Certification Report

Certified Reference Material

BAM-M365a

Refined Copper

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Summary

This report describes preparation, analysis and certification of copper reference material BAM-M365a, refined copper.
The certified reference material (CRM) is available in the form of chips. It is intended for calibration and quality control of wet chemical analysis procedures.

The following mass fractions and uncertainties have been certified:

Element	Mass fraction in %	
	Certified value [1]	Uncertainty [2]
Cu	99.73	0.07
	Mass fraction in mg/kg	
Ag	159	5
As	40.4	0.8
Bi	30.0	1.2
Co	2.13	0.14
Fe	6.1	1.3
Ni	235	5
Pb	141	4
Sb	12.1	1.0
Se	179	12
Te	1.27	0.12
Zn	30	4

[1] Unweighted mean value of the means of accepted sets of data, each set being obtained by at least 5 laboratories and/or with different methods of measurement. The values are traceable to the SI (Système International d'Unités) by the use of pure substances of known stoichiometry for calibration.

[2] Estimated expanded uncertainty U with a coverage factor of k = 2 (Cu: k = 3, Zn: k = 2.5), corresponding to a level of confidence of about 95 %, as defined in the ISO/IEC Guide 98-3:2008 [Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)].

The certified values are based on the results of 8 laboratories which participated in the certification interlaboratory comparison.

The mass fractions of Sn and O are given as indicative values.

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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
GDMS	glow discharge mass 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
A	FAAS
I	ICP-OES (Tables 4 – 17)
I(R)	ICP-OES, revised value (Tables 4 – 17)
IMS	ICP-MS (Tables 4 – 17)
EA	ETAAS (Tables 4 – 17)
EG	electrogravimetry (Tables 4 – 17)
P	spectrophotometry (Tables 4 – 17)
GD	GD-MS (Tables 4 – 17)
GD*	GD-MS (Tables 4 – 17) calibrated with other BAM-CRMs

1. Introduction

BAM-M365a replaces CRM BAM-365 which is no longer available. The new CRM is available in chip form and can be used for calibration and validation of wet chemical analytical methods.
Certification was carried out in cooperation with the German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB), especially with the working group „Copper“ of the Committee of Chemists within GDMB. Participating laboratories were recruited from this group. Since all of these laboratories are highly experienced with copper analysis and had participated in earlier inter-laboratory comparisons, there was no preceding round for qualification.
Certification of reference material BAM-M365a was carried out on the basis of the relevant ISO-Guides [1-3], and the „Guidelines for the development and production of BAM Reference Materials“ [4].

2. Companies/laboratories involved

Manufacturing of the material

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

Test for homogeneity

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

Participants in the certification inter-laboratory comparison

– Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim, Germany
– Aurubis AG, Hamburg, Germany
– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
– Currenta GmbH & Co. OHG, Leverkusen, Germany
– Institut für Materialprüfung Glörfeld GmbH, Willich, Germany
– KM Europa Metal AG, Osnabrück, Germany
– Montanwerke Brixlegg, Brixlegg, Austria
– Wieland-Werke AG, Vöhringen, Germany

Statistical evaluation of the data

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

3. Candidate material

The candidate material was produced by SUS Nell by casting of pure copper doped with the desired impurities. A block of approx. 100 kg of copper was casted. After removing the casting skin the material was sewed into blocks and machined to chips. The chips were sieved with a 0.5 mm sieve to remove the fines. The chips were then bottled. Each bottle contains 100 g of chips, in total 677 bottles were filled.

4. Homogeneity testing

A total of 15 (Sn, Zn: 10) bottled units (see Table 1) of the candidate material were randomly selected for homogeneity testing. From each bottle three (Sn, Zn: two) sub-samples were analysed using ICP-OES or ICP-MS. 1 g of sample was weighed and dissolved in nitric acid. (Originally the elements Sn and Zn were not part of the certification project. They were identified as impurities in BAM-M365a at a later stage of the project. Therefore, an additional homogeneity investigation for these two elements was performed with a fewer number of samples.)

Tab. 1a: Bottles analysed for homogeneity testing of BAM-M365a

12	147	242	512	562
27	154	330	528	584
117	207	340	560	637

Tab. 1b: Bottles analysed for homogeneity testing of BAM-M365a (Sn, Zn)

Zn						Sn				
11	154	330	364	577		32	154	268	330	340
32	268	348	476	584		364	476	577	584	

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budgets were 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 bottles (from 1-way ANOVA)
MS_{within}	mean of squared deviations within bottles (from 1-way ANOVA)
n	number of replicate sub-samples per bottle
N	number of bottles selected for homogeneity study

s_{bb} signifies the between-bottle 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}. Eq. (1) does not apply if MS_{within} is larger than MS_{among}.
The calculated relative values of s_{bb}, u^*_{bb} , and u_{bb} are given in the following Table 2.

In accordance with ISO Guide 35 [3] high purity materials (especially metals), which are certified for purity and not for impurities of individual elements, are expected to be homogeneous on thermodynamic grounds. In case of BAM-M365a this is valid only for copper but not for the impurities. Therefore, a specific homogeneity test for Cu was not performed, i.e. the uncertainty contribution u_{bb}. for this element is zero.

Table 2: Relative uncertainty contributions due to possible sample inhomogeneity

Element	$s_{bb,r}$ (%)	$u^*_{bb,r}$ (%)	$u_{bb,r}$ (%)
Ag	1.411	0.461	1.411
As	0.557	0.521	0.557
Bi	1.021	0.437	1.021
Co	2.712	1.161	2.712
Fe	7.53	5.33	7.53
Ni	0.775	0.239	0.775
Pb	0.481	0.459	0.481
Sb	2.758	1.496	2.758
Se	2.367	2,740	2.740
Te	3.286	1.715	3.286
Zn	0	2.698	2.698
Sn	1.105	0.515	1.105

Annex 1 shows the results of the calculations.

5. Characterisation study

5.1 Analytical methods

Eight 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 for their determinations. Table 3 shows the analytical methods used by the participating laboratories.

Table 3: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Ag, As, Bi, Co, Fe, Ni, Pb, Sb, Se, Te	1 g	Dissolution with HNO_3	ICP-MS, calibration with commercial solutions (Merck)
	Cu	2.5 g	Dissolution with H_2SO_4/HNO_3	Electrogravimetry, determination of residue with ICP-OES
	Ag, As, Bi, Co, Ni, Pb, Sb	1 g	Dissolution with HNO_3	ICP-OES, calibration with commercial solutions (Merck)
	As, Bi, Co, Ni, Pb, Sb	0.5 g	Dissolution with HNO_3	ETAAS, commercial mono-element solutions (Merck)
	Sn	1 g	Dissolution with HNO_3	ETAAS, commercial mono-element solution (Merck)
	Zn	1 g	Dissolution with HNO_3	FAAS, commercial mono-element solution (Merck)
	O	0.8 g		Carrier gas hot extraction, calibration with Fe_2O_3
	Sb	1 g	Dissolution with HCl/H_2O_2	Spectrophotometry, calibration with commercial solution (Merck)
	Fe	5 g	Dissolution with HCl/ H_2O_2	Spectrophotometry, calibration with commercial solution (Merck)

Table 3 (cont.): Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Ag, Bi, Fe, Pb, Sb, Se, Te			GDMS, calibration with pressed powder pellets
	As, Co, Ni			GDMS, calibration with BAM-365
2	As, Bi, Co, Fe, Ni, Pb, Sb, Se, Sn, Zn	1 g	Dissolution with HCl/H_2O_2	ICP-OES with matrix matched standards (Cu), commercial mono-element solution
	Ag	1 g	Dissolution with HCl/H_2O_2 (HCl conc.to fill up)	ICP-OES with matrix matched standards (Cu), commercial mono-element solution
	Cu	1 g	Dissolution with HNO_3	Electrogravimetry
	O			Carrier gas hot extraction
3	Cu	2 g	Dissolution with HNO_3	Electrogravimetry
	Te	1 g	Dissolution with HNO_3	ICP-MS, calibration with commercial solution (Agilent)
	As, Bi, Co, Ni, Pb, Sb	1 g	Dissolution with HNO_3/HF	ICP-OES with matrix matched standards (Cu), commercial mono-element solution (Spex)
	Ag, Fe, Se	1 g	Dissolution with HCl/H_2O_2 (HCl conc.to fill up)	ICP-OES with matrix matched standards (Cu), commercial mono-element solution (Spex)
5	Cu	5 g	Dissolution with H_2SO_4/HNO_3	Electrogravimetry, determination of residue with FAAS
	Ag	2.5 g	Dissolution with HNO_3	ICP-OES, mono-element solution prepared from $AgNO_3$ (matrix-matched)
	Ag	5 g	Dissolution with HNO_3	Fire assay, lead-collection, calibration with Ag-metal
	As	2.5 g	Dissolution with HNO_3	ICP-OES, mono-element solution prepared from As_2O_3 (matrix-matched)
	Bi, Fe, Ni, Se	2.5 g	Dissolution with HNO_3	ICP-OES, mono-element solutions prepared from metal-powder (matrix-matched)
	Co, Sb, Te	2.5 g	Dissolution with HNO_3	ETAAS, mono-element solutions prepared from metal-powder (matrix-matched)
	Pb	2.5 g	Dissolution with HNO_3	ICP-OES, mono-element solution prepared from metal-granules (matrix-matched)
6	Ag, As, Bi, Co, Ni, Pb, Sb; Se, Te	0.5 g	Dissolution with HNO_3	ICP-MS, calibration with commercial solutions
7	Cu	5 g	Dissolution with $HNO_3/HBO_3/HF$ Separation of Ag with HCl	Electrogravimetry
	Ni, Pb, Se	1 g	Dissolution with HNO_3/HCl	ICP-OES, mono-element solutions prepared from metal
	Ag, As, Bi, Co, Ni, Pb, Sb, Se, Te			GDMS, calibration with pressed powder pellets
8	Cu	1 g	Dissolution with HNO_3	Electrogravimetry
	Bi, Sb, As	0.05 g	Dissolution with HNO_3	ETAAS (DIN EN 14935), calibration with matrix-matched standards
	Pb, Se, Ni	1.0 g	Dissolution with HCl/ $HNO_3/HBO_3/HF$	ICP-OES (DIN EN 15605), calibration with matrix-matched standards (Spex)
	Sn, Zn	2 g	Dissolution with $HNO_3/HCl/HF$	ICP-OES, calibration with matrix-matched standards (Spex)
	Ag	1 g	Dissolution with HNO_3/HF	ICP-OES (DIN EN 15605), calibration with matrix-matched standards (Spex)
	Co	0.2 g	Dissolution with HNO_3	ETAAS (DIN EN 14935), calibration with matrix-matched standards (Spex)
10	Cu, Ag, As, Bi, Co, Fe, Ni, Pb, Sb, Se, Sn, Zn	2.5 g	Dissolution with HNO_3/HCl	ICP-OES, mono-element solutions. Prepared from pure metals

For all analytical methods where a calibration was necessary this 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.

