BAM

Certification Report

Certified Reference Material

BAM-M112

Pure Lead

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Summary

This report describes preparation, analysis and certification of the lead reference material BAM-M112. The certified reference material (CRM) is available in the form of discs (ca. 40 mm diameter and 30 mm height). It is intended for establishing and checking the calibration of optical emission spectrometry for the analysis of samples of similar matrix composition. It is also suitable for validation of wet chemical analysis methods.

The following mass fractions and uncertainties have been certified:

Certified Values

Element	Mass fraction [1)] in mg/kg	Uncertainty [2)] in mg/kg
Cu	8.2	0.6
Ni	5.3	0.4
Pt	5.4	0.5
Se	5.2	0.4
Te	5.3	0.3

1) Unweighted mean value of the means of accepted sets of data (consisting of at least 4 single results), each set being obtained by a different laboratory and/or a different method of measurement.

2) Estimated expanded uncertainty *U* with a coverage factor of *k* = 2, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement, (GUM, ISO/IEC Guide 98-3:2008).

This report contains detailed information on the preparation of the CRM as well as on homogeneity investigations and on the analytical methods used for certification.
The certified values are based on the results of eight laboratories which participated in the certification inter-laboratory comparison.
Mass fractions of Ag, Bi, S and Tl are given for information.

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List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
ETAAS	electrothermal atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
SOES	spark optical emission spectrometry
M	mean value
n	number of accepted data sets
s	standard deviation of an individual data set
s_M	standard deviation of laboratory means
s_{rel}	relative standard deviation
$\bar{s}_i$	square root of mean of variances of data sets under repeatability conditions
M_i	single result
I	ICP-OES (Tables 2 – 6)
I-D	ICP-OES after fire assay (Tables 2 – 6)
I(R)	ICP-OES, revised value (Tables 2 – 6)
IMS	ICP-MS (Tables 2 – 6)
IMS(R)	ICP-MS, revised value (Tables 2 – 6)
EA	ETAAS (Tables 2 – 6)

1. Introduction

In the metal-producing and metal-working industry mainly spark emission spectrometry (SOES) is used for reception inspection of raw materials, e.g. scrap, for quality control of end products and production control. This time-saving analytical technique requires suitable reference materials for calibration and recalibration. The certified reference material BAM-M112 is based on pure lead and is beside other elements certified for its Pt-content. Pt becomes more and more important for lead battery production.

The idea to produce the reference material for BAM-M112 was the outcome of discussions within the working group „Lead" of the Committee of Chemists within the Society of Metallurgists und Miners (GDMB). The needs are defined by this working group, since the members are potential users of the prepared CRMs. Participating laboratories were recruited from this group. Since all these laboratories are highly experienced with lead analysis and had participated in earlier interlaboratory comparisons, there was no preceding proficiency test for qualification necessary.

Certification was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2. Companies/laboratories involved

Manufacturing of the material:

– SUS Nell, Oberhausen, Germany

Test for homogeneity:

– Aurubis AG and participating laboratories

Participants in the certification inter-laboratory comparison:

Aurubis AG, Hamburg, Germany
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
Berzelius Stolberg, Stolberg, Germany
Clarios Germany GmbH & Co. KGaA, Hannover, Germany
Clarios Zwickau GmbH & Co. KG, Zwickau, Germany
Hoppecke Batterien GmbH & Co. KG, Brilon-Hoppecke, Germany
Muldenhütten Recycling und Umwelttechnik GmbH, Freiberg, Germany
WESER METALL GmbH, Nordenham, Germany

Statistical evaluation of the data:

– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

3. Candidate material

A pure lead was used as basic material for the preparation of the candidate material. This material was milled, melted and doped with the desired impurities by SUS Nell, Oberhausen. Five sub-batches were produced (1 – 5), from which cylinders were casted.
In total, 240 discs of BAM-M112 with a diameter of ca. 38 mm and 38 mm height were obtained.

4. Homogeneity testing

Possible reasons for an inhomogeneous distribution of elements in the raw material may be a change of the composition of the melt during the casting procedure because some elements may volatize or because of possible segregation during the solidification of the material. Since the raw material was produced by casting of a rod, concentration gradients can occur over the length of the rod (axial) as well as over the area of the rod (radial, see Figure 1):

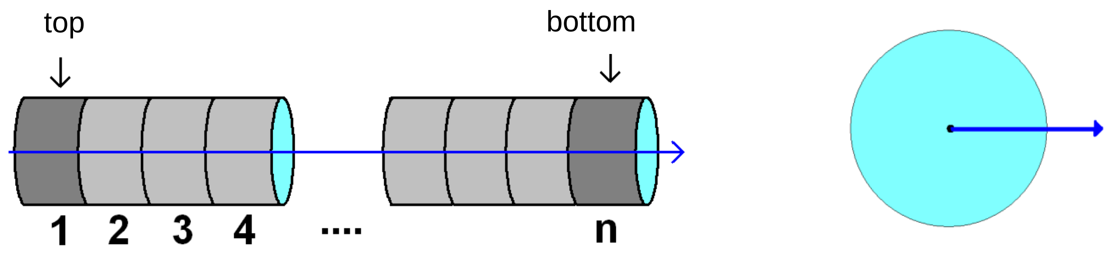


Fig. 1: Axial and radial composition gradient

Therefore, it is necessary to investigate the raw material for both axial and radial inhomogeneities. Radial as well as axial homogeneity testing of the candidate material was done using spark emission spectrometry. In total 10 discs (two of each sub-batch) of BAM-M112 were investigated (4 sparks per disc).

The estimate of analyte-specific inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [4] using Eq. (1) and Eq. (2):

$$s_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \qquad (1)$$

$$u_{bb}^{*} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

where:

MS_{among}	mean of squared deviations between discs (from 1-way ANOVA, see Annex 1)
MS_{within}	mean of squared deviations within one disc (from 1-way ANOVA)
n	number of replicate measurements per disc
N	number of discs selected for homogeneity study

s_{bb} signifies the between-discs standard deviation whereas u^*_{bb} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as $u_{bb}(1)$ for inhomogenity over the length. Eq. (1) does not apply if MS_{within} is larger than MS_{among}.

