2 Statistical evaluation

The homogeneity study had demonstrated the equivalence of ERM-EB530A, B and C. Therefore, all values obtained on all three materials were pooled per laboratory and evaluated together. The datasets accepted based on technical reasons were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots. In addition, they were tested for outlying means using the Grubbs test and using 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 4.

Table 4: Statistical evaluation of the technically accepted datasets for gold mass fraction in ERM-EB530A, B and C. p : number of technically valid datasets

ERM-EB530A, B and C	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [mg/kg]	s [mg/kg]	s_{between} [mg/kg]	s_{within} [mg/kg]
Au	16	None	Yes, L15	Unimodal	1005.39	5.74	5.11	11.73

The laboratory means follow normal distributions. None of the data contains outlying means. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value.

The statistical evaluation flags laboratory L15 as outlying variance for gold mass fraction in ERM-EB530A, B and C. This merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained.

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table 5).

Table 5: Uncertainty of characterisation for the gold mass fraction in ERM-EB530A, B and C

	ρ	Mean [mg/kg]	s [mg/kg]	U_{char} [mg/kg]
Au mass fraction in ERM-EB530A, B and C	16	1005.39	5.74	1.43

6.5 Material composition information

During the processing of the material and the intercomparison of expert laboratories, information was gathered about the composition of ERM-EB530A, B and C.

The following information was obtained by two laboratories using INAA and ICP-OES. It corresponds to less than three independent analyses. It should be regarded as informative only on the general composition of the material.

Table 6: Material composition information

Elements	Range	Unit	Analytical method
Ag	1 - 3	mg/kg	INAA
Ce	0.37 - 0.47	mg/kg	INAA
Co	< 0.07	mg/kg	INAA
Cr	0.3 - 0.6	mg/kg	INAA
Cs	< 0.01	mg/kg	INAA
Cu	2 - 4	mg/kg	ICP-OES
Eu	< 0.002	mg/kg	INAA
Fe	4 - 6	mg/kg	ICP-OES
Hf	< 0.02	mg/kg	INAA
Hg	0.3 - 0.8	mg/kg	INAA
Nd	< 0.5	mg/kg	INAA
Rb	< 0.5	mg/kg	INAA
Sb	0.1 - 0.14	mg/kg	INAA
Sc	0.12 - 0.14	mg/kg	INAA
Se	< 0.05	mg/kg	INAA
Sr	< 4	mg/kg	INAA
Ta	0.002 - 0.02	mg/kg	INAA
Tb	0.002 - 0.005	mg/kg	INAA
Th	0.05 - 0.07	mg/kg	INAA
Zn	0.4 - 0.9	mg/kg	INAA
Zr	< 7	mg/kg	INAA

7 Value Assignment

One certified value was assigned.

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

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, would fall under this category.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 4 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during transport (u_{sts}) and long-term storage, u_{its} (Section 5). The uncertainties related to degradation during transport and long-term storage were found to be negligible as described in Section 4. These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{\text{CRM,rel}}$) with a coverage factor k as:

$$U_{\text{CRM,rel}} = k \cdot \sqrt{u_{\text{char,rel}}^2 + u_{\text{bb,rel}}^2} \quad \text{Equation 6}$$

- u_{char} was estimated as described in Section 6,
- u_{bb} 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 6.

Table 7: Certified value and its uncertainty for ERM-ERB530A, B and C

	Certified value [mg/kg]	$u_{\text{char,rel}}$ [%]	$u_{\text{bb,rel}}$ [%]	$U_{\text{CRM,rel}}$ [%]	U_{CRM} [mg/kg] ¹⁾
Au mass fraction in ERM-EB530A, B and C	1005	0.143	0.302	0.668	7

¹⁾ Expanded ($k = 2$) and rounded uncertainty.

7.2 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.

Material dimension compliance (wire diameter and foil thickness)

During the processing, the diameter of the wire material (ERM-EB530B and ERM-EB530C) and the thickness of the foil (ERM-EB530A) were checked to determine their compliance with

the nominal gauges and tolerances. The units tested were randomly selected. IRMM measured thickness or diameter in 5 different locations on 5 units.

For ERM-EB530A: the foil nominal thickness is (0.100 ± 0.005) mm. The producer measured a thickness of (0.101 ± 0.003) mm (standard deviation of 16 measurements). IRMM measured a thickness of (0.101 ± 0.003) mm (standard deviation of 25 measurements).

ERM-EB530B: the wire nominal thickness is (0.500 ± 0.025) mm. The producer measured a diameter of (0.499 ± 0.002) mm (standard deviation of 8 measurements). IRMM measured a diameter of (0.502 ± 0.002) mm (standard deviation of 25 measurements).

ERM-EB530C: the wire nominal thickness is (1.00 ± 0.05) mm. The producer measured a diameter of (0.995 ± 0.005) mm (standard deviation of 12 measurements). IRMM measured a diameter of (1.000 ± 0.004) mm (standard deviation of 25 measurements).

The units tested by IRMM and FRANSOR comply with the nominal values for thickness and diameter according to the tolerances.

Molybdenum mass fraction

Three laboratories of the characterisation study (L0, L2 and L13) measured Molybdenum mass fraction by ICP-OES in 2 units of ERM-EB530A, 2 units of ERM-EB530B and 2 units of ERM-EB530C.

L0 reported a Mo mass fraction below 0.7 mg/kg for all units; L2 reported Mo mass fraction below 1 mg/kg for all units and L13 reported Mo mass fraction below 2 mg/kg.

As additional information, the Molybdenum mass fraction is below 2 mg/kg in ERM-EB530A, B and C.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

Gold is a chemically clearly defined analyte. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The identity of 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 of 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 it is 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.

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 fully 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 [21] 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.

The CRM is prepared from pure aluminium and pure gold and the analytical behaviour will be the same as for previous Al-0.1%Au calibrants (IRMM-530R and IRMM530). For other types of samples the commutability has to be assessed.

9 Consistency of k_0 -NAA comparators

For any new calibrant or k_0 -NAA comparator, it is extremely important to evaluate its performance as calibrant before releasing it on the market. A dedicated study was done to compare k_0 -NAA results on different certified reference materials using ERM-EB530 and the existing gold k_0 -comparators: IRMM-530 [11] and IRMM-530R [12]. The first objective of the study is to demonstrate that the comparator is giving results in agreement with the certified values of different CRMs. Secondly, it will inform about the significance of bias between the results obtained by the different gold k_0 comparators.

The selected reference materials covered a wide range of matrixes (fly ash, food and sediments) and elements commonly analysed by k_0 -NAA. Three certified reference materials for trace elements in mussel tissue (ERM-CE278k [22]), fly ash (BCR-176R [23]) and sediments (BCR-320R [24]) and one reference material for trace elements in Bakelite (SMELS [25]) were selected to be analysed by k_0 -NAA using IRMM-530, IRMM-530R and ERM-530 as k_0 -comparators. Three independent replicates from 1 unit were analysed for each material. To avoid bias due to different subsamples or neutron flux fluctuation, the analyses were performed at the same time with the same subsamples for all comparators.

The results are presented in Annex F in tabular version with expanded uncertainty ($k=2$) reported by the INAA laboratory and in graphical version after normalisation to the certified value for presentation purposes.

The data evaluation was focused on two questions:

- Agreement of the results of k_0 -NAA with the certified values. It was done by comparing the average of the three replicates with the certified values for each elements and matrices. To determine if a difference is significant (95% confidence level), the difference between the certified and the measured mean value (Δ_{meas}) was compared to the combination of the two uncertainties (u_{meas} and u_{CRM}) expanded by a coverage factor of 2 (U_Δ). Measurement was considered unbiased at 95% confidence level if $\Delta_{meas} \leq U_\Delta$. Results are reported in Annex F (Tables F1 – F4)

All results using k_0 comparators IRMM-530, IRMM-530R and ERM-EB530 were compliant with the certified value at 95% confidence level for all elements.

- Agreement of the results obtained using different k_0 gold comparators (IRMM-530, IRMM-530R and ERM-EB530). For each matrix, a paired comparison was performed between the results obtained between IRMM-530 and ERM-EB530 and between IRMM-530R and ERM-EB530. The difference between ERM-EB530 and IRMM-530 or IRMM-530R was calculated according to the equation 7 or 8.

$$d_{\Delta 1;y} = \frac{X_{ERM-EB530;y} - X_{IRMM-530;y}}{X_{ERM-EB530;y} + X_{IRMM-530;y}} \quad \text{or} \quad d_{\Delta 2;y} = \frac{X_{ERM-EB530;y} - X_{IRMM-530R;y}}{X_{ERM-EB530;y} + X_{IRMM-530R;y}} \quad \text{Equations 7 and 8}$$

$d_{\Delta 1;y}$ relative difference between results on element y obtained using k_0 comparators ERM-EB530 and IRMM-530

$d_{\Delta 2;y}$ relative difference between results on element y obtained using k_0 comparators ERM-EB530 and IRMM-530R

y chemical elements

$X_{ERM-EB530;y}$ mean results obtained for elements y using the k_0 comparator ERM-EB530

$X_{IRMM-530;y}$ mean results obtained for elements y using the k_0 comparator IRMM-530

$x_{IRMM-530R;y}$ mean results obtained for elements y using the k_0 comparator IRMM-530R

To determine if the difference between k_0 comparators results is significant, the t-value was calculated using equation 9 or 10.

$$t_{\Delta 1} = \frac{\bar{d}_{\Delta 1}}{s_{\Delta 1} / \sqrt{n}} \quad \text{or} \quad t_{\Delta 2} = \frac{\bar{d}_{\Delta 2}}{s_{\Delta 2} / \sqrt{n}} \quad \text{Equations 9 and 10}$$

$t_{\Delta 1}$ calculated t – value for the relative difference between IRMM-530 and ERM-EB530

$t_{\Delta 2}$ calculated t – value for the relative difference between IRMM-530R and ERM-EB530

$\bar{d}_{\Delta 1}$ and $\bar{d}_{\Delta 2}$ mean value of $d_{\Delta 1;y}$ and $d_{\Delta 2;y}$ respectively

$s_{\Delta 1}$ and $s_{\Delta 2}$ standard deviation of $d_{\Delta 1;y}$ and $d_{\Delta 2;y}$ respectively

n number of analysis

The t-value calculated was compared to the critical t-value from student's table with confidence level of 95%. Results are reported for each matrix in Tables 8 – 11.

Table 8: Comparison of results obtained using ERM-EB530 as k_0 comparators with the two existing gold k_0 comparators IRMM-530 and IRMM-530R in fly ash certified reference material (BCR-176R).

	ERM-EB530 vs IRMM-530	ERM-EB530 vs IRMM-530R
Matrix	Fly ash (BCR-176R)	Fly ash (BCR-176R)
Mean of relative difference [%]	0.75	0.07
Standard deviation of the relative differences [%]	1.60	0.25
Significant difference (95% confidence level)	No	No

Table 9: Comparison of results obtained using ERM-EB530 as k_0 comparators with the two existing gold k_0 comparators IRMM-530 and IRMM-530R in mussel tissue certified reference material (ERM-CE278k).

	ERM-EB530 vs IRMM-530	ERM-EB530 vs IRMM-530R
Matrix	Mussel tissue (ERM-CE278k)	Mussel tissue (ERM-CE278k)
Mean of relative difference [%]	-0.55	-0.76
Standard deviation of the relative differences [%]	0.40	0.39
Significant difference (95% confidence level)	Yes	Yes

Table 10: Comparison of results obtained using ERM-EB530 as k_0 comparators with the two existing gold k_0 comparators IRMM-530 and IRMM-530R in sediment certified reference material (BCR-320).

	ERM-EB530 vs IRMM-530	ERM-EB530 vs IRMM-530R
Matrix	Sediment (BCR-320)	Sediment (BCR-320)
Mean of relative difference [%]	0.45	-1.16
Standard deviation of the relative differences [%]	3.20	0.95
Significant difference (95% confidence level)	No	Yes

Table 11: Comparison of results obtained using ERM-EB530 as k_0 comparators with the two existing gold k_0 comparators IRMM-530 and IRMM-530R in bakelite reference material (SMELS).

	ERM-EB530 vs IRMM-530	ERM-EB530 vs IRMM-530R
Matrix	bakelite (SMELS)	bakelite (SMELS)
Mean of relative difference [%]	0.06	0.42
Standard deviation of the relative differences [%]	0.77	0.79
Significant difference (95% confidence level)	No	No

No significant difference at 95% confidence level was observed between the results obtained in fly ash, sediment and bakelite matrix using k_0 comparator IRMM-530 and k_0 comparator ERM-EB530 (Table 8, 10-11). For mussel tissue matrix, significant difference (95% confidence level) was observed between the results obtained using k_0 comparators IRMM-530 and ERM-EB530 (Table 9). In mussel tissue, the results are approximately 0.5% higher for ERM-EB530 compare to results obtained using IRMM-530.

No significant difference at 95% confidence level was observed between the results obtained in fly ash and bakelite matrix using k_0 comparator IRMM-530R and k_0 comparator ERM-EB530 (Table 8, 11). In mussel tissue and sediment matrix, significant differences at 95% confidence level were observed between results obtained using k_0 comparator IRMM-530R and k_0 comparator ERM-EB530. The results are approximately 0.8% lower in mussel tissue and 1.2% lower in sediment compare to IRMM-530R.

The bias between the existing k_0 comparators and ERM-EB530 is extremely low. When the bias is statically significant, it represents maximum 1.2% and is covered by the expanded uncertainty of IRMM-530 or IRMM-530R.

This study shows that INAA analysis using k_0 comparator ERM-EB530 give accurate and reliable results in different matrixes (food, environment and engineering product). It demonstrates too that no major bias should be observed between the results obtained using the existing k_0 gold comparators (IRMM-530 or IRMM-530R) and the new k_0 comparator ERM-EB530.

10 Instructions for use

10.1 Safety information

The usual laboratory safety measures apply.

10.2 Storage conditions

The materials shall be stored at $18\text{ °C} \pm 5\text{ °C}$ 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.

10.3 Preparation and use of the material

The units shall be cleaned prior to analysis (ethanol, rinsed in water and dried prior to analysis). Surface contamination should be avoided, particularly gold or easily activated heavy metals from cutting tools.

Users should take into consideration the effects of epithermal self-shielding due to the amount of Au in the material.

10.4 Minimum sample intake

The minimum sample intake representative for gold mass fraction is 0.55 mg.

10.5 Use of the certified value

The main purpose of these materials is for the calibration of methods (k_0 -neutron activation analysis) and to assess method performance. As any reference material, ERM-EB530A, B and C can also be used for control charts or validation studies.

Use as a calibrant

If used as calibrant or “comparator” for k_0 -NAA, the uncertainty of the certified value shall 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 [21]).

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}): $u_{\Delta} = \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2}$
- 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 $\Delta_{\text{meas}} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use in 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.

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Annexes

Annex A: Results of the homogeneity measurements

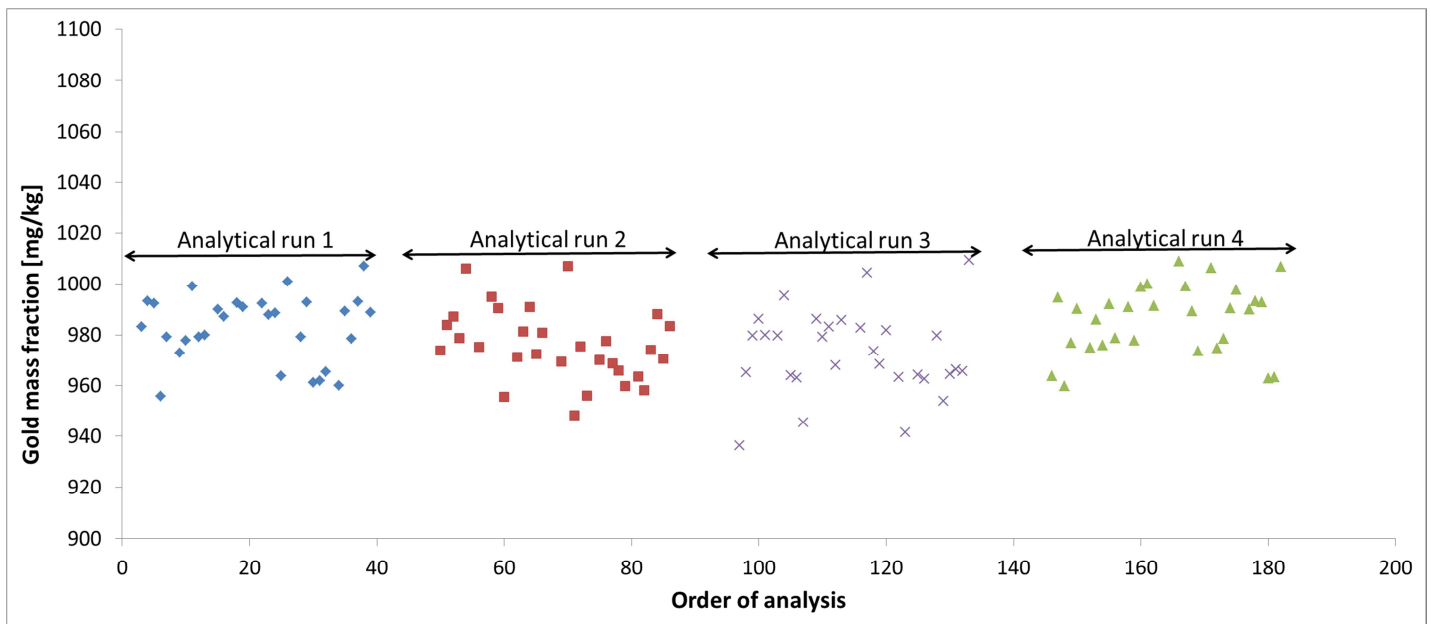


Figure A1. Gold mass fraction in ERM-EB530A, B and C homogeneity study replicates are plotted in function of the analytical run. The order of analysis is correct in each analytical run (30 independent analyses per analytical run). The complete order of analysis (0 to 180) is used to separate graphically the analytical runs.