5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 4 to 17. 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 ($\overline{s}_i$) 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.

Lab./Meth.	3/EG	7/EG	5/EG	2/EG	10/I	8/EG	1/EG		
M_i [%]	99.69	99.60	99.68	99.71	99.747	99.77	99.84		*n*
	99.64	99.70	99.71	99.72	99.747	99.77	99.81		7
	99.67	99.71	99.70	99.72	99.746	99.77	99.80		
	99.67	99.63	99.67	99.73	99.746	99.79	99.85		
	99.67		99.71	99.72	99.746	99.75	99.81		
	99.64		99.74	99.72	99.747	99.76			
M [%]	**99.66**	**99.66**	**99.70**	**99.72**	**99.75**	**99.77**	**99.82**		**99.73**
s [%]	0.0217	0.0535	0.0248	0.0063	0.0005	0.0133	0.0221	s_M [%]	0.0583
								$\bar{s}_i$ [%]	0.0258
s_{rel}	0.00022	0.00054	0.00025	0.00006	0.00001	0.00013	0.00022		0.00058

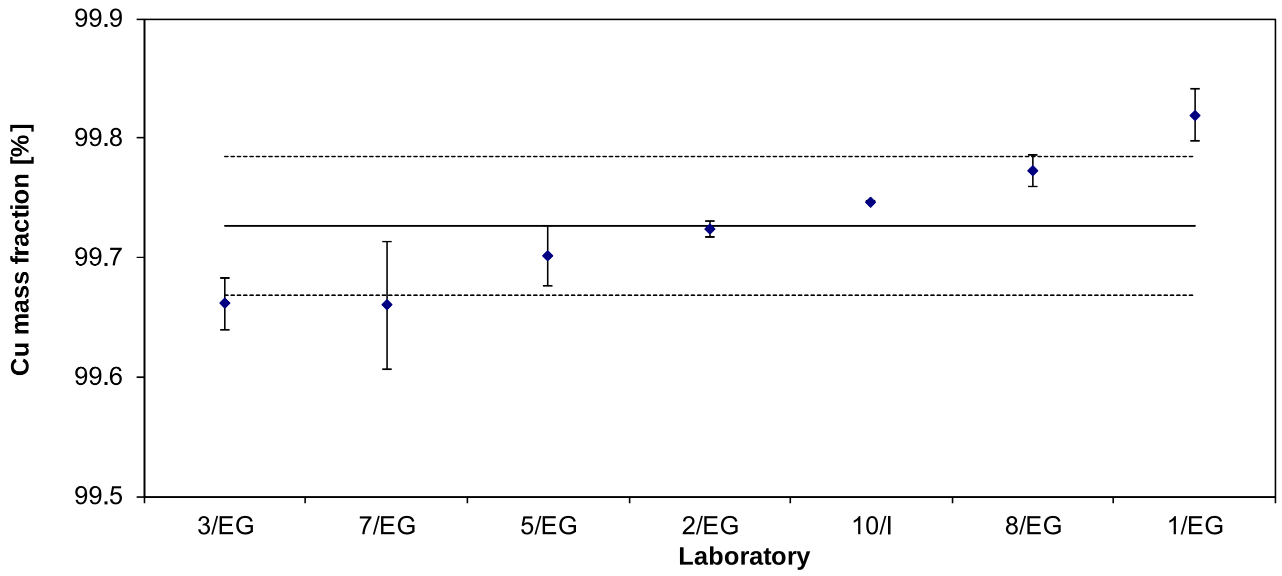

Table 4: Results for Cu

Lab./Meth.	6/IMS	10/I	5/I	5/D	1/GD	1/I	2/I	8/I	1/IMS	3/I	7/GD		
M_i [mg/kg]	149.3	157.0	155.4	156.0	153.1	159.5	160.1	158.0	161.7	162.9	164.0		*n*
	156.6	155.0	156.0	154.0	158.1	160.4	159.1	163.0	161.9	162.8	162.0		11
	155.0	154.0	157.8	157.0	152.9	162.5	159.6	160.0	162.8	162.7	165.0		
	155.3	157.0	155.7		159.3	156.0	162.3	160.0	161.4	162.7	164.0		
	151.9	154.0	153.6		158.8	158.2	160.6	160.0	161.9	162.4			
	155.3	153.0	154.9		162.3	158.5	161.7	166.0	163.0	161.7			
					161.4								
					160.1								
***M* [mg/kg]**	**153.9**	**155.0**	**155.6**	**155.7**	**158.2**	**159.2**	**160.6**	**161.2**	**162.1**	**162.5**	**163.8**		**159.4**
s [mg/kg]	2.742	1.673	1.381	1.528	3.522	2.185	1.232	2.858	0.622	0.441	1.258	s_M [mg/kg]	3.161
												$\bar{s}_i$ [mg/kg]	1.9905
s_{rel}	0.018	0.011	0.009	0.010	0.022	0.014	0.008	0.018	0.004	0.003	0.008		0.020

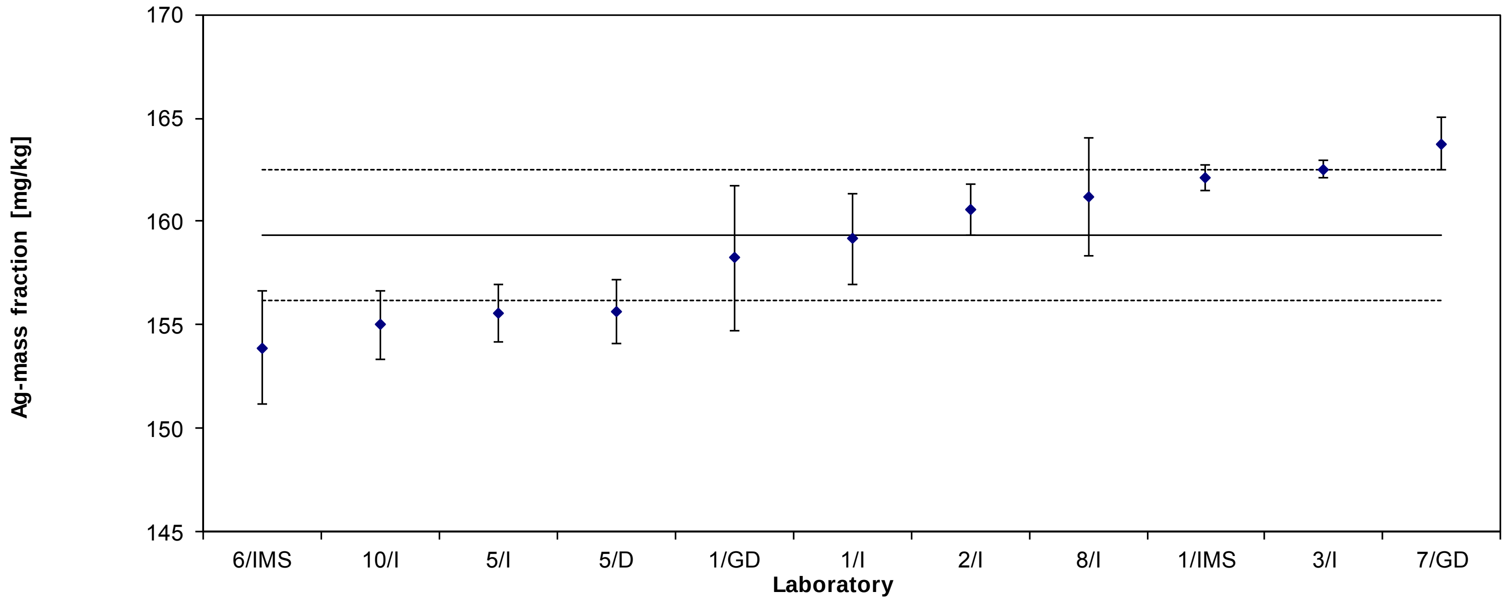

Table 5: Results for Ag

Lab./Meth.	**7/I**	**3/I**	**5/I**	**1/EA**	**1/IMS**	**6/IMS**	**2/I**	**1/I**	**10/I**	**1/GD***	**8/I**		
M_i [mg/kg]	38.0	39.20	39.63	40.7	39.9	41.0	40.8	41.0	41.0	*40.1*	42.3		*n*
	39.0	38.63	40.49	40.0	40.2	39.5	40.9	40.1	41.0	*43.3*	39.8		11
	38.0	38.88	40.87	39.6	40.1	40.4	40.3	41.2	41.0	*41.6*	42.7		
	36.0	39.88	39.75	40.4	40.2	40.3	40.6	40.3	41.0	*43.1*	39.2		
	40.0	39.07	39.62	40.2	40.7	40.7	40.9	41.5	41.0	*41.5*	43.7		
	39.0	38.82	40.02	40.5	40.7	40.7	41.0	40.4	42.0	*41.8*	43.3		
				40.3						*40.9*			
										41.0			
***M* [mg/kg]**	**38.33**	**39.08**	**40.06**	**40.26**	**40.30**	**40.42**	**40.75**	**40.76**	**41.17**	**41.66**	**41.83**		**40.42**
s [mg/kg]	1.366	0.439	0.513	0.349	0.348	0.508	0.259	0.554	0.408	1.085	1.880	s_M [mg/kg]	1.031
												$\overline{s}_i$ [mg/kg]	0.8569
s_{rel}	0.036	0.011	0.013	0.009	0.009	0.013	0.006	0.014	0.010	0.026	0.045		0.026