In addition to the tests performed over the length of the rods nine laboratories participated in a spark OES round robin. They were asked to perform the analysis following the given routine: outer circle: 4 sparks, inner circle: 4 sparks; centre: 1 spark. From this investigation no hint to any inhomogeneity over the area was obtained. The uncertainty contribution was calculated with the data obtained from two of the laboratories (Aurubis AG (Lab. A), Clarios Hannover (Lab. B)).

The analyte-specific within-disc uncertainty component $u_{bb}(2)$ was calculated in the same way as for the total batch. To calculate the necessary data an unbalanced ANOVA was carried out considering that the number of single measurements is different for the centre, the inner and the outer circle. For technical reasons, at r_0 (centre) only one measurement is possible. An ANOVA requires a minimum of two measurements per factor value. Thus, the value for r_0 should be replaced by a dummy. This dummy is defined as follows:

The two values replacing the measured one have a mean equal to the value measured, and a standard deviation equal to the average within-variation. This resembles the situation where one could take two independent measurements at the same place, with values deviating by the average standard deviation (non-destructive testing method). A measure for the average standard deviation is calculated from the data for r_in (inner circle) and r_out (outer circle). The result from these calculations is an inhomogeneity component for the radius of the disc. From these values, a combined inhomogeneity component is calculated. This component is compared with the within standard deviation calculated from the ANOVA-data. The higher component (square root of the mean of variances from the two labs) is used for the uncertainty calculation.

The results of the calculations are given in the annex.

5. Characterisation study

5.1 Analytical methods

Nine laboratories participated in the certification inter-laboratory comparison. For some elements part of the laboratories used more than one analytical method reporting more than one data set.
The laboratories were asked to analyse six subsamples. They were free to choose any suitable analytical method. Table 1 shows the analytical methods used by the participating laboratories.
For all analytical methods where a calibration was necessary this calibration was performed using liquid standard solutions. All participating laboratories were asked to use only standard solutions prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 1: Analytical procedures used by the participating laboratories

Lab-No.	Element	Sample mass	Sample pretreatment	Analytical method
1	Cu, Ni, Pt, Se, Te	2 g	Dissolution HNO_3/HCl	ICP-OES with matrix matched standards (Pb 99.9995%), calibration with commercial solutions (Spex certified)
	Pt	5 g	Melting with 10 mg Ag to collect Pt, separation of lead, dissolution of Ag in HNO_3/HCl	ICP-OES, calibration with commercial solutions (Spex certified)
2	Cu, Ni, Se, Te	0.5 g	Dissolution HNO_3	ICP-MS, calibration with commercial solutions (Merck certipur)
	Pt	2 g	Dissolution with HNO_3 and HCl at 200 °C	ICP-OES with matrix matched standards (Pb 99.999%), calibration with commercial solutions (Merck certipur)
	Pt	0.5 g	Dissolution with HNO_3 and HCl at 200 °C	ICP-MS, calibration with commercial solutions (Merck certipur)
3	Cu, Ni, Se, Te	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, with matrix matched standards, calibration with commercial solutions (Merck, NIST traceable)
	Pt	5 g	Melting with 10 mg Ag to collect Pt, separation of lead, dissolution of Ag in HNO_3/HCl	ICP-OES, calibration with commercial solutions (Merck, NIST traceable)
4	Cu, Ni, Se, Te	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800) precipitation of Pb as sulfate	ICP-OES, calibration with commercial solutions (Merck certipur)
	Pt	2 g	Dissolution with aqua regia, precipitation of Pb as sulfate	ICP-OES, calibration with commercial solutions (Merck certipur)
5	Cu, Ni, Pt, Se, Te	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, commercial mono-element solutions (Merck)
6	Cu, Ni, Pt, Se, Te	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Kraft)
7	Cu, Ni, Se, Te, Ag, Bi, Tl	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck, Kraft)
9	Cu	0.25 g	Dissolution with HNO_3	ETAAS with commercial mono-element solution (Merck certipur)
	Ni	0.1 g	Dissolution with HNO_3	ETAAS with commercial mono-element solution (Merck certipur)

5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 2 to 6. These tables show the single results (M_i) of each laboratory, the respective laboratories' mean values (M), absolute and relative intra-laboratory standard deviation (s and s_{rel}, respectively), the standard deviation of laboratory means (s_M), and in addition the square root of mean of variances of data sets under repeatability conditions ($\bar{s}_i$) where n is the number of accepted data sets. The continuous line marks the certified value (mean of the laboratories' means), the broken lines mark the standard deviation, calculated from the laboratories' means.
In the related figures for each laboratory its mean value and single standard deviation is given. Outliers which have been excluded are highlighted in yellow. This was the case for two values for Pt where the laboratories had problems to completely dissolve the platinum.

Table 2: Results for Cu in BAM-M112

Lab./Meth.	**7/I(R)**	**6/I**	**1/I**	**9/EA**	**3/I**	**2/IMS**	**4/I**	**5/I**		
M_i [mg/kg]	7.8	7.8	8.2	8.0	8.3	8.3	8.4	8.6		*n*
	7.7	7.9	8.1	8.9	8.2	8.4	8.3	8.6		8
	7.7	7.6	8.1	8.9	8.2	8.4	8.9	8.6		
	7.6	7.9	8.2	8.1	8.3	8.2	8.5	8.6		
	7.5	7.9	8.4	7.9	8.2	8.1	8.4	8.5		
		7.8	8.4	7.6	8.3	8.1	8.1	8.7		
M [mg/kg]	**7.66**	**7.82**	**8.22**	**8.22**	**8.25**	**8.25**	**8.43**	**8.58**		**8.18**
s [mg/kg]	0.114	0.117	0.150	0.539	0.055	0.158	0.258	0.046	s_M [mg/kg]	0.303
									$\bar{s}_i$ [mg/kg]	0.234
s_{rel}	0.015	0.015	0.018	0.066	0.007	0.019	0.031	0.005		0.037

