Certification Report

Certified Reference Material

BAM-M603

Zinc powder

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Summary

This report describes preparation, analysis and certification of zinc powder reference material BAM-M603.
The certified reference material (CRM) is available in the form of powder (d_{50} = 148 µm). It is intended for establishing and checking the calibration of wet chemical methods for the analysis of samples of similar materials.

The following mass fractions and uncertainties have been certified:

Element	Mass fraction [1) in mg/kg	Uncertainty [2) in mg/kg
Pb	15.8	0.5
Ag	1.00	0.09
Cd	1.69	0.12
Cu	3.69	0.21
Fe	2.18	0.14
Ni	0.43	0.05
Tl	3.81	0.23

1) Unweighted mean value of the means of accepted sets of data (consisting of at least 4 but usually 5 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).

The certified values are based on the results of 14 laboratories which participated in the certification inter-laboratory comparison.

The mass fractions of Al, As, Bi, Co, In, Sb, Sn, and V are given for information.

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List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
ETAAS	electrothermal atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
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
ICP	ICP-OES (Tables 5 – 19)
u_{ilc}	uncertainty contribution from inter-laboratory comparison
u_{stab}	uncertainty contribution from possible instability
u_{bb}	uncertainty contribution from possible inhomogeneity

1. Introduction

Zinc powder is mainly used in alkaline batteries and in button cells, in thermal spraying for corrosion protection and in the chemical industry. DIN EN 1179 (Primary zinc) defines the maximum contents of the elements Pb, Cd, Fe, Sn, Cu, and Al [1]. For 99.995 % zinc (Z1 acc. to the standard) the following mass fractions are defined:
Pb: max. 30 mg/kg
Cd: max. 30 mg/kg
Fe: max. 20 mg/kg
Sn: max. 10 mg/kg
Cu: max. 10 mg/kg
Al: max. 10 mg/kg
The sum of all six elements must not be higher than 50 mg/kg.

The idea to produce a zinc powder reference material was the outcome of discussions within the German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB), especially of the working group „Zinc“ 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 zinc analysis and had participated in earlier inter-laboratory comparisons, there was no preceding round robin for qualification.
Certification of reference material BAM-M603 was carried out on the basis of ISO 17034 [2] and the relevant ISO-Guides [3, 4].

2. Companies/laboratories involved

Manufacturing of the material

- Grillo AG, Goslar, Germany

Test for homogeneity and stability

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

Participants in the certification inter-laboratory comparison

- Agilent GmbH AG, Waldbronn, Germany
- AMCO united, Duisburg, Germany
- Boliden Odda, Norway
- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
  Division „Inorganic Reference Materials“
  Division „Inorganic Trace Analysis
- Chemad GmbH, Duisburg, Germany
- Inspectorate International Limited, Witham, Essex, United Kingdom
- MKM Mansfelder Kupfer und Messing GmbH, Hettstedt, Germany
- Norzinco GmbH, Goslar, Germany
- revierlabor GmbH, Essen, Germany
- Thyssenkrupp Steel Europe AG, Duisburg, Germany
- TU Clausthal, Institut für Aufbereitung, Deponietechnik und Geomechanik, Clausthal, Germany
- VARTA Consumer Batteries GmbH & Co. KGaA, Dischingen, Germany
- VARTA Microbattery GmbH, Ellwangen, Germany

Statistical evaluation of the data

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

3. Candidate material

The starting material in form of fine powder was taken from the normal production process within Grillo-Werke Goslar. The particle size was determined by the producer using dry sieve analysis according to ASTM B214 [5].

Tab. 1: Particle size distribution of BAM-M603

range	amount
> 425 µm	0 %
425-250 µm	12 %
250-180 µm	25 %
180-150 µm	11 %
150-106 µm	25 %
106-75 µm	14 %
75-45 µm	9 %
45-25 µm	3 %
< 25 µm	1 %
d 10	66 µm
d 50	148 µm
d 90	284 µm

The powder was homogenised and bottled in BAM using a spinning riffler. In total 495 bottles containing 200 g of powder were obtained from the whole batch.

4. Homogeneity testing

A total of 15 bottled units (see Table 2) of the candidate material were randomly selected for homogeneity testing.

Tab. 2: Bottles analysed for homogeneity testing of BAM-M603

3	114	206	334	417
36	133	253	350	461
79	165	277	394	482

From each bottle three sub-samples were analysed using ICP-MS. 0.25 g of sample was weighed and dissolved in nitric acid. The homogeneity contribution to the total uncertainty was calculated using a 1-way-ANOVA (see Annex 1).

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budgets were calculated according to ISO Guide 35 [4] using Eq. (1):

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

with:

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

In cases, where $s_{within} > s_{between}$ the inhomogeneity contribution to the combined uncertainty is set to zero. This was the case for the elements Pb, Ag, Cd, Fe, Ni, Sb, Bi, Co, and V.

5. Stability testing

According to the producer of the material zinc powder should be stable because of the oxide layer on the surface of the particles. A possible instability could be the oxidation of Zn to ZnO.
To ensure the stability of the material the content of zinc oxide of the material was determined in February 2018 and in May 2019, using the following test:

1) 4 g of zinc powder was taken from the same bottle and transferred into a beaker filled with 20 ml of ammonia and 30 ml of water followed by strong mixing for 40 s.
2) The whole mixture was transferred immediately into a 100-ml-volumetric flask, filled up to the mark with water and mixed well.
3) 50 ml of this mixture were filtered, transferred into a 100-ml-volumetric flask filled with 10 ml of concentrated HCl.
4) The zinc-content of the solution was measured using ICP-OES

Table 3: Results of stability measurements

	Sample	1	2	3	Mean	s
02/2018	1	0.130	0.121	0.117	0.114	0.012
	2	0.112	0.103	0.101		
05/2019	1	0.097	0.139	0.120	0.117	0.017
	2	0.133	0.109	0.104		

The test results don't indicate an additional oxidation within 15 months of storage.
To consider a possible oxidation it was assumed that the mass fraction of ZnO increases from 0.1 % in 02/2018 to 0.5 % within ten years. This would increase the weight of the material by 0.1 %. As a result, the mass fractions of the certified impurities will decrease by 0.1 %. Therefore, an uncertainty contribution of 0.1 % is added to the combined uncertainty.
The stability test will be repeated regularly.

6. Characterisation study

6.1 Analytical methods

14 laboratories participated in the certification inter-laboratory comparison. All laboratories were highly experienced in the analysis of zinc or 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 five subsamples. They were free to choose any suitable analytical method for their determinations. Table 4 shows the analytical methods used by the participating laboratories.

Table 4: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Ag, Al, As, Bi, Cd, Co, Cu, Fe, Ni, Pb, Sb, Sn, V	5 g	Dissolution with HCl/HNO_3,	ICP-OES, calibration with commercial solutions (Carl Roth), standard addition
2	Pb, Cd, Fe, Cu, Ni, Sn	1 g	Dissolution with HNO_3/tartaric acid according to DIN ISO 3815-2	ICP-OES, calibration with commercial solutions
3	Pb, Cd, Fe, Cu, Ni, Sn, Sb, Ag, Al, As, Bi, Tl, V	5 g	Dissolution with HCl/HNO_3,	ICP-OES, calibration with commercial solutions (Merck)
	Pb, Cd, Fe, Cu, Ni, Sn, Sb, Ag, Al, As, Bi, Tl, V	5 g	Dissolution with HCl/HNO_3,	ICP-MS, calibration with commercial solutions (Merck)
4	Pb, Cd, Fe, Cu, Ni, Sn, Sb	2.5 g	Dissolution with HCl/HNO_3,	ICP-OES, calibration with commercial solutions (Kraft)
5	Pb, Cd, Fe, Cu, Ni, Sn	2.5 g	Dissolution with HCl/HNO_3	ICP-OES, calibration with commercial mono-element solutions
6	Pb, Cd, Fe, Cu, Ni, Sn	1 g	Dissolution with HCl/H_2O_2	ICP-OES, matrix matched calibration with commercial mono-element solutions (traceable to NIST standards)
7	Al, Sb, As, Bi, Pb, Cd, Co, Fe, In, Cu, Ni, Ag, Tl, V, Sn	10 g	Dissolution with HNO_3, HCl	ICP-MS, calibration with commercial solutions (Merck)
8	Pb, Cd, Fe, Cu, Ni, Sn, Sb	1 g	Dissolution with HNO_3	ICP-MS, matrix matched calibration with commercial mono-element solutions
	Pb, Cd, Fe, Cu, Ni	1 g	Dissolution with HNO_3	ICP-OES, matrix matched calibration with commercial mono-element solutions
9	Pb, Cd, Fe, Cu, Ni, Sb	10 g	Dissolution with HNO_3, HCl	ICP-OES with matrix matched standards, prepared from pure metals
	Sn	5 g	Dissolution with HCl	ICP-OES with matrix matched standards, prepared from pure metal
10	Pb, Cd, Fe, Cu, Ni, Sn, Sb	2 g	Dissolution with HNO_3	ICP-MS, calibration with matrix matched commercial solution standards
11	Pb, Cd, Fe, Cu, Ni, Tl	0.5 g	Dissolution with HNO_3	ETAAS, calibration with commercial solutions (Merck)
	Pb, Ag, Cd, Cu, Fe, Ni, Sb, Tl, Bi, Co, V	0.25 g	Dissolution with HNO_3	ICP-MS, calibration with commercial solutions (Merck)
12	Pb, Cd, Fe, Cu, Ni, Sn, Sb, Tl, Al, Bi, Co, V	2 g	Dissolution with HCl/HNO_3	ICP-MS, calibration with matrix matched commercial solution standards
13	Pb, Cd, Fe, Cu, Ni, Sb	1 g	Dissolution with HNO_3	ICP-OES, calibration with commercial mono-element solutions
14	Pb, Cd, Fe, Cu, Ni, Sn, Sb, Ag, Al, As, Bi, Co, In, Tl, V	2 g	Dissolution with HNO_3	ICP-OES, calibration with commercial mono-element solutions

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 internally checked commercial calibration solutions.

6.2 Analytical results and statistical evaluation

The analytical results of the inter-laboratory certification comparison are listed in Tables 5 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 5: Results for Pb

Lab./Meth.	1_ICP	5_ICP	7_ICP-MS	11_ETAAS	11_ICP-MS	6_ICP	8_ICP-MS	14_ICP	13_ICP	10_ICP-MS	8_ICP	12_ICP-MS	3_ICP-MS	3_ICP	2_ICP	9_ICP	4_ICP		
M_i [mg/kg]	12.6	14	14.6	14.92	15.09	15	15.36	15.70	16.15	16.11	15.83	16.03	16.95	16.72	17	17.3	20		*n*
	12.7	15	14.6	14.75	15.06	16	15.82	15.77	15.52	16.02	15.68	16.12	16.24	16.71	17	17.3	20		15
	12.7	14	14.4	14.90	14.95	15	15.51	15.75	15.56	15.95	15.88	16.02	15.92	16.87	17	17.2	20		
	12.7	14	14.7	14.39	15.09	16	15.83	15.75	15.83	15.72	15.96	16.03	17.49	16.76	16	17.3	19		
	12.8	14	14.4	14.75	15.07	16	15.94	15.76	16.03	15.61	16.07	16.09			17	17.2	20		
				14.98	15.02			15.78	15.82										
					15.08														
M [mg/kg]	12.68	14.20	14.54	14.78	15.05	15.60	15.69	15.75	15.82	15.88	15.88	16.06	16.65	16.76	16.80	17.26	19.80		15.78
s [mg/kg]	0.073	0.447	0.134	0.213	0.049	0.548	0.247	0.028	0.249	0.209	0.144	0.045	0.706	0.073	0.447	0.055	0.447	s_M [mg/kg]	0.872
																		$\bar{s}_i$ [mg/kg]	0.312
s_{rel}	0.006	0.031	0.009	0.014	0.003	0.035	0.016	0.002	0.016	0.013	0.009	0.003	0.042	0.004	0.027	0.003	0.023		0.055

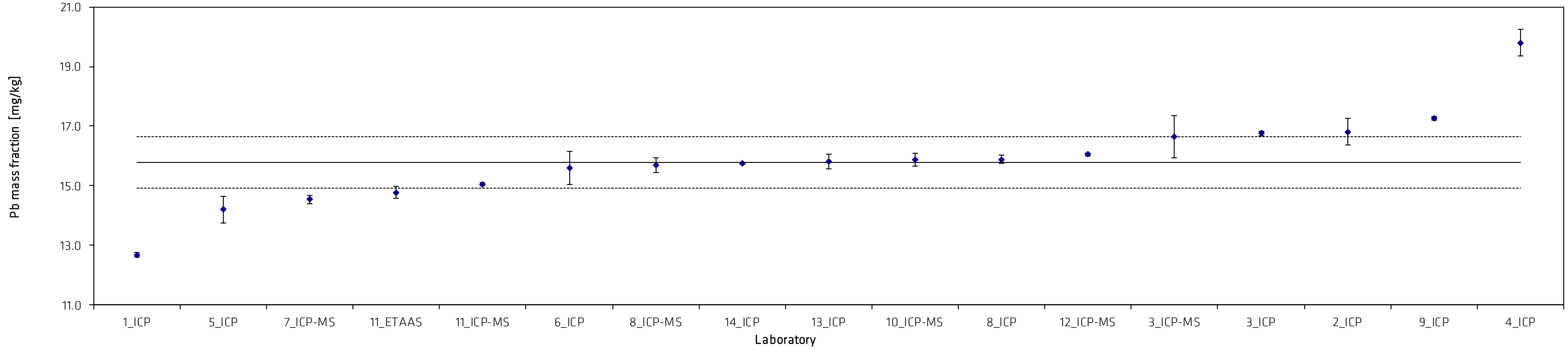


Table 6: Results for Ag

Lab./Meth.	1_ICP	3_ICP	11_ICP-MS	14_ICP	3_ICP-MS		
M_i [mg/kg]	0.84	1.01	1.10	1.06	1.12		*n*
	0.83	1.00	1.01	1.03	1.02		5
	0.85	1.01	1.02	1.02	1.03		
	0.84	1.01	1.00	1.03	1.11		
	0.85		1.00	1.04			
	0.84		0.97	1.11			
			1.02				
M [mg/kg]	**0.84**	**1.01**	**1.02**	**1.05**	**1.07**		**1.00**
s [mg/kg]	0.008	0.007	0.040	0.033	0.052	s_M [mg/kg]	0.090
						$\bar{s}_i$ [mg/kg]	0.033
s_{rel}	0.009	0.007	0.039	0.032	0.049		0.091

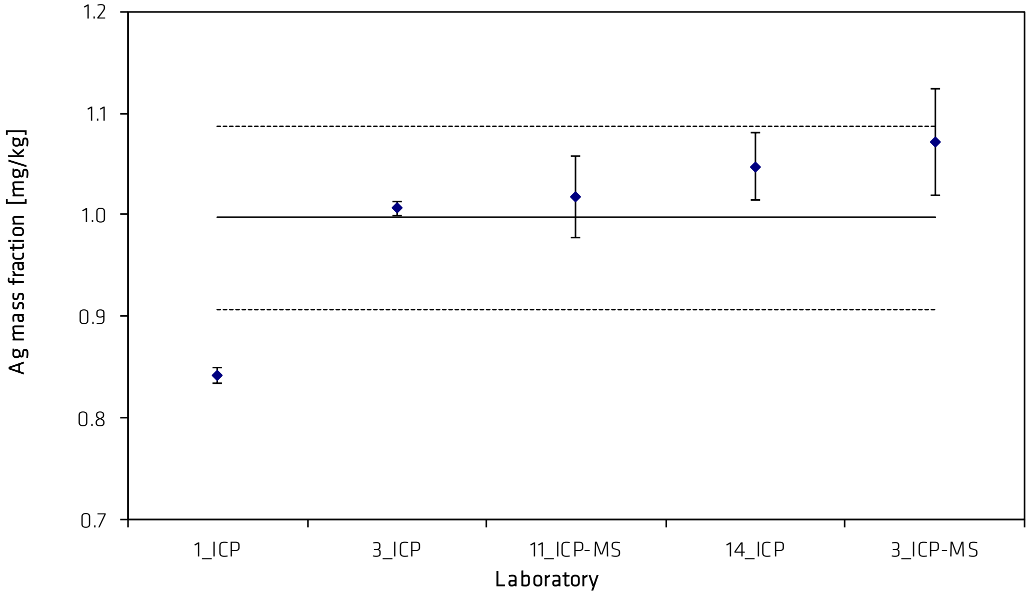


Table 7: Results for Cd

Lab./Meth.	6_ICP	11_ICP-MS	1_ICP	9_ICP	13_ICP	8_ICP	10_ICP-MS	12_ICP-MS	8_ICP-MS	14_ICP	3_ICP	3_ICP-MS	7_ICP-MS	11_ETAAS	5_ICP	4_ICP		
M_i [mg/kg]	0.8	1.27	1.34	1.4	1.67	1.62	1.67	1.71	1.71	1.74	1.76	1.86	1.8	1.96	2	2		*n*
	0.8	1.27	1.34	1.4	1.59	1.66	1.64	1.70	1.68	1.75	1.75	1.66	1.8	1.94	2	2		15
	0.8	1.28	1.35	1.4	1.61	1.62	1.65	1.69	1.73	1.74	1.77	1.69	1.8	2.04	2	2		
	0.8	1.29	1.34	1.4	1.63	1.66	1.64	1.69	1.71	1.74	1.77	1.86	1.8	1.95	2	2		
	0.8	1.26	1.36	1.4	1.64	1.66	1.68	1.70	1.73	1.75			1.8	1.97		2		
		1.28	1.35		1.59					1.75				2.10				
		1.28																
M [mg/kg]	**0.80**	**1.28**	**1.35**	**1.40**	**1.62**	**1.64**	**1.65**	**1.70**	**1.71**	**1.75**	**1.76**	**1.77**	**1.80**	**1.99**	**2.00**	**2.00**		**1.69**
s [mg/kg]	0.000	0.009	0.008	0.000	0.031	0.023	0.016	0.010	0.019	0.004	0.009	0.108	0.000	0.063	0.000	0.000	s_M [mg/kg]	0.222
																	$\bar{s}_i$ [mg/kg]	0.035
s_{rel}	0.000	0.007	0.006	0.000	0.019	0.014	0.010	0.006	0.011	0.002	0.005	0.061	0.000	0.032	0.000	0.000		0.131

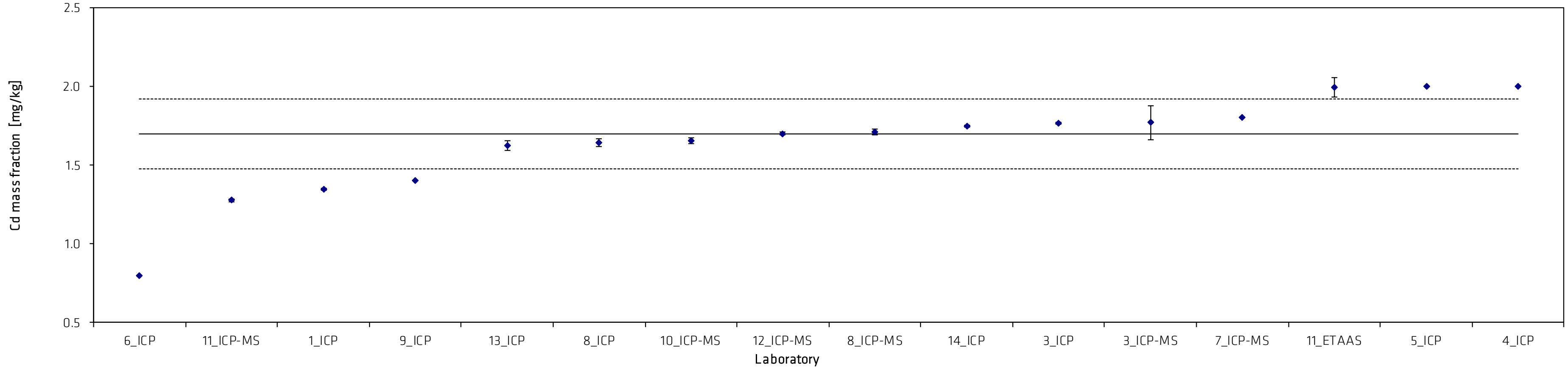


Table 8: Results for Cu

Lab./Meth.	1_ICP	4_ICP	7_ICP-MS	10_ICP-MS	11_ICP-MS	13_ICP	3_ICP	14_ICP	12_ICP-MS	8_ICP	8_ICP-MS	5_ICP	11_ETAAS	3_ICP-MS	9_ICP		
M_i [mg/kg]	3.0	3	3.1	3.06	3.69	3.70	3.68	3.82	3.88	3.86	4.02	4	4.28	4.23	3.8		*n*
	2.9	3	3.3	3.15	3.64	3.64	3.67	3.83	3.86	4.03	3.99	4	4.08	3.97	3.8		15
	3.0	3	3.2	3.53	3.61	3.61	3.73	3.81	3.87	4.09	3.94	4	3.86	3.84	3.7		
	2.9	3	3.2	3.47	3.62	3.71	3.74	3.83	3.89	3.92	4.04	4	4.18	4.21	4.4		
	3.0	3	3.2	3.45	3.59	3.63		3.83	3.81	3.93	3.93	4	3.92		5.1		
	3.0				3.62	3.61		3.95					4.05				
					3.60												
M [mg/kg]	**2.96**	**3.00**	**3.20**	**3.33**	**3.62**	**3.65**	**3.71**	**3.84**	**3.86**	**3.97**	**3.98**	**4.00**	**4.06**	**4.07**	**4.16**		**3.69**
s [mg/kg]	0.022	0.000	0.071	0.212	0.030	0.044	0.037	0.052	0.031	0.093	0.047	0.000	0.157	0.191	0.594	s_M [mg/kg]	0.396
																$\bar{s}_i$ [mg/kg]	0.179
s_{rel}	0.007	0.000	0.022	0.064	0.008	0.012	0.010	0.013	0.008	0.023	0.012	0.000	0.039	0.047	0.143		0.107

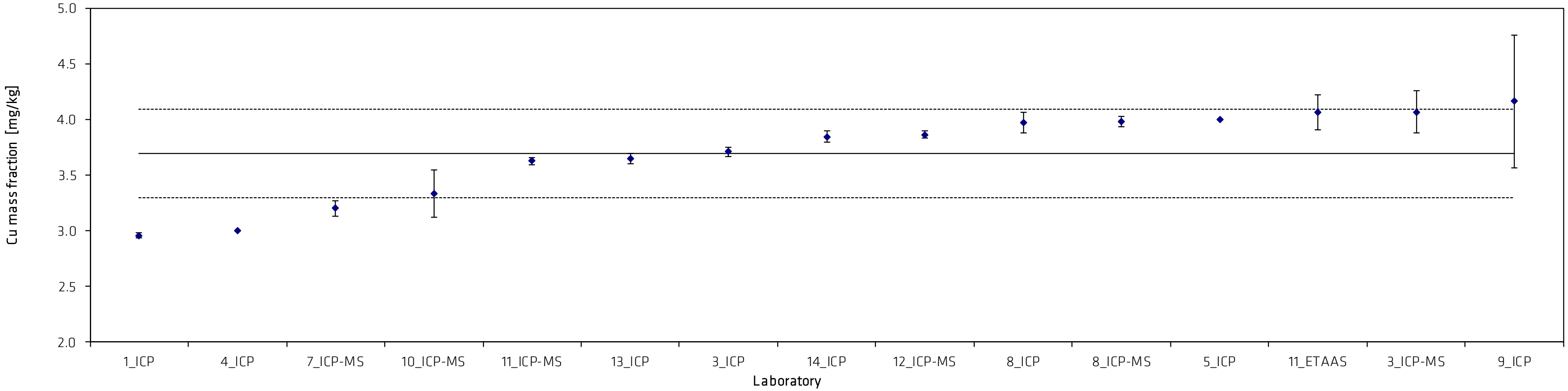


Table 9: Results for Fe

Lab./Meth.	2_ICP	9_ICP	4_ICP	8_ICP-MS	14_ICP	7_ICP-MS	8_ICP	12_ICP-MS	1_ICP	11_ICP-MS	13_ICP	11_ETAAS	3_ICP	3_ICP-MS	10_ICP-MS	5_ICP	6_ICP		
M_i [mg/kg]	1	1.9	2	2.02	2.01	2.0	1.98	2.07	2.80	2.44	2.19	2.59	2.61	2.67	2.63	3	4		*n*
	1	1.8	2	2.06	2.01	2.1	2.11	2.07	2.78	1.77	2.20	2.58	2.40	2.36	2.45	4	3		14
	1	1.6	2	1.84	2.02	2.0	2.05	2.07	1.76	2.16	2.24	2.49	2.62	2.52	2.58	2	3		
	1	1.7	2	2.13	2.02	2.0	2.10	2.06	1.73	2.23	2.18	2.59	2.42	2.52		2	3		
	1	1.7	2	2.05	2.02	2.0	2.04	2.06	1.87	2.00	2.22	2.38				2			
		1.4			2.03				1.91	2.16	2.24	2.39							
										2.621									
M [mg/kg]	1.00	1.68	2.00	2.02	2.02	2.02	2.06	2.07	2.14	2.20	2.21	2.50	2.51	2.52	2.56	2.60	3.25		2.18
s [mg/kg]	0.000	0.189	0.000	0.108	0.009	0.045	0.054	0.004	0.507	0.278	0.026	0.097	0.118	0.124	0.091	0.894	0.500	s_M [mg/kg]	0.258
																		$\bar{s}_i$ [mg/kg]	0.176
s_{rel}	0.000	0.113	0.000	0.054	0.004	0.022	0.026	0.002	0.237	0.127	0.012	0.039	0.047	0.049	0.036	0.344	0.154		0.119

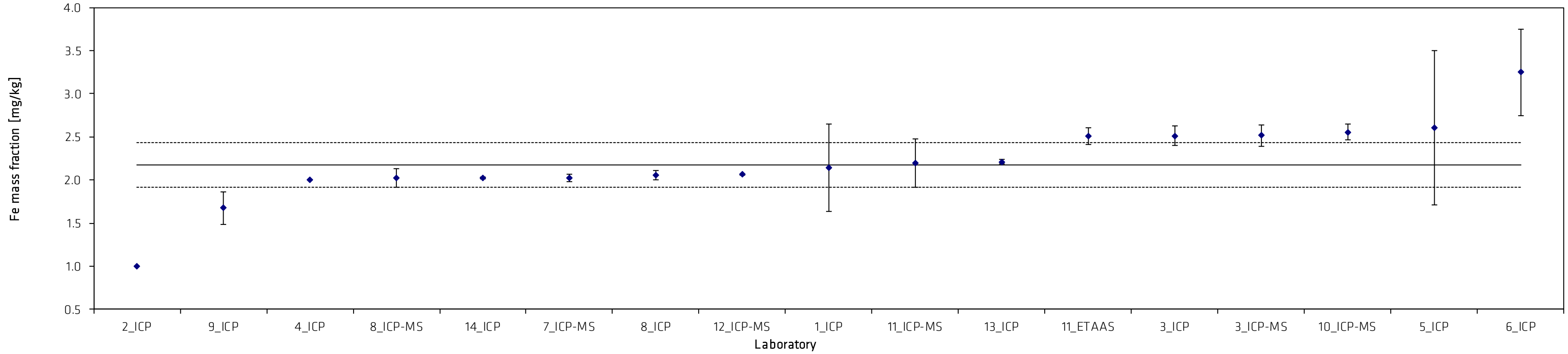


Table 10: Results for Ni

Lab./Meth.	7_ICP-MS	9_ICP	10_ICP-MS	13_ICP	8_ICP-MS	8_ICP	12_ICP-MS	11_ICP-MS	1_ICP	14_ICP	3_ICP-MS	3_ICP	11_ETAAS		
M_i [mg/kg]	0.31	0.31	0.50	0.36	0.39	0.36	0.40	0.48	0.42	0.51	0.58	0.57	0.56		*n*
	0.31	0.36	0.41	0.40	0.41	0.39	0.41	0.42	0.48	0.52	0.53	0.59	0.58		13
	0.30	0.32	0.31	0.41	0.36	0.40	0.41	0.33	0.45	0.53	0.49	0.54	0.59		
	0.29	0.34	0.35	0.40	0.41	0.44	0.40	0.49	0.39	0.52	0.48	0.49	0.55		
	0.28	0.34	0.36	0.39	0.40	0.41	0.39	0.32	0.42	0.51			0.52		
				0.36				0.34	0.40	0.54					
								0.44							
M [mg/kg]	**0.30**	**0.33**	**0.38**	**0.39**	**0.39**	**0.40**	**0.40**	**0.40**	**0.43**	**0.52**	**0.52**	**0.55**	**0.56**		**0.43**
s [mg/kg]	0.013	0.019	0.077	0.022	0.019	0.027	0.008	0.073	0.033	0.010	0.046	0.041	0.026	s_M [mg/kg]	0.082
														$\bar{s}_i$ [mg/kg]	0.038
s_{rel}	0.044	0.058	0.199	0.056	0.048	0.067	0.019	0.182	0.078	0.019	0.087	0.075	0.047		0.191

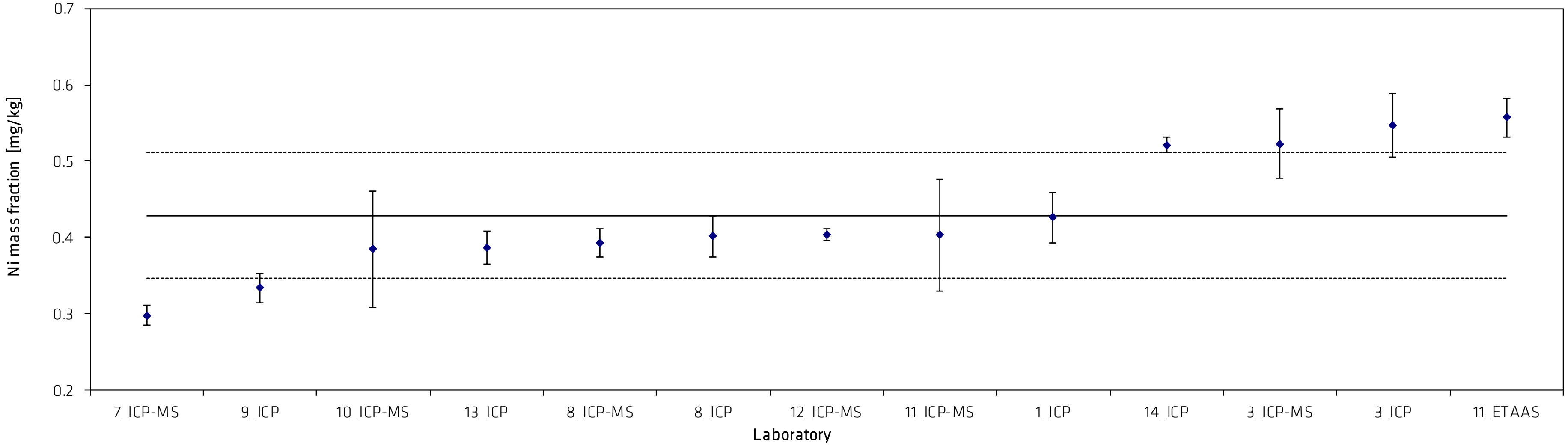


Table 11: Results for Sb

Lab./Meth.	7_ICP-MS	11_ICP-MS	12_ICP-MS	3_ICP-MS	8_ICP-MS	13_ICP	9_ICP	14_ICP	6_ICP	10_ICP-MS	1_ICP		
M_i [mg/kg]	0.02	0.02	0.04	0.06	0.07	0.18	0.19	1.41	2	< 0.3	< 0.5		*n*
	0.01	0.02	0.04	0.05	0.05	0.03	0.14	1.07	1	< 0.3	< 0.5		5
		0.04	0.04	0.05	0.05	0.23	0.22	0.98	1	< 0.3	< 0.5		
		0.03	0.04	0.05	0.06	-0.06	0.28	1.52	1	< 0.3	< 0.5		
		0.07	0.04		0.06	0.48	0.22	1.30	1		< 0.5		
		0.03				0.21		1.42					
		0.04											
***M* [mg/kg]**	**0.02**	**0.04**	**0.04**	**0.05**	**0.06**	**0.18**	**0.21**	**1.28**	**1.20**	**< 0.3**	**< 0.5**		**0.040**
s [mg/kg]	0.007	0.016	0.001	0.003	0.006	0.186	0.051	0.211	0.447			s_M [mg/kg]	0.016
												$\bar{s}_i$ [mg/kg]	0.008
s_{rel}	0.471	0.447	0.014	0.048	0.106	1.045	0.243	0.165	0.373				0.407

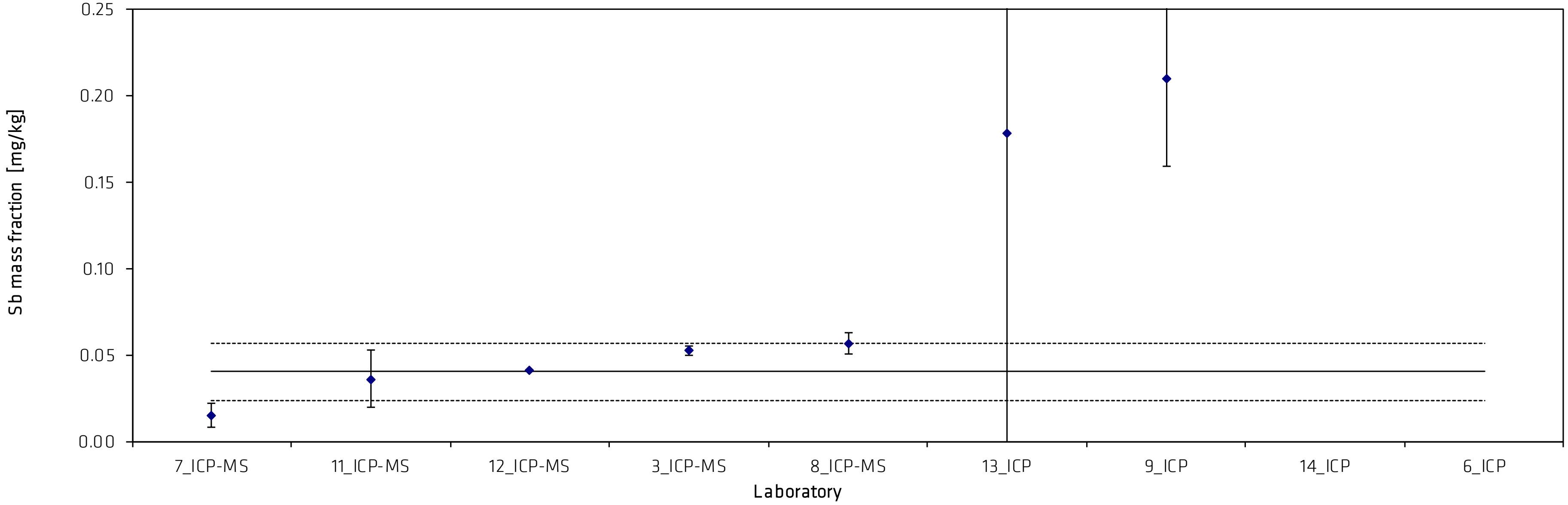


Table 12: Results for Tl

Lab./Meth.	7_ICP-MS	11_ICP-MS	3_ICP	3_ICP-MS	12_ICP-MS	11_ETAAS	14_ICP		
M_i [mg/kg]	3.5	3.65	3.73	3.82	3.82	3.84	4.31		*n*
	3.5	3.58	3.74	3.69	3.83	4.01	4.35		7
	3.4	3.60	3.81	3.66	3.83	3.95	4.30		
	3.5	3.59	3.83	4.03	3.78	3.71	4.37		
	3.4	3.57			3.83	3.98	4.37		
		3.63				3.95	4.31		
		3.57							
M [mg/kg]	**3.46**	**3.60**	**3.78**	**3.80**	**3.82**	**3.91**	**4.34**		**3.81**
s [mg/kg]	0.055	0.032	0.052	0.166	0.021	0.112	0.032	s_M [mg/kg]	0.276
								$\bar{s}_i$ [mg/kg]	0.083
s_{rel}	0.016	0.009	0.014	0.044	0.006	0.029	0.007		0.072

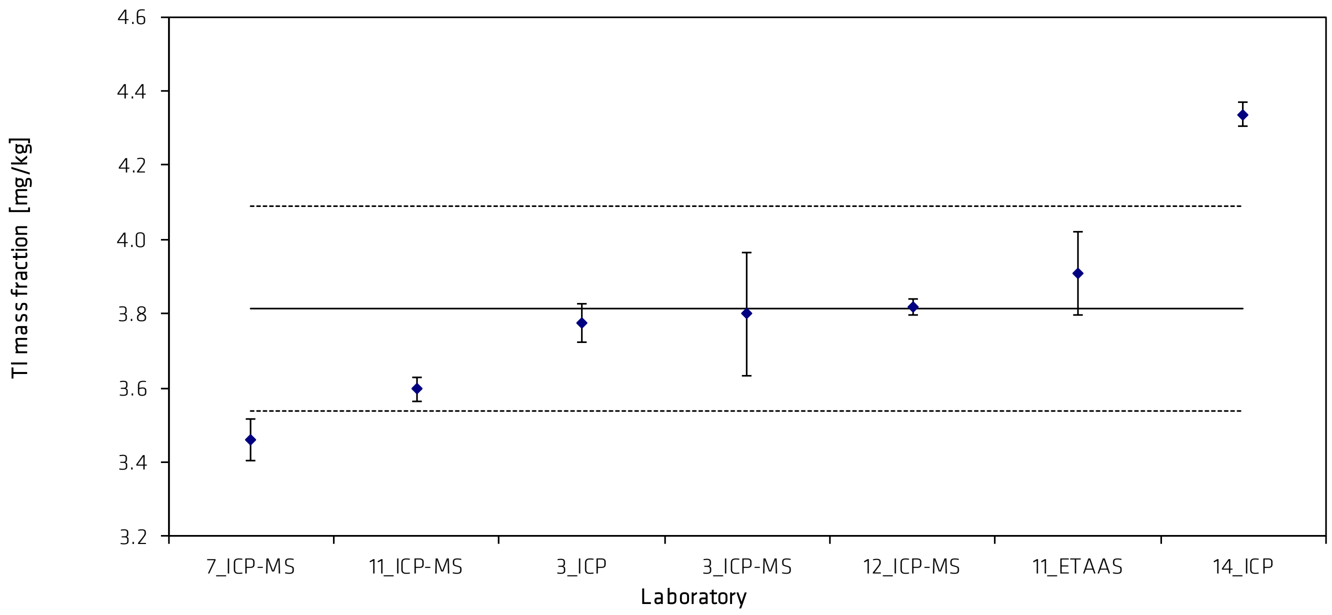


Table 13: Results for Al

Lab./Meth.	12_ICP-MS	1_ICP	7_ICP-MS	14_ICP	3_ICP		
M_i [mg/kg]	< 0.15	0.200	0.140	0.219	< 0.25		*n*
	< 0.15	0.200	0.130	0.293	< 0.25		3
	< 0.15	0.180	0.160	0.336	< 0.25		
	< 0.15	0.170	0.180	0.441	< 0.25		
	< 0.15	0.260	0.240	0.402	< 0.25		
		0.130		0.288			
		0.008					
M [mg/kg]	**< 0.15**	**0.164**	**0.170**	**0.330**	**< 0.25**		**0.221**
s [mg/kg]		0.079	0.044	0.081		s_M [mg/kg]	0.094
						$\bar{s}_i$ [mg/kg]	0.070
s_{rel}		0.482	0.256	0.246			0.424

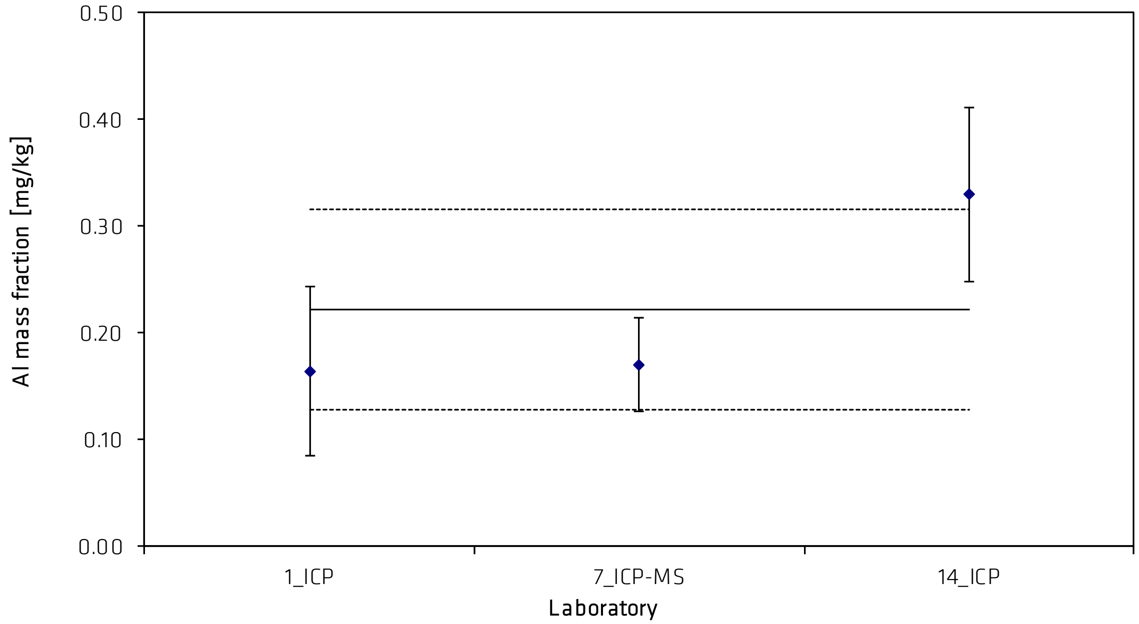


Table 14: Results for As

Lab./Meth.	7_ICP-MS	3_ICP-MS	14_ICP	1_ICP	1_ICP	3_ICP			
M_i [mg/kg]	< 0.01	< 0.02	0.128	0.200	< 0.5	< 1			*n*
	< 0.01	< 0.02	0.128	0.200	< 0.5	< 1			1
	< 0.01	< 0.02	0.154	0.180	< 0.5	< 1			
	< 0.01	< 0.02	0.136	0.170	< 0.5	< 1			
	< 0.01	< 0.02	0.107	0.260	< 0.5	< 1			
			0.160	0.130					
				0.008					
M [mg/kg]	**< 0.01**	**< 0.02**	**0.135**	**0.164**	**< 0.5**	**< 1**			**0.150**
s [mg/kg]			0.019	0.079				s_M [mg/kg]	0.020
								$\bar{s}_i$ [mg/kg]	0.014
s_{rel}			0.143	0.482					0.135

Table 15: Results for In

Lab./Meth.	14_ICP	7_ICP-MS	3_ICP-OES		
M_i [mg/kg]	0.113	0.50	< 0.2		*n*
	0.124	0.40	< 0.2		2
	0.085	0.40	< 0.2		
	0.115	0.40	< 0.2		
	0.113	0.50			
	0.137				
M [mg/kg]	**0.114**	**0.440**	**< 0.2**		**0.277**
s [mg/kg]	0.017	0.055		s_M [mg/kg]	0.230
				$\bar{s}_i$ [mg/kg]	0.041
s_{rel}	0.150	0.124			0.831

Table 16: Results for Bi

Lab./Meth.	12_ICP-MS	11_ICP-MS	3_ICP-MS	1_ICP	14_ICP		
M_i [mg/kg]	0.093	0.111	0.109	< 0.2	0.541		*n*
	0.094	0.103	0.099	< 0.2	0.529		3
	0.128	0.105	0.099	< 0.2	0.548		
	0.093	0.100	0.104	< 0.2	0.417		
	0.100	0.103		< 0.2	0.488		
		0.089		< 0.2	0.538		
		0.108					
M [mg/kg]	**0.102**	**0.103**	**0.103**	**< 0.2**	**0.510**		**0.102**
s [mg/kg]	0.015	0.007	0.005		0.051	s_M [mg/kg]	0.001
						$\bar{s}_i$ [mg/kg]	0.010
s_{rel}	0.150	0.068	0.050		0.099		0.006

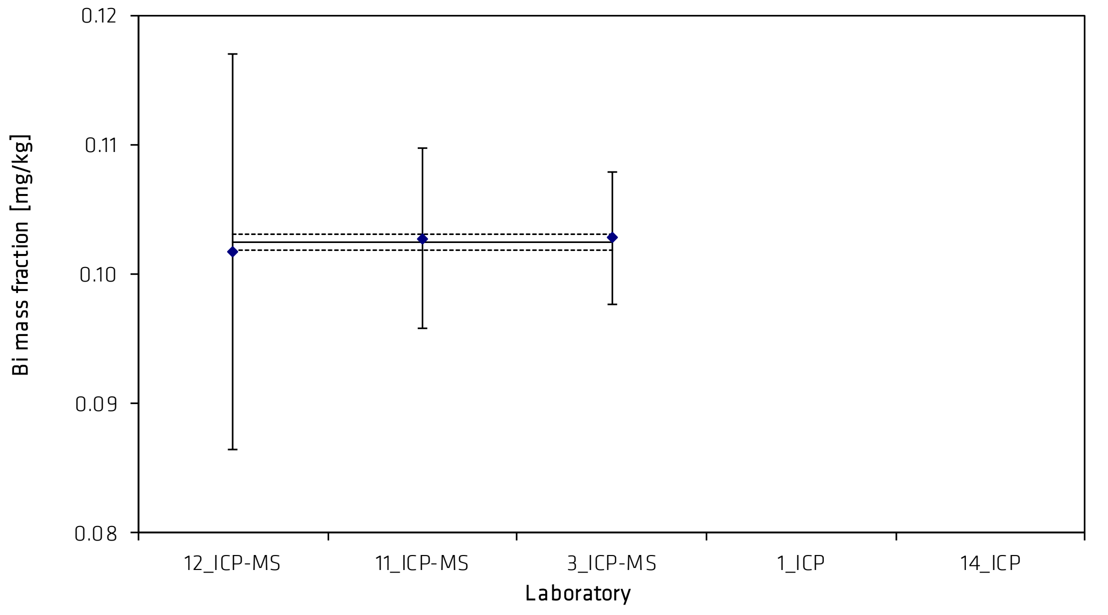


Table 17 Results for Co

Lab./Meth.	7_ICP-MS	11_ICP-MS	12_ICP-MS	14_ICP	1_ICP	3_ICP		
M_i [mg/kg]	0.030	0.041	0.044	0.117	< 0.2	<0.2		*n*
	0.040	0.041	0.044	0.125	< 0.2	<0.2		3
	0.040	0.040	0.042	0.111	< 0.2	<0.2		
	0.040	0.040	0.043	0.108	< 0.2	<0.2		
	0.040	0.040	0.043	0.118	< 0.2			
		0.040		0.113	< 0.2			
		0.041						
M [mg/kg]	**0.038**	**0.040**	**0.043**	**0.115**	**< 0.2**	**<0.2**		**0.041**
s [mg/kg]	0.004	0.001	0.001	0.006			s_M [mg/kg]	0.003
							$\bar{s}_i$ [mg/kg]	0.004
s_{rel}	0.118	0.013	0.017	0.052				0.064

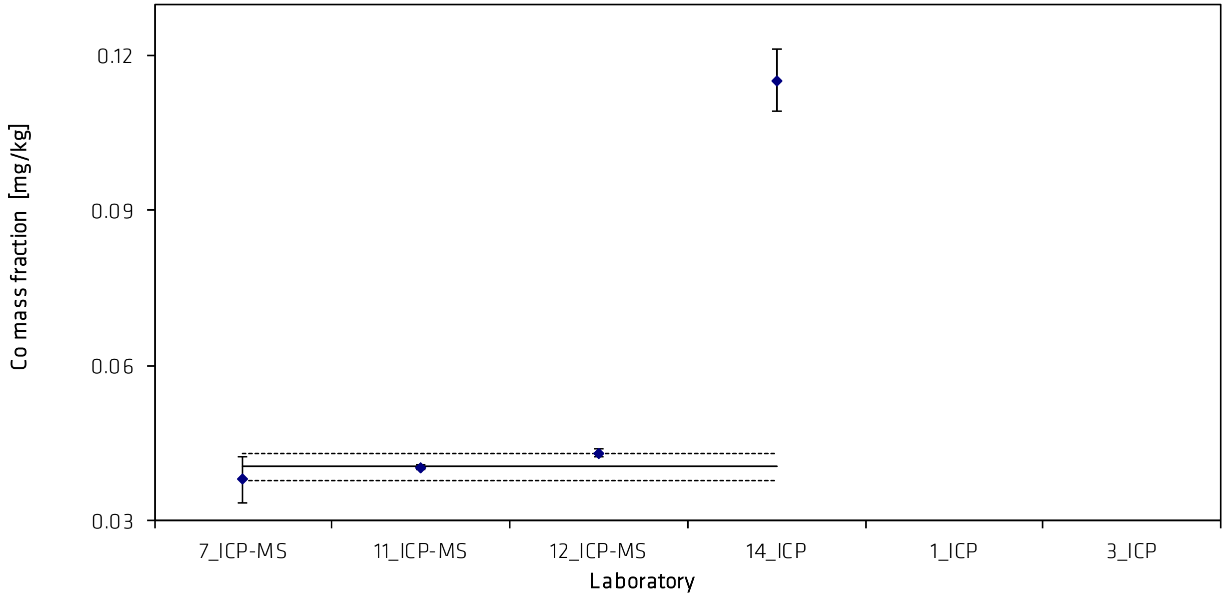


Table 18: Results for Sn

Lab./Meth.	8_ICP-MS	7_ICP-MS	14_ICP	9_ICP	10_ICP-MS	1_ICP	6_ICP		
M_i [mg/kg]	0.022	0.03	0.34	1.24	< 0.3	< 1	1		*n*
	0.027	0.03	0.42	1.15	< 0.3	< 1	1		4
	0.016	0.03	0.92	1.08	< 0.3	< 1	< 1		
	0.037	0.03	0.37	1.16	< 0.3	< 1	< 1		
	0.021	0.03	0.40	1.33		< 1	< 1		
			0.64			< 1			
M [mg/kg]	**0.025**	**0.030**	**0.515**	**1.192**	**< 0.3**	**< 1**	**< 1**		**0.440**
s [mg/kg]	0.008	0.000	0.224	0.096				s_M [mg/kg]	0.551
								$\bar{s}_i$ [mg/kg]	0.099
s_{rel}	0.324	0.000	0.434	0.080					1.252

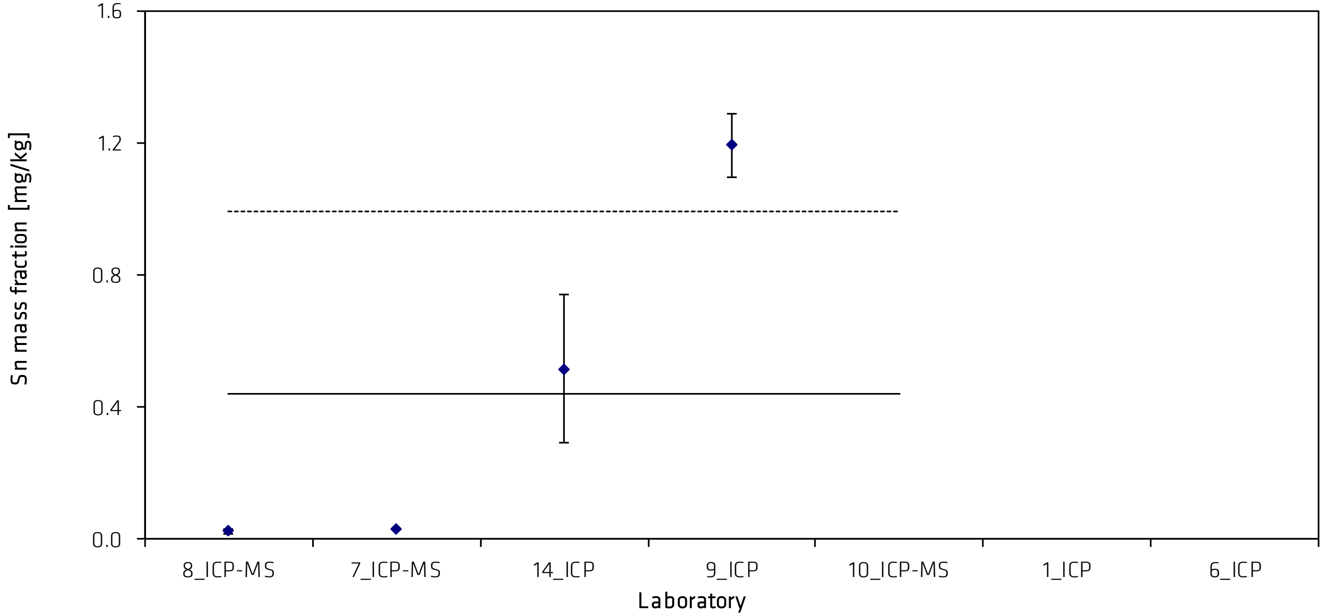
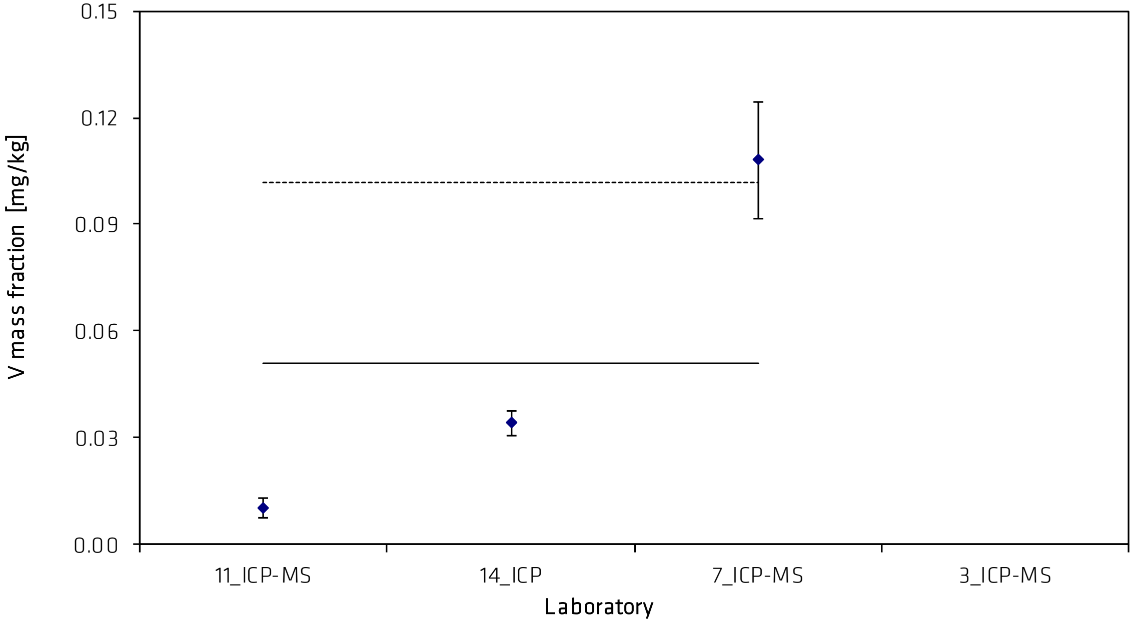


Table 19: Results for V

Lab./Meth.	11_ICP-MS	14_ICP	7_ICP-MS	3_ICP-MS	3_ICP-OES		
M_i [mg/kg]	0.008	0.034	0.110	< 0.02	< 0.2		*n*
	0.008	0.032	0.120	< 0.02	< 0.2		3
	0.016	0.032	0.120	< 0.02	< 0.2		
	0.009	0.041	0.110	< 0.02	< 0.2		
	0.012	0.033	0.080				
	0.010	0.033					
	0.008						
M [mg/kg]	**0.010**	**0.034**	**0.108**	**< 0.02**	**< 0.2**		**0.051**
s [mg/kg]	0.003	0.004	0.016			s_M [mg/kg]	0.051
						$\bar{s}_i$ [mg/kg]	0.010
s_{rel}	0.273	0.104	0.152				1.004



The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [6]. The following results were obtained:

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

	1st run	2nd run
Number of data sets	16	14
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 4	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 4, Lab. 1	---
Nalimov (α = 0.01)	Lab. 4	---
Grubbs (α = 0.05)	Lab. 4	---
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: not 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 (Lab. 4 and Lab. 1) were removed.

Tab. 21: Outcome of statistical tests on the results obtained for Ag and Cu

	Ag	Cu
Number of data sets	5	15
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 1	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 1	---
Nalimov (α = 0.01)	Lab. 1	---
Grubbs (α = 0.05)	Lab. 1	---
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	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: insuff. data	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: insuff. data	Distribution: normal

The outlier (Lab. 1; Ag) was not removed.

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

	1st run	2nd run
Number of data sets	16	15
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. 11_ICP-MS
Nalimov (α = 0.01)	Lab. 6	---
Grubbs (α = 0.05)	Lab. 6	---
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	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: normal	Distribution: normal

The outlier (Lab. 6) was removed, the straggler (Lab. 11) was not removed.

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

	1st run	2nd run
Number of data sets	17	14
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, Lab. 6	---
Dixon (α = 0.01)	Lab. 2	---
Nalimov (α = 0.05)	Lab. 2, Lab. 6	Lab. 9
Nalimov (α = 0.01)	Lab. 2	---
Grubbs (α = 0.05)	Lab. 2	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Lab. 5	---
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: normal	Distribution: normal

The outliers (Labs. 5, 2 and 6, 1st run) were removed, the straggler (Lab. 9, 2nd run) was not removed.

Tab. 24: Outcome of statistical tests on the results obtained for Ni and Sb (without all ICP-OES results since this method was not suitable to analyse this element)

	Ni	Sb
Number of data sets	13	5
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. 25: Outcome of statistical tests on the results obtained for Tl

	Tl
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)	Lab. 14
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. 14, Tl) was not removed.

For the other elements no statistical evaluation using SoftCRM was performed because the number of data sets was too low.

The resp. combined uncertainties were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contribution from possible inhomogeneity of the material using Equation 2.

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

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 26: Uncertainty calculation

	uncertainty contribution from								uncertainty contribution from
	M	n	s_M	u_{ilc}	u_{bb}	u_{stab}	u (comb)	U	homogeneity test (rel. %)
	mg/kg		mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	
Pb	15.780	15	0.8720	0.2251	0.00000	0.01578	0.2257	0.4514	0.0000
Ag	1.000	5	0.0900	0.0402	0.00000	0.00100	0.0403	0.0805	0.0000
Cd	1.690	15	0.2220	0.0573	0.00000	0.00169	0.0573	0.1147	0.0000
Cu	3.690	15	0.3960	0.1022	0.02013	0.00369	0.1043	0.2085	0.5454
Fe	2.180	14	0.2580	0.0690	0.00000	0.00218	0.0690	0.1380	0.0000
Ni	0.430	13	0.0820	0.0227	0.00000	0.00043	0.0227	0.0455	0.0000
Sb	0.040	6	0.0160	0.0065	0.00000	0.00004	0.0065	0.0131	0.0000
Tl	3.810	7	0.2760	0.1043	0.03543	0.00381	0.1102	0.2205	0.9300
Al	0.221	3	0.0940	0.0543	0.04738	0.00022	0.0720	0.1441	21.4401
Bi	0.102	3	0.0010	0.0006	0.00000	0.00010	0.0006	0.0012	0.0000
Co	0.041	3	0.0030	0.0017	0.00000	0.00004	0.0017	0.0035	0.0000

The expanded uncertainties U are calculated by multiplication of $u_{combined}$ with a coverage factor of k = 2 using Equation 3.

$$U = k \cdot u_{\text{combined}} \qquad (3)$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 3 of this report. Rounding was done according to DIN 1333 [7].

7. Instructions for users

The certified reference material BAM-M603 is intended for the development, validation and quality control of analytical methods and procedures for the determination of trace components in pure zinc. For wet chemical analysis, a minimum sample intake of 0.25 g should be used.

8. Metrological Traceability

To ensure traceability 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.

9. Information on and purchase of the CRM

Certified reference material BAM-M603 is 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 bottle of BAM-M603 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.

10. References

[1] DIN EