Certification Report

Certified Reference Material

BAM-M397/397a

CuSn4Zn2PS

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Summary

This report describes preparation, analysis and certification of copper-based reference materials BAM-M397 and BAM-M397a, CuSn4Zn2PS.
The certified reference materials (CRM) are available in the form of discs (40 mm diameter and 30 mm height). They are intended for establishing and checking the calibration of spark optical emission and X-ray fluorescence spectrometers for the analysis of samples of similar materials. They are also suitable for wet chemical analysis.

The following mass fractions and uncertainties have been certified:

BAM-M397

Element	Mass fraction [1] in %	Uncertainty [2] in %
Zn	1.96	0.05
Pb	0.229	0.008
Sn	3.99	0.08
Ni	0.336	0.006
Sb	0.097	0.004
S	0.459	0.029

[1] Unweighted mean value of the means of accepted sets of data (consisting of at least 5 but usually 6 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).

BAM-M397a

Element	Mass fraction [1] in %	Uncertainty [2] in %
Zn	1.87	0.06
Pb	0.227	0.008
Sn	3.98	0.10
Ni	0.337	0.007
Sb	0.097	0.004
S	0.45	0.04

[3] Unweighted mean value of the means of accepted sets of data (consisting of at least 5 but usually 6 single results), each set being obtained by a different laboratory and/or a different method of measurement.

[4] 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).

The certified values are based on the results of ten laboratories (BAM-M397a: nine) which participated in the certification inter-laboratory comparison.

The mass fractions of As (2.9 mg/kg), Te and Se are given as value for information (both < 1 mg/kg).

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List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
ETAAS	electrothermal atomic absorption spectrometry
FAAS	flame atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
GD-MS	glow discharge mass spectrometry
SOES	spark optical emission spectrometry
XRF	X-ray fluorescence 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 – 19)
IMS	ICP-MS (Tables 2 – 19)
A	FAAS (Tables 2 – 19)
EA	ETAAS (Tables 2 – 19)
P	spectrophotometry (Tables 2 – 19)
GD	GD-MS (Tables 2 – 19)
V	combustion (Tables 2 – 19)

1. Introduction

In the metal-producing and metal-working industry mainly spark optical emission spectrometry (SOES) and X-ray fluorescence spectrometry (XRF) are used for reception inspection of raw materials, e.g. scrap, for quality control of end products and production control. These time-saving analytical techniques require suitable reference materials for calibration and recalibration.

The gunmetal CuSn4Zn2PS is foreseen as a material for drinking water applications. The idea to produce a CuSn4Zn2PS reference material was the outcome of discussions within the German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB), especially of the working group „Copper" of the Committee of Chemists within 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 the laboratories participating in this certification project are highly experienced with copper and brass analysis and had participated in earlier inter-laboratory comparisons or had a laboratory accreditation, there was no preceding round robin for qualification.

Certification of reference materials BAM-M397/BAM-M397a was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2. Companies/laboratories involved

<u>Manufacturing of the material</u>

– Gebr. Kemper GmbH + Co. KG, Olpe, Germany

<u>Test for homogeneity</u>

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

<u>Participants in the certification inter-laboratory comparison</u>

– Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim, Germany
– Aurubis AG, Hamburg, Germany
– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
– Diehl Metall Stiftung & Co KG, Röthenbach, Germany
– Institut für Materialprüfung Glörfeld GmbH, Willich, Germany
– KME Germany GmbH & Co. KG, Osnabrück, Germany
– Montanwerke Brixlegg AG, Brixlegg, Austria
– RIO GmbH, Siegen, Germany
– VDM-Metals GmbH, Werdohl, Germany
– Wieland-Werke AG, Vöhringen, Germany

<u>Additional participants in the spark emission inter-laboratory comparison</u>

– Gebr. Kemper GmbH + Co. KG, Olpe, Germany
– TAZ GmbH, Eurasburg, Germany

<u>Statistical evaluation of the data</u>

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

3. Candidate material

CuSn4Zn2PS was taken from the normal production process within Gebr. Kemper GmbH + Co. KG, Olpe. From the raw material 10 rods with a diameter of ca. 40 mm, but different length were produced by Gebr. Kemper GmbH + Co. KG (Rods 1, 6-10: length 3 m, Rods 2 and 3: length 1.1 m, Rod 4: length 1.8 m). From these rods one (Rods 2 and 3), two (Rod 4) or three (Rods 1, 6-10) samples per rod (in total 25) were cut for homogeneity testing and chemical analysis.
Due to some inhomogeneities not all of the rods were suitable as candidate RM. Rods 2, 8, 10 and the first part of Rod 4 were taken as CRM BAM-M397, Rod 9 and the second parts of Rods 1 and 6 were taken as BAM-M397a.

In total, about 460 discs with a diameter of ca. 40 mm and 30 mm were received from the total batch.

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 volatise 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):

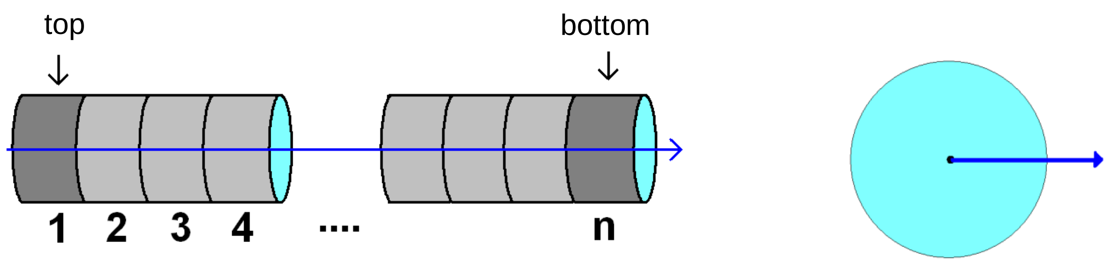

Fig. 1: Axial and radial composition gradient

Therefore, it is necessary to investigate the raw material for both axial and radial inhomogeneities. Axial homogeneity testing of the candidate material was performed on the 25 discs using spark emission spectrometry. All tests were carried out with a SpectroLab spark emission spectrometer. Each disc was analysed six times.
Homogeneity testing of zinc, lead, tin, nickel, and antimony was done using XRF (see Annex 1). An estimation of inhomogeneity was obtained by subtracting the variance of the element contents in the samples tested for homogeneity from the variance obtained by measuring the same sample 23 times (s(instrument). This was done only over the length of the rods.

The estimate of analyte-specific inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [3] 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). 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, two discs were tested for homogeneity over the area (possible segregation from the outer part to the centre). To perform this test, SOES analysis was carried out in circles (outer circle: 4 sparks, inner circle: 4 sparks; centre: 1 spark).

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 taking into account 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 one measured have a mean equal to the value measured, and a standard deviation equal to the average within-variation. This resembles the situation were one could take two independent measurements at the same place, with values deviating by the average standard deviation (non-destructive testing method). A first guess for the average standard deviation may be calculated from the data for r_in (inner circle) and r_out (outer circle). As results from these calculations an inhomogeneity factor for the radius and one for the height of the disc is obtained. From these values a combined inhomogeneity factor is calculated. This factor is compared with the within standard deviation calculated from the ANOVA data. The higher factor is used for uncertainty calculation. Annex 2 shows the results of the calculations.

5. Characterisation study

5.1 Analytical methods

Ten laboratories participated in the certification inter-laboratory comparison. All laboratories were highly experienced in the analysis of copper and copper alloys and participated successfully in former certification inter-laboratory comparisons. 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 for their determinations. Table 1 shows the analytical methods used by the participating laboratories.

Table 1: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Sn, Zn	0.25 g	Dissolution with $HCl/HNO_3/H_3BO_3/HF$	ICP-OES (DIN EN 15605), calibration with commercial solutions (Merck), matrix matching with Cu
	Ni, Sb, Pb, S	1 g	Dissolution with HCl, HNO_3, H_3BO_3, HF	ICP-OES (DIN EN 15605), calibration with commercial solutions (Merck), matrix matching with Cu
	As, Te, Se	0.5 g	Dissolution with HNO_3	ETAAS (DIN EN 14935), calibration with commercial solutions (Merck), matrix matching with Cu
2	As, Ni, P, Pb, S, Sb, Se, Zn	0.1 g	Dissolution with HNO_3/HCl (3:1)	ICP-OES, calibration with commercial solutions (Merck), matrix matching with Cu
	Ni, Pb, Zn	1 g	Dissolution with HCl/HNO_3 (2:1)	FAAS, calibration with commercial solutions (Merck), matrix matching with Cu
	Sb	0.4 g	Dissolution with HCl/H_2O_2	Spectrophotometry (DIN EN 14937-1), calibration with commercial solution (Merck), matrix matching with Cu
3	Pb, Ni, Sb	0.5 g	Dissolution with $HNO_3/HF/HCl$	ICP-OES, calibration with commercial solutions (Spex), matrix matching with Cu
	Sn, Zn, S	0.25 g	Dissolution with $HNO_3/HF/HCl$	ICP-OES, calibration with commercial solutions (Spex)
5	Zn,Sn,Se,As,Te,Sb, Ni,Pb	0.5 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), mono-element solutions prepared from pure Zn and pure Sn, other elements commercial mono-element solutions
6	Sn, Zn, Pb, Ni, S, Sb	1 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), mono-element solutions prepared from Zn 99.99 %, Sn 99.99 %, Pb 99.99 %, Ni 99.9 %, K_2SO_4 s.p. and Sb 99.9 %
	S	1 g	Combustion with subsequent titration of H_2SO_4 with NaOH	Titration, calibration with K_2SO_4 s.p.
7	Zn, Pb, Sn, Ni, S, Sb	1 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), mono-element solutions prepared from pure substances
	Sb	1 g	Dissolution with HCl/HNO_3 (3:1)	ICP-MS with matrix matched standards (Cu), commercial mono-element solution (Bernd Kraft)
	As, Se, Te			GD-MS, calibration with standards prepared from pure substances
8	Sn, Zn, S	0.1 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), commercial mono-element solutions (traceable via NIST-SRM)
	Pb, Ni	0.5 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), commercial mono-element solutions (traceable via NIST-SRM)
10	Zn, Ni, Pb, Sb, Sn, S	0.25 g	Dissolution with HNO_3/HF	ICP-OES, with matrix matched standards (Cu, Zn), commercial certified mono-element solutions

Table 1: Analytical procedures used by the participating laboratories (continued)

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
11	Ni, Pb, Sb, Sn, Zn	1 g	Dissolution with HCl/H_2O_2	ICP-OES with matrix matched standards (Cu), commercial mono-element solutions (Alfa Aesar)
14	Zn, Ni, Pb, Sb, Sn, S	0.5 g	Dissolution with HCl/HNO_3 (3:1)	ICP-OES with matrix matched standards (Cu), commercial mono-element solutions (Roth)
	S			Combustion with infrared detection

For all analytical methods where a calibration was necessary it was performed using liquid standard solutions. All participating laboratories were asked to use only standard solutions prepared from pure metals or stoichiometric compounds or internally checked commercial calibration solutions.

5.2 Analytical results and statistical evaluation

The analytical results of the inter-laboratory certification comparison are listed in Tables 2 to 19. 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 ($\bar{s}_i$). 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. Outliers which have been excluded are highlighted.
In the related figures for each laboratory its mean value and single standard deviation is given.

Table 2: Results for Zn in BAM-M397

Lab./Meth.	1/I	8/I	5/I	11/I	10/I	2/I	2/A	14/I	7/I	6/I	3/I		
M_i [%]	1.84	1.92	1.927	1.95	1.936	1.99	1.979	1.99	2.00	2.011	2.015		*n*
	1.89	1.93	1.914	1.94	1.937	1.97	1.977	2.03	2.02	2.023	2.017		11
	1.91	1.91	1.922	1.92	1.940	1.98	1.982	2.01	1.99	2.044	2.025		
	1.90	1.91	1.910	1.92	1.937	1.91	1.997	1.96	1.96	2.009	2.041		
	1.90	1.91	1.906	1.93	1.954	1.95	1.976	1.95	1.96	2.052	2.061		
	1.90	1.92	1.913	1.93	1.944		1.969	1.95	1.97	2.033	2.072		
							1.959						
M [%]	**1.89**	**1.91**	**1.92**	**1.93**	**1.94**	**1.96**	**1.98**	**1.98**	**1.98**	**2.03**	**2.04**		**1.96**
s[%]	0.0253	0.0071	0.0078	0.0088	0.0069	0.0308	0.0117	0.0353	0.0243	0.0175	0.0238		0.047
												s_M [%]	0.021
s_{rel}	0.0134	0.0037	0.0041	0.0045	0.0035	0.0157	0.0059	0.0178	0.0122	0.0086	0.0117	$\bar{s}_i$ [%]	0.0241

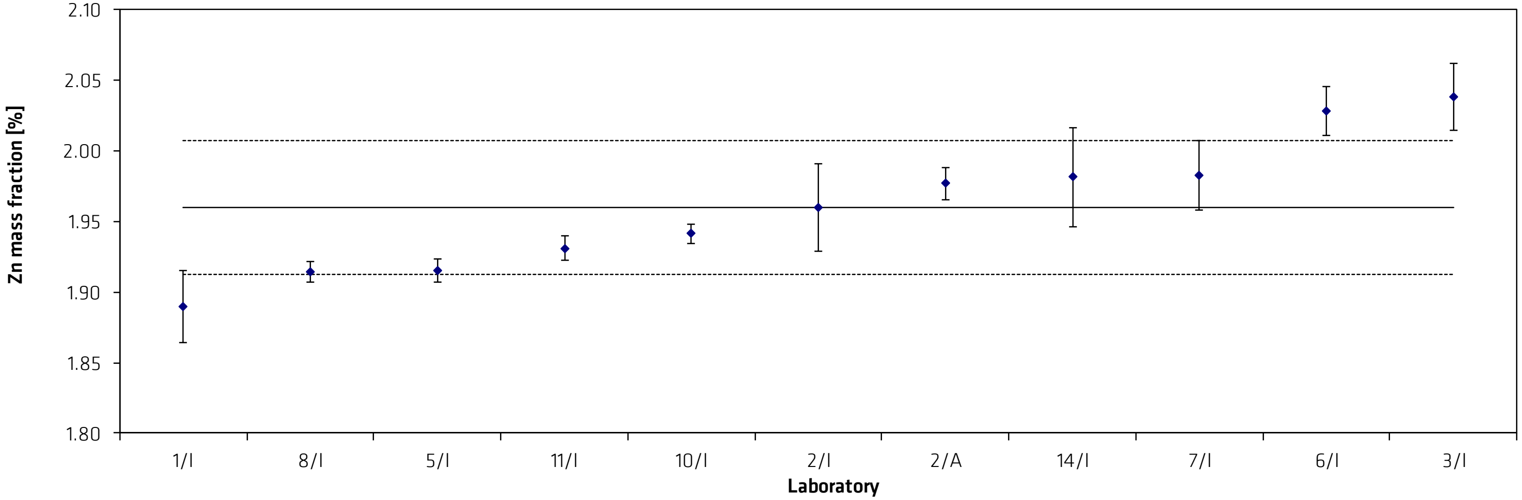

Table 3: Results for Pb in BAM-M397

Lab./Meth.	14/I	8/I	5/I	2/I	3/I	11/I	1/I	2/A	7/I	10/I	6/I		
M_i [%]	0.200	0.209	0.218	0.229	0.222	0.226	0.230	0.225	0.234	0.236	0.240		*n*
	0.204	0.208	0.218	0.225	0.223	0.225	0.250	0.232	0.236	0.236	0.242		9
	0.204	0.207	0.218	0.228	0.221	0.224	0.230	0.229	0.235	0.235	0.238		
	0.197	0.207	0.215	0.211	0.228	0.224	0.220	0.233	0.233	0.237	0.241		
	0.194	0.207	0.215	0.220	0.223	0.224	0.230	0.228	0.233	0.234	0.237		
	0.193	0.206	0.216	0.217	0.224	0.225	0.220	0.232	0.238	0.239	0.239		
								0.231					
M [%]	0.199	0.207	0.217	0.222	0.224	0.225	0.230	0.230	0.235	0.236	0.240		0.229
s[%]	0.005	0.001	0.002	0.007	0.002	0.001	0.011	0.003	0.002	0.002	0.002		0.008
												s_M [%]	0.005
s_{rel}	0.025	0.005	0.007	0.032	0.011	0.004	0.048	0.012	0.008	0.008	0.008	$\bar{s}_i$ [%]	0.033

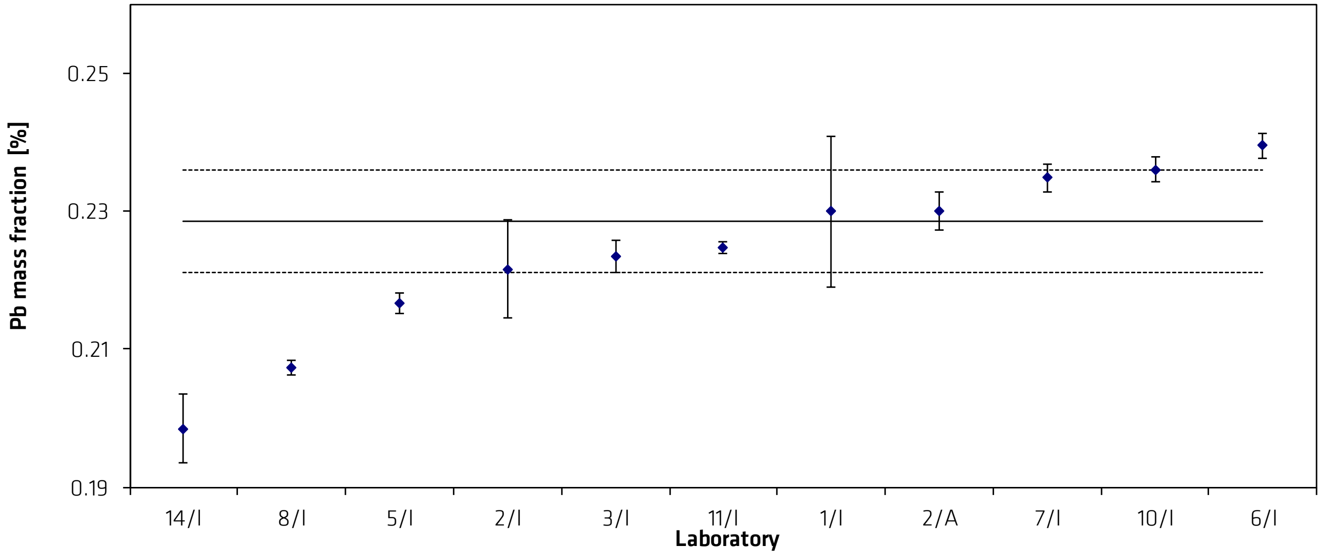

Table 4: Results for Sn in BAM-M397

Lab./Meth.	8/I	6/I	10/I	5/I	1/I	7/I	14/I	11/I	3/I		
M_i [%]	3.823	3.922	3.921	3.958	3.96	4.01	4.09	4.074	4.092		*n*
	3.835	3.905	3.908	3.966	3.94	4.01	4.04	4.070	4.104		9
	3.843	3.891	3.893	3.963	3.92	4.01	4.10	4.081	4.128		
	3.860	3.911	3.928	3.959	3.98	4.01	4.06	4.056	4.199		
	3.868	3.876	3.883	3.948	3.98	4.00	4.00	4.097	4.149		
	3.865	3.917	3.948	3.957	4.00	4.00	4.09	4.047	4.145		
M [%]	**3.849**	**3.904**	**3.913**	**3.959**	**3.963**	**4.007**	**4.066**	**4.071**	**4.136**		**3.985**
s[%]	0.0181	0.0173	0.0238	0.0062	0.0294	0.0060	0.0370	0.0177	0.0381		0.0926
										s_M [%]	0.0242
s_{rel}	0.0047	0.0044	0.0061	0.0016	0.0074	0.0015	0.0091	0.0043	0.0092	$\bar{s}_i$ [%]	0.023

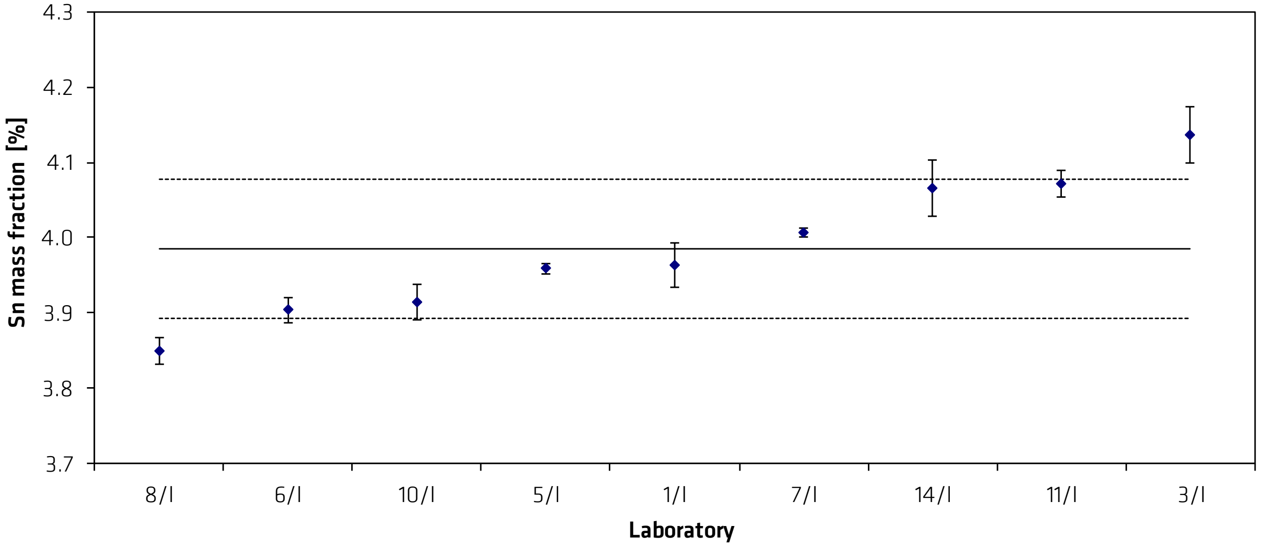

Table 5: Results for Ni in BAM-M397

Lab./Meth.	1/I	8/I	10/I	14/I	2/I	3/I	2/A	11/I	6/I	5/I	7/I		
M_i [%]	0.32	0.325	0.330	0.34	0.339	0.336	0.340	0.341	0.345	0.346	0.347		*n*
	0.32	0.323	0.329	0.34	0.333	0.335	0.337	0.340	0.344	0.344	0.345		11
	0.32	0.324	0.332	0.34	0.336	0.338	0.339	0.341	0.341	0.346	0.347		
	0.32	0.325	0.330	0.33	0.327	0.338	0.335	0.343	0.340	0.343	0.346		
	0.33	0.322	0.333	0.32	0.329	0.335	0.338	0.341	0.344	0.342	0.348		
	0.32	0.323	0.328	0.33	0.338	0.336	0.338	0.343	0.342	0.342	0.348		
							0.339						
M [%]	0.322	0.324	0.330	0.333	0.334	0.336	0.338	0.341	0.343	0.344	0.347		0.336
s[%]	0.0041	0.0012	0.0018	0.0060	0.0047	0.0014	0.0016	0.0011	0.0020	0.0018	0.0012		0.0081
												s_M [%]	0.0029
s_{rel}	0.0127	0.0037	0.0055	0.0179	0.0141	0.0041	0.0048	0.0033	0.0057	0.0053	0.0034	$\bar{s}_i$ [%]	0.024

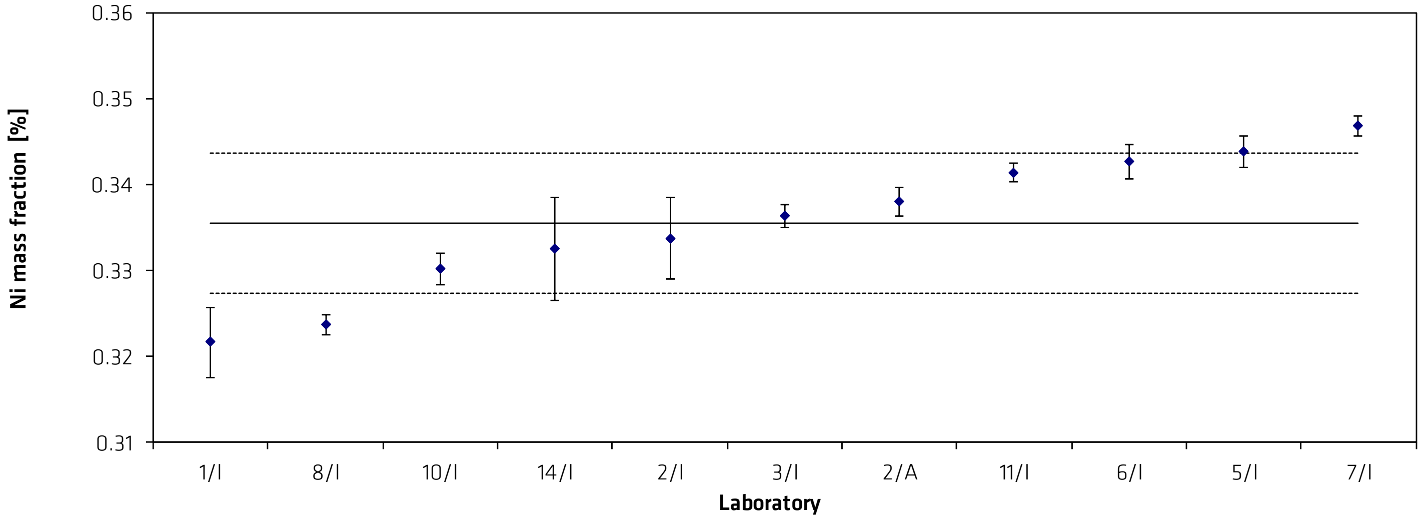

Table 6: Results for Sb in BAM-M397

Lab./Meth.	2/I	6/I	10/I	5/I	2/P	1/I	7/IMS	14/I	7/I	3/I	11/I	8/I		
M_i [%]	0.091	0.088	0.096	0.096	0.0975	0.096	0.097	0.093	0.100	0.100	0.1080	0.102		*n*
	0.089	0.090	0.095	0.096	0.0952	0.097	0.099	0.101	0.100	0.100	0.1037	0.104		12
	0.090	0.089	0.095	0.096	0.0984	0.096	0.096	0.102	0.100	0.102	0.0964	0.104		
	0.087	0.088	0.095	0.096	0.0974	0.096	0.097	0.099	0.100	0.102	0.1003	0.102		
	0.086	0.090	0.094	0.096	0.0975	0.099	0.096	0.098	0.100	0.100	0.1039	0.103		
		0.089	0.095	0.096	0.0938	0.096	0.098	0.100	0.099	0.102	0.1047	0.105		
M [%]	**0.089**	**0.089**	**0.095**	**0.096**	**0.097**	**0.097**	**0.097**	**0.099**	**0.100**	**0.101**	**0.103**	**0.103**		**0.097**
s[%]	0.0021	0.0009	0.0005	0.0000	0.0017	0.0012	0.0012	0.0033	0.0004	0.0011	0.0040	0.0012		0.0047
													s_M [%]	0.0019
s_{rel}	0.0239	0.0100	0.0054	0.0000	0.0180	0.0125	0.0120	0.0338	0.0041	0.0107	0.0389	0.0117	$\bar{s}_i$ [%]	0.048

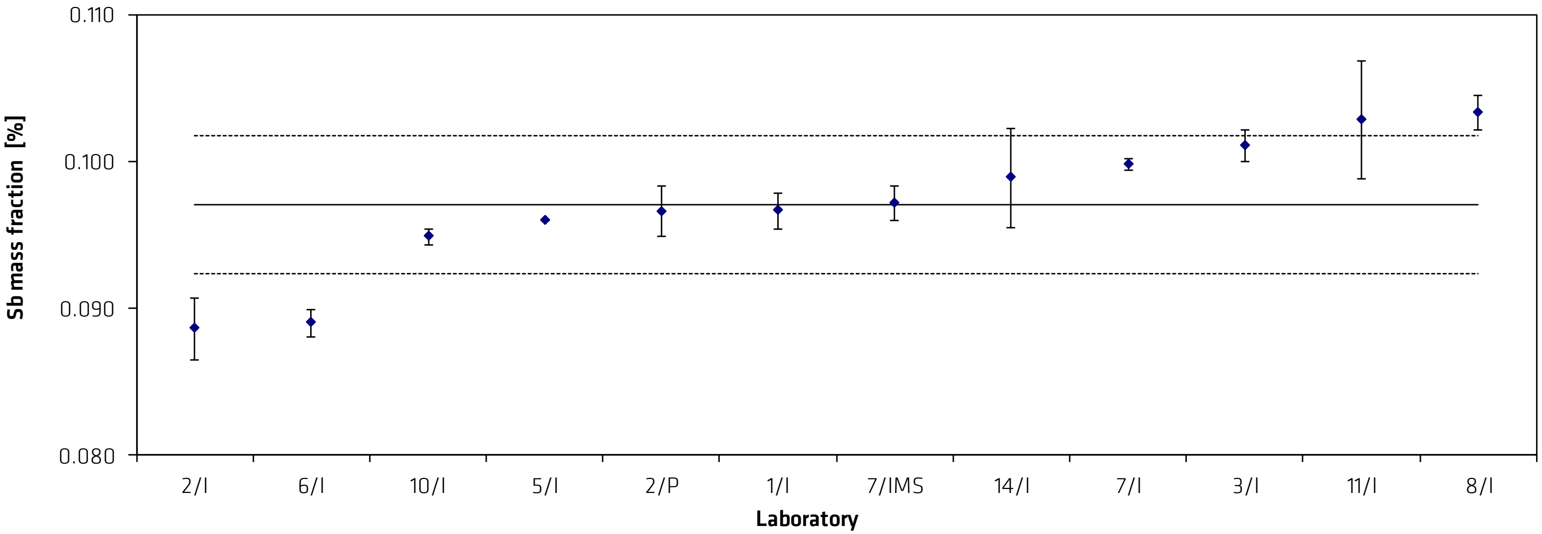

Table 7: Results for S in BAM-M397

Lab./Meth.	14/I	6/I	6/V	3/I	1/I	2/I	14/V	8/I		
M_i [%]	0.162	0.406	0.417	0.451	0.46	0.500	0.498	0.498		*n*
	0.162	0.407	0.420	0.454	0.45	0.495	0.489	0.501		7
	0.164	0.410	0.411	0.451	0.47	0.500	0.486	0.500		
	0.155	0.406	0.410	0.459	0.46	0.448	0.489	0.500		
	0.153	0.409	0.414	0.460	0.48	0.482	0.491	0.502		
	0.157	0.412	0.419	0.440	0.47	0.477		0.500		
M [%]	**0.159**	**0.408**	**0.415**	**0.453**	**0.465**	**0.483**	**0.491**	**0.500**		**0.459**
s[%]	0.0048	0.0024	0.0042	0.0072	0.0105	0.0198	0.0047	0.0013		0.0362
									s_M [%]	0.0088
s_{rel}	0.0300	0.0059	0.0100	0.0160	0.0226	0.0409	0.0095	0.0027	$\bar{s}_i$ [%]	0.079

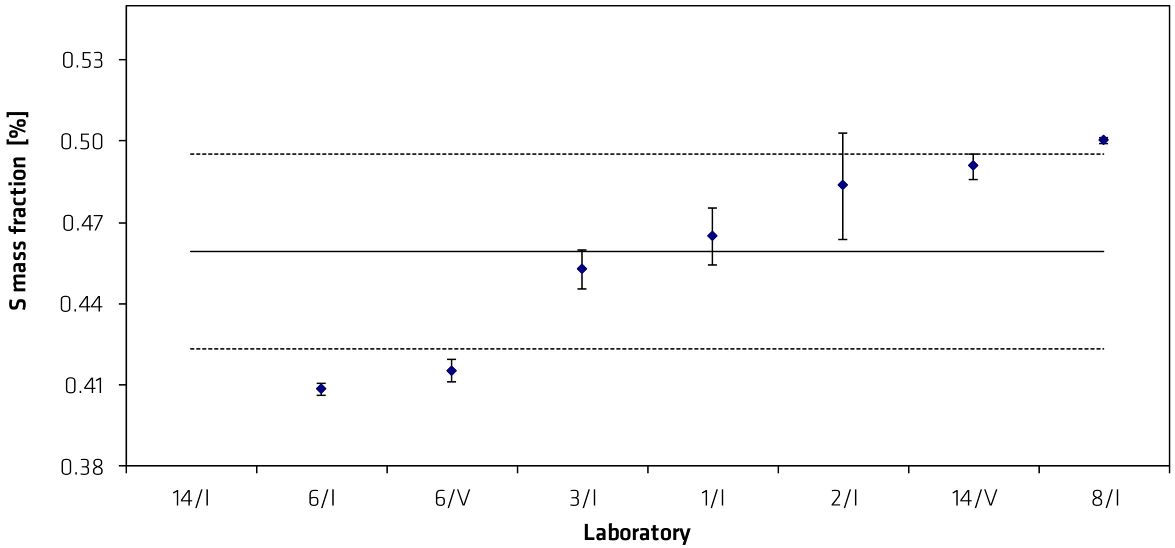

Table 8: Results for As in BAM-M397

Lab./Meth.	7/GD	8/I	2/I	1/EA	5/I		
M_i [mg/kg]	2.5	2.8	3.8	3.2	< 10		*n*
	2.7	2.7	3.1	3.3	< 10		4
	2.7	2.7	3.2	2.8	< 10		
	2.6	2.8	2.7	3.4	< 10		
	2.6	2.8	2.5	3.0	< 10		
	2.9	2.7	2.7	2.6	< 10		
M [mg/kg]	2.67	2.72	3.02	3.06	< 10		2.87
s[mg/kg]	0.137	0.051	0.468	0.298			0.199
						s_M [%]	0.287
s_{rel}	0.0512	0.0187	0.1552	0.0975		$\bar{s}_i$ [%]	0.069

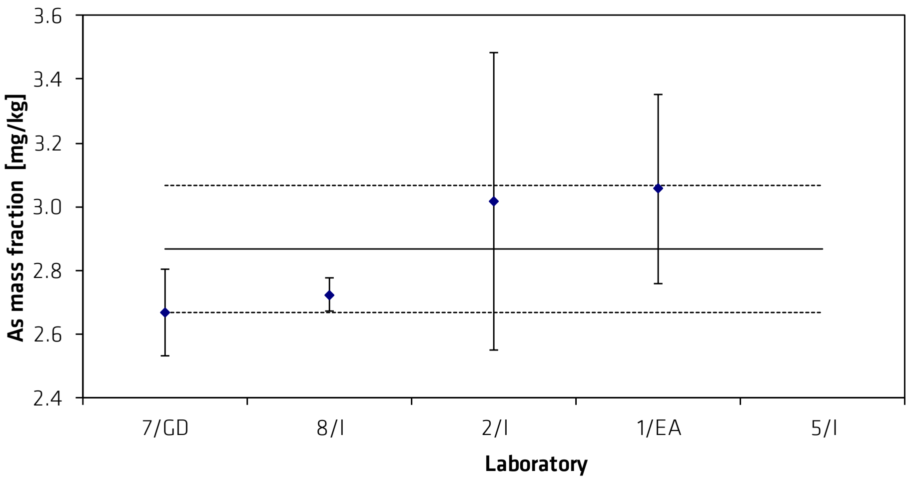

Table 9: Results for Te in BAM-M397

Lab./Meth.	7/GD	8/I	1/EA	5/I		
M_i [mg/kg]	0.1	< 0.1	< 1	< 10		*n*
	0.1	< 0.1	< 1	< 10		1
	0.1	< 0.1	< 1	< 10		
	0.1	< 0.1		< 10		
	0.1	< 0.1		< 10		
	0.1	< 0.1		< 10		
M [mg/kg]	**0.10**	**< 0.1**	**< 1**	**< 10**		**0.10**
s[mg/kg]	0.000					
					s_M [%]	0.000
s_{rel}	0.0000				$\bar{s}_i$ [%]	0.000

Table 10: Results for Se in BAM-M397

Lab./Meth.	7/GD	8/I	1/EA	5/I		
M_i [mg/kg]	0.3	0.50	< 1	< 10		*n*
	0.2	0.32	< 1	< 10		2
	0.3	0.30	< 1	< 10		
	0.3	0.36		< 10		
	0.4	0.46		< 10		
	0.4	0.36		< 10		
M [mg/kg]	**0.32**	**0.38**	**< 1**	**< 10**		**0.35**
s[mg/kg]	0.080	0.079				
					s_M [%]	0.000
s_{rel}	0.2508	0.2071			$\bar{s}_i$ [%]	0.000

Table 11: Results for Zn in BAM-M397a

Lab./Meth.	5/I	1/I	8/I	2/I	10/I	11/I	3/I	7/I	2/A	6/I		
M_i [%]	1.802	1.80	1.82	1.83	1.83	1.85	1.871	1.909	1.928	1.981		*n*
	1.801	1.77	1.82	1.87	1.85	1.86	1.887	1.906	1.926	2.020		10
	1.769	1.81	1.80	1.87	1.86	1.87	1.882	1.917	1.923	1.999		
	1.802	1.81	1.82	1.82	1.85	1.87	1.885	1.917	1.912	1.977		
	1.781	1.81	1.80	1.86	1.87	1.86	1.870	1.923	1.929	1.975		
	1.806	1.81	1.81	1.85	1.86	1.88	1.875	1.920	1.941	1.988		
									1.924			
M [%]	**1.79**	**1.80**	**1.81**	**1.85**	**1.85**	**1.87**	**1.88**	**1.92**	**1.93**	**1.99**		**1.87**
s[%]	0.0149	0.0160	0.0107	0.0216	0.0140	0.0104	0.0073	0.0065	0.0086	0.0171		0.0614
											s_M [%]	0.0135
s_{rel}	0.00832	0.00889	0.00587	0.01169	0.00753	0.00560	0.00390	0.00341	0.00448	0.00859	$\bar{s}_i$ [%]	0.03287

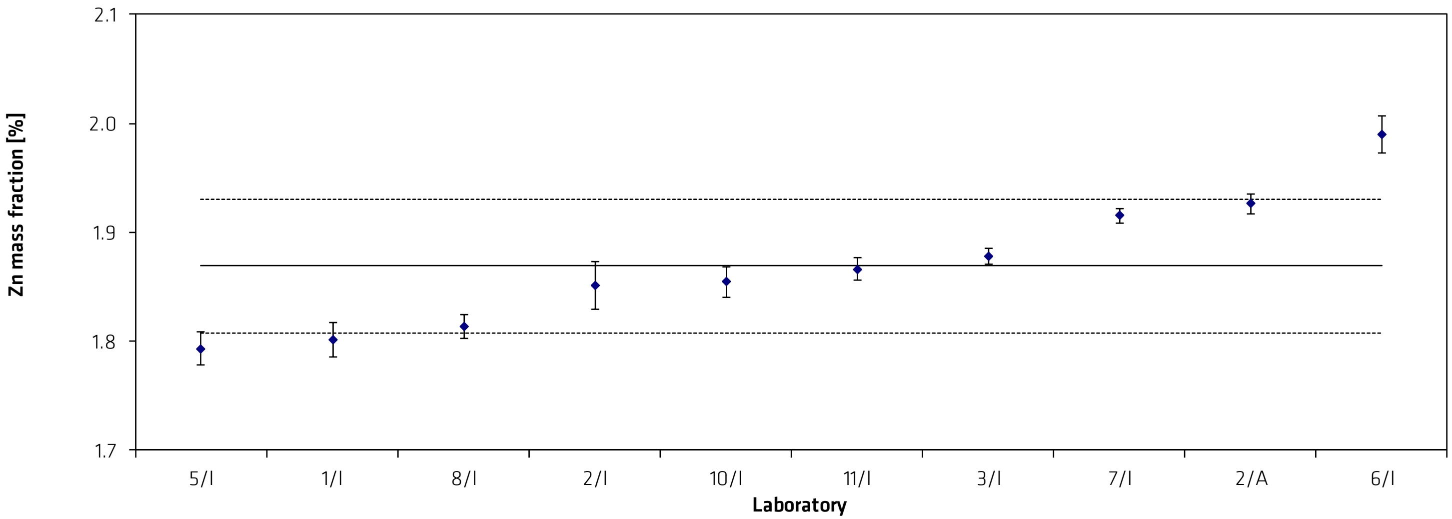

Table 12: Results for Pb in BAM-M397a

Lab./Meth.	8/I	5/I	2/I	1/I	3/I	11/I	2/A	7/I	6/I	10/I		
M_i [%]	0.206	0.219	0.210	0.230	0.227	0.226	0.229	0.233	0.234	0.236		*n*
	0.206	0.216	0.218	0.220	0.228	0.226	0.231	0.231	0.236	0.237		9
	0.206	0.215	0.229	0.230	0.225	0.227	0.235	0.233	0.233	0.236		
	0.206	0.217	0.205	0.220	0.224	0.228	0.233	0.234	0.235	0.240		
	0.207	0.216	0.226	0.220	0.229	0.229	0.228	0.232	0.230	0.238		
	0.207	0.218	0.226	0.220	0.229	0.228	0.232	0.232	0.232	0.235		
							0.229					
M [%]	0.206	0.217	0.219	0.223	0.227	0.227	0.231	0.233	0.233	0.237		0.227
s[%]	0.001	0.001	0.010	0.005	0.002	0.001	0.003	0.001	0.002	0.002		0.007
											s_M [%]	0.0040
s_{rel}	0.003	0.007	0.044	0.023	0.009	0.006	0.011	0.005	0.009	0.007	$\bar{s}_i$ [%]	0.030