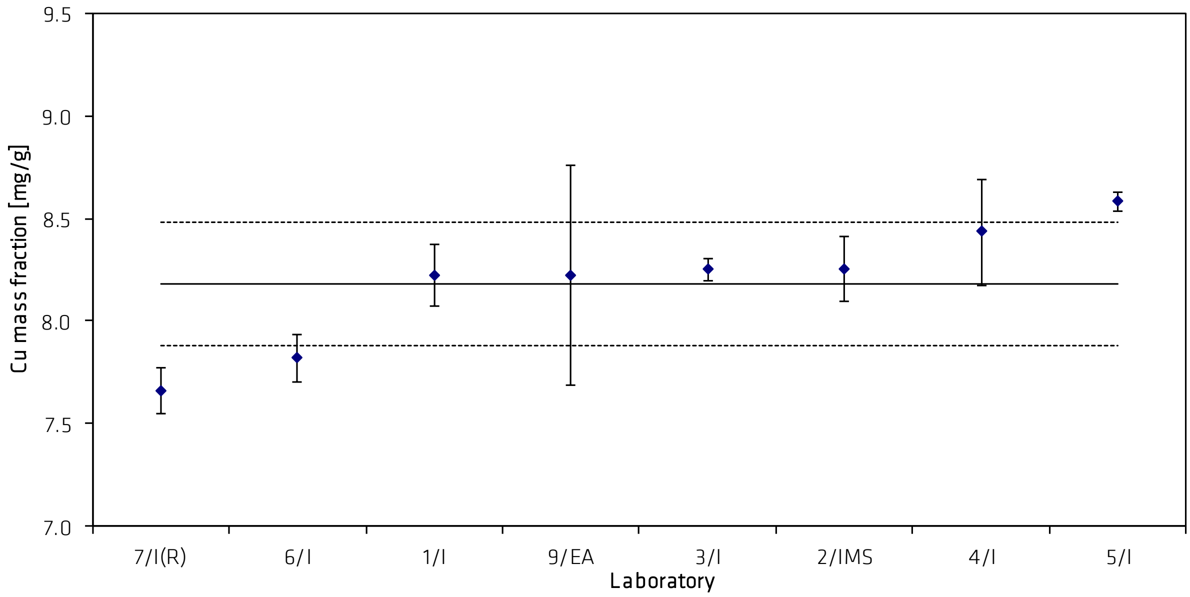


Table 3: Results for Ni in BAM-M112

Lab./Meth.	1/I	2/IMS	7/I	6/I	4/I	3/I	5/I	9/EA		
M_i [mg/kg]	5.0	5.2	5.2	5.3	5.3	5.4	5.4	5.6		*n*
	5.0	5.2	5.3	5.3	5.4	5.3	5.4	6.6		8
	5.1	5.2	5.2	5.3	5.2	5.3	5.5	5.4		
	5.1	5.2	5.2	5.3	5.4	5.3	5.4	5.2		
	5.1	5.2	5.2	5.3	5.3	5.3	5.5	5.5		
	5.1	5.2	5.2	5.2	5.2	5.4	5.5	6.1		
M [mg/kg]	**5.06**	**5.21**	**5.22**	**5.28**	**5.30**	**5.33**	**5.46**	**5.74**		**5.33**
s [mg/kg]	0.027	0.027	0.041	0.041	0.087	0.052	0.043	0.512	s_M [mg/kg]	0.205
									$\bar{s}_i$ [mg/kg]	0.187
s_{rel}	0.005	0.005	0.008	0.008	0.016	0.010	0.008	0.089		0.038