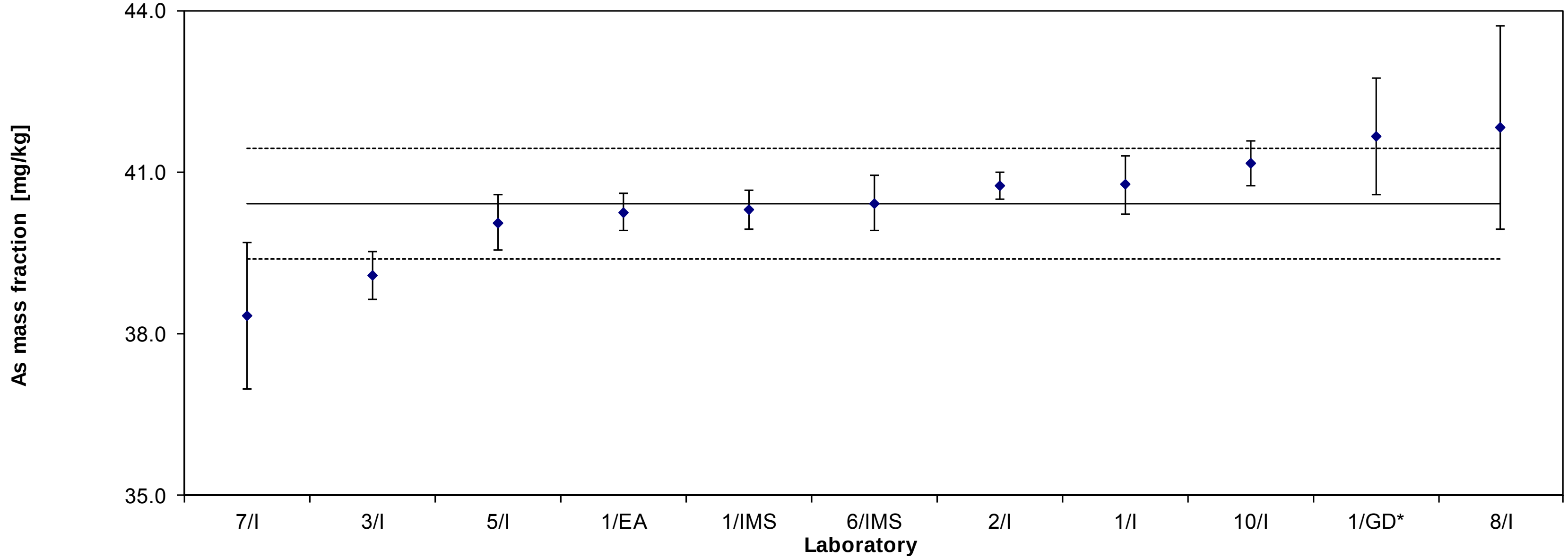

Table 6: Results for As

Lab./Meth.	6/IMS	5/I	1/IMS	1/EA	1/GD	3/I	2/I	8/EA	1/I	10/I	7/GD		
M_i [mg/kg]	26.1	30.0	29.6	30.3	28.0	29.9	29.9	30.0	30.6	31.0	32.9		*n*
	25.3	28.3	29.5	29.9	27.9	30.1	30.4	29.6	30.8	31.0	33.0		11
	26.3	29.4	29.4	30.0	28.9	30.1	29.9	28.3	30.8	30.0	33.2		
	26.4	28.8	29.3	28.7	31.5	30.3	30.0	33.8	31.0	31.0	34.3		
	26.8	27.7	29.5	29.3	31.2	30.0	30.4	30.8	31.1	31.0			
	26.8	29.3	29.2	29.1	30.3	30.4	30.4	31.7	30.4	31.0			
***M* [mg/kg]**	**26.27**	**28.91**	**29.43**	**29.55**	**29.63**	**30.14**	**30.17**	**30.70**	**30.78**	**30.83**	**33.35**		**29.98**
s [mg/kg]	0.573	0.818	0.143	0.622	1.585	0.174	0.258	1.902	0.257	0.408	0.645	s_M [mg/kg]	1.698
												$\bar{s}_i$ [mg/kg]	0.8676
s_{rel}	0.022	0.028	0.005	0.021	0.054	0.006	0.009	0.062	0.008	0.013	0.019		0.057

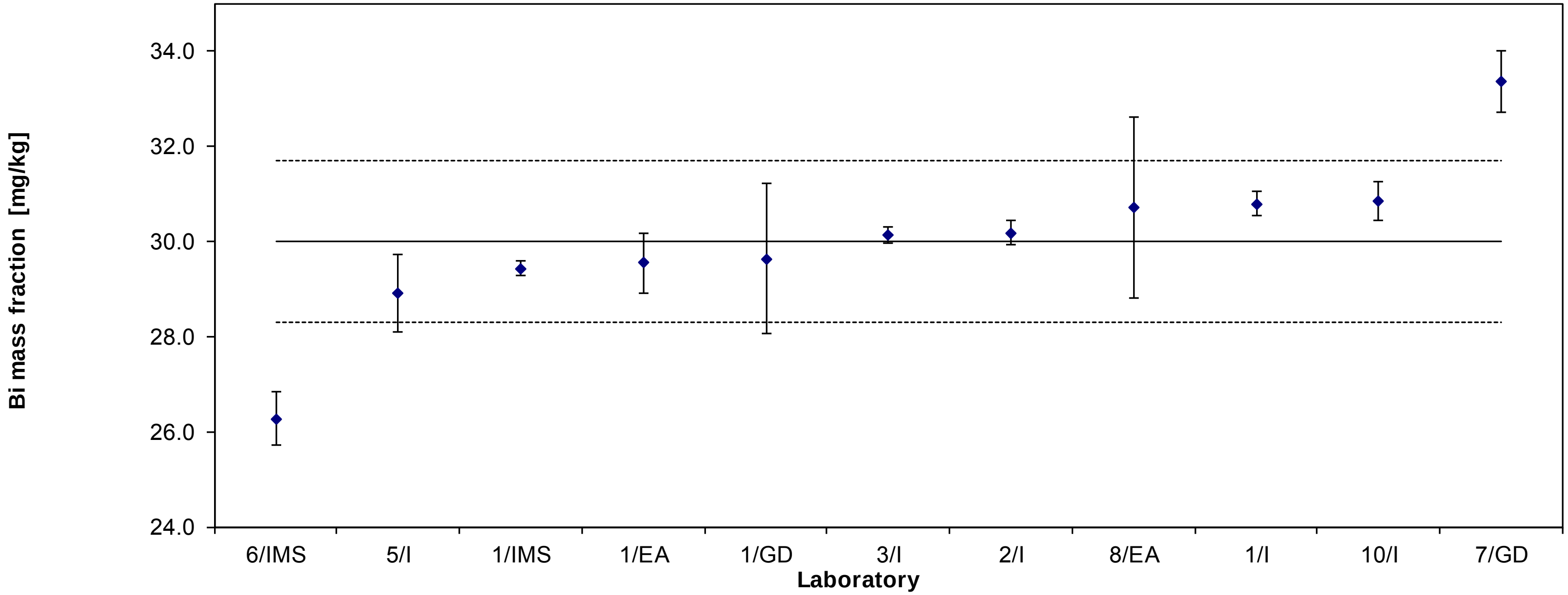

Table 7: Results for Bi

Lab./Meth.	10/I	8/EA	1/IMS	3/I	2/I	6/IMS	1/I	1/GD*	7/GD	5/EA		
M_i [mg/kg]	1.80 1.90 1.90 1.90 1.90 2.30	2.11 2.02 1.99 2.08 1.99 1.91	2.04 2.02 1.98 2.13 1.99 2.15	2.08 2.12 2.09 2.03 2.12 2.17	2.24 2.15 2.11 2.11 1.97 2.04	2.16 2.06 2.10 2.11 2.11 2.12	2.16 2.01 2.07 2.17 2.23 2.16	*2.16* *2.23* *2.22* *2.24* *2.14* *2.15* *2.13* *2.21*	2.30 2.20 2.30 2.40	2.29 2.34 2.33 2.27 2.41 2.31		*n* 10
***M* [mg/kg]**	**1.95**	**2.02**	**2.05**	**2.10**	**2.10**	**2.11**	**2.13**	**2.19**	**2.30**	**2.33**		**2.127**
s [mg/kg]	0.1761	0.0715	0.0731	0.0475	0.0924	0.0322	0.0800	0.0441	0.0816	0.0489	s_M [mg/kg]	0.1172
											$\overline{s}_i$ [mg/kg]	0.0841
s_{rel}	0.09029	0.03544	0.03568	0.02262	0.04395	0.01528	0.03752	0.02017	0.03550	0.02103		0.055

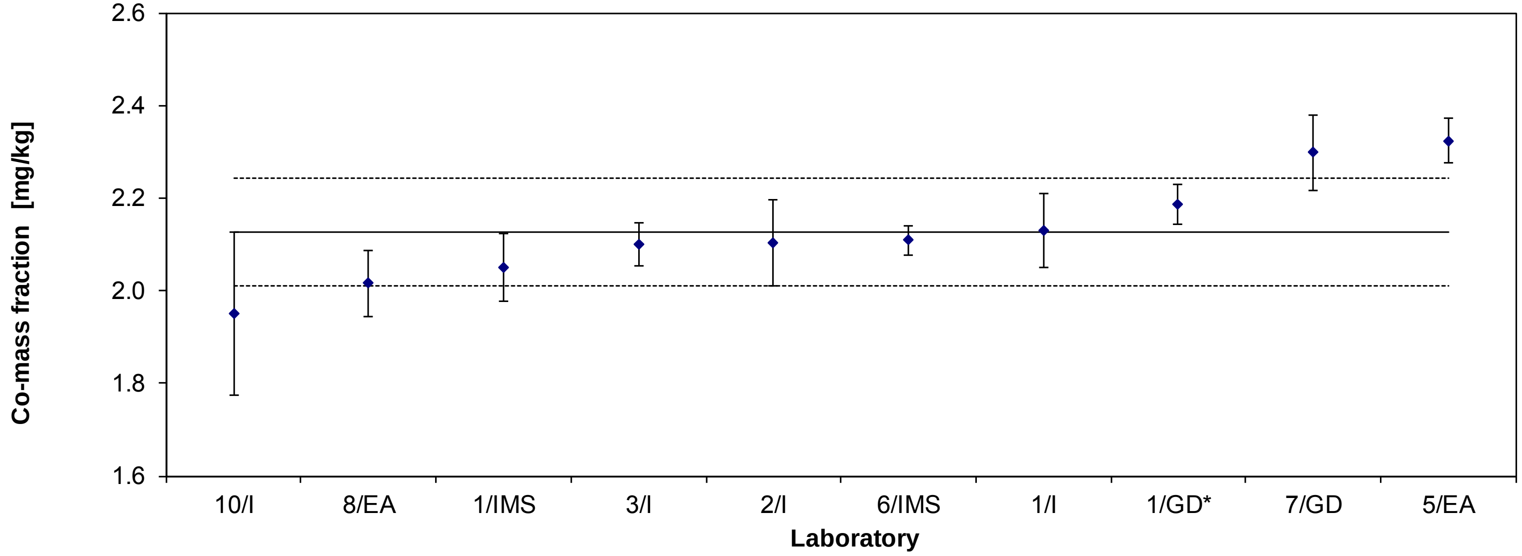

Table 8: Results for Co

Lab./Meth.	8/I	5/I	1/P	10/I	1/GD	1/IMS	2/I	3/I	6/IMS		
M_i [mg/kg]	4.70	5.04	5.93	6.0	5.72	6.98	5.90	5.19	7.60		*n*
	4.50	5.52	5.54	6.0	7.53	6.49	7.60	7.67	5.97		9
	3.40	5.54	5.55	6.0	6.49	4.48	6.80	7.35	7.80		
	4.00	4.99	5.55	6.0	5.87	7.68	7.00	7.54	8.77		
	6.20	4.97	5.44	6.0	5.62	6.91	6.10	6.98	6.58		
	6.20	5.11	4.84	6.0	6.15	7.22	6.60	6.64	7.44		
					5.76						
M [mg/kg]	**4.83**	**5.20**	**5.47**	**6.00**	**6.16**	**6.63**	**6.67**	**6.89**	**7.36**		**6.13**
s [mg/kg]	1.1501	0.2640	0.3541	0.0000	0.6717	1.1213	0.6186	0.9169	0.9784	s_M [mg/kg]	0.8393
										$\bar{s}_i$ [mg/kg]	0.7751
s_{rel}	0.23795	0.05082	0.06470	0.00000	0.10904	0.16921	0.09279	0.13301	0.13293		0.137

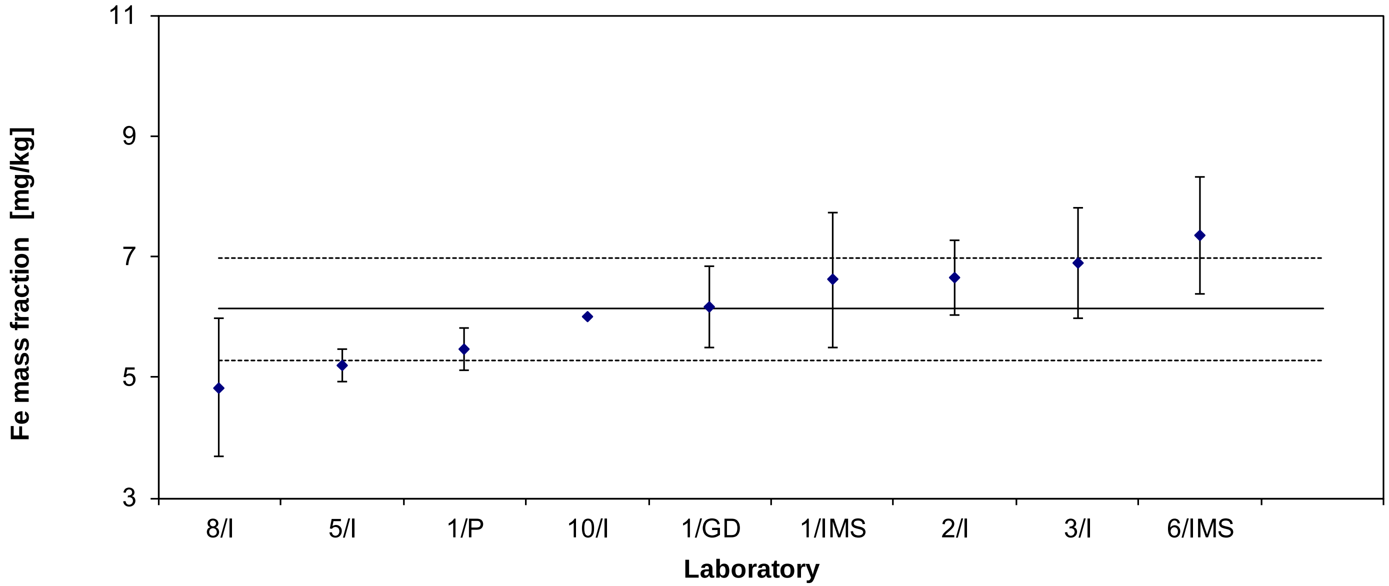

Table 9: Results for Fe

Lab./Meth.	1/I	7/GD	7/I	6/IMS	1/IMS	5/I	8/I(R)	10/I	3/I	1/EA	1/GD*	2/I		
M_i [mg/kg]	229.2	232.0	230.1	235.7	233.2	234.9	237.0	235.0	237.1	240.3	*236.4*	245.5		*n*
	229.8	231.0	230.8	225.8	234.1	235.3	237.0	237.0	236.3	235.4	*252.2*	244.1		12
	230.5	230.0	231.4	233.5	231.9	235.9	238.0	235.0	236.0	234.5	*252.9*	241.8		
	227.7	228.0	232.5	232.0	232.1	235.9	236.0	238.0	236.3	236.7	*251.3*	243.2		
	229.2		232.0	233.6	234.7	231.9	232.0	235.0	236.0	236.7	*229.9*	243.5		
	227.9		230.4	231.5	236.9	235.3	237.0	237.0	235.8	240.7	*226.4*	243.1		
											227.3			
											234.1			
***M* [mg/kg]**	**229.0**	**230.3**	**231.2**	**232.0**	**233.8**	**234.9**	**236.2**	**236.2**	**236.2**	**237.4**	**238.8**	**243.5**		**235.0**
s [mg/kg]	1.11	1.71	0.94	3.38	1.86	1.50	2.14	1.33	0.46	2.56	11.52	1.22	s_M [mg/kg]	4.05
													$\overline{s}_i$ [mg/kg]	3.90
s_{rel}	0.00484	0.00742	0.00405	0.01456	0.00797	0.00640	0.00905	0.00563	0.00195	0.01077	0.04824	0.00503		0.017

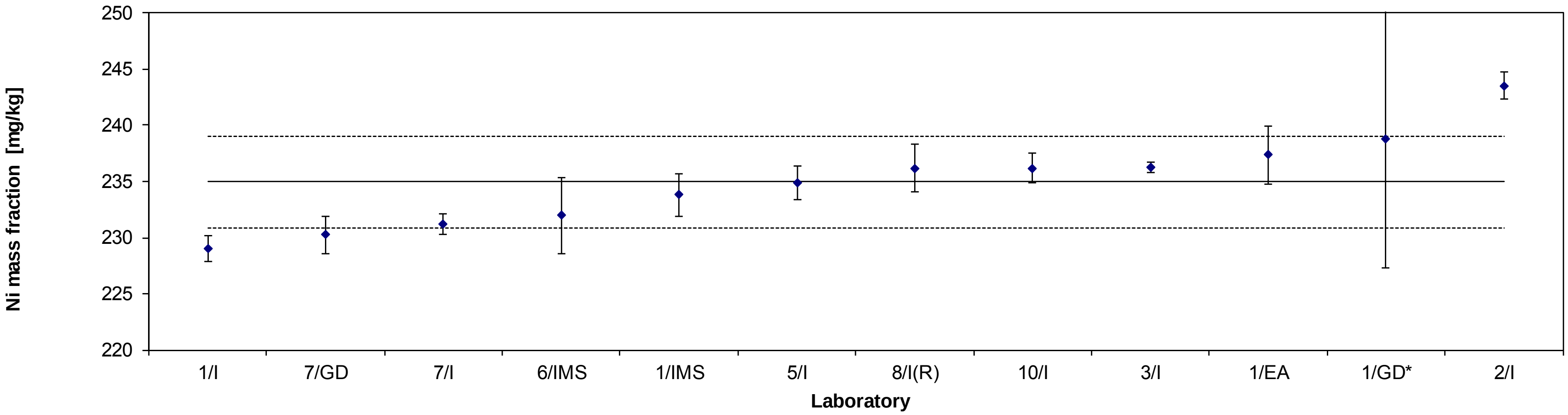

Table 10: Results for Ni

Lab./Meth.	7/I	1/EA	6/IMS	1/GD	1/I	5/I	10/I	1/IMS	3/I	8/I	2/I		
M_i [mg/kg]	132.0	134.8	129.7	141.8	144.1	141.6	142.0	142.0	143.6	148.0	147.3		*n*
	132.0	133.2	135.8	124.6	141.8	142.7	143.0	146.3	145.0	147.0	146.8		11
	124.0	137.7	135.4	126.6	144.0	144.4	144.0	142.2	144.9	146.0	146.2		
	143.0	133.3	135.8	139.6	141.8	144.2	143.0	142.5	145.5	148.0	146.0		
		130.2	133.3	140.7	143.1	141.6	146.0	143.0	145.4	142.0	146.2		
		133.5	135.8	157.4	141.0	142.9	145.0	148.2	144.5	143.0	145.9		
				156.0									
				154.1									
M [mg/kg]	**132.8**	**133.8**	**134.3**	**142.6**	**142.6**	**142.9**	**143.8**	**144.0**	**144.8**	**145.7**	**146.4**		**141.2**
s [mg/kg]	7.805	2.444	2.454	12.682	1.294	1.213	1.472	2.594	0.713	2.582	0.540	s_M [mg/kg]	5.059
												$\bar{s}_i$ [mg/kg]	4.7982
s_{rel}	0.059	0.018	0.018	0.089	0.009	0.008	0.010	0.018	0.005	0.018	0.004		0.036

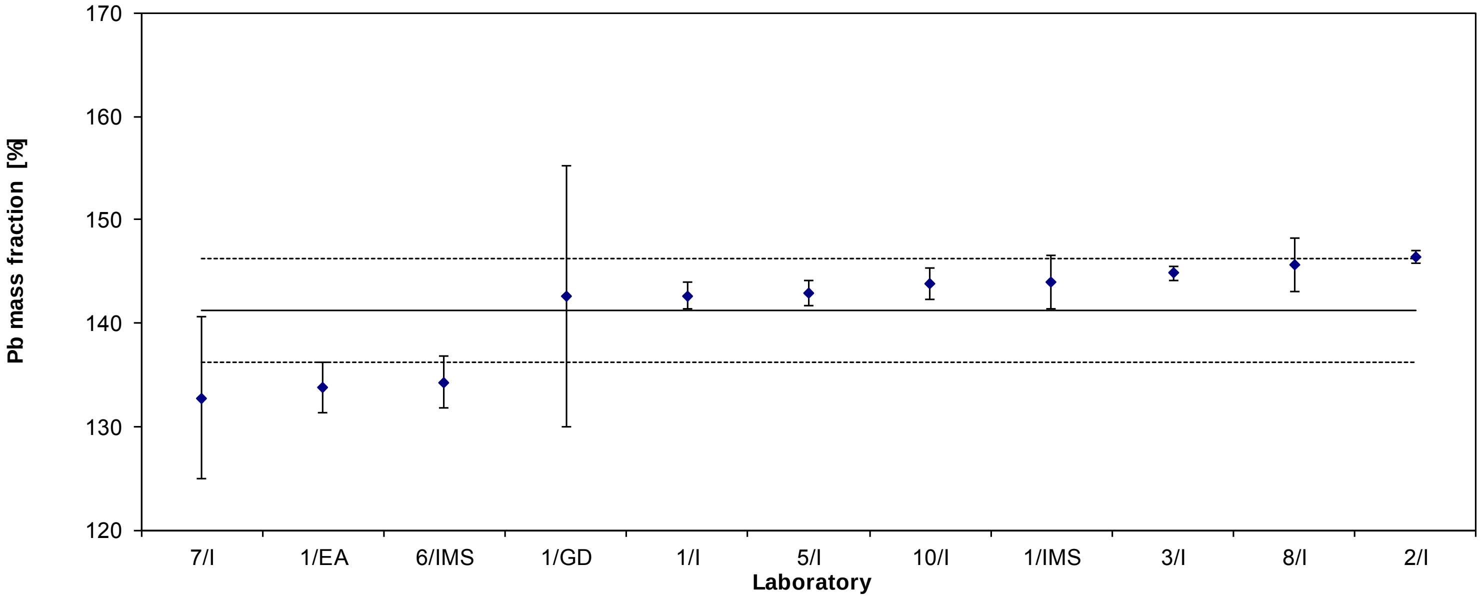

Table 11: Results for Pb

Lab./Meth.	10/I	3/I	1/I	1/GD	1/IMS	5/EA	8/EA	1/P	6/IMS	2/I	7/I		
M_i [mg/kg]	10	10.4	11.5	11.2	11.7	11.8	12.6	12.8	13.01	13.2	13.7		*n*
	9	11.1	10.7	11.3	11.7	11.9	12.6	12.8	12.58	13.4	13.7		11
	10	11.9	11.5	11.4	11.6	12.2	13.2	12.7	12.99	13.2	13.8		
	10	11.2	11.8	12.1	11.7	12.4	13.7	12.6	12.93	13.7	14.0		
	8	12.1	11.4	11.8	11.6	12.3	11.9	12.7	13.20	13.4			
	10	11.1	11.5	11.7	11.6	12.1	11.5	12.8	13.10	13.9			
								12.7					
***M* [mg/kg]**	**9.5**	**11.3**	**11.4**	**11.6**	**11.6**	**12.1**	**12.6**	**12.7**	**13.0**	**13.5**	**13.8**		**12.1**
s [mg/kg]	0.837	0.623	0.345	0.355	0.047	0.219	0.808	0.070	0.212	0.280	0.141	s_M [mg/kg]	1.204
												$\bar{s}_i$ [mg/kg]	0.4458
s_{rel}	0.088	0.055	0.030	0.031	0.004	0.018	0.064	0.006	0.016	0.021	0.010		0.100