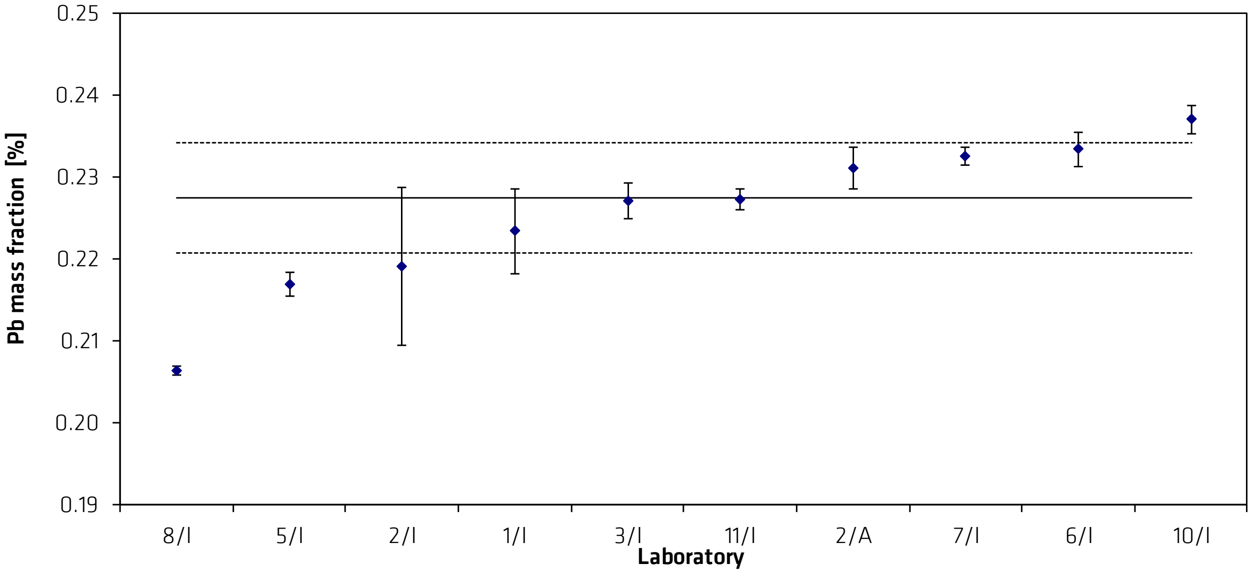

Table 13: Results for Sn in BAM-M397a

Lab./Meth.	8/I	6/I	10/I	5/I	1/I	7/I	11/I	3/I		
M_i [%]	3.825	3.891	3.930	3.980	4.02	4.016	4.092	4.119		*n*
	3.745	3.880	3.925	3.980	3.91	4.019	4.100	4.164		8
	3.756	3.873	3.931	3.940	3.91	4.012	4.088	4.181		
	3.810	3.901	3.933	3.930	3.99	4.012	4.079	4.158		
	3.839	3.860	3.963	3.910	3.97	4.014	4.052	4.123		
	3.847	3.896	3.936	3.970	4.00	4.010	4.108	4.239		
M [%]	3.80	3.88	3.94	3.95	3.97	4.01	4.09	4.16		3.98
s[%]	0.043	0.015	0.014	0.029	0.047	0.003	0.020	0.044		0.113
									s_M [%]	0.031
s_{rel}	0.0114	0.0040	0.0035	0.0074	0.0118	0.0008	0.0048	0.0106	$\bar{s}_i$ [%]	0.028

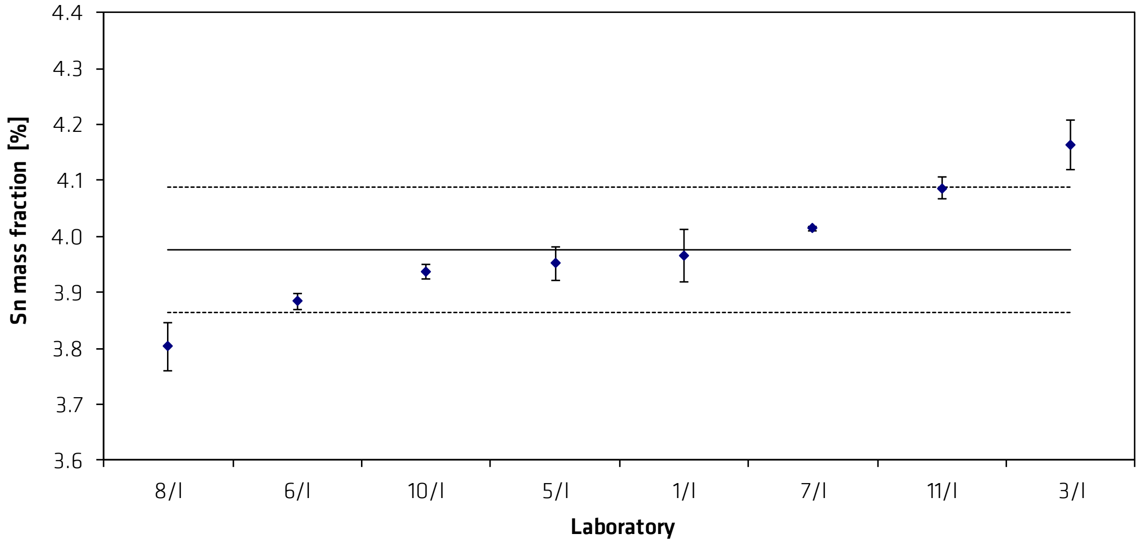

Table 14: Results for Ni in BAM-M397a

Lab./Meth.	1/I	8/I	10/I	2/I	3/I	2/A	11/I	6/I	7/I	5/I		
M_i [%]	0.32	0.330	0.328	0.333	0.335	0.338	0.340	0.341	0.349	0.352		*n*
	0.32	0.329	0.330	0.338	0.339	0.339	0.340	0.342	0.346	0.359		10
	0.32	0.328	0.330	0.335	0.336	0.342	0.340	0.343	0.347	0.350		
	0.32	0.328	0.330	0.331	0.340	0.342	0.343	0.340	0.348	0.349		
	0.32	0.331	0.330	0.332	0.339	0.340	0.341	0.344	0.350	0.352		
	0.32	0.329	0.331	0.331	0.336	0.339	0.342	0.340	0.351	0.348		
						0.347						
M [%]	0.320	0.329	0.330	0.334	0.338	0.341	0.341	0.342	0.349	0.352		0.337
s[%]	0.0000	0.0012	0.0009	0.0028	0.0020	0.0031	0.0015	0.0016	0.0019	0.0039		0.0095
											s_M [%]	0.0022
s_{rel}	0.0000	0.0036	0.0027	0.0083	0.0059	0.0090	0.0044	0.0048	0.0054	0.0112	$\bar{s}_i$ [%]	0.028

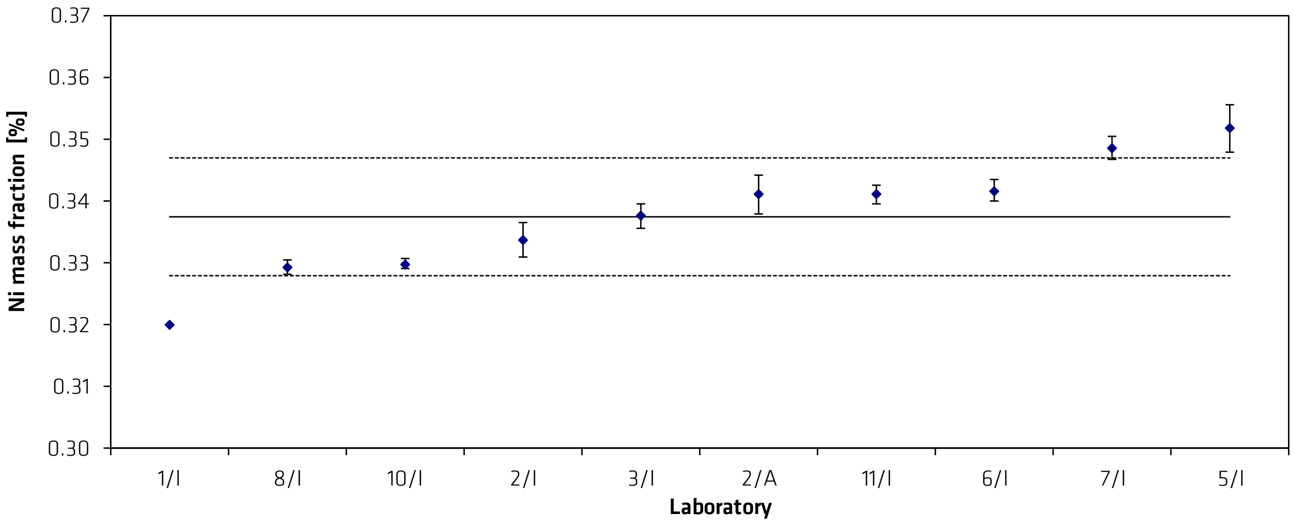

Table 15: Results for Sb in BAM-M397a

Lab./Meth.	2/I	6/I	5/I	7/IMS	10/I	1/I	2/P	11/I	7/I	3/I	8/I		
M_i [%]	0.0839	0.087	0.095	0.097	0.096	0.098	0.0982	0.1017	0.101	0.104	0.105		n
	0.0868	0.090	0.095	0.095	0.096	0.096	0.0980	0.0984	0.100	0.101	0.105		11
	0.0910	0.088	0.095	0.097	0.096	0.097	0.0989	0.1023	0.100	0.100	0.106		
	0.0820	0.088	0.095	0.094	0.096	0.096	0.0960	0.1012	0.101	0.101	0.105		
	0.0898	0.089	0.092	0.095	0.095	0.096	0.0968	0.0996	0.101	0.103	0.105		
	0.0896	0.087	0.094	0.096	0.096	0.096	0.0964	0.0973	0.101	0.102	0.106		
M [%]	0.0872	0.0882	0.0943	0.0956	0.0959	0.0965	0.0974	0.1001	0.1006	0.1020	0.1053		0.0966
s[%]	0.0036	0.0012	0.0012	0.0011	0.0002	0.0008	0.0011	0.0020	0.0005	0.0014	0.0005		0.0055
												s_M [%]	0.0015
s_{rel}	0.0413	0.0133	0.0128	0.0117	0.0025	0.0087	0.0117	0.0198	0.0047	0.0136	0.0049	$\bar{s}_i$ [%]	0.057

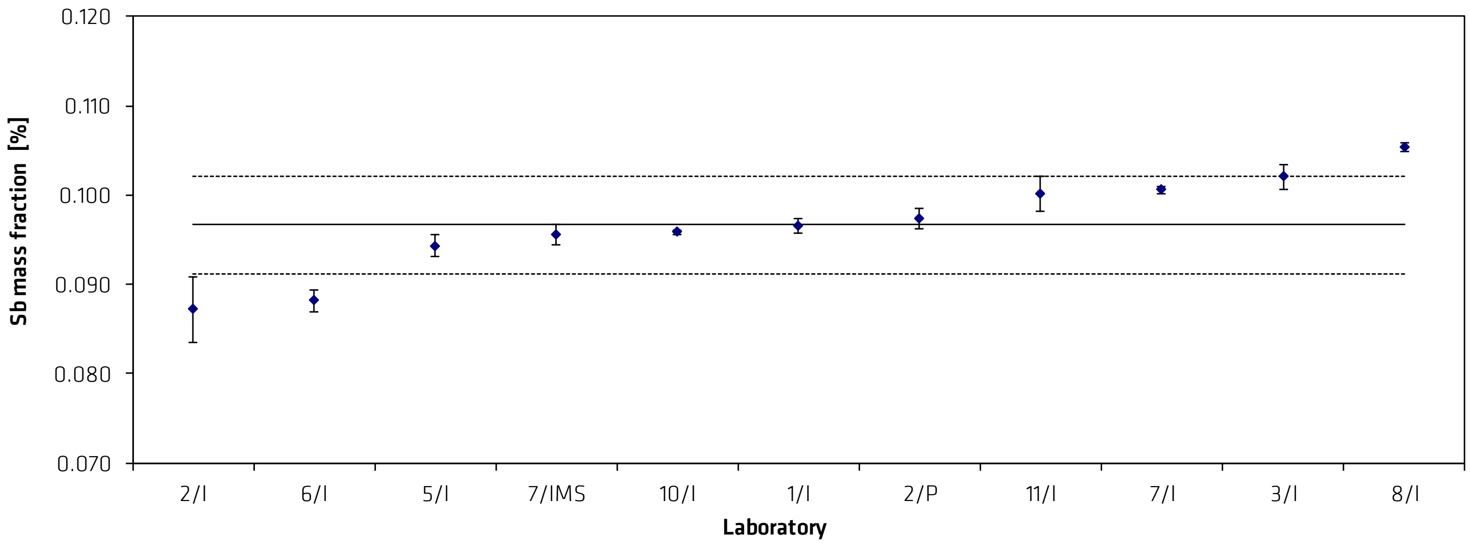

Table 16: Results for S in BAM-M397a

Lab./Meth.	6/I	6/V	1/I	3/I	2/I	8/I		
M_i [%]	0.393	0.400	0.46	0.472	0.484	0.496		*n*
	0.398	0.400	0.46	0.472	0.490	0.497		6
	0.394	0.409	0.45	0.470	0.493	0.495		
	0.399	0.406	0.45	0.470	0.443	0.504		
	0.391	0.405	0.45	0.466	0.470	0.495		
	0.390	0.402	0.44	0.467	0.493	0.495		
M [%]	0.394	0.404	0.452	0.470	0.479	0.497		0.449
s[%]	0.0037	0.0036	0.0075	0.0025	0.0195	0.0035		0.0417
							s_M [%]	0.0090
s_{rel}	0.0093	0.0090	0.0167	0.0053	0.0408	0.0071	$\bar{s}_i$ [%]	0.093