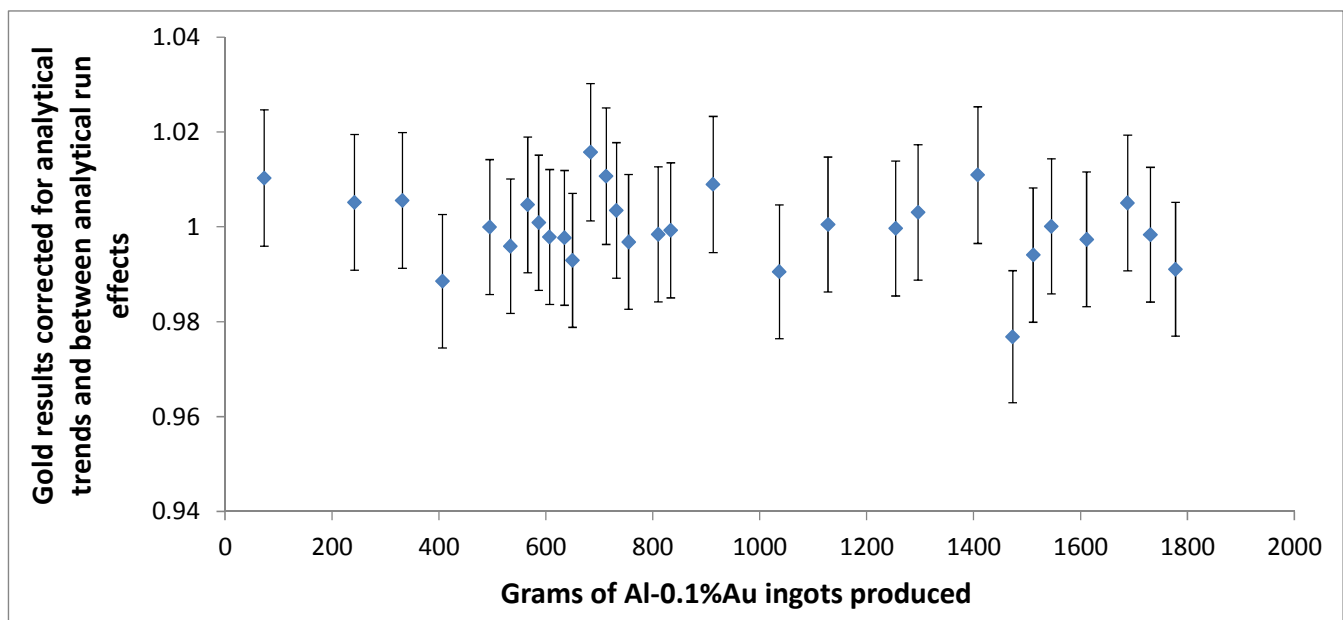


Figure A2. Mean of normalised gold results per ERM-EB530A, B and C unit in function of the unit position in the original Al-0.1%Au ingot (position determined using unit mass and production order). The mean gold results are calculated using the dataset corrected for analytical trend and for analytical runs effects. The unit means are plotted with the confidence interval of the means (s_{wb} from ANOVA for all units).

Table A1. Gold mass fraction results for ERM-EB530A, B and C as a function of the analytical run (series 1 – 4). The unit number is given with the corresponding position in the production. The position is given in grams to take into account the sample mass and the rejected units for non-compliance with production specifications.

CRM	Unit number	Mass of Al-0.1%Au ingots produced [grams]	Series 1 Au mass fraction [mg/kg]	Series 2 Au mass fraction [mg/kg]	Series 3 Au mass fraction [mg/kg]	Series 4 Au mass fraction [mg/kg]
ERM-EB530	A015	73	961.87	994.81	991.26	1009.47
ERM-EB530	A86	242	990.06	955.51	1009.00	983.22
ERM-EB530	A124	332	989.30	974.16	989.85	985.83
ERM-EB530	A154	407	979.12	955.98	973.53	963.89
ERM-EB530	A175	495	972.96	972.31	1006.83	965.26
ERM-EB530	A253	534	983.10	965.83	998.88	953.98
ERM-EB530	A310	566	992.66	983.46	993.17	966.39
ERM-EB530	A363	587	979.22	983.81	977.82	979.84
ERM-EB530	A389	607	1001.03	980.87	962.92	964.17
ERM-EB530	A434	635	991.01	970.64	978.67	968.04
ERM-EB530	B036	650	961.13	970.12	978.54	979.77
ERM-EB530	B109	684	992.20	1006.97	1006.40	973.50
ERM-EB530	B170	713	993.08	990.53	992.78	982.81
ERM-EB530	B209	732	987.19	987.24	976.79	979.66
ERM-EB530	B247	755	992.37	988.16	959.85	964.52
ERM-EB530	B300	810	965.38	969.31	990.34	986.12
ERM-EB530	B328	834	979.99	973.86	997.59	963.30
ERM-EB530	B392	913	993.24	977.48	999.96	981.88
ERM-EB530	B447	1037	977.84	948.23	974.87	979.30
ERM-EB530	B483	1128	988.56	990.94	994.65	945.38
ERM-EB530	C4	1254	978.47	975.51	999.16	963.07
ERM-EB530	C30	1296	999.08	958.09	986.07	986.15
ERM-EB530	C41	1408	1007.08	981.41	991.96	979.74
ERM-EB530	C68	1473	955.90	971.32	963.22	936.28
ERM-EB530	C86	1512	987.90	959.84	975.94	968.34
ERM-EB530	C102	1546	992.64	968.73	990.86	965.65
ERM-EB530	C133	1612	979.18	975.22	990.15	962.63
ERM-EB530	C169	1688	988.88	963.45	989.30	995.43
ERM-EB530	C189	1731	963.72	978.83	963.63	1004.36
ERM-EB530	C211	1778	960.00	1006.01	974.73	941.57

Table A2. Summary of the method used for the homogeneity study

Parameter	Sample mass (mg)	Sample preparation	Calibration	Instrumentation and measurement method
Au	3	Dissolution in aqua regia (HNO ₃ and HCl)	6-points external calibration with Certipur Gold ICP Standard (Merck)	ICP-OES IRIS Intrepid II XDL (ThermoFischer Scientific)

Annex B: Results of the minimum sample intake measurements

Table B1. Individual results for Au mass fraction in ERM-EB530B unit. Results are reported in function of the sample intake (mean sample intake) and rounded to 1 digit.

ERM-EB530B unit 209	Gold mass fraction for sample intake of 3.1 mg [mg/kg]	Gold mass fraction for sample intake of 1.1 mg [mg/kg]	Gold mass fraction for sample intake of 0.55 mg [mg/kg]
Replicate 1	1008.0	998.4	1019.9
Replicate 2	1003.8	996.7	973.7
Replicate 3	993.1	1025.0	989.4
Replicate 4	982.3	1018.6	985.3
Replicate 5	986.2	1004.6	998.6
Replicate 6	1023.9	985.2	972.2
Replicate 7	972.2	998.4	1011.2
Replicate 8	1009.0	995.4	1036.5
Replicate 9	998.0	989.1	936.5
Replicate 10	982.9	989.7	1020.5
Replicate 11	966.5	992.3	994.6
Replicate 12	992.4	998.5	1005.1
Replicate 13	958.6	990.6	n.d.
Replicate 14	994.9	1030.5	955.3
Replicate 15	978.6	1022.9	1014.1
Replicate 16	1012.6	984.6	963.3
Replicate 17	965.0	1000.0	966.8
Replicate 18	1013.1	1005.8	983.7
Replicate 19	953.3	982.5	996.4
Replicate 20	1020.9	990.2	1021.8

n.d.: not determined due to technical problems

Annex C: Results of the long-term stability study

Table C1. Individual results for Au mass fraction in IRMM-530 for laboratories L0, L2, L7, L12 and L14 (after 21 years of storage). Results are reported in mg/kg, together with the mean value and the expanded uncertainty budget. Expanded uncertainty is calculated as 2 times the standard deviation of the measurements. The results are rounded to 1 digit after the coma.