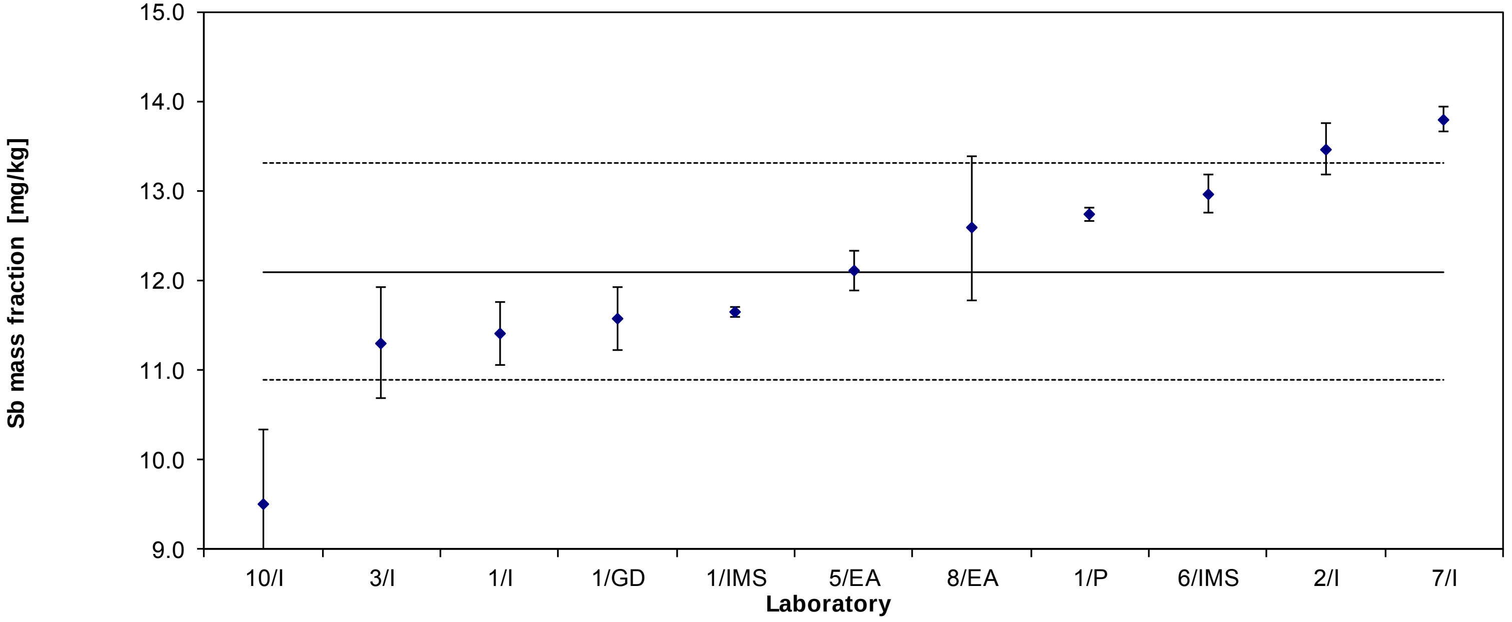

Table 12: Results for Sb

Lab./Meth.	6/IMS	1/GD	1/IMS	3/I(R)	7/I	10/I	8/I	5/I	2/I	7/GD		
M_i [mg/kg]	168.3	166.0	174.1	174.8	174.3	181.0	183.0	183.3	185.6	191.0		*n*
	163.1	170.3	167.0	171.0	175.5	183.0	185.0	185.2	188.2	190.0		10
	166.1	167.0	169.6	178.3	175.3	184.0	188.0	188.9	186.3	193.0		
	164.6	171.9	163.8	176.7	176.2	187.0	188.0	190.2	187.8	195.0		
	166.7	165.8	166.1	175.2	176.7	184.0	178.0	183.2	187.1			
	166.9	165.8	168.1	173.2	176.4	184.0	181.0	186.5	188.2			
M [mg/kg]	**166.0**	**167.8**	**168.1**	**174.9**	**175.7**	**183.8**	**183.8**	**186.2**	**187.2**	**192.3**		**178.6**
s [mg/kg]	1.8415	2.6170	3.5199	2.5679	0.8824	1.9408	3.9707	2.8910	1.0714	2.2174	s_M [mg/kg]	9.320
											$\bar{s}_i$ [mg/kg]	2.5290
s_{rel}	0.0111	0.0156	0.0209	0.0147	0.0050	0.0106	0.0216	0.0155	0.0057	0.0115		0.052

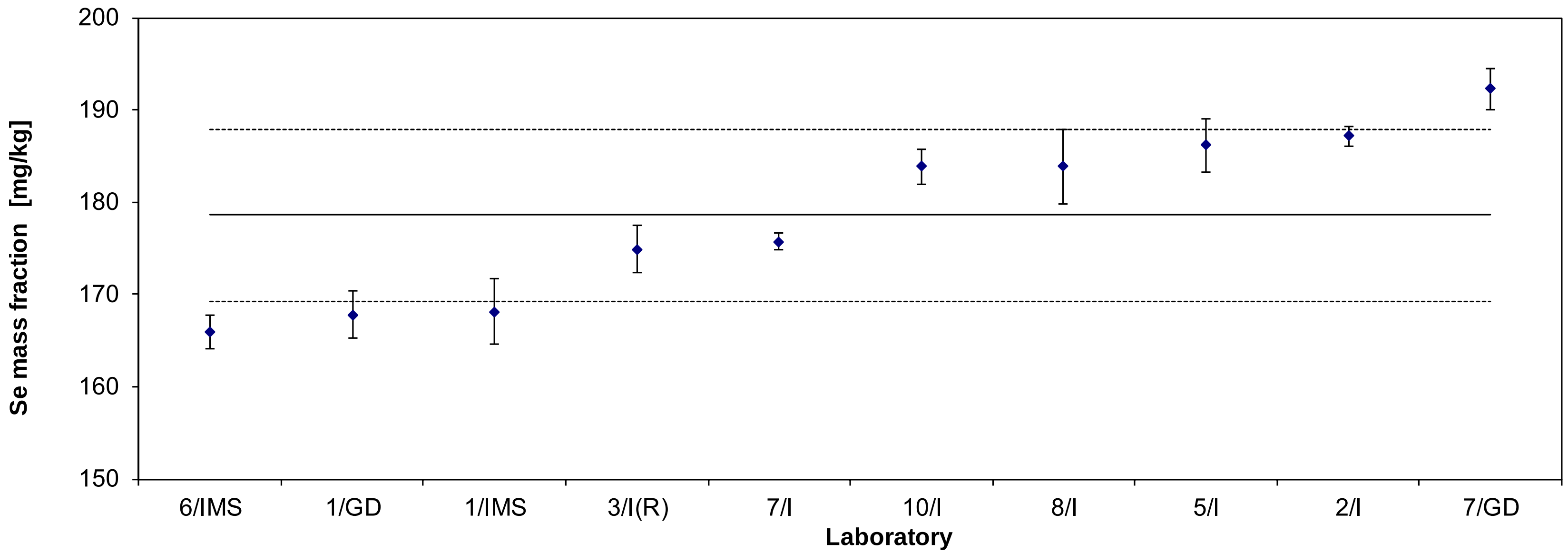

Table 13: Results for Se

Lab./Meth.	3/IMS	5/EA	1/GD	1/IMS	1/IMS(II)	6/IMS	7/GD	10/I		
M_i [mg/kg]	1.13	1.24	1.17	1.23	1.33	1.31	1.40	< 2		*n*
	1.13	1.19	1.22	1.23	1.31	1.43	1.40	< 2		7
	1.14	1.29	1.20	1.26	1.37	1.36	1.40	< 2		
	1.14	1.08	1.25	1.24	1.34	1.34	1.40	< 2		
	1.14	1.14	1.22	1.25	1.34	1.35		< 2		
	1.13	1.17	1.21	1.17	1.33	1.38		< 2		
***M* [mg/kg]**	**1.14**	**1.19**	**1.21**	**1.23**	**1.34**	**1.36**	**1.40**	**< 2**		**1.27**
s [mg/kg]	0.006	0.074	0.026	0.032	0.019	0.041	0.000		s_M [mg/kg]	0.100
									$\overline{s}_i$ [mg/kg]	0.028
s_{rel}	0.005	0.062	0.021	0.026	0.014	0.030	0.000			0.079

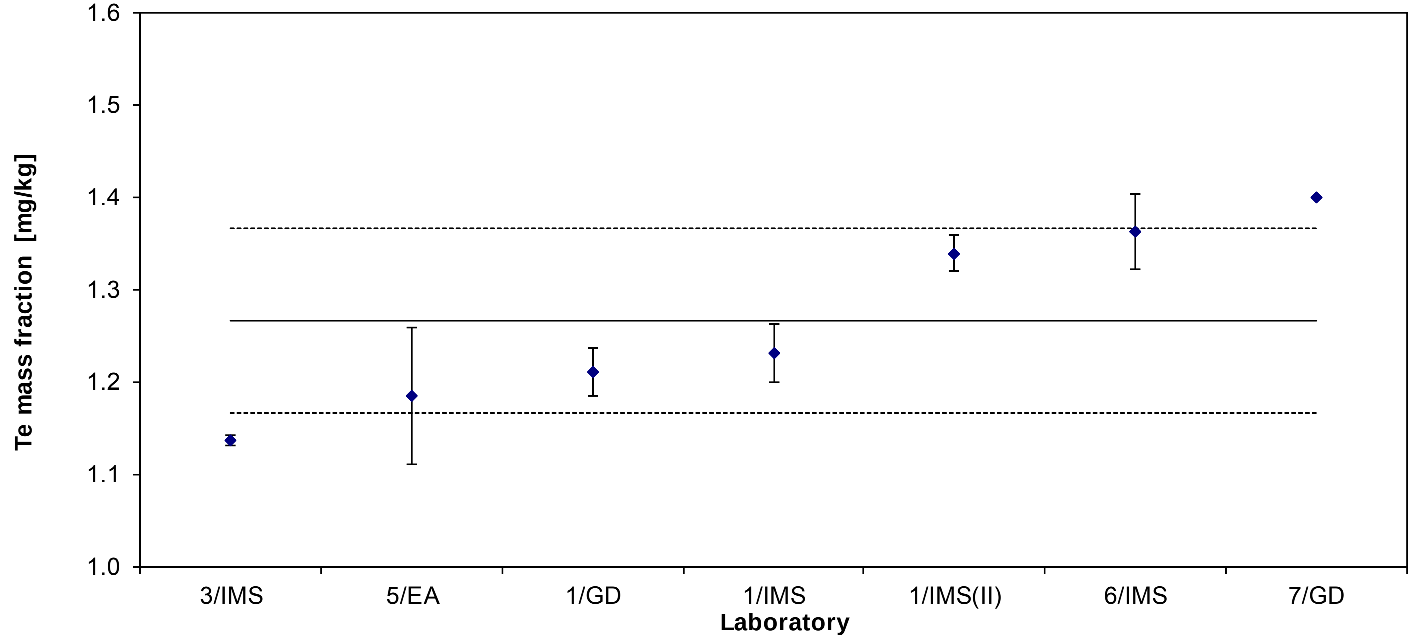

Table 14: Results for Te

Lab./Meth.	10/I	2/I	1/EA	8/I	1/I		
M_i [mg/kg]	23.0	29.3	27.4	33.0	35.6		*n*
	24.0	28.6	31.0	31.1	32.2		5
	23.0	29.0	28.4	33.4	30.8		
	23.0	28.0	31.8	30.8	32.9		
	24.0	28.6	27.8	30.3	33.2		
	24.0	28.7	28.6	30.3	32.3		
					32.8		
					30.9		
***M* [mg/kg]**	**23.5**	**28.7**	**29.2**	**31.5**	**32.6**		**29.1**
s [mg/kg]	0.548	0.440	1.824	1.370	1.512	s_M [mg/kg]	3.515
						$\bar{s}_i$ [mg/kg]	1.2637
s_{rel}	0.023	0.015	0.063	0.044	0.046		0.121

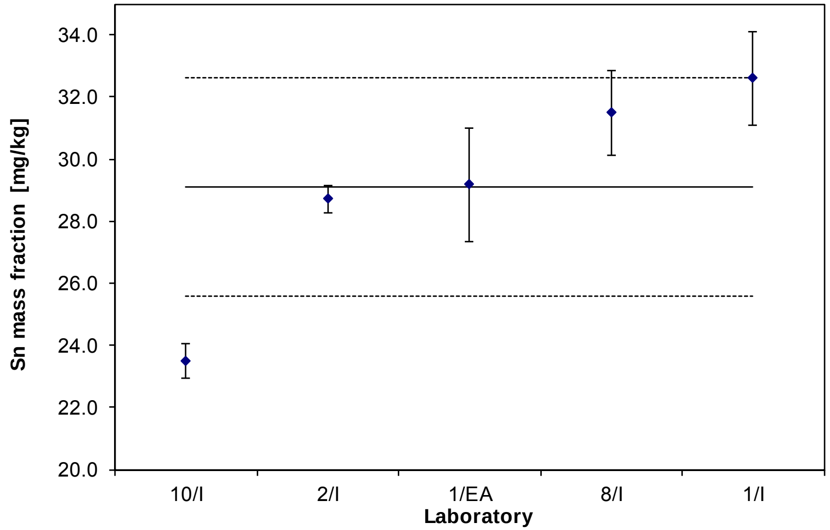

Table 15: Results for Sn

Lab./Meth.	8/I	10/I	1/I	1/A	2/I		
M_i [mg/kg]	27.9	28.0	32.4	31.9	32.8		*n*
	26.2	29.0	31.3	31.5	32.2		5
	22.9	28.0	30.4	33.6	32.8		
	26.2	28.0	32.3	31.6	31.6		
	26.6	28.0	32.0	32.5	32.8		
	27.6	29.0	31.9	31.2	31.9		
			31.5				
			31.2				
***M* [mg/kg]**	**26.2**	**28.3**	**31.6**	**32.0**	**32.4**		**30.1**
s [mg/kg]	1.783	0.516	0.644	0.871	0.548	s_M [mg/kg]	2.701
						$\bar{s}_i$ [mg/kg]	0.9919
s_{rel}	0.068	0.018	0.020	0.027	0.017		0.090

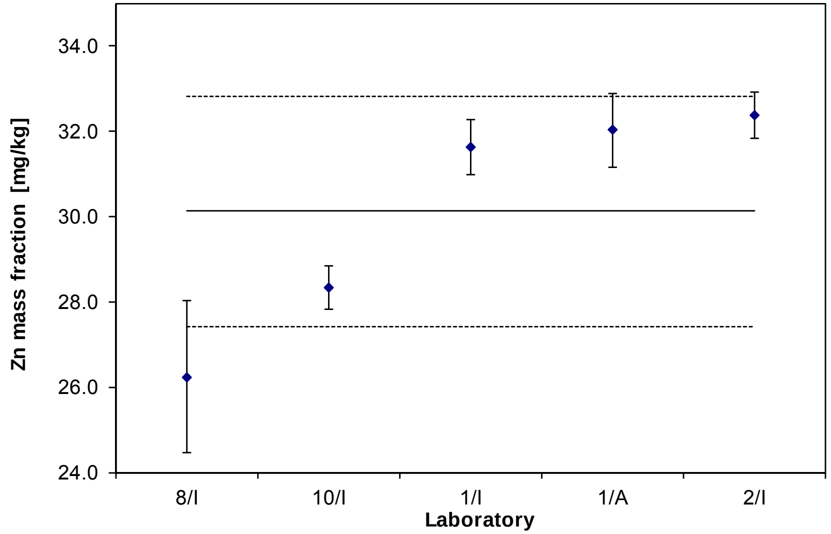

Table 16: Results for Zn

Lab./Meth.	5/TG	2/TG-2	2/TG-1	1/TG	3/TG		
M_i [mg/kg]	1660 1560 1650 1560 1670 1550	1690 1630 1642	1693 1630 1684	1774 1793 1771 1748 1767 1775	1860 1860 1850		*n* 5
***M* [mg/kg]**	**1608**	**1654**	**1669**	**1771**	**1857**		**1712**
s [mg/kg]	57.1	31.7	34.1	14.4	5.8	s_M [mg/kg]	100.5
						$\bar{s}_i$ [mg/kg]	33.7
s_{rel}	0.035	0.019	0.020	0.008	0.003		0.059

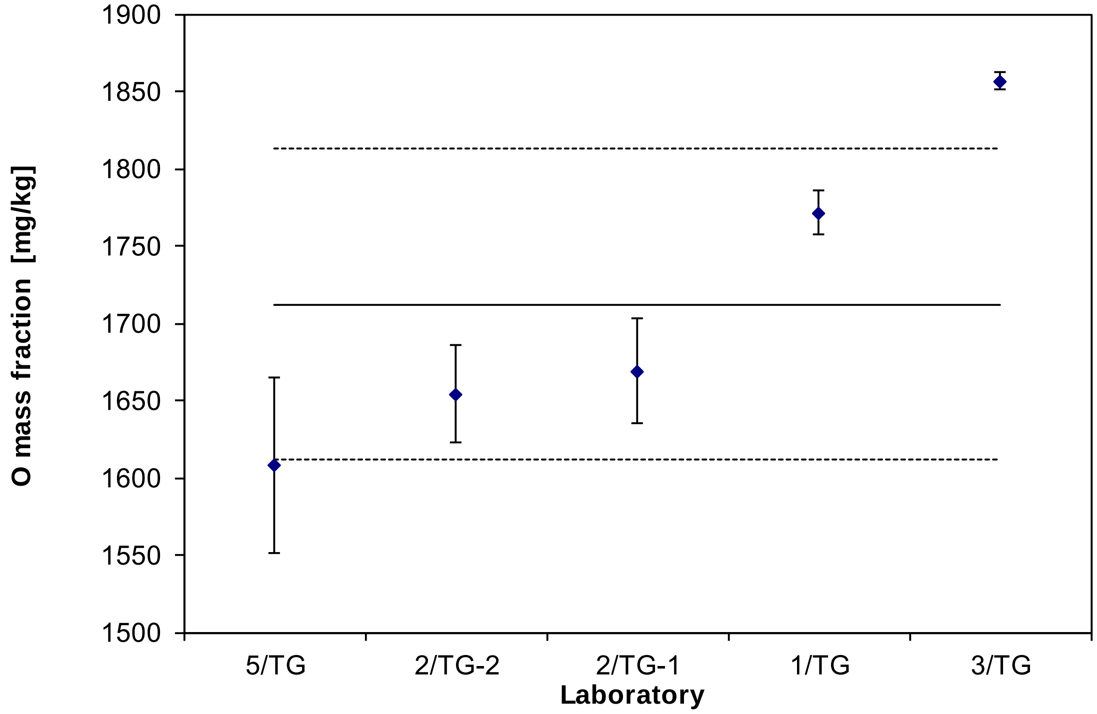

Table 17: Results for O

The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [5]. The following results were obtained:

Tab. 18: Outcome of statistical tests on the results obtained for Cu

Number of data sets	7
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

Tab. 19: Outcome of statistical tests on the results obtained for Ag

Number of data sets	11
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

Tab. 20: Outcome of statistical tests on the results obtained for As

Number of data sets	11
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)	Laboratory 7
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 straggler (Lab. 7) was not removed.

Tab. 21: Outcome of statistical tests on the results obtained for Bi

Number of data sets	11
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	Laboratories 6 and 7
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	Laboratories 6 and 7
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: not normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: not normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: not normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The stragglers (Labs. 6 and 7) were not removed.

Tab. 22: Outcome of statistical tests on the results obtained for Co

Number of data sets	10
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

Tab. 23: Outcome of statistical tests on the results obtained for Fe

Number of data sets	9
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

Tab. 24: Outcome of statistical tests on the results obtained for Ni

Number of data sets	12
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)	Laboratory 2
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 straggler (Lab. 2) was not removed.

Tab. 25: Outcome of statistical tests on the results obtained for Pb

Number of data sets	10
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

Tab. 26: Outcome of statistical tests on the results obtained for Sb

Number of data sets	11
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)	Laboratory 10
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 straggler (Lab. 10) was not removed.

Tab. 27: Outcome of statistical tests on the results obtained for Se

Number of data sets	10
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

Tab. 28: Outcome of statistical tests on the results obtained for Te

Number of data sets	7
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

Tab. 29: Outcome of statistical tests on the results obtained for Sn

Number of data sets	5
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)	Lab. 10
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)	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Insufficient data

The straggler (Lab. 10) was not removed.

Tab. 30: Outcome of statistical tests on the results obtained for Zn

Number of data sets	5
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)	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Insufficient data

Tab. 31: Outcome of statistical tests on the results obtained for O

Number of data sets	5
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)	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Insufficient data

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.

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

with

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

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

Table 32: Uncertainty calculation

			uncertainty contribution from						
	M	n	s_{M}	u_{ilc}	u_{bb}	u(comb)	U		u_{bb} (rel)
	%		%	%	%	%	%		
Cu	99.730	7	0.0583	0.0220	0.0000	0.0220	0.0661		
	mg/kg		mg/kg	mg/kg	mg/kg				
Ag	159.4	11	3.1610	0.9531	2.2488	2.4424	4.8848		1.4108
As	40.42	11	1.0310	0.3109	0.2251	0.3838	0.7676		0.5570
Bi	29.98	11	1.6980	0.5120	0.3060	0.5965	1.1929		1.0208
Co	2.127	10	0.1172	0.0371	0.0577	0.0685	0.1371		2.7111
Fe	6.134	9	0.8393	0.2798	0.5593	0.6254	1.2508		9.1185
Ni	235.0	12	4.0490	1.1688	1.8199	2.1629	4.3258		0.7745
Pb	141.3	11	5.0590	1.5253	0.6787	1.6695	3.3390		0.4805
Sb	12.10	11	1.2040	0.3630	0.3337	0.4931	0.9862		2.7581
Se	178.6	10	9.3200	2.9472	4.8929	5.7120	11.4240		2.7396
Te	1.270	7	0.1000	0.0378	0.0417	0.0563	0.1126		3.2856
Sn	29.09	5	3.5200	1.5742	0.3215	1.6067	4.0167		1.1051
Zn	30.11	5	2.7010	1.2079	0.8122	1.4556	3.6389		2.6973
O	1712.0	5	100.5000	44.9450	0.0000	44.9450	134.8349		

The expanded uncertainties U are calculated by multiplication of u_{combined} with a coverage factor of k = 2 (Sn, Zn: k = 2.5 and Cu, O: k = 3 due to a lower number of degrees of freedom) using Equation 4.

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

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

6. Metrological Traceability

The values are traceable to the SI (Système International d'Unités) via calibration using pure metals or substances of known stoichiometry including certified commercial monoelemental solutions in most cases (exception: some of the GDMS measurements).

7. Instructions for users and stability statement

The certified reference material BAM-M365a is intended for calibration and quality control of wet chemical analysis procedures.
For wet chemical analysis, the minimum sample intake is 1 g.
The material will remain stable provided that it is not subjected to excessive heat.

8. References

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

[2] ISO Guide 34, General requirements for the competence of reference material producers, 2009

[3] ISO Guide 35, Reference materials - General and statistical principles for certification. Third edition, 2006

[4] Guidelines for the development and production of BAM Reference Materials, 2016

[5] Bonas G, Zervou M, Papaeoannou T, Lees M: Accred Qual Assur (2003) 8:101-107

9. Information on and purchase of the CRM

Certified reference material BAM-M365a is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
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 bottle of BAM-M365a 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
www.webshop.bam.de
Tel. +49 30 8104 1111.

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity

Silver:

Bottle	1	2	3
12	153.32	155.88	157.40
27	155.97	157.26	157.62
117	153.52	156.69	
147	156.82	158.52	159.60
154	154.52		152.76
207	160.07	160.59	159.62
242	161.27	158.79	160.46
330	161.55	160.37	160.15
340	157.99	161.32	161.73
512	157.54	159.74	159.06
528	165.91	160.50	156.80
560	157.00	157.56	162.50
562	157.48	160.93	160.58
584	160.48	161.48	163.31
637	156.90	159.02	159.70

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	466.6	155.5	4.3		
27	3	470.8	156.9	0.8		
117	2	310.2	155.1	5.0		
147	3	474.9	158.3	2.0		
154	2	307.3	153.6	1.5		
207	3	480.3	160.1	0.2		
242	3	480.5	160.2	1.6		
330	3	482.1	160.7	0.6		
340	3	481.0	160.3	4.2		
512	3	476.3	158.8	1.3		
528	3	483.2	161.1	21.0		
560	3	477.1	159.0	9.2		
562	3	479.0	159.7	3.6		
584	3	485.3	161.8	2.1		
637	3	475.6	158.5	2.1		
			158.6			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	196.357013	14	14.0255009	3.49990004	0.00232114	2.06354083
Within groups	112.207212	28	4.00740043			
Total	308.564225	42				
within-sd	2.001849					
effective n	2.00					
s_bb	2.238091			1.41076		
s_bb_min	0.731786			0.461275		
u_bb	2.238091	2238.091				
u_bb(rel.)	1.41075998					

Arsenic:

Bottle	1	2	3
12	39.63	40.13	40.50
27	40.65	39.93	40.34
117	40.41	40.05	40.40
147	40.41	41.42	40.86
154	40.46	41.18	40.80
207	41.30	41.50	40.51
242	41.73	40.46	41.10
330	41.90	41.57	40.79
340	40.98	40.69	40.92
512	40.65	40.66	39.65
528	41.98	40.76	39.75
560	39.94	40.26	42.14
562	41.46	41.43	40.97
584	41.06	40.45	41.43
637	40.55	41.35	40.86

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	120.25	40.08	0.19		
27	3	120.92	40.31	0.13		
117	3	120.86	40.29	0.04		
147	3	122.68	40.89	0.26		
154	3	122.44	40.81	0.13		
207	3	123.32	41.11	0.27		
242	3	123.28	41.09	0.40		
330	3	124.25	41.42	0.33		
340	3	122.59	40.86	0.02		
512	3	120.95	40.32	0.34		
528	3	122.49	40.83	1.24		
560	3	122.34	40.78	1.41		
562	3	123.86	41.29	0.07		
584	3	122.94	40.98	0.24		
637	3	122.77	40.92	0.16		
			40.80			

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.33808298	14	0.45272021	1.29552239	0.26668858	2.03742044
Within groups	10.483498	30	0.34944993			
Total	16.821581	44				
within-sd	0.591143					
effective n	2.00					
s_bb	0.227234			0.556967		
s_bb_min	0.2124			0.520609		
u_bb	0.227234	227.2337				
u_bb(rel.)	0.5569668					

Bismuth:

Bottle	1	2	3
12	29.47	30.09	29.56
27	30.24	30.13	30.79
117	30.47	29.90	30.24
147	30.10	30.99	30.96
154	30.24	31.04	31.33
207	31.20	30.99	30.75
242	30.19	30.26	30.63
330	31.01	30.80	30.19
340	30.76	30.92	31.14
512	30.72	30.96	30.15
528	31.38	30.51	30.54
560	30.07	30.19	30.90
562	30.51	30.34	30.87
584	30.57	30.80	30.84
637	30.98	31.11	30.41

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	89.12	29.71	0.11		
27	3	91.16	30.39	0.12		
117	3	90.62	30.21	0.08		
147	3	92.05	30.68	0.25		
154	3	92.61	30.87	0.32		
207	3	92.93	30.98	0.05		
242	3	91.09	30.36	0.06		
330	3	91.99	30.66	0.18		
340	3	92.83	30.94	0.04		
512	3	91.83	30.61	0.17		
528	3	92.43	30.81	0.24		
560	3	91.16	30.39	0.20		
562	3	91.72	30.57	0.07		
584	3	92.21	30.74	0.02		
637	3	92.49	30.83	0.14		
			30.58			

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4.66118298	14	0.33294164	2.4119972	0.02109007	2.03742044
Within groups	4.14107	30	0.13803567			
Total	8.80225298	44				
within-sd	0.371532					
effective n	2.00					
s_bb	0.312175			1.02076		
s_bb_min	0.133493			0.4365		
u_bb	0.312175	312.1746				
u_bb(rel.)	1.02075964					

Cobalt:

Bottle	1	2	3
12	2.046	2.158	2.118
27	2.103	2.189	2.139
117	2.048	2.052	2.114
147	2.131	2.190	2.155
154	2.119	2.258	2.217
207	2.237	2.126	2.143
242	2.140	2.093	2.239
330	2.247	2.284	2.255
340	2.209	2.135	2.275
512	2.164	2.249	2.310
528	2.388	2.190	2.187
560	2.162	2.060	2.259
562	2.167	1.985	2.149
584	2.195	2.073	2.070
637	2.237	2.338	2.235

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	6.322	2.107	0.0032		
27	3	6.431	2.144	0.0019		
117	3	6.214	2.071	0.0014		
147	3	6.476	2.159	0.0009		
154	3	6.594	2.198	0.0051		
207	3	6.506	2.169	0.0036		
242	3	6.472	2.157	0.0056		
330	3	6.786	2.262	0.0004		
340	3	6.619	2.206	0.0049		
512	3	6.723	2.241	0.0054		
528	3	6.765	2.255	0.0133		
560	3	6.481	2.160	0.0099		
562	3	6.301	2.100	0.0101		
584	3	6.338	2.113	0.0051		
637	3	6.810	2.270	0.0035		
			2.174			

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.16635791	14	0.01188271	2.40828818	0.02126974	2.03742044
Within groups	0.14802267	30	0.00493409			
Total	0.31438058	44				
within-sd	0.070243					
effective n	2.00					
s_bb	0.058943			2.71106		
s_bb_min	0.025239			1.160835		
u_bb	0.058943	58.94327				
u_bb(rel.)	2.71106045					

Iron:

Bottle	1	2	3
12	4.4712	4.9253	5.7062
27	4.9874	5.5802	5.5207
117	4.8282	5.1692	6.9618
147	4.5522	5.1124	4.7594
154	5.4121	6.4748	7.9250
207	8.8248	5.8438	6.1457
242	5.0323	4.8286	4.8739
330	5.7891	5.6546	6.6873
340	4.9718	5.0648	9.5866
512	7.1773	6.8883	
528	6.5986	6.2959	5.7782
560	6.5239	4.9941	6.4547
562	6.0083	5.0294	5.7764
584	6.9792	6.4908	4.4807
637	7.6786	6.9087	7.2203

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	15.1028	5.0343	0.3902		
27	3	16.0884	5.3628	0.1066		
117	3	16.9592	5.6531	1.3137		
147	3	14.4240	4.8080	0.0803		
154	3	19.8120	6.6040	1.5912		
207	3	20.8143	6.9381	2.6924		
242	3	14.7348	4.9116	0.0114		
330	3	18.1311	6.0437	0.3152		
340	3	19.6232	6.5411	6.9587		
512	2	14.0656	7.0328	0.0418		
528	3	18.6727	6.2242	0.1721		
560	3	17.9727	5.9909	0.7464		
562	3	16.8141	5.6047	0.2616		
584	3	17.9508	5.9836	1.7536		
637	3	21.8076	7.2692	0.1499		
			6.0001			

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	24.3745591	14	1.74103993	1.5240734	0.16411124	2.05000359
Within groups	33.1284294	29	1.14235963			
Total	57.5029885	43				
within-sd	1.068812					
effective n	2.00					
s_bb	0.54712			7.526553		
s_bb_min	0.387297			5.327925		
u_bb	0.54712	547.1199				
u_bb(rel.)	9.11846001					

Nickel:

Bottle	1	2	3
12	224.35	225.31	227.76
27	227.61	223.56	226.43
117	227.99	227.94	227.27
147	228.39	227.69	229.31
154	228.60	229.40	229.87
207	229.69	229.23	230.84
242	226.66	228.30	228.64
330	227.48	228.14	230.04
340	227.25	225.18	229.29
512	227.95	228.63	228.24
528	235.93	231.84	229.44
560	228.25	227.81	231.00
562	229.19	230.78	229.84
584	229.57	230.64	228.39
637	225.79	228.74	226.90

Bottle	*Number*	*Sum*	*Mean*	*Variance*
12	3	677.41	225.80	3.10
27	3	677.60	225.87	4.35
117	3	683.21	227.74	0.16
147	3	685.39	228.46	0.66
154	3	687.87	229.29	0.41
207	3	689.76	229.92	0.69
242	3	683.60	227.87	1.13
330	3	685.66	228.55	1.77
340	3	681.72	227.24	4.22
512	3	684.82	228.27	0.12
528	3	697.22	232.41	10.76
560	3	687.06	229.02	2.99
562	3	689.81	229.94	0.64
584	3	688.60	229.53	1.27
637	3	681.43	227.14	2.22
			228.47	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	119.852111	14	8.5608651	3.72535495	0.00122246	2.03742044
Within groups	68.9399953	30	2.29799984			
Total	188.792107	44				
within-sd	1.515916					
effective n	2.00					
s_bb	1.769585			0.774538		
s_bb_min	0.544675			0.238401		
u_bb	1.769585	1769.585				
u_bb(rel.)	0.77453824					

Lead:

Bottle	1	2	3
12	139.35	140.40	140.20
27	141.57	138.76	139.63
117	140.67	138.82	140.63
147	139.93	142.13	142.15
154	140.92	145.02	143.97
207	143.73	142.35	142.81
242	142.51	138.93	140.98
330	142.91	143.59	140.05
340	142.01	144.36	143.73
512	140.17	142.65	140.71
528	146.50	140.40	138.04
560	138.82	139.11	143.19
562	142.74	142.26	140.93
584	143.37	140.74	143.21
637	142.78	142.96	141.22

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	419.96	139.99	0.31		
27	3	419.97	139.99	2.07		
117	3	420.11	140.04	1.12		
147	3	424.21	141.40	1.62		
154	3	429.91	143.30	4.53		
207	3	428.89	142.96	0.49		
242	3	422.42	140.81	3.22		
330	3	426.56	142.19	3.53		
340	3	430.10	143.37	1.49		
512	3	423.53	141.18	1.69		
528	3	424.93	141.64	19.05		
560	3	421.11	140.37	5.97		
562	3	425.93	141.98	0.88		
584	3	427.31	142.44	2.17		
637	3	426.96	142.32	0.92		
			141.60			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	58.7493378	14	4.19638127	1.28301936	0.2738038	2.03742044
Within groups	98.12123	30	3.27070767			
Total	156.870568	44				
within-sd	1.80851					
effective n	2.00					
s_bb	0.680321			0.48046		
s_bb_min	0.649805			0.458909		
u_bb	0.680321	680.3211				
u_bb(rel.)	0.4804603					

Antimony:

Bottle	1	2	3
12	11.531	11.804	11.105
27	11.187	11.236	11.406
117	11.354	11.002	12.010
147	11.192	11.848	12.212
154	11.815	11.556	11.920
207	12.514	10.932	10.702
242	11.517	11.855	11.417
330	11.242	11.610	10.975
340	10.167	11.300	10.623
512	10.569	11.430	11.785
528	11.752	11.162	11.680
560	12.600	11.739	12.188
562	10.877	10.369	11.207
584	11.090	10.644	11.824
637	11.900	11.585	11.854

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	34.440	11.480	0.124		
27	3	33.829	11.276	0.013		
117	3	34.366	11.455	0.262		
147	3	35.252	11.751	0.267		
154	3	35.291	11.764	0.035		
207	3	34.148	11.383	0.973		
242	3	34.789	11.596	0.053		
330	3	33.827	11.276	0.102		
340	3	32.090	10.697	0.325		
512	3	33.784	11.261	0.391		
528	3	34.594	11.531	0.104		
560	3	36.527	12.176	0.185		
562	3	32.453	10.818	0.178		
584	3	33.558	11.186	0.355		
637	3	35.339	11.780	0.029		
			11.429			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	5.95164213	14	0.4251173	1.87770703	0.07234762	2.03742044
Within groups	6.79207067	30	0.22640236			
Total	12.7437128	44				
within-sd	0.475818					
effective n	2.00					
s_bb	0.31521			2.758082		
s_bb_min	0.170963			1.495924		
u_bb	0.31521	315.2102				
u_bb(rel.)	2.75808235					

Selenium:

Bottle	1	2	3
12	151.04	156.93	168.23
27	151.60	156.42	164.62
117	120.23	136.05	165.35
147	143.38	156.81	144.13
154	140.59	167.27	162.17
207	160.84	162.83	156.29
242	168.63	163.86	171.02
330	156.65	157.42	164.34
340	138.65	147.41	157.60
512	147.62	163.58	175.45
528	164.36	161.34	159.99
560	149.33	153.60	160.83
562	118.89	161.61	168.66
584	162.17	166.09	174.26
637	147.27	149.74	166.05

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
12	3	476.20	158.73	76.33		
27	3	472.64	157.55	43.30		
117	3	421.62	140.54	524.04		
147	3	444.32	148.11	56.90		
154	3	470.04	156.68	200.61		
207	3	479.96	159.99	11.26		
242	3	503.52	167.84	13.28		
330	3	478.40	159.47	17.93		
340	3	443.66	147.89	89.99		
512	3	486.65	162.22	195.05		
528	3	485.69	161.90	5.00		
560	3	463.75	154.58	33.77		
562	3	449.15	149.72	725.33		
584	3	502.52	167.51	38.09		
637	3	463.06	154.35	104.17		
			156.47			

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2376.55592	14	169.753995	1.19261858	0.32999266	2.03742044
Within groups	4270.11614	30	142.337205			
Total	6646.67206	44				

within-sd	11.93052					
effective n	2.00					
s_bb	3.702485			2.366251		
s_bb_min	4.286683			2.739611		
u_bb	4.286683	4286.683				
u_bb(rel.)	2.7396114					

Tellurium:

Bottle	1	2	3
12	1.2603	1.3380	1.3516
27	1.2632	1.3026	1.3185
117	1.1630	1.0815	1.3072
147	1.2489	1.3135	1.1685
154	1.2469	1.3216	1.3389
207		1.3898	1.2989
242		1.3439	1.3376
330	1.3177	1.3242	1.3369
340	1.2645	1.2834	1.4162
512	1.2974	1.3733	1.3695
528	1.4146	1.3980	1.3496
560	1.3274	1.3044	1.3731
562	1.1196	1.2928	1.3552
584	1.3346	1.3136	1.3727
637	1.3430	1.3355	1.3323

Bottle	*Number*	*Sum*	*Mean*	*Variance*
12	3	3.9499	1.3166	0.0024
27	3	3.8843	1.2948	0.0008
117	3	3.5516	1.1839	0.0131
147	3	3.7308	1.2436	0.0053
154	3	3.9074	1.3025	0.0024
207	2	2.6887	1.3444	0.0041
242	2	2.6814	1.3407	0.0000
330	3	3.9787	1.3262	0.0001
340	3	3.9641	1.3214	0.0068
512	3	4.0403	1.3468	0.0018
528	3	4.1622	1.3874	0.0011
560	3	4.0050	1.3350	0.0012
562	3	3.7676	1.2559	0.0149
584	3	4.0210	1.3403	0.0009
637	3	4.0108	1.3369	0.0000
			1.3118	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.10500582	14	0.00750042	1.98147086	0.06010701	2.06354083
Within groups	0.10598775	28	0.00378528			
Total	0.21099358	42				

within-sd	0.061525					
effective n	2.00					
s_bb	0.0431			3.28564		
s_bb_min	0.022491			1.714547		
u_bb	0.0431	43.09953				
u_bb(rel.)	3.28564048					

Zinc:

Bottle	1	2
11	33.8500	32.4100
32	33.2900	32.1100
154	33.8900	33.8100
268	31.8700	32.7800
330	32.9900	30.6300
348	31.7900	35.7400
364	33.6700	32.7400
476	31.4600	34.2900
584	33.2600	32.4000
577	32.4600	32.1600

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
11	2	66.26	33.13	1.0368		
32	2	65.4	32.70	0.6962		
154	2	67.7	33.85	0.0032		
268	2	64.65	32.33	0.41405		
330	2	63.62	31.81	2.7848		
348	2	67.53	33.77	7.80125		
364	2	66.41	33.21	0.43245		
476	2	65.75	32.88	4.00445		
584	2	65.66	32.83	0.3698		
577	2	64.62	32.31	0.045		
			32.88			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	7.41	9	0.82333333	0.4681222	0.86570093	3.02038295
Within groups	17.588	10	1.7588			
Total	24.998	19				
within-sd	1.326198					
effective n	1.00					
s_bb	0			0		
s_bb_min	0.886882			2.697329		
u_bb	0.886882	886.8818				
u_bb(rel.)	2.69732898					

Tin:

Bottle	1	2
32	32.3800	32.4400
154	33.1700	32.9300
268	32.5800	
330	33.0300	32.9900
340	33.0800	33.5400
364	32.8000	32.1700
476	32.4800	
577	32.9600	32.8300
584	32.4900	32.7300

Bottle	*Number*	*Sum*	*Mean*	*Variance*		
32	2	64.82	32.41	0.0018		
154	2	66.1	33.05	0.0288		
268	1	32.58	32.58	#DIV/0!		
330	2	66.02	33.01	0.0008		
340	2	66.62	33.31	0.1058		
364	2	64.97	32.485	0.19845		
476	1	32.48	32.48	#DIV/0!		
577	2	65.79	32.895	0.00845		
584	2	65.22	32.61	0.0288		
			32.76			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.4746	8	0.184325	3.46010995	0.05966789	3.72572532
Within groups	0.3729	7	0.05327143			
Total	1.8475	15				
within-sd	0.230806					
effective n	1.00					
s_bb	0.362013			1.105084		
s_bb_min	0.168745			0.515111		
u_bb	0.362013	362.0132				
u_bb(rel.)	1.10508394					