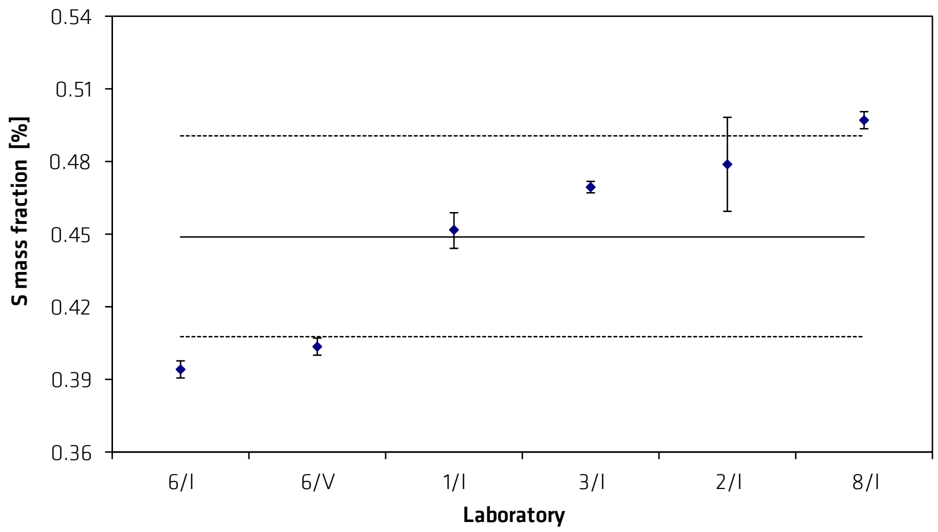

Table 17: Results for As in BAM-M397a

Lab./Meth.	8/I	7/GD	1/EA	2/I	5/I		
M_i [mg/kg]	2.9	2.6	2.9	3.2	< 10		*n*
	2.9	2.8	2.9	3.7	< 10		4
	2.8	3.0	2.7	3.3	< 10		
	2.8	2.8	2.9	2.3	< 10		
	2.8	3.0	2.9	2.8	< 10		
	2.8	2.8	2.8	3.4	< 10		
M [mg/kg]	**2.82**	**2.83**	**2.85**	**3.11**	**< 10**		**2.90**
s[mg/kg]	0.030	0.151	0.074	0.482			0.139
						s_M [%]	0.228
s_{rel}	0.0107	0.0531	0.0258	0.1547		$\bar{s}_i$ [%]	0.048

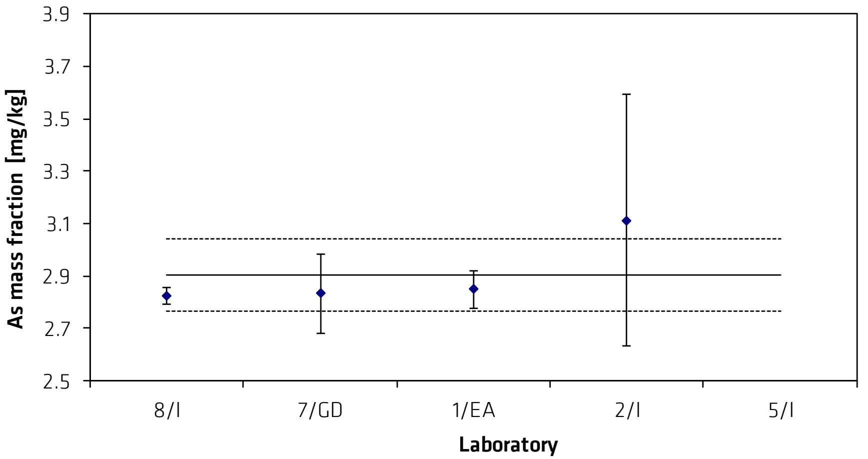

Table 18: Results for Te in BAM-M397a

Lab./Meth.	7/GD	8/I	1/EA	5/I		
M_i [mg/kg]	0.1	< 0.1	< 1	< 10		*n*
	0.1	< 0.1	< 1	< 10		1
	0.2	< 0.1	< 1	< 10		
	0.1	< 0.1		< 10		
	0.1	< 0.1		< 10		
	0.1	< 0.1		< 10		
M [mg/kg]	0.12	< 0.1	< 1	< 10		0.12
s[mg/kg]	0.052					
					s_M [%]	0.000
s_{rel}	0.4356				$\bar{s}_i$ [%]	0.000

Table 19: Results for Se in BAM-M397a

Lab./Meth.	7/GD	8/I	1/EA	5/I		
M_i [mg/kg]	0.4	0.48	< 1	< 10		*n*
	0.3	0.50	< 1	< 10		2
	0.3	0.55	< 1	< 10		
	0.3	0.41		< 10		
	0.4	0.46		< 10		
	0.3	0.52		< 10		
M [mg/kg]	0.34	0.49	< 1	< 10		0.41
s[mg/kg]	0.055	0.052				
					s_M [%]	0.000
s_{rel}	0.1645	0.1068			$\bar{s}_i$ [%]	0.000

The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [4]. The following results were obtained:

Tab. 20: Outcome of statistical tests on the results obtained for Zn and Pb in BAM-M397

	Zn	Pb
Number of data sets	11	11
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. 14
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	Labs. 8 and 14
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The outliers (Labs. 8 and 14, Pb) were removed.

Tab. 21: Outcome of statistical tests on the results obtained for Sn and Ni in BAM-M397

	Sn	Ni
Number of data sets	9	11
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)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: not normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: not normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

Tab. 22: Outcome of statistical tests on the results obtained for Sb and As in BAM-M397 ("<"-values were not considered)

	Sb	As
Number of data sets	12	4
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)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Insufficient data

Tab. 23: Outcome of statistical tests on the results obtained for S in BAM-M397

	1^{st} run	2^{nd} run
Number of data sets	8	7
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 14/I	---
Dixon (α = 0.01)	Lab. 14/I	---
Nalimov (α = 0.05)	Lab. 14/I	---
Nalimov (α = 0.01)	Lab. 14/I	---
Grubbs (α = 0.05)	Lab. 14/I	---
Grubbs (α = 0.01)	Lab. 14/I	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: not normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: not normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: not normal	Distribution: normal

The outlier (Lab. 14/I) was removed.

Tab. 24: Outcome of statistical tests on the results obtained for Zn and Pb in BAM-M397a

	Zn	Pb
Number of data sets	10	10
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	Lab. 8
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The straggler (Lab. 6, Zn) was not removed, the straggler (Lab. 8, Pb) was removed, because the results of this laboratory was an outlier in case of BAM-M397.

Tab. 25: Outcome of statistical tests on the results obtained for Sn and Ni in BAM-M397a

	Sn	Ni
Number of data sets	8	10
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. 1
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: not normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: not normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The straggler (Lab. 1, Ni) was not removed.

Tab. 26: Outcome of statistical tests on the results obtained for Sb and As in BAM-M397a ("<"-values were not considered)

	Sb	As
Number of data sets	11	4
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	Lab. 2
Dixon (α = 0.01)	---	Lab. 2
Nalimov (α = 0.05)	---	Lab. 2
Nalimov (α = 0.01)	---	Lab. 2
Grubbs (α = 0.05)	---	Lab. 2
Grubbs (α = 0.01)	---	Lab. 2
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Insufficient data

The outlier (Lab. 2, As) was not removed.

Tab. 27: Outcome of statistical tests on the results obtained for S in BAM-M397a

	S
Number of data sets	6
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The resp. combined uncertainties were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity of the material using Equation 3.

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

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 28: Uncertainty calculation (u_{bb}(rel) with the data from the homogeneity test and used for the calculation of u_{bb}(2) and u_{bb}(2) by multiplication with M)

		uncertainty contribution from									u_{bb} (rel)	
		M	n	s_M	u_{ilc}	u_{bb} (1) Length	u_{bb} (2) Area	u(comb)	U		Length	Area
		%		%	%	%	%	%	%			
BAM-M397	Zn	1.9601	11	0.0472	0.0142	0.0179	0.0086	0.0244	0.0488		0.9119	0.4368
	Pb	0.2285	9	0.0075	0.0025	0.0023	0.0022	0.0040	0.0080		0.9956	0.9531
	Sn	3.9852	9	0.0926	0.0309	0.0168	0.0143	0.0379	0.07583		0.4213	0.3579
	Ni	0.3355	11	0.0081	0.0025	0.0005	0.0011	0.0028	0.00550		0.1568	0.3352
	Sb	0.0971	12	0.0047	0.0014	0.0007	0.0008	0.0017	0.0035		0.7260	0.8426
	S	0.4593	7	0.0362	0.0137	0.0019	0.0033	0.0142	0.02839		0.4082	0.7219
		mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
	As	2.9	4	0.20	0.0994	0.0211	0.0400	0.1092	0.2183		0.7355	1.3952
BAM-M397a	Zn	1.8691	10	0.0614	0.0194	0.0170	0.0082	0.0271	0.0542		0.9119	0.4368
	Pb	0.2275	9	0.0067	0.0022	0.0023	0.0022	0.0039	0.0077		0.9956	0.9531
	Sn	3.9757	8	0.1130	0.0400	0.0167	0.0142	0.0456	0.09121		0.4213	0.3579
	Ni	0.3374	10	0.0095	0.0030	0.0005	0.0011	0.0033	0.00651		0.1568	0.3352
	Sb	0.0966	11	0.0055	0.0017	0.0007	0.0008	0.0020	0.0039		0.7260	0.8426
	S	0.4491	6	0.0417	0.0170	0.0018	0.0032	0.0174	0.03482		0.4082	0.7219
		mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
	As	2.9	4	0.14	0.0696	0.0214	0.0405	0.0833	0.1666		0.7355	1.3952

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

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

The calculated mass fractions and their respective expanded uncertainties are given on Page 3 of this report.
Rounding was done according to DIN 1333 [5].

In addition to the wet chemical characterisation an accompanying inter-laboratory comparison with spark emission was performed on BAM-M397 to check if there is agreement between SOES and wet chemistry. Three additional laboratories participated in this comparison. Tab. 29 shows the mean values of wet chemical and SOES results as well as their standard deviations. The results obtained with wet chemistry are consistent with the results obtained with SOES all elements except of As where the results obtained with SOES have a very wide spread.

Tab. 29: Comparison wet chemistry vs. SOES

Element	**Wet chemical analysis**			**Spark emission**		
	Mass fraction in %	**Std.-dev.** in %	***n***	**Mass fraction** in %	**Std.-dev.** in %	***n***
Zn	1.96	0.05	11	1.96	0.12	7
Pb	0.229	0.008	9	0.238	0.029	7
Sn	3.99	0.10	10	4.12	0.12	7
Ni	0.336	0.009	11	0.325	0.018	7
Sb	0.097	0.005	12	0.095	0.017	7
S	0.459	0.037	7	0.474	0.036	7
	in mg/kg	in mg/kg		in mg/kg	in mg/kg	
As	2.9	0.2	4	27.2	14.4	3

6. Instructions for users and stability statement

The certified reference materials BAM-M397 and BAM-M397a are intended for the calibration and quality control of spark emission and X-ray fluorescence spectrometry used for the analysis of similar materials. They can also be used for wet chemical analysis.
Before analysis the surface of the materials should be cleaned by turning or milling. The preparation of the surface has to be done slowly to avoid heating of the disc.
If chips prepared from the compact material are used for wet chemical analysis, a minimum sample intake of 0.2 g should 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 traceablility of the certified mass fractions to the SI (Système International d'Unités) calibration was done using standard solutions prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

8. Information on and purchase of the CRM

Certified reference materials BAM-M397 and BAM-M397a are supplied by
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 „Inorganic Reference Materials"
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 – 8104 72061
E-Mail: sales.crm@bam.de

Each disc of BAM-M397 and BAM-M397a 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.

9. References

[1] DIN EN ISO 17034, Allgemeine Anforderungen an die Kompetenz von Referenzmaterial-herstellern, 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] Bonas G, Zervou M, Papaeoannou T, Lees M: Accred Qual Assur (2003) 8:101-107

[5] DIN 1333:1992-02 Zahlenangaben

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity (length), XRF

Seq.			Zn (%)	Pb (%)	Sn (%)	Ni (%)	Sb (%)		
47	M-397 1AE	Concentration	1.998	0.353	4.106	0.35	0.101		
46	M-397 1AE	Concentration	1.998	0.347	4.102	0.351	0.1		
45	M-397 1AE	Concentration	2.001	0.349	4.103	0.349	0.101		
44	M-397 1AE	Concentration	2	0.351	4.102	0.35	0.1		
43	M-397 1AE	Concentration	1.998	0.35	4.097	0.35	0.1		
42	M-397 1AE	Concentration	1.997	0.351	4.103	0.349	0.1		
41	M-397 1AE	Concentration	2.001	0.35	4.105	0.351	0.1		
40	M-397 1AE	Concentration	2.003	0.349	4.101	0.349	0.101		
39	M-397 1AE	Concentration	1.999	0.351	4.106	0.349	0.101		
38	M-397 1AE	Concentration	2	0.349	4.1	0.35	0.101		
29	M-397 1AE	Concentration	2.001	0.35	4.099	0.35	0.101		
20	M-397 1AE	Concentration	2.002	0.352	4.104	0.351	0.101		
11	M-397 1AE	Concentration	2.002	0.351	4.099	0.35	0.1		
10	M-397 1AE	Concentration	2	0.351	4.096	0.35	0.101		
9	M-397 1AE	Concentration	1.999	0.35	4.104	0.35	0.101		
8	M-397 1AE	Concentration	2.002	0.35	4.098	0.35	0.1		
7	M-397 1AE	Concentration	2.001	0.35	4.107	0.351	0.101		
6	M-397 1AE	Concentration	2.003	0.349	4.1	0.35	0.1		
5	M-397 1AE	Concentration	2.004	0.351	4.099	0.35	0.1		
4	M-397 1AE	Concentration	2.002	0.347	4.105	0.35	0.1		
3	M-397 1AE	Concentration	1.998	0.35	4.102	0.35	0.1		
2	M-397 1AE	Concentration	2.002	0.348	4.106	0.351	0.1		
1	M-397 1AE	Concentration	2.003	0.35	4.098	0.351	0.1		
27	M-397 1BE	Concentration	2.255	0.346	4.111	0.35	0.101		
37	M-397 1CE	Concentration	2.354	0.35	4.116	0.349	0.102		
19	M-397 2AE	Concentration	2.413	0.343	4.075	0.349	0.099		
18	M-397 3AE	Concentration	2.187	0.358	4.099	0.349	0.1		
17	M-397 4AE	Concentration	2.393	0.344	4.067	0.35	0.099		
26	M-397 4BE	Concentration	2.358	0.338	4.091	0.349	0.1		
16	M-397 5AE	Concentration	2.039	0.344	4.12	0.349	0.101		
25	M-397 5BE	Concentration	1.952	0.346	4.111	0.351	0.1		
36	M-397 5CE	Concentration	1.926	0.346	4.116	0.349	0.101		
15	M-397 6AE	Concentration	2.26	0.351	4.083	0.349	0.1		
30	M-397 6BE	Concentration	2.283	0.349	4.104	0.349	0.1		
35	M-397 6CE	Concentration	2.302	0.347	4.108	0.35	0.101		
14	M-397 7AE	Concentration	2.401	0.34	4.233	0.341	0.099		
24	M-397 7BE	Concentration	2.406	0.339	4.227	0.341	0.099		
34	M-397 7CE	Concentration	2.4	0.349	4.251	0.341	0.1		
13	M-397 8AE	Concentration	2.421	0.348	4.097	0.35	0.101		
23	M-397 8BE	Concentration	2.411	0.35	4.116	0.35	0.101		
33	M-397 8CE	Concentration	2.403	0.354	4.106	0.351	0.101		
12	M-397 9AE	Concentration	2.333	0.35	4.091	0.349	0.101		
22	M-397 9BE	Concentration	2.318	0.353	4.088	0.35	0.1		
32	M-397 9CE	Concentration	2.306	0.357	4.105	0.349	0.101		
28	M-397 10AE	Concentration	2.372	0.348	4.098	0.35	0.1		
21	M-397 10BE	Concentration	2.392	0.347	4.093	0.35	0.1		
31	M-397 10CE	Concentration	2.408	0.352	4.115	0.349	0.101		
		Mean Concentration	2.155	0.349	4.110	0.349	0.100		
		Min. Concentration	1.926	0.338	4.067	0.341	0.099		
		Max. Concentration	2.421	0.358	4.251	0.351	0.102		
		s Concentration	0.1835	0.0038	0.035	0.0022	0.0006		
		RSD rel. Concentration	8.515	1.093	0.853	0.642	0.592		
	6 and 8 and 9 and 10		2.344	0.351	4.101	0.350	0.101		
		s	0.057	0.003	0.010	0.001	0.001		
		RSD	2.417	0.872	0.254	0.186	0.512		
	2AE and 4AE and 8 and 10		2.402	0.348	4.096	0.350	0.100		397
		s	0.015	0.004	0.018	0.001	0.001		
		RSD	0.645	1.072	0.429	0.183	0.884		
	1CE and 6CE and 9		2.323	0.351	4.102	0.349	0.101		397a
		s	0.021	0.004	0.012	0.001	0.001		
		RSD	0.917	1.076	0.288	0.157	0.700		
		Instrument	2.001	0.350	4.102	0.350	0.100		
		s	0.002	0.001	0.003	0.001	0.001		
		RSD	0.099	0.408	0.079	0.191	0.505		
	Contribution inhomog. (RSD)		0.912	0.996	0.421		0.726		

Calculation of uncertainty contribution of potential inhomogeneity (length), Arsenic (FOES)

Sample	1 in %	2 in %	3 in %	4 in %	5 in %	6 in %	Mean in %	Standard deviation in %
1AE	0.00410	0.00440	0.00410	0.00410	0.00410	0.00420	0.00417	0.00012
2AE	0.00410	0.00430	0.00410	0.00420	0.00410	0.00420	0.00417	0.00008
3AE	0.00410	0.00420	0.00420	0.00410	0.00430	0.00420	0.00418	0.00008
4AE	0.00420	0.00420	0.00400	0.00400	0.00420	0.00410	0.00412	0.00010
5AE	0.00410	0.00420	0.00410	0.00410	0.00420	0.00430	0.00417	0.00008
6AE	0.00410	0.00440	0.00390	0.00410	0.00410	0.00410	0.00412	0.00016
7AE	0.00410	0.00420	0.00410	0.00420	0.00430	0.00420	0.00418	0.00008
8AE	0.00410	0.00420	0.00410	0.00430	0.00420	0.00440	0.00422	0.00012
9AE	0.00410	0.00420	0.00400	0.00420	0.00430	0.00430	0.00418	0.00012
10AE	0.00410	0.00420	0.00430	0.00410	0.00420	0.00440	0.00422	0.00012
1BE	0.00420	0.00420	0.00420	0.00400	0.00410	0.00420	0.00415	0.00008
4BE	0.00410	0.00400	0.00400	0.00400	0.00440	0.00430	0.00413	0.00018
5BE	0.00390	0.00410	0.00410	0.00430	0.00420	0.00430	0.00415	0.00015
6BE	0.00420	0.00430	0.00390	0.00400	0.00410	0.00410	0.00410	0.00014
7BE	0.00410	0.00430	0.00420	0.00410	0.00420	0.00430	0.00420	0.00009
8BE	0.00400	0.00410	0.00430	0.00420	0.00430	0.00410	0.00417	0.00012
9BE	0.00420	0.00450	0.00410	0.00420	0.00420	0.00420	0.00423	0.00014
10BE	0.00410	0.00420	0.00420	0.00410	0.00430	0.00420	0.00418	0.00008
1CE	0.00410	0.00410	0.00410	0.00410	0.00420	0.00420	0.00413	0.00005
5CE	0.00390	0.00410	0.00410	0.00410	0.00420	0.00430	0.00412	0.00013
6CE	0.00400	0.00390	0.00400	0.00400	0.00410	0.00410	0.00402	0.00008
7CE	0.00430	0.00440	0.00400	0.00410	0.00440	0.00420	0.00423	0.00016
8CE	0.00410	0.00410	0.00400	0.00410	0.00430	0.00410	0.00412	0.00010
9CE	0.00380	0.00410	0.00410	0.00400	0.00420	0.00420	0.00407	0.00015
10CE	0.00380	0.00390	0.00400	0.00410	0.00430	0.00420	0.00405	0.00019

Sample	*Number*	*Sum*	*Mean*	*Variance*
1AE	6	0.025	0.00417	1.46667E-08
2AE	6	0.025	0.00417	6.66667E-09
3AE	6	0.0251	0.00418	5.66667E-09
4AE	6	0.0247	0.00412	9.66667E-09
5AE	6	0.025	0.00417	6.66667E-09
6AE	6	0.0247	0.00412	2.56667E-08
7AE	6	0.0251	0.00418	5.66667E-09
8AE	6	0.0253	0.00422	1.36667E-08
9AE	6	0.0251	0.00418	1.36667E-08
10AE	6	0.0253	0.00422	1.36667E-08
1BE	6	0.0249	0.00415	7E-09
4BE	6	0.0248	0.00413	3.06667E-08
5BE	6	0.0249	0.00415	0.000000023
6BE	6	0.0246	0.00410	0.00000002
7BE	6	0.0252	0.00420	8E-09
8BE	6	0.025	0.00417	1.46667E-08
9BE	6	0.0254	0.00423	1.86667E-08
10BE	6	0.0251	0.00418	5.66667E-09
1CE	6	0.0248	0.00413	2.66667E-09
5CE	6	0.0247	0.00412	1.76667E-08
6CE	6	0.0241	0.00402	5.66667E-09
7CE	6	0.0254	0.00423	2.66667E-08
8CE	6	0.0247	0.00412	9.66667E-09
9CE	6	0.0244	0.00407	2.26667E-08
10CE	6	0.0243	0.00405	0.000000035
			0.00415	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4.38267E-07	24	1.82611E-08	1.256498471	0.20863876	1.604785732
Within groups	1.81667E-06	125	1.45333E-08			
Total	2.25493E-06	149				

within-sd	0.0001206			status:	homogeneous
effective n	4.00				
s_bb	3.053E-05				
s_bb_min	2.144E-05				
u_bb	3.053E-05	0.030527765			
u_bb(rel.)	0.735490647				

Calculation of uncertainty contribution of potential inhomogeneity (length), Sulfur (FOES)

Sample	1 in %	2 in %	3 in %	4 in %	5 in %	6 in %	Mean in %	Standard deviation in %
1AE	0.52000	0.52000	0.50000	0.51000	0.51000	0.51000	0.51167	0.00753
2AE	0.51000	0.50000	0.49700	0.50000	0.51000	0.50000	0.50283	0.00567
3AE	0.52000	0.52000	0.50000	0.50000	0.51000	0.50000	0.50833	0.00983
4AE	0.51000	0.52000	0.50000	0.49800	0.51000	0.50000	0.50633	0.00852
5AE	0.52000	0.51000	0.51000	0.49600	0.51000	0.50000	0.50767	0.00852
6AE	0.52000	0.52000	0.51000	0.51000	0.51000	0.51000	0.51333	0.00516
7AE	0.51000	0.51000	0.51000	0.50000	0.51000	0.51000	0.50833	0.00408
8AE	0.51000	0.51000	0.50000	0.50000	0.51000	0.49900	0.50483	0.00567
9AE	0.51000	0.51000	0.50000	0.50000	0.50000	0.51000	0.50500	0.00548
10AE	0.52000	0.52000	0.51000	0.50000	0.49800	0.51000	0.50967	0.00942
1BE	0.51000	0.51000	0.51000	0.50000	0.50000	0.51000	0.50667	0.00516
4BE	0.51000	0.51000	0.51000	0.51000	0.51000	0.51000	0.51000	0.00000
5BE	0.52000	0.52000	0.51000	0.50000	0.51000	0.51000	0.51167	0.00753
6BE	0.51000	0.51000	0.49800	0.49600	0.51000	0.51000	0.50567	0.00674
7BE	0.51000	0.51000	0.50000	0.49900	0.50000	0.50000	0.50317	0.00531
8BE	0.51000	0.51000	0.50000	0.49700	0.51000	0.51000	0.50617	0.00601
9BE	0.51000	0.51000	0.51000	0.49900	0.50000	0.50000	0.50483	0.00567
10BE	0.51000	0.51000	0.49400	0.49800	0.51000	0.49900	0.50350	0.00731
1CE	0.51000	0.51000	0.51000	0.51000	0.51000	0.51000	0.51000	0.00000
5CE	0.52000	0.51000	0.51000	0.51000	0.52000	0.51000	0.51333	0.00516
6CE	0.51000	0.49900	0.51000	0.50000	0.51000	0.49600	0.50417	0.00652
7CE	0.51000	0.51000	0.51000	0.51000	0.50000	0.50000	0.50667	0.00516
8CE	0.51000	0.51000	0.51000	0.49900	0.51000	0.50000	0.50650	0.00543
9CE	0.50000	0.51000	0.51000	0.50000	0.51000	0.51000	0.50667	0.00516
10CE	0.50000	0.51000	0.49500	0.50000	0.51000	0.51000	0.50417	0.00665

Sample	*Number*	*Sum*	*Mean*	*Variance*
1AE	6	3.07	0.51167	5.66667E-05
2AE	6	3.017	0.50283	3.21667E-05
3AE	6	3.05	0.50833	9.66667E-05
4AE	6	3.038	0.50633	7.26667E-05
5AE	6	3.046	0.50767	7.26667E-05
6AE	6	3.08	0.51333	2.66667E-05
7AE	6	3.05	0.50833	1.66667E-05
8AE	6	3.029	0.50483	3.21667E-05
9AE	6	3.03	0.50500	3E-05
10AE	6	3.058	0.50967	8.86667E-05
1BE	6	3.04	0.50667	2.66667E-05
4BE	6	3.06	0.51000	1.47911E-32
5BE	6	3.07	0.51167	5.66667E-05
6BE	6	3.034	0.50567	4.54667E-05
7BE	6	3.019	0.50317	2.81667E-05
8BE	6	3.037	0.50617	3.61667E-05
9BE	6	3.029	0.50483	3.21667E-05
10BE	6	3.021	0.50350	5.35E-05
1CE	6	3.06	0.51000	1.47911E-32
5CE	6	3.08	0.51333	2.66667E-05
6CE	6	3.025	0.50417	4.25667E-05
7CE	6	3.04	0.50667	2.66667E-05
8CE	6	3.039	0.50650	0.0000295
9CE	6	3.04	0.50667	2.66667E-05
10CE	6	3.025	0.50417	4.41667E-05
			0.50725	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.001371707	24	5.71544E-05	1.428813484	0.1067809	1.604785732
Within groups	0.005000167	125	4.00013E-05			
Total	0.006371873	149				
within-sd	0.0063247			status:	homogeneous	
effective n	4.00					
s_bb	0.0020708					
s_bb_min	0.0011247					
u_bb	0.0020708	2.070815728				
u_bb(rel.)	0.408246296					

Annex 2: Calculation of uncertainty contribution of potential inhomogeneity (area)

Zinc:

r_0	1.90662	1.96278				
r_middle	1.92040	1.91050	1.94540	1.95130		
r_out	1.94320	1.94650	1.94430	1.92590		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.000132861	2	6.64307E-05	0.155246643	0.85907237	4.737414128
Within groups	0.002995332	7	0.000427905			
Total	0.003128194	9				
within-sd	0.020685855			status:	homogeneous	
effective n	3.20					
s_bb	0					
s_bb_min	0.008454374					
u_bb	0.008454374			1.93569		
u_bb(rel.)	0.436762821					

Lead:

r_0	0.26710	0.28285				
r_middle	0.28915	0.28685	0.28216	0.27746		
r_out	0.28024	0.28666	0.27766	0.29010		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.000124262	2	6.2131E-05	1.436293477	0.300147516	4.737414128
Within groups	0.000302805	7	4.32579E-05			
Total	0.000427067	9				
within-sd	0.006577071			status:	homogeneous	
effective n	3.20					
s_bb	0.002428549					
s_bb_min	0.00268807					
u_bb	0.00268807			0.282021681		
u_bb(rel.)	0.953142968					

Tin:

r_0	3.96433	4.03881				
r_middle	4.01757	3.99657	4.05066	4.02966		
r_out	4.02686	4.07015	3.98108	4.00327		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.000687766	2	0.000343883	0.277752599	0.765457107	4.737414128
Within groups	0.008666633	7	0.00123809			
Total	0.009354399	9				
within-sd	0.035186509			status:	homogeneous	
effective n	3.20					
s_bb	0					
s_bb_min	0.014380838					
u_bb	0.014380838			4.017897155		
u_bb(rel.)	0.357919504					

Nickel:

r_0	0.31200	0.31886				
r_middle	0.31332	0.31147	0.31658	0.31596		
r_out	0.31605	0.31719	0.31658	0.31385		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	5.16451E-06	2	2.58225E-06	0.386417133	0.693130825	4.737414128
Within groups	4.67779E-05	7	6.68255E-06			
Total	5.19424E-05	9				
within-sd	0.002585064			status:	homogeneous	
effective n	3.20					
s_bb	0					
s_bb_min	0.001056524					
u_bb	0.001056524			0.315186449		
u_bb(rel.)	0.335205939					

Antimony

r_0	0.09394	0.09726				
r_middle	0.09870	0.09812	0.09725	0.09725		
r_out	0.09579	0.09734	0.09560	0.10131		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	7.05186E-06	2	3.52593E-06	0.877057623	0.457193693	4.737414128
Within groups	2.81413E-05	7	4.02018E-06			
Total	3.51931E-05	9				
within-sd	0.002005039			status:	homogeneous	
effective n	3.20					
s_bb	0					
s_bb_min	0.000819466					
u_bb	0.000819466			0.097256155		
u_bb(rel.)	0.842585201					

Sulfur:

r_0	0.46979	0.48521				
r_middle	0.46680	0.46710	0.47280	0.47750		
r_out	0.48130	0.47470	0.47620	0.48660		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00015687	2	0.000078435	1.928097345	0.215264026	4.737414128
Within groups	0.00028476	7	4.068E-05			
Total	0.00044163	9				
within-sd	0.006378087			status:	homogeneous	
effective n	3.20					
s_bb	0.003434885					
s_bb_min	0.002606745					
u_bb	0.003434885			0.4758		
u_bb(rel.)	0.7219179					

Arsenic:

r_0	0.00314	0.00333				
r_in	0.00304	0.00314	0.00314	0.00314		
r_out	0.00304	0.00304	0.00333	0.00314		
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.98225E-08	2	9.91126E-09	0.86	0.463484743	4.737414128
Within groups	8.0673E-08	7	1.15247E-08			
Total	1.00496E-07	9				
within-sd	0.000107353			status:	homogeneous	
effective n	3.20					
s_bb	0					
s_bb_min	4.38756E-05					
u_bb	4.38756E-05			0.003144845		
u_bb(rel.)	1.395159482					