Lab code / Technique	Replicate 1 [mg/kg]	Replicate 2 [mg/kg]	Replicate 3 [mg/kg]	Replicate 4 [mg/kg]	Lab mean value [mg/kg]	Uncertainty (k=2) [mg/kg]
L0-ICP-OES	998.1	1002.7			1000.4	4.6
L2-ICP-OES	1004.6	999.3			1001.9	5.3
L7-INAA	1000.0	1025.0			1012.5	25.0
L12-Fire assay	984.0	991.0			987.5	7.0
L-14-Fire assay	992.0	990.0	989.0	990.0	990.3	2.5

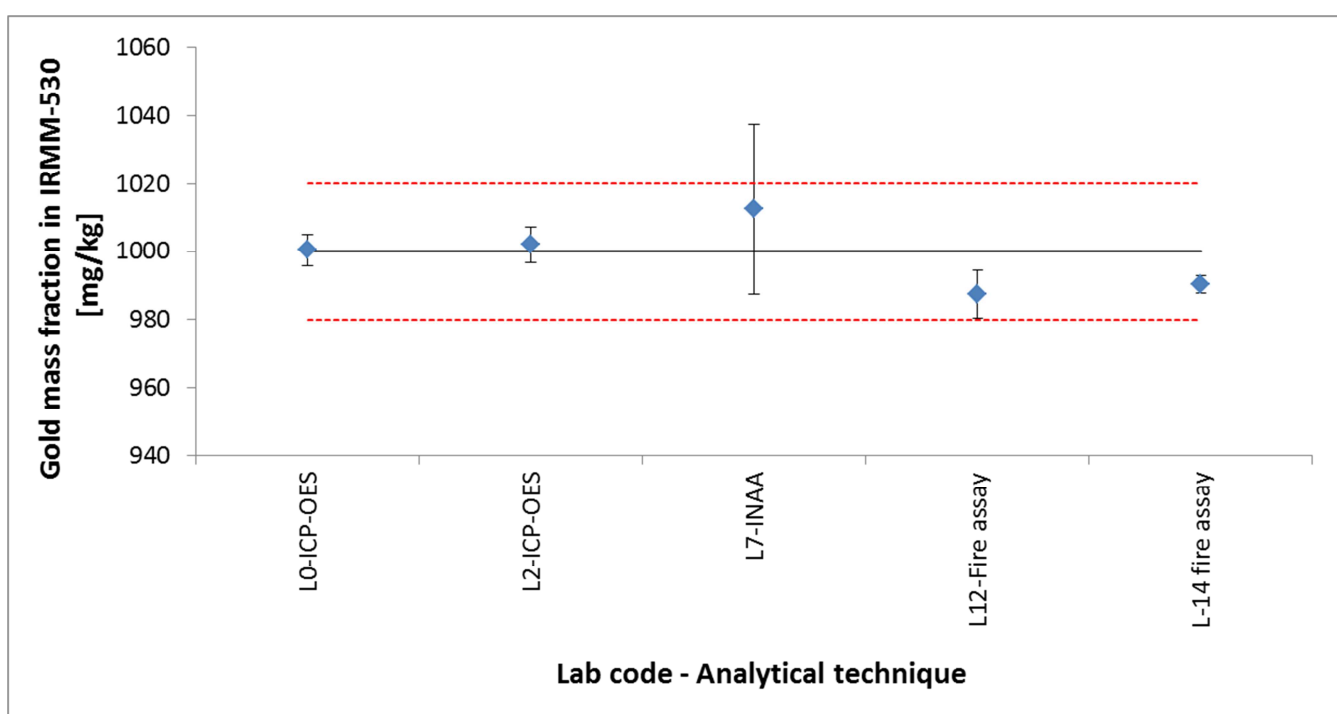


Figure C1. Results for Au mass fraction in IRMM-530 are presented as mean value (♦), with expanded uncertainty budget (□); certified value (—) and expanded uncertainty of the certified value (---).

Table C2. Individual results for Au mass fraction in IRMM-530R for laboratories L1, L3, L4, L5, L6, L8, L9, L10, L11, L13 and L15 (after 13 years of storage). Results are reported in mg/kg, together with the mean value and the expanded uncertainty budget. Expanded uncertainty is calculated as 2 times the standard deviation of the measurements. The results are rounded to 1 digit after the coma.

Lab code / Technique	Replicate 1 [mg/kg]	Replicate 2 [mg/kg]	Replicate 3 [mg/kg]	Lab mean value [mg/kg]	Uncertainty (k=2) [mg/kg]
L1-INAA	1001.0	1006.0		1003.5	6.0
L3-ICP-OES	986.2	994.3	1015.6	998.7	24.8
L4-ICP-OES	999.0	1004.0		1001.5	5.0
L5-ICP-OES	979.0	994.0		986.5	15.0
L6-INAA	997.0	991.0		994.0	6.0
L8-INAA	1005.0	999.7		1002.4	5.3
L13-ICP-OES	1014.0	999.0		1006.5	15.0
L15-INAA	1000	1021		1010.5	21.0

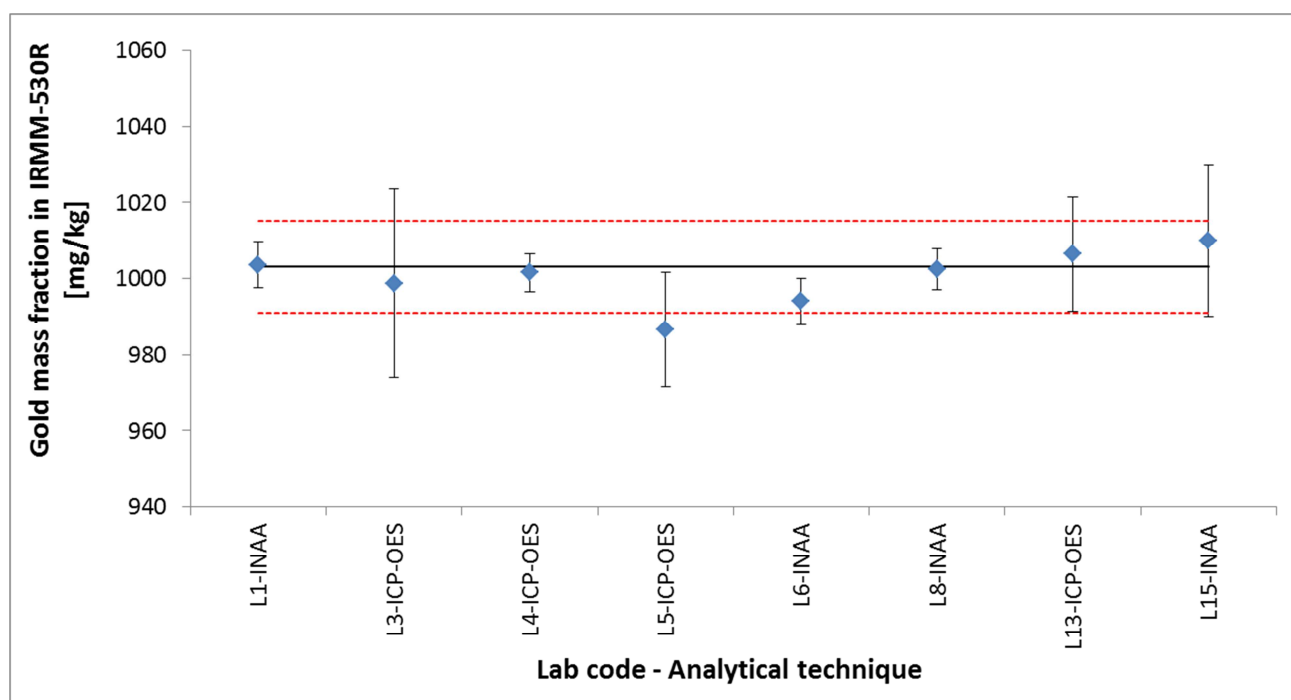


Figure C2. Results for Au mass fraction in IRMM-530R are presented as mean value (♦), with expanded uncertainty budget (□); certified value (—) and expanded uncertainty of the certified value (---).

Annex D: Summary of methods used in the characterisation study

The method information is reported as given by laboratories.

Lab / Method code	Technique	Sample mass [mg]	Sample preparation	Calibration	Instrumentation
L0	ICP-OES	100	Digestion in aqua regia	2-points external calibration (bracketing), with Inorganic Venture standard	ICAP 6500 ThermoFisher Scientific
L1	INAA	8 - 16	n.a.	NIST 3121 gold standard solution	Reactor with thermal neutron flux of $5 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$ Detector: HPGe coaxial
L2	ICP-OES	100	Overnight digestion in aqua regia	2-points external calibration (bracketing), with Certipur gold ICP Standard (Merck) Internal standard (Be)	Varian E730
L3	ICP-OES	100 - 150	HNO ₃ + HF	Matrix matching using CPI International Peak Performance™ Standards of aluminium and gold	Perkin Elmer Optima 5300V
L4	ICP-OES	50 - 100	Digestion in diluted HCl and nitric acid	3-points external calibration, with matrix matched standard prepared from gold (purity 99.99%) and aluminium metal Internal standard: Yttrium	Perkin Elmer 4300DV
L5	ICP-OES	100 - 250	Digestion in aqua regia	2-points external calibration, with standards prepared from solid gold (purity 99.9%)	VARIAN Vista MPX radial
L6	INAA	10	n.a.	NIST 3121 gold standard solution	Reactor with neutron fluence rates of thermal, epithermal and fast neutrons were $3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, and $8 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ Detector: coaxial HPGe
L7	INAA	10	n.a.	IRMM-530R	TRIGA Mark II reactor with a thermal neutron flux of $1.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ Detector: coaxial HPGe
L8	INAA	10	n.a.	IRMM-530	Reactor with neutron fluence rate of $5.4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ (day 1), $2.8 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ (day 2)
L9	INAA	10	n.a.	IRMM-530R shape C	Reactor with fluence rate $2.2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ Detector: 2 HPGe calibrated