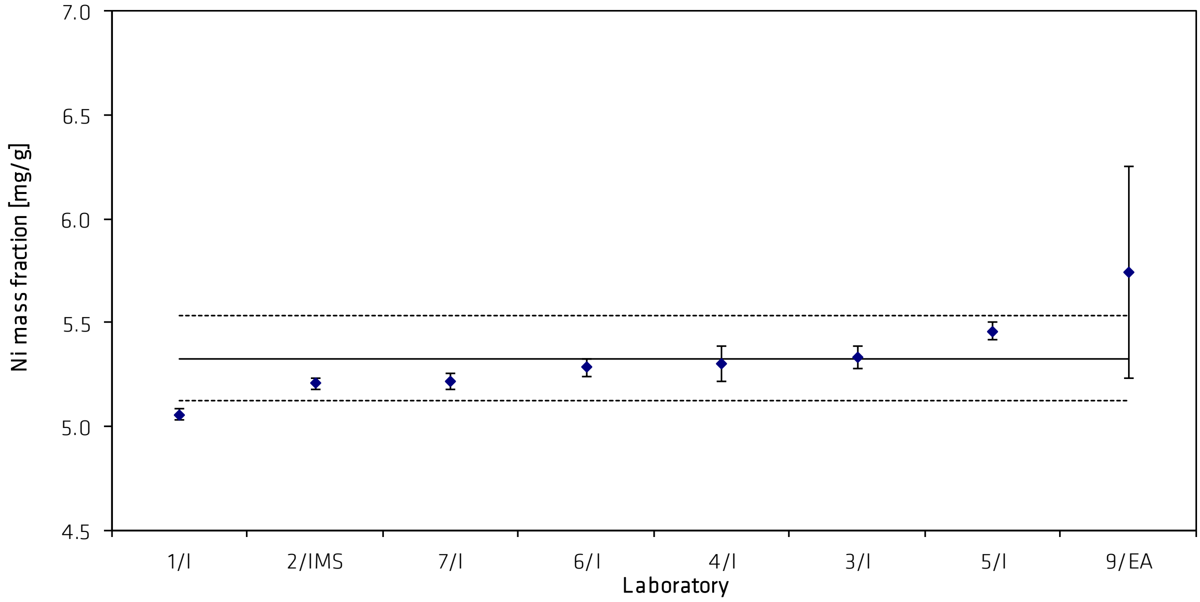


Table 4: Results for Pt in BAM-M112

Lab./Meth.	6/I	5/I	4/I (R)	3/I-D	2/IMS(R)	1/I-D	2/I	1/I		
M_i [mg/kg]	*1.6*	*2.6*	4.8	5.4	*5.5*	*5.4*	5.1	5.8		*n*
	1.7	*2.3*	4.5	5.4	*5.5*	*5.6*	6.1	5.8		6
	1.5	*2.6*	4.6	5.3	*5.5*	*5.6*	5.3	6.0		
	2.2	*3.0*	4.3	5.3	*5.5*	*5.6*	6.3	6.0		
	1.6	*2.7*	4.2	5.4	*5.5*		5.8	5.8		
	1.5	*2.6*	4.3	5.3	*5.5*		5.7	5.8		
M [mg/kg]	1.68	2.64	4.46	5.35	5.49	5.55	5.71	5.85		5.40
s [mg/kg]	0.264	0.240	0.218	0.055	0.019	0.100	0.459	0.087	s_M [mg/kg]	0.496
									$\bar{s}_i$ [mg/kg]	0.216
s_{rel}	0.157	0.091	0.049	0.010	0.004	0.018	0.080	0.015		0.092

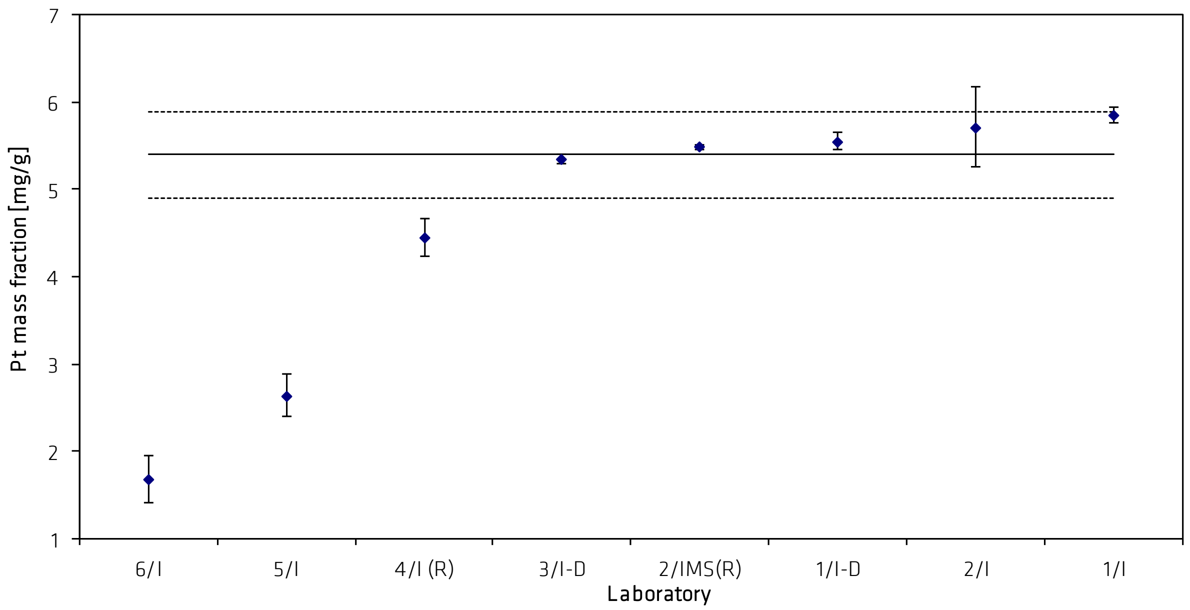


Table 5: Results for Se in BAM-M112

Lab./Meth.	6/I	4/I	2/IMS	1/I	7/I	3/I	5/I		
M_i [mg/kg]	4.8	5.2	5.3	5.2	5.4	5.3	5.6		n
	4.9	5.0	5.1	5.1	5.3	5.4	5.2		7
	4.4	5.1	5.2	5.3	5.4	5.5	5.6		
	4.7	4.8	5.3	5.4	5.5	5.3	5.7		
	4.8	4.7	5.2	5.3	5.6	5.9	5.6		
	4.7	5.1	5.2	5.2	5.6	5.5	5.6		
M [mg/kg]	**4.72**	**4.98**	**5.22**	**5.23**	**5.47**	**5.48**	**5.52**		**5.23**
s [mg/kg]	0.172	0.191	0.067	0.109	0.121	0.223	0.168	s_M [mg/kg]	0.297
								$\bar{s}_i$ [mg/kg]	0.158
s_{rel}	0.037	0.038	0.013	0.021	0.022	0.041	0.030		0.057