Lab / Method code	Technique	Sample mass [mg]	Sample preparation	Calibration	Instrumentation
L10	INAA	5-10	n.a	IRMM-530R	Reactor with neutron fluence rate $3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ Detector: HPGe
L11	INAA	5 - 50	n.a	IRMM-530R	Medium Flux Nuclear Reactor in thermal irradiation conditions Detector: coaxial HPGe
L12	Fire Assay with Gravimetric Finished	70-250	Fusion of the sample with PbO, Silica, Borax, Soda ash, CaF ₂ and Ag. Separation of the button and the slag. Then separation of Au from other metals by fusion and acid digestion steps. The final Au button is weighted	Certified geological reference materials (Rocklabs Ltd)	Microbalance Mettler Toledo Model MT5
L13	ICP-OES	500	Digestion in HNO ₃ and HCl HF	Gold standard solution Certipur (Merck)	ICP-OES Agilent 720
L14	Fire Assay with Gravimetric Finished	500 - 1000	Fire assay lead collection of Au with addition of Ag. Separation of Au from Ag by using nitric acid. The final Au button is weighted	Microbalance calibrated using certified reference weight	Mettler Toledo XP6
L15	INAA	15 - 25	n.a.	NIST 3121 gold standard solution	Reactor MTR type neutron flux with thermal, epithermal, and fast components: $\phi_{\text{thermal}} \approx 2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, $\phi_{\text{epithermal}} \approx 1 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$, $\phi_{\text{fast}} \approx 1 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ Detector: HPGe coaxial
L16	Fire assay with ICP-OES finished	100 - 300	Lead collection fire assay with Ag co-collection, followed by inductively coupled plasma optical emission spectroscopy	External, linear, 7 points plus blank using NIST SRM 3121 gold standard solution	SPECTRO Arcos

Annex E: Results of the characterisation measurements

Table E1. Individual results for gold mass fraction in ERM-EB530 provided by each laboratory. The mean value was calculated as the unweighted mean of all individual results and, the expanded uncertainty is reported as stated by the laboratory.

Laboratory code	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Replicate 6	Replicate 7	Replicate 8	Replicate 9	Mean [mg/kg]	Uncertainty (k=2) [mg/kg]
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]		
	Replicate 10	Replicate 11	Replicate 12	Replicate 13	Replicate 14	Replicate 15	Replicate 16	Replicate 17	Replicate 18		
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]		
L0-ICP-OES	984.4 1020.0	995.3 1007.1	996.0 1007.7	1017.4 1018.5	1003.6 991.8	1017.0 1003.1	1037.2 1001.5	995.0 996.3	1020.9 1013.2	1007	24
L1-INAA	1016 1010	1019 990	996 1007	999 1020	992 1022	1010 993	1005 1004	1007 1007	1019 1002	1007	12
L2-ICP-OES	1017 1003	1014 1001	1012 1011	1013 1012	1008 1013	1015 1007	1009 1011	1013 1015	1014 1011	1011	7
L3-ICP-OES	995 1016	1008	999	1007	1009	991	985	1013	1002	1002	31
L4-ICP-OES	1004 1013	1004 1015	1008 1012	1003 1017	1004 1013	1002 1015	985 1003	989 1005	991 1006	1005	5
L5-ICP-OES	980 1006	989 1011	992 969	993 1007	986 987	993 1016	996 1005	982 993	972 997	993	26
L6-INAA	1005 998	993 1008	994 1006	992 1008	999 1005	1003 1002	1010 989	1006 995	1006 992	1001	5
L7-INAA	1025 1011	1015 1010	1013 1009	1017 1003	1036 1008	1000 1013	999 1022	1005 1015	1007 1003	1012	27
L8-INAA	1017.1 997.5	1010.2 1004.9	1007.3 1000.4	995.2 1012.2	1006.4 999.4	993.4 1005.3	1005.4 1002.6	1010.7 995.8	1017.3 1002.8	1005	11
L9-INAA	988 1018	1007 1009	984 1034	991 994	1000 1005	1005 983	1006 999	1023 983	1008 1011	1003	33
L10-INAA	1016.04 997.76	1020.05 1011.02	1022.06 1007.26	998.44 1014.53	1001.19 1015.04	1013.53 1014.79	1008.77 1015.54	1017.29 1021.30	1007.76 1016.29	1012	14
L11-INAA	1006 1010	1016 1009	1008 1006	1017 1003	1015 1019	1005 993	990 996	1021 1023	999 1004	1008	87
L12-Fire assay	1003 1011	1010 1025	995 1005	1005 1006	978 1005	962 997	960 988	1011 1002	988 998	997	7
L13-ICP-OES	1025 984	1003 987	1005 997	1012 1008	1006 1004	998 999	1007 1030	1020 1023	1021 1035	1009	28
L14-Fire assay	1005	1003	1004	997	997	1003				1002	8
L15-INAA	990.00 1006.00	1011.00 1035.00	1007.00 1050.00	1017.00 1021.00	1011.00 1002.00	1029.00 1029.00	998.00 980.00	1006.00 1016.00	1060.00 986.00	1014	32
<i>Results not used for certification</i>											
L16-Fire assay	736 845	714 820	725 766	772 857	810 808	818 843	813 863	826 909	801 843	779	44

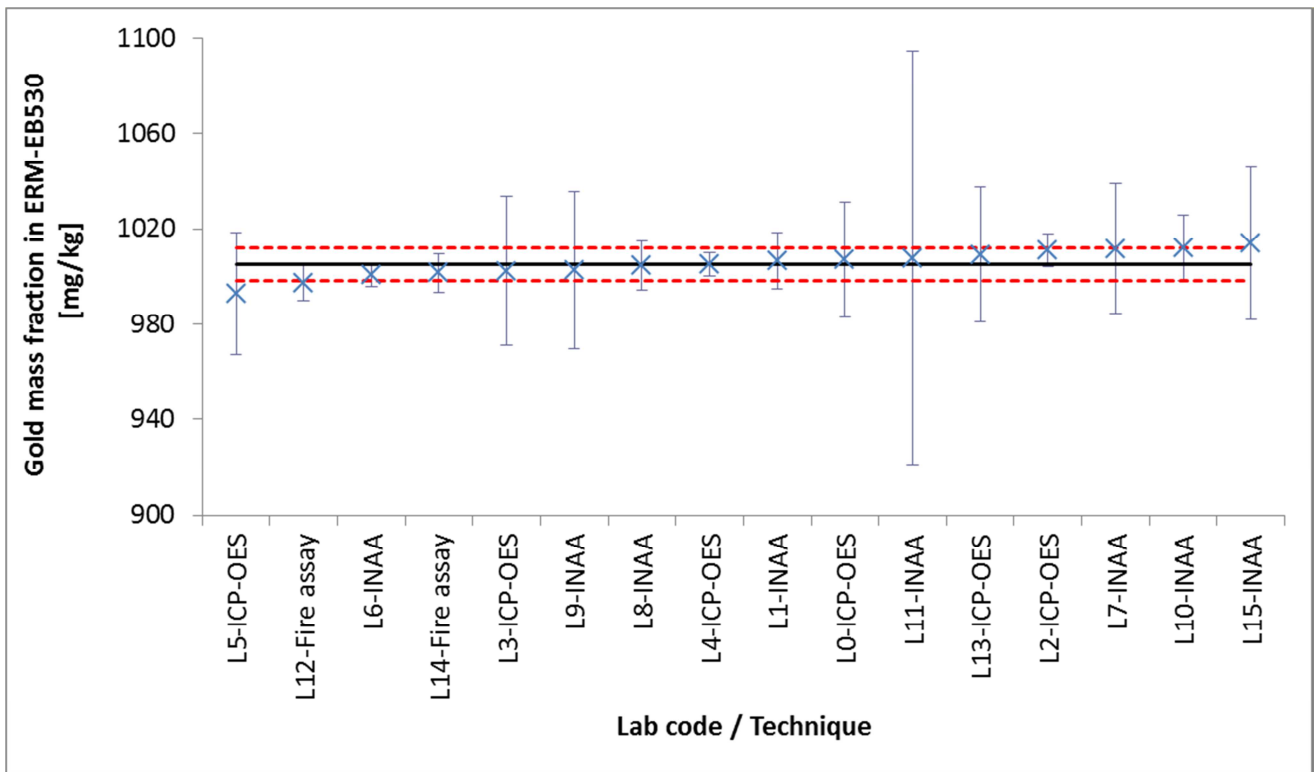


Figure E1. Mean gold mass fraction in ERM-EB530 reported by participating laboratories. Error bars represent expanded uncertainties as reported by participating laboratories. The solid line represents the certified values (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value. Each laboratory is represented by its code and technique used.

Annex F: Consistency of k_0 gold comparator study

Table F1. Mean results of k_0 -NAA analysis in mussel tissue CRM (ERM-CE278k). Expanded uncertainty is given with k factor of 2 as reported by laboratory.

Elements	Certified values			IRMM-530			IRMM-530R			ERM-EB530		
	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]
Fe	161	±	8	165	±	9	165	±	9	164	±	9
Zn	71	±	4	73	±	3	73	±	3	72	±	3
Se	1.62	±	0.12	1.71	±	0.15	1.71	±	0.15	1.71	±	0.14
Rb	2.46	±	0.16	2.44	±	0.28	2.45	±	0.28	2.43	±	0.27
Sr	19	±	1.2	21.1	±	3.9	21.2	±	3.9	21.0	±	3.9

Table F2. Mean results of k_0 -NAA analysis in bakelite RM (SMELS). Expanded uncertainty is given with k factor of 2 as reported by laboratory.

Elements	Certified values			IRMM-530			IRMM-530R			ERM-EB530		
	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]	Mass fraction [mg/kg]		uncertainty (k=2) [mg/kg]
Sc	1.140	±	0.031	1.116	±	0.059	1.111	±	0.058	1.121	±	0.057
Cr	86.7	±	2.6	82.5	±	6.5	82.0	±	6.3	81.3	±	6.3
Fe	8200	±	190	8093	±	432	8062	±	422	8140	±	417
Co	24.3	±	0.33	24.23	±	1.27	24.14	±	1.25	24.39	±	1.20
Zn	618	±	11	606	±	39	604	±	38	604	±	34
Se	131	±	6	132	±	7	131	±	7	133	±	7
Sr	8150	±	200	7839	±	520	7800	±	519	7775	±	451
Zr	4580	±	100	4570	±	289	4560	±	280	4554	±	262
In	462	±	19	451	±	22	449	±	21	454	±	21
Sb	51.2	±	1.3	51.2	±	2.9	51.0	±	2.9	51.5	±	2.9
Cs	20.80	±	0.34	19.91	±	1.06	19.83	±	1.04	20.05	±	1.02
Yb	20.7	±	0.5	21.0	±	1.5	21.0	±	1.5	20.9	±	1.4
Au	0.901	±	0.016	0.878	±	0.042	0.876	±	0.042	0.870	±	0.041
Th	26.2	±	0.9	25.7	±	1.2	25.6	±	1.2	25.9	±	1.2

Table F3. Mean results of k_0 -NAA analysis in sediment CRM (BCR-320R). Expanded uncertainty is given with k factor of 2 as reported by laboratory.

Elements	Certified values			IRMM-530			IRMM-530R			ERM-EB530		
	Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]	
Sc	5.2	±	0.4	5.2	±	0.2	5.2	±	0.2	5.1	±	0.2
Cr	59	±	4	60	±	3	60	±	3	60	±	3
Fe	25700	±	1300	25226	±	1162	25280	±	1169	25045	±	1159
Co	9.7	±	0.6	9.8	±	0.5	9.8	±	0.5	9.7	±	0.5
Zn	319	±	20	316	±	15	317	±	15	314	±	15
As	21.7	±	2	24	±	1	24	±	1	23.41	±	1
Se	0.96	±	0.18	0.79	±	0.09	0.79	±	0.09	0.79	±	0.09
Th	5.3	±	0.4	5.3	±	0.2	5.3	±	0.3	5.3	±	0.3
U	1.56	±	0.20	1.44	±	0.21	1.63	±	0.37	1.57	±	0.33

Table F4. Mean results of k_0 -NAA analysis in fly ash CRM (BCR-176R). Expanded uncertainty is given with k factor of 2 as reported by laboratory.

Elements	Certified values			IRMM-530			IRMM-530R			ERM-EB530		
	Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]		Mass fraction [mg/kg]	uncertainty (k=2) [mg/kg]	
Sc	2.91	±	0.30	2.84	±	0.14	2.86	±	0.13	2.87	±	0.13
Cr	810	±	70	786	±	36	787	±	36	788	±	36
Fe	13100	±	500	12690	±	624	12710	±	609	12723	±	610
Co	26.7	±	1.6	26.9	±	1.3	27.0	±	1.3	27.0	±	1.3
Zn	16800	±	400	16034	±	738	16060	±	739	16076	±	740
Se	18.3	±	1.9	16.8	±	0.8	17.8	±	0.9	18.0	±	0.9
Ag	33.1	±	3.0	33.6	±	1.6	33.6	±	1.6	33.6	±	1.6
Sb	850	±	50	835	±	42	837	±	42	837	±	42
Cs	8.27	±	0.80	8.35	±	0.39	8.36	±	0.39	8.37	±	0.39
Ba	4650	±	460	4470	±	210	4479	±	210	4481	±	210
La	30.2	±	0.3	30.2	±	1.7	30.5	±	1.7	30.4	±	1.7
Ce	47.7	±	4.8	48.8	±	2.3	48.8	±	2.3	48.8	±	2.3
Hf	4.85	±	0.50	4.77	±	0.22	4.78	±	0.22	4.79	±	0.22
Ta	2.02	±	0.20	2.06	±	0.25	2.06	±	0.26	2.07	±	0.26
Au	0.60	±	0.06	0.61	±	0.04	0.61	±	0.04	0.61	±	0.04
Th	5.28	±	0.50	5.30	±	0.25	5.31	±	0.25	5.31	±	0.25

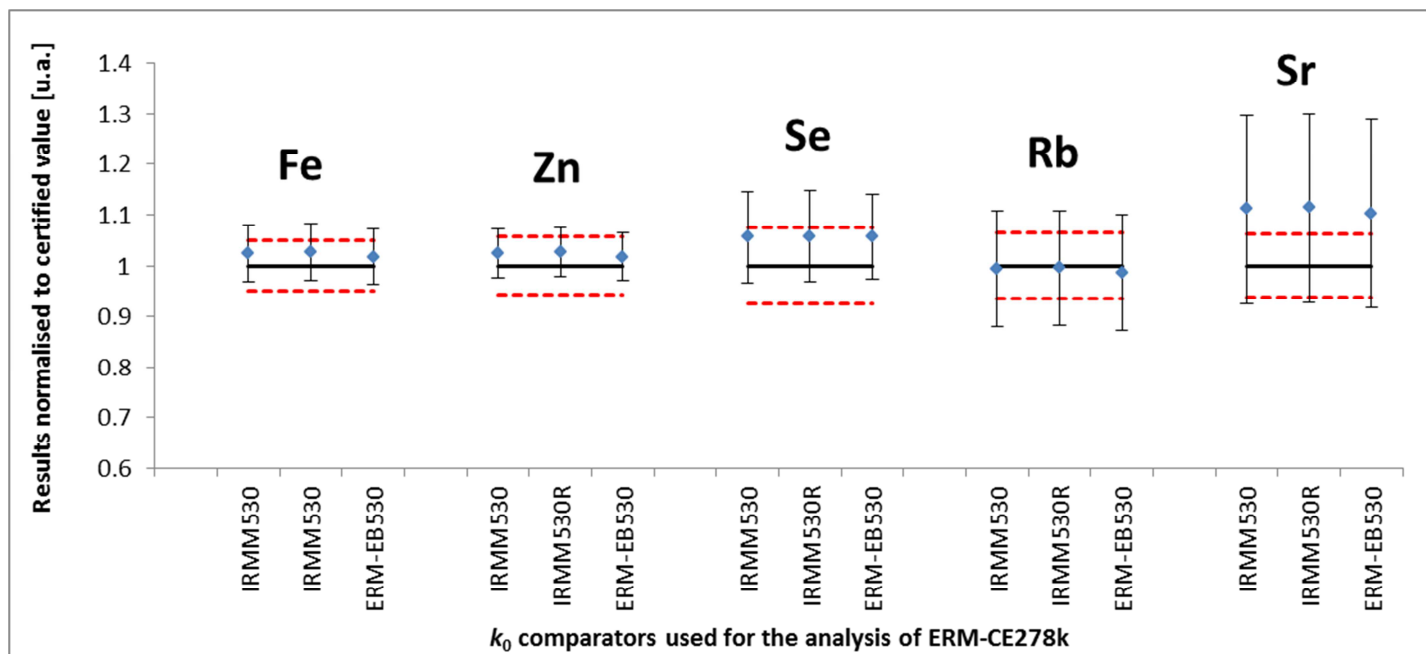


Figure F1. Results normalised to certified value for Fe, Zn, Se, Rb and Sr in mussel tissue CRM (ERM-CE278k). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

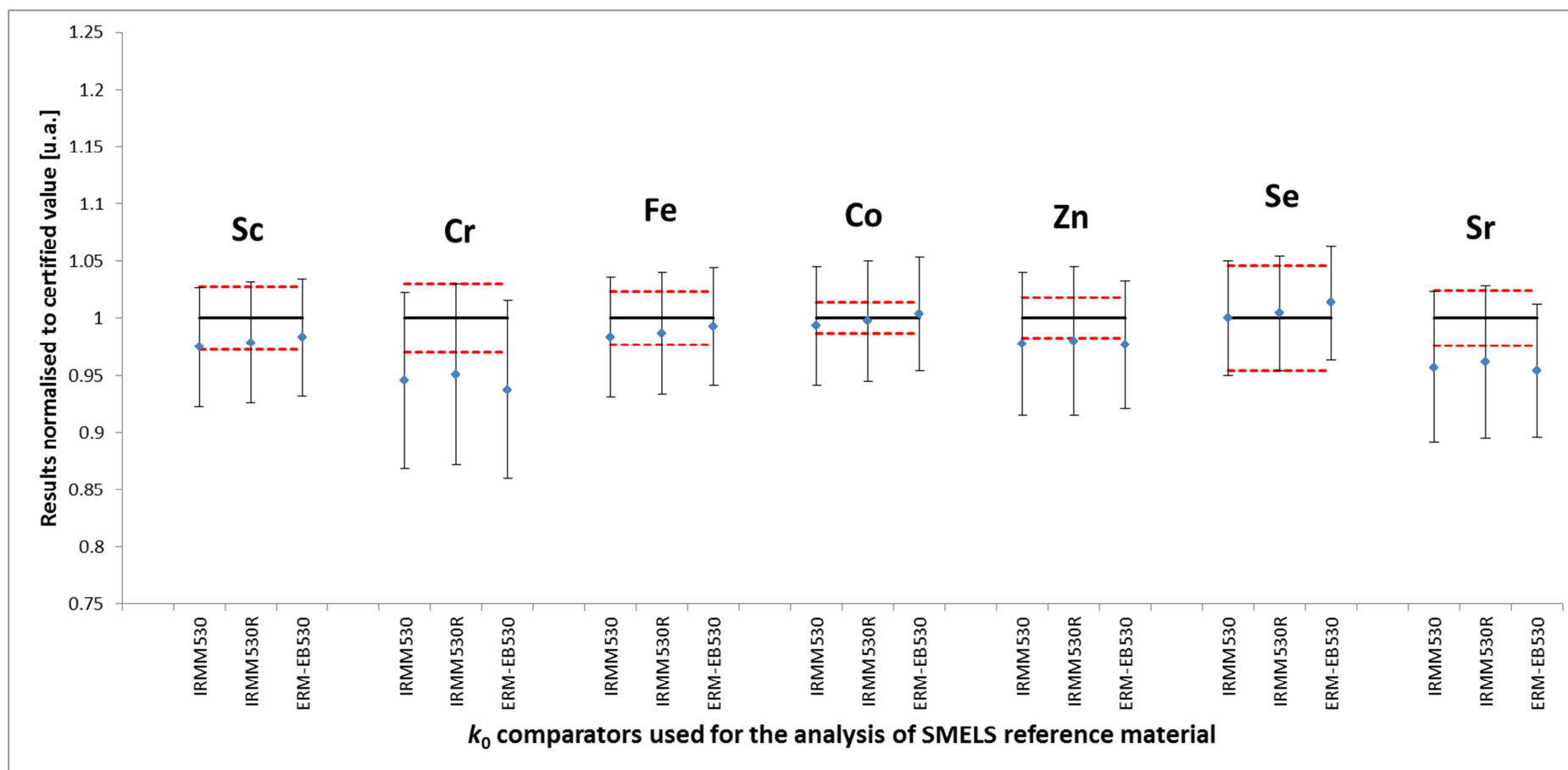


Figure F2a. Results normalised to certified value for Sc, Cr, Fe, Co, Zn, Se and Sr in Bakelite RM (SMELS). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

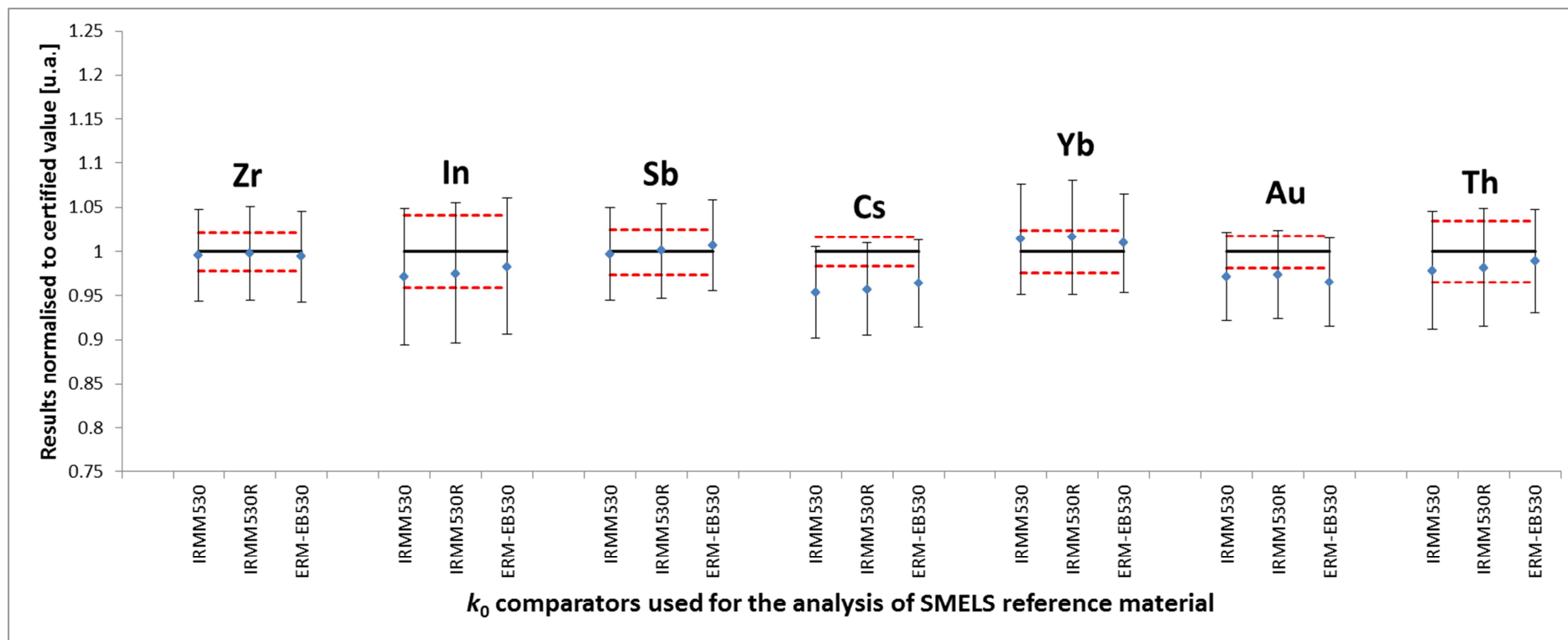


Figure F2b. Results normalised to certified value for Zr, In, Sb, Cs, Yb, Au and Th in Bakelite RM (SMELS). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

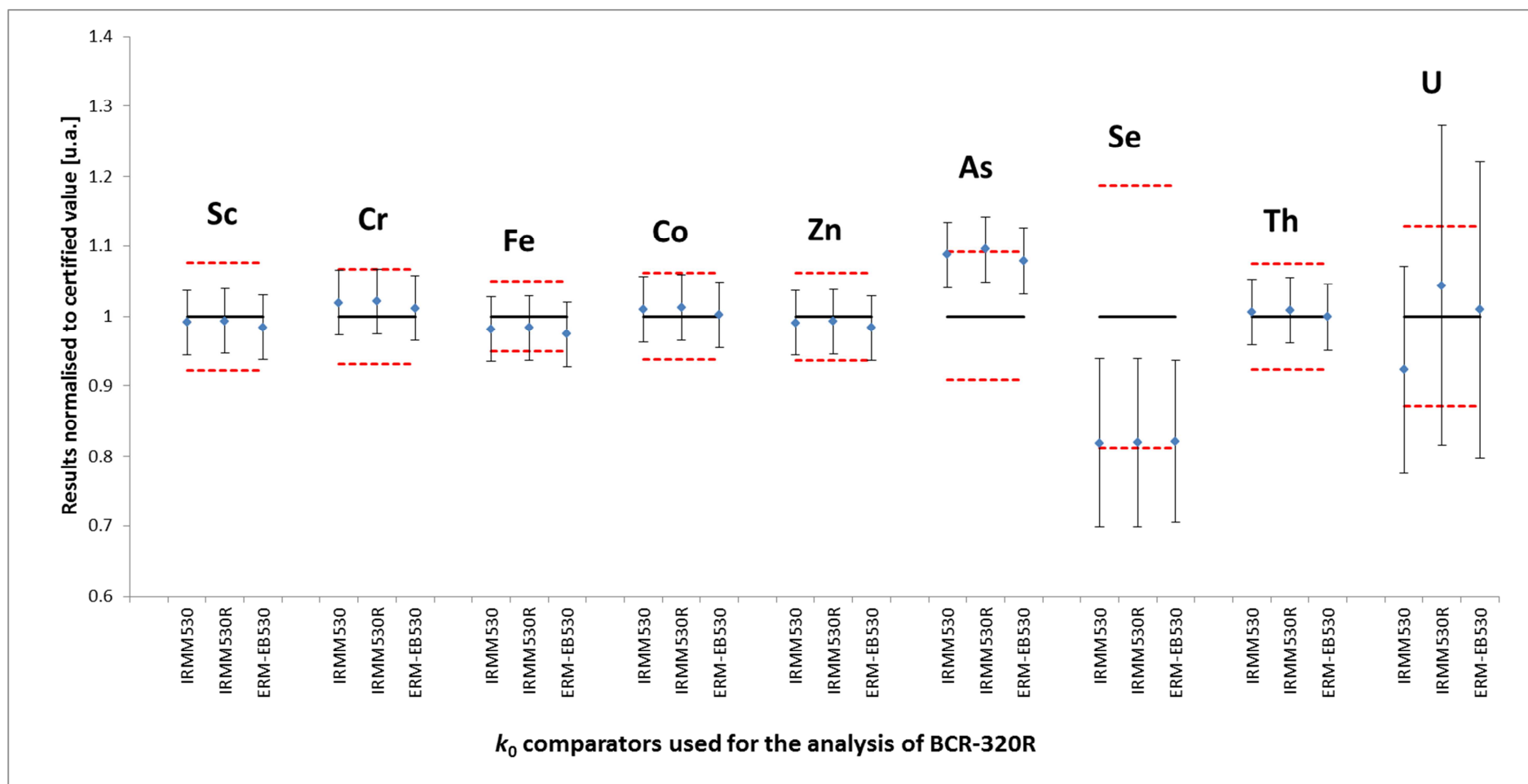


Figure F3. Results normalised to certified value for Sc, Cr, Fe, Co, Zn, As, Se, Th and U in sediment CRM (BCR-320R). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

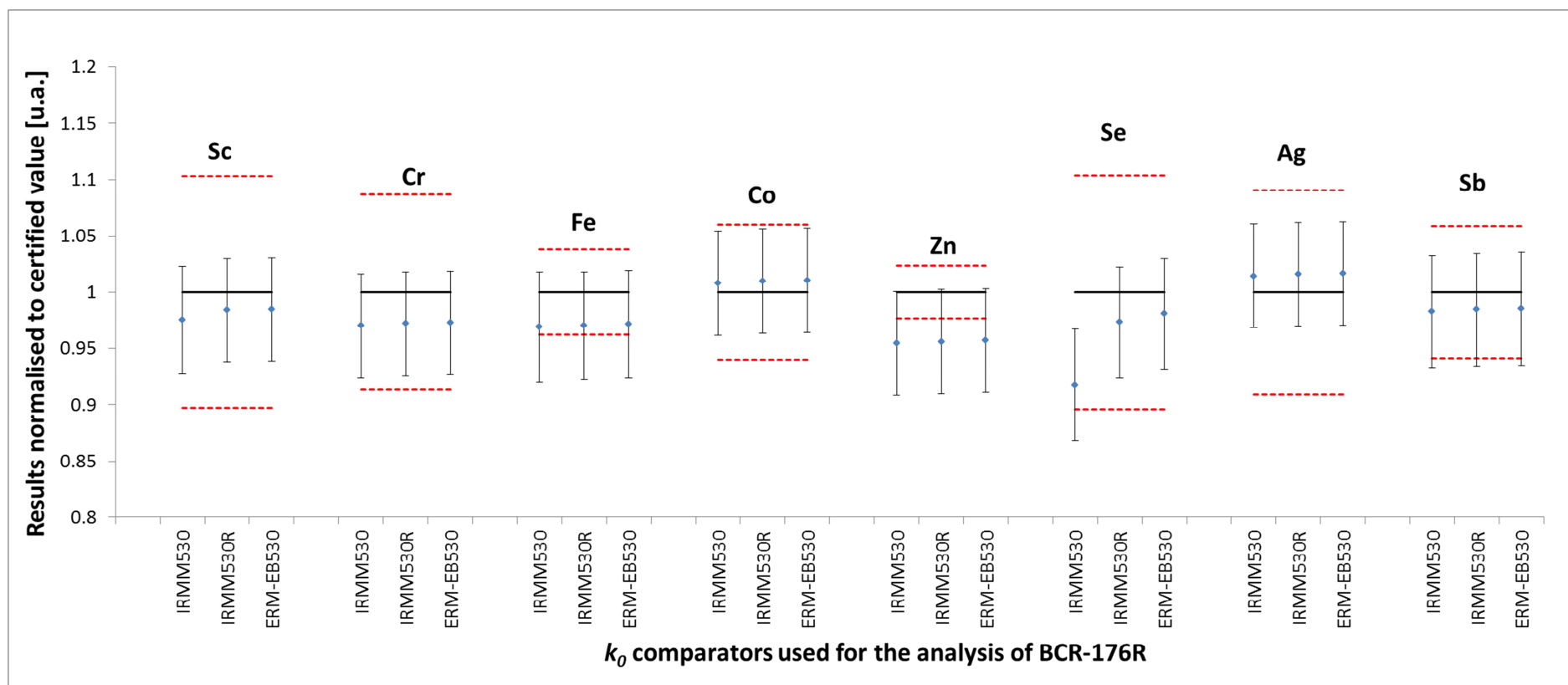


Figure F4a. Results normalised to certified value for Sc, Cr, Fe, Co, Zn, Se, Ag and Sb in fly ash CRM (BCR-176R). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

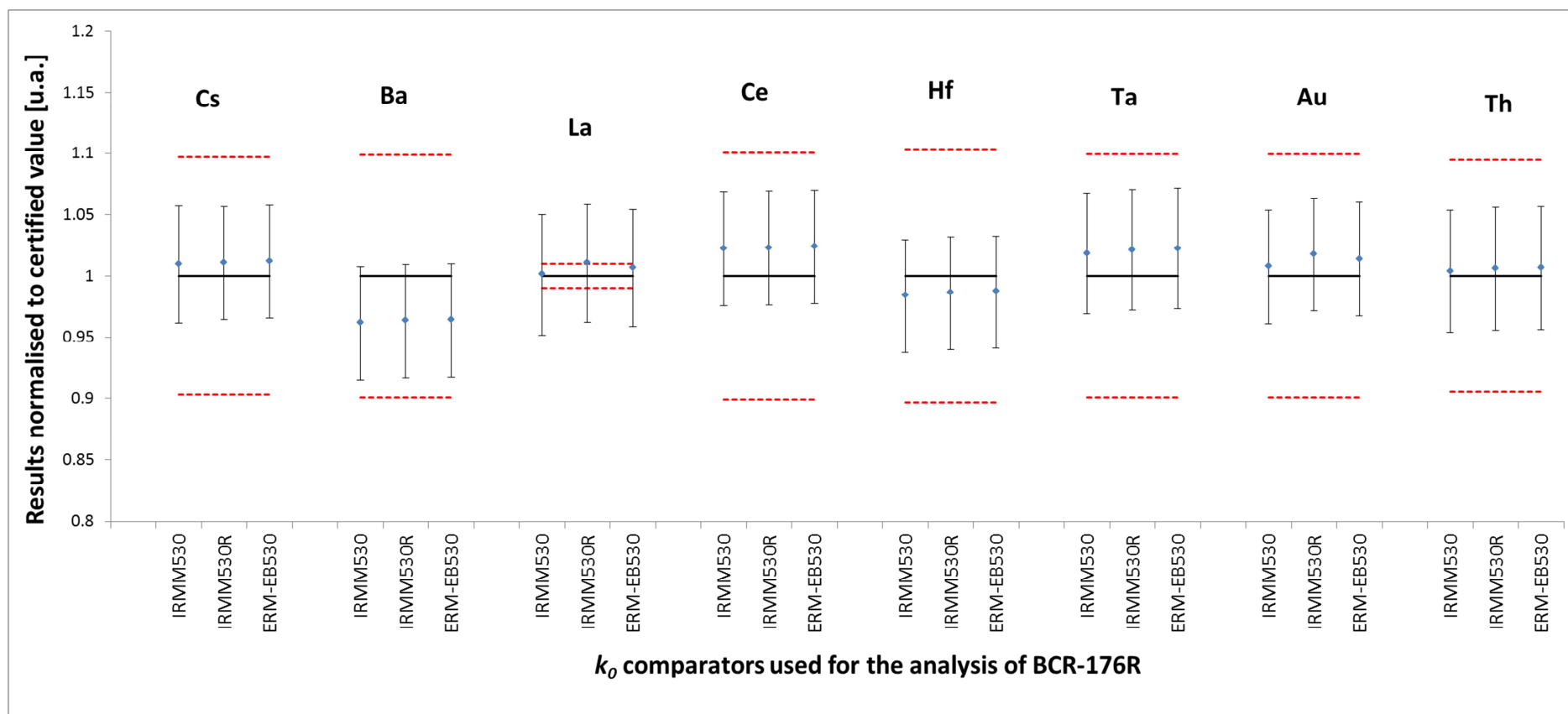


Figure F4b. Results normalised to certified value for Cs, Ba, La, Ce, Hf, Ta, Au and Th in fly ash CRM (BCR-176R). Results obtained using k_0 -NAA analysis with k_0 comparators IRMM-530, IRMM530R and ERM-EB530. The results are represented as the mean of three independent analysis with expanded uncertainty ($k=2$). The dark line is the certified value, red dot line represent the expanded uncertainty ($k=2$) of the certified value.

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Abstract

This report describes the production of ERM®-EB530A, B and C, aluminium gold alloy material certified for the mass fraction of gold. The material was produced following ISO Guide 34:2009.

Pure aluminium and pure gold were arc melted together to obtain a master alloy Al-5%Au (mass percent). The master alloy was melted with pure aluminium in a resistance furnace, casted in ingot and heat treated. The ingot was processed mechanically (wire drawing or rolling) to obtain thin wire (diameter 0.5 mm and 1.0 mm) and thin foil (thickness 0.1 mm).

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with 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 estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, and instability and to characterisation.

The material is intended for the calibration of methods (k_0 -neutron activation analysis). As any reference material, it can also be used for control charts or validation studies. The CRM is packed in plastic boxes and available in three different versions:

ERM-EB530A: foil of 50 cm², thickness: 0.100 mm

ERM-EB530B: 1 meter of wire diameter 0.500 mm

ERM-EB530C: 1 meter of wire diameter 1.000 mm

The minimum amount of sample to be used is 0.55 mg.

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

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