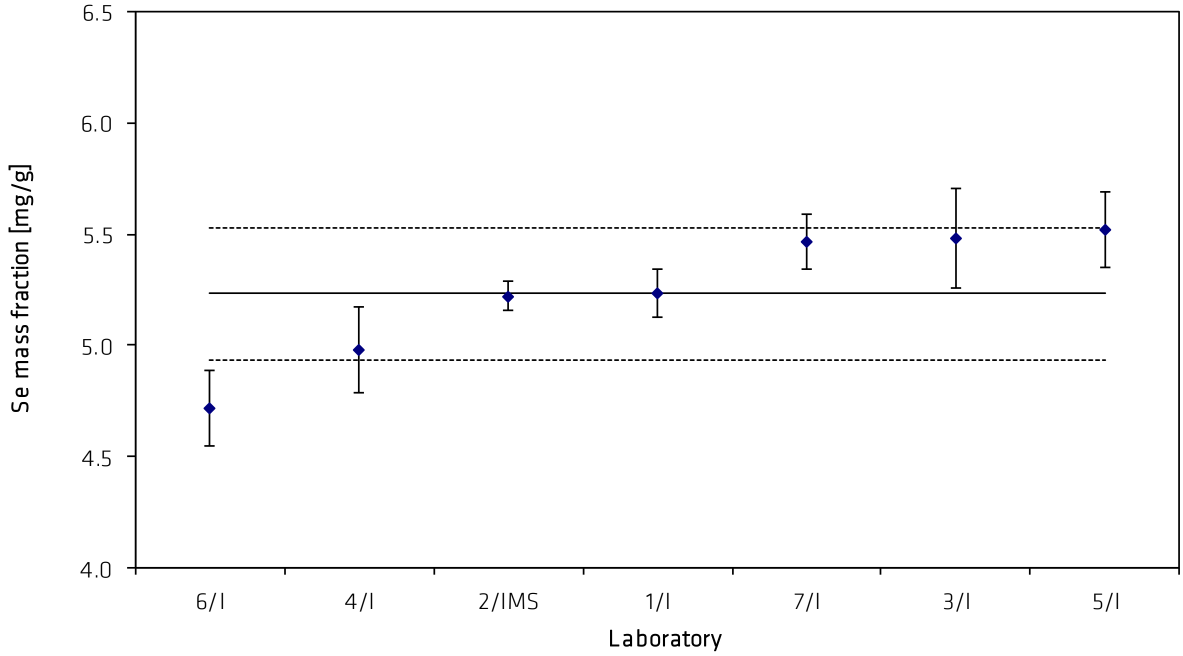
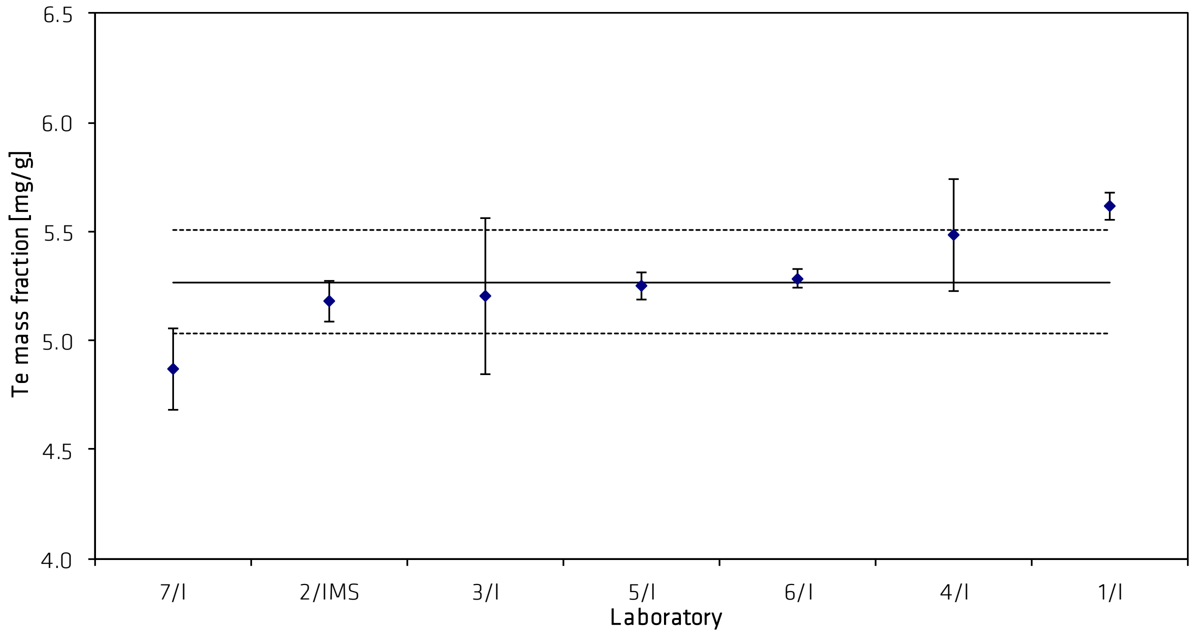


Table 6: Results for Te in BAM-M112

Lab./Meth.	7/I	2/IMS	3/I	5/I	6/I	4/I	1/I		
M_i [mg/kg]	4.9	5.1	5.8	5.21	5.3	5.6	5.6		*n*
	5.1	5.1	5.1	5.34	5.3	5.6	5.6		7
	5.0	5.1	4.9	5.17	5.3	5.3	5.5		
	4.9	5.3	4.8	5.21	5.3	5.9	5.7		
	4.7	5.2	5.3	5.30	5.3	5.4	5.7		
	4.6	5.3	5.3	5.27	5.2	5.1	5.6		
M [mg/kg]	**4.87**	**5.18**	**5.20**	**5.25**	**5.28**	**5.48**	**5.61**		**5.27**
s [mg/kg]	0.186	0.092	0.358	0.064	0.041	0.257	0.063	s_M [mg/kg]	0.237
								$\bar{s}_i$ [mg/kg]	0.188
s_{rel}	0.038	0.018	0.069	0.012	0.008	0.047	0.011		0.045



One laboratory determined the elements Ag, Bi and Tl with ICP-OES as well. These elements are given for information.
The data was statistically evaluated to detect outlying values (Grubbs, Nalimov, Dixon, Cochran). The Cochran-test was performed only once. The following results were obtained:

Tab. 7: Outcome of statistical tests on the results obtained for Cu and Ni

	Cu	Ni
Number of data sets	8	8
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	Lab. 9
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	Lab. 9
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	Lab. 9	Lab. 9
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outliers were not removed.

Table 8: Outcome of statistical tests of results obtained for Pt in BAM-M112

	1st run	2nd run
Number of data sets	8	6
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	Lab. 4
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	Lab. 4
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	Lab. 4
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	Labs. 6 and 5	---
Grubbs Pair (α = 0.01)	Labs. 6 and 5	---
Cochran (α = 0.01)	Lab. 2	Lab. 2
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The Grubbs-outliers (Labs. 6 and 5, 1st run) were removed, the outlier (Lab. 4, 2nd run) was not removed.

Tab. 9: Outcome of statistical tests on the results obtained for Se and Te

	Se	Te
Number of data sets	7	7
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 6	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran (α = 0.01)	---	Lab. 3
Kolmogorov-Smirnov-Lilliefors Test	Distribution: normal	Distribution: normal

The outliers were not removed.

The certified mass fractions of all elements were calculated as mean of the accepted data sets. These values are given in Table 10.
The respective combined uncertainties (u_{comb}) were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity over the length ($u_{bb}(1)$) and over area ($u_{bb}(2)$) of the material using Equation 3.

$$u_{comb} = \sqrt{u_{ilc}^2 + u_{bb}^2(1) + u_{bb}^2(2)} \qquad (3)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$: uncertainty contribution resulting from inter-laboratory comparison

n : number of data sets used for calculating the certified mass fraction of each element

Table 10: Uncertainty calculation for BAM-M112

		uncertainty contribution from								u_{bb} (rel)	
					u_{bb} (1)	u_{bb} (2)					
	M	n	s_M	u_{ilc}	Length	Area	u (comb)	U		Length	Area*
	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
Cu	8.18	8	0.30	0.1072	0.2341	0.1003	0.2763	0.5527		2.8619	1.2267
Ni	5.33	8	0.20	0.0724	0.1160	0.0629	0.1505	0.3010		2.1760	1.1804
Pt	5.40	6	0.50	0.2024	0.0365	0.1124	0.2343	0.4687		0.6751	2.0816
Se	5.23	7	0.30	0.1123	0.1272	0.0780	0.1868	0.3735		2.4314	1.4916
Te	5.27	7	0.24	0.0897	0.0907	0.0641	0.1428	0.2856		1.7218	1.2166

*calculated as mean of Labs. A and B

The expanded uncertainties U are calculated by multiplication of u_{comb} with a coverage factor of $k = 2$ using Equation 4.

$$U = k \cdot u_{comb} \qquad (4)$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 3 of this report. Rounding was done according to DIN 1333 [4].

In addition to the wet chemical characterization some of the laboratories analysed the material with spark emission spectrometry to check if there is agreement between SOES and wet chemistry. Tab. 11 shows the mean values of wet chemical and spark emission results as well as their standard deviations. The agreement between wet chemistry and SOES is given for all elements.

Tab. 11: Comparison wet chemistry vs. SOES (BAM-M112)

Element	**Wet chemical analysis**			**Spark emission**		
	Mass fraction in %	**Std.-dev.** in %	***n***	**Mass fraction** in %	**Std.-dev.** in %	***n***
Cu	8.2	0.3	8	8.8	1.8	13
Ni	5.33	0.21	8	5.6	0.5	11
Pt	5.4	0.5	6	5.44	0.24	7
Se	5.23	0.30	7	4.8	1.4	11
Te	5.27	0.24	7	5.5	2.1	13

Three laboratories determined the elements Ag, Bi, S and Tl with SOES as well. These elements are given for information.

6. Instructions for users and stability

The certified reference material BAM-M112 is intended for the calibration and quality control of spark emission spectrometers used for the analysis of materials with similar matrix composition. It is also suitable for validation of wet chemical analysis methods.
The surface of the material should be cleaned by turning or milling before analysis.
If chips prepared from the compact material are used for wet chemical analysis, a minimum sample intake of 0.1 g has to be used.
The material will remain stable provided that it is not subjected to excessive heat (e.g, during preparation of the working surface).

7. Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

8. References

[1] DIN EN ISO 17034, General requirements for the competence of reference material producers, 2016

[2] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[3] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[4] DIN 1333:1992-02 Zahlenangaben

9. Information on and purchase of the CRM

Certified reference materials BAM-M112 are supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 „Inorganic Reference Materials"
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Each disc of BAM-M112 will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.
Tel. +49 30 8104 1111.

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity (length)
Copper in BAM-M112:

1A	9.13	9.52	9.15	9.5
1E	9.27	9.48	9.37	9.48
2A	9.07	9.42	9.29	9.53
2E	9.39	9.4	9.1	9.41
3A	8.84	9.31	8.8	9.1
3E	8.88	8.96	8.45	9.01
4A	8.88	8.72	8.39	8.95
4E	8.79	8.63	8.37	8.86
5A	8.83	8.95	8.64	8.98
5E	8.98	9.16	8.46	9.07

Sample	*Number*	*Sum*	*Mean*	*Variance*		
Sample 1A	4	37.3	9.325	0.04576667		
Sample 1B	4	37.6	9.4	0.0102		
Sample 2A	4	37.31	9.3275	0.03909167		
Sample 2B	4	37.3	9.325	0.02256667		
Sample 3A	4	36.05	9.0125	0.057025		
Sample 3B	4	35.3	8.825	0.06536667		
Sample 4A	4	34.94	8.735	0.06216667		
Sample 4B	4	34.65	8.6625	0.04729167		
Sample 5A	4	35.4	8.85	0.0238		
Sample 5B	4	35.67	8.9175	0.098425		
			9.038			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.83314	9	0.314793333	6.67359197	3.4032E-05	2.21069698
Within groups	1.4151	30	0.04717			
Total	4.24824	39				
within-sd	0.217186556					
effective n	4.00					
s_bb	0.258661619					
s_bb_min	0.055179801					
u_bb	0.258661619	258.661619				
u_bb(rel.)	2.86193427					

Nickel in BAM-M112:

1A	6.48	6.45	6.54	6.3
1E	6.51	6.38	6.51	6.33
2A	6.51	6.4	6.45	6.35
2E	6.2	6.31	6.61	6.34
3A	6.47	6.18	6.44	6.29
3E	6.38	6.16	6.36	6.18
4A	6.05	6.11	6.32	6.1
4E	5.96	6.09	6.26	6.14
5A	6.17	5.98	6.34	6.11
5E	5.96	6.08	6.2	5.93

Sample	*Number*	*Sum*	*Mean*	*Variance*		
Sample 1A	4	25.77	6.4425	0.010425		
Sample 1B	4	25.73	6.4325	0.008425		
Sample 2A	4	25.71	6.4275	0.00469167		
Sample 2B	4	25.46	6.365	0.0303		
Sample 3A	4	25.38	6.345	0.0183		
Sample 3B	4	25.08	6.27	0.01346667		
Sample 4A	4	24.58	6.145	0.0143		
Sample 4B	4	24.45	6.1125	0.015425		
Sample 5A	4	24.6	6.15	0.02233333		
Sample 5B	4	24.17	6.0425	0.015225		
			6.27325			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.8084025	9	0.0898225	5.87491143	0.00010307	2.21069698
Within groups	0.458675	30	0.015289167			
Total	1.2670775	39				
within-sd	0.12364937					
effective n	4.00					
s_bb	0.136503968					
s_bb_min	0.031415147					
u_bb	0.136503968	136.503968				
u_bb(rel.)	2.175968887					

Platinum in BAM-M112:

1A	6.72	6.85	6.69	6.59
1E	6.98	6.7	6.86	6.48
2A	6.91	6.82	6.73	6.43
2E	6.63	6.57	6.83	6.74
3A	7.06	6.58	6.73	6.69
3E	6.53	6.55	6.95	6.61
4A	6.58	6.46	6.77	6.55
4E	6.41	6.37	6.9	6.56
5A	6.6	6.59	6.79	6.51
5E	6.6	6.5	6.83	6.45

Sample	*Number*	*Sum*	*Mean*	*Variance*		
Sample 1A	4	26.85	6.7125	0.01149167		
Sample 1B	4	27.02	6.755	0.04676667		
Sample 2A	4	26.89	6.7225	0.043425		
Sample 2B	4	26.77	6.6925	0.01335833		
Sample 3A	4	27.06	6.765	0.0427		
Sample 3B	4	26.64	6.66	0.03853333		
Sample 4A	4	26.36	6.59	0.017		
Sample 4B	4	26.24	6.56	0.05806667		
Sample 5A	4	26.49	6.6225	0.01409167		
Sample 5B	4	26.38	6.595	0.02843333		
			6.6675			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.19095	9	0.021216667	0.67597706	0.72400949	2.21069698
Within groups	0.9416	30	0.031386667			
Total	1.13255	39				
within-sd	0.177162825					
effective n	4.00					
s_bb	0					
s_bb_min	0.045011117					
u_bb	0.045011117	45.0111166				
u_bb(rel.)	0.675082364					

Selenium in BAM-M112:

1A	4.65	4.73	4.83	4.78
1E	4.82	4.79	4.81	4.93
2A	4.67	5.03	4.78	4.89
2E	4.77	4.87	4.63	4.83
3A	4.8	4.68	4.7	4.8
3E	4.7	4.5	4.57	4.59
4A	4.8	4.7	4.51	4.8
4E	4.52	4.57	4.66	4.81
5A	4.69	4.64	4.8	4.67
5E	4.52	4.4	4.45	4.33

Sample	*Number*	*Sum*	*Mean*	*Variance*		
Sample 1A	4	18.99	4.7475	0.00589167		
Sample 1B	4	19.35	4.8375	0.00395833		
Sample 2A	4	19.37	4.8425	0.02369167		
Sample 2B	4	19.1	4.775	0.01103333		
Sample 3A	4	18.98	4.745	0.0041		
Sample 3B	4	18.36	4.59	0.00686667		
Sample 4A	4	18.81	4.7025	0.01869167		
Sample 4B	4	18.56	4.64	0.0162		
Sample 5A	4	18.8	4.7	0.00486667		
Sample 5B	4	17.7	4.425	0.00643333		
			4.7005			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.56179	9	0.062421111	6.13575797	7.1177E-05	2.21069698
Within groups	0.3052	30	0.010173333			
Total	0.86699	39				
within-sd	0.100862943					
effective n	4.00					
s_bb	0.114288864					
s_bb_min	0.025625882					
u_bb	0.114288864	114.288864				
u_bb(rel.)	2.431419297					

Tellurium in BAM-M112:

1A	6.52	6.3	6.46	6.53
1E	6.38	6.56	6.41	6.39
2A	6.25	6.36	6.31	6.52
2E	6.38	6.45	6.53	6.43
3A	6.41	6.46	6.46	6.33
3E	6.22	6.22	6.29	6.33
4A	6.17	6.04	6.08	6.28
4E	6.19	6.26	6.21	6.2
5A	6.09	6.4	6.18	6.32
5E	6.02	6.43	6.17	6.06

Sample	*Number*	*Sum*	*Mean*	*Variance*		
Sample 1A	4	25.81	6.4525	0.01129167		
Sample 1B	4	25.74	6.435	0.0071		
Sample 2A	4	25.44	6.36	0.0134		
Sample 2B	4	25.79	6.4475	0.00389167		
Sample 3A	4	25.66	6.415	0.00376667		
Sample 3B	4	25.06	6.265	0.00296667		
Sample 4A	4	24.57	6.1425	0.01135833		
Sample 4B	4	24.86	6.215	0.00096667		
Sample 5A	4	24.99	6.2475	0.01929167		
Sample 5B	4	24.68	6.17	0.03406667		
			6.315			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.5229	9	0.0581	5.3746531	0.00021471	2.21069698
Within groups	0.3243	30	0.01081			
Total	0.8472	39				
within-sd	0.10397115					
effective n	4.00					
s_bb	0.10873132					
s_bb_min	0.026415573					
u_bb	0.10873132	108.73132				
u_bb(rel.)	1.721794461					

Annex 2: Calculation of uncertainty contribution of potential inhomogeneity (area)
Copper in BAM-M112:

at:	Lab. A				
r_0	8.6				
r_in	8.58	8.67	8.8	8.7	
r_out	8.55	8.73	8.78	8.64	
at:	Lab. B				
r_0	9				
r_in	9.3	9.3	9.3	9.9	
r_out	9.1	9.3	9.5	9.3	

at:	Lab. A					
r_0	*8.53*	*8.67*				
r_in	8.58	8.67	8.80	8.70		
r_out	8.55	8.73	8.78	8.64		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.010875	2	0.0054375	0.584582895	0.582399717	4.737414128
Within groups	0.065110526	7	0.009301504			
Total	0.075985526	9				
within-sd	0.096444304					
effective n	3.20					
s_bb	0			u_bb(rel.)	0.4549	
s_bb_min	0.039417092					
u_bb	0.039417092					
at:	Lab. B					
r_0	*8.84*	*9.16*				
r_in	9.30	9.30	9.30	9.90		
r_out	9.10	9.30	9.50	9.30		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.27	2	0.135	2.350746269	0.165576512	4.737414128
Within groups	0.402	7	0.057428571			
Total	0.672	9				
within-sd	0.239642591					
effective n	3.20					
s_bb	0.155695444			u_bb(rel.)	1.6741	
s_bb_min	0.097942685					
u_bb	0.155695444					
			u_bb (rel.), mean (Labs. 1 + 5):			1.2267

Nickel in BAM-M112:

at:	Lab. A				
r_0	5.4				
r_in	5.49	5.56	5.57	5.55	
r_out	5.46	5.47	5.54	5.53	
at:	Lab. B				
r_0	5				
r_in	5.1	5.2	5.1	5.2	
r_out	5.1	5.1	5.1	5.2	

at:	Lab. A					
r_0	*5.37*	*5.43*				
r_in	5.49	5.56	5.57	5.55		
r_out	5.46	5.47	5.54	5.53		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.027135	2	0.0135675	9.128891231	0.011206239	4.737414128
Within groups	0.010403509	7	0.001486216			
Total	0.037538509	9				
within-sd	0.038551466					
effective n	3.20					
s_bb	0.061444295			u_bb(rel.)	1.1178	
s_bb_min	0.015756106					
u_bb	0.061444295					
at:	Lab. B					
r_0	*4.96*	*5.04*				
r_in	5.10	5.20	5.10	5.20		
r_out	5.10	5.10	5.10	5.20		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.0315	2	0.01575	5.422131148	0.037809249	4.737414128
Within groups	0.020333333	7	0.002904762			
Total	0.051833333	9				
within-sd	0.053895843					
effective n	3.20					
s_bb	0.063357217			u_bb(rel.)	1.2399	
s_bb_min	0.022027402					
u_bb	0.063357217					
			u_bb (rel.), mean (Labs. 1 + 5):			1.1804

Platinum in BAM-M112:

at:	Lab. A				
r_0	5.61				
r_in	5.88	6.07	6.06	5.8	
r_out	5.57	5.92	5.87	5.89	

at:	Lab. B				
r_0	5.2				
r_in	5.3	5.4	5.4	5.3	
r_out	5.3	5.4	5.6	5.5	

at:	Lab. A					
r_0	*5.50*	*5.72*				
r_in	5.88	6.07	6.06	5.80		
r_out	5.57	5.92	5.87	5.89		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.15801	2	0.079005	3.523864592	0.087341712	4.737414128
Within groups	0.156939912	7	0.022419987			
Total	0.314949912	9				
within-sd	0.149733054					
effective n	3.20					
s_bb	0.132976751			u_bb(rel.)	2.2817	
s_bb_min	0.061196373					
u_bb	0.132976751					

at:	Lab. B					
r_0	*5.12*	*5.28*				
r_in	5.30	5.40	5.40	5.30		
r_out	5.30	5.40	5.60	5.50		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.084	2	0.042	4.121495327	0.065629259	4.737414128
Within groups	0.071333333	7	0.010190476			
Total	0.155333333	9				
within-sd	0.100947888					
effective n	3.20					
s_bb	0.099701937			u_bb(rel.)	1.8601	
s_bb_min	0.041257721					
u_bb	0.099701937					
			u_bb (rel.), mean (Labs. 1 + 5):			2.0816

Selenium in BAM-M112:

at:	Lab. A				
r_0	4.52				
r_in	4.6	4.58	4.66	4.49	
r_out	4.65	4.48	4.46	4.5	
at:	Lab. B				
r_0	4.2				
r_in	4.16	4.41	4.66	4.72	
r_out	4.41	4.28	4.53	4.66	

at:	Lab. A					
r_0	*4.46*	*4.58*				
r_in	4.60	4.58	4.66	4.49		
r_out	4.65	4.48	4.46	4.50		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00889	2	0.004445	0.708635415	0.524497698	4.737414128
Within groups	0.043908333	7	0.006272619			
Total	0.052798333	9				
within-sd	0.079199868					
effective n	3.20					
s_bb	0			u_bb(rel.)	0.7120	
s_bb_min	0.032369237					
u_bb	0.032369237					
at:	Lab. B					
r_0	*4.05*	*4.35*				
r_in	4.16	4.41	4.66	4.72		
r_out	4.41	4.28	4.53	4.66		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.124364198	2	0.062182099	1.346935159	0.319965329	4.737414128
Within groups	0.323159351	7	0.046165622			
Total	0.447523548	9				
within-sd	0.214861866					
effective n	3.20					
s_bb	0.070747079			u_bb(rel.)	1.9856	
s_bb_min	0.087814725					
u_bb	0.087814725					
			u_bb (rel.), mean (Labs. 1 + 5):			1.4916

Tellurium in BAM-M112:

at:		Lab. A			
r_0	7.18				
r_in	7.06	6.94	7.22	7.13	
r_out	7.07	6.94	6.94	6.96	

at:		Lab. B			
r_0	4.8				
r_in	4.8	4.9	4.9	5	
r_out	5	4.9	4.9	5.1	

at:		Lab. A				
r_0	*7.12*	*7.24*				
r_in	7.06	6.94	7.22	7.13		
r_out	7.07	6.94	6.94	6.96		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.05901	2	0.029505	3.377490084	0.094022815	4.737414128
Within groups	0.061150439	7	0.008735777			
Total	0.120160439	9				
within-sd	0.093465378					
effective n	3.20					
s_bb	0.080562908			u_bb(rel.)	1.1408	
s_bb_min	0.038199596					
u_bb	0.080562908					
at:		Lab. B				
r_0	*4.74*	*4.86*				
r_in	4.80	4.90	4.90	5.00		
r_out	5.00	4.90	4.90	5.10		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.0415	2	0.02075	2.609281437	0.142322214	4.737414128
Within groups	0.055666667	7	0.007952381			
Total	0.097166667	9				
within-sd	0.089176123					
effective n	3.20					
s_bb	0.063239671			u_bb(rel.)	1.2880	
s_bb_min	0.036446564					
u_bb	0.063239671					
			u_bb (rel.), mean (Labs. 1 + 5):			1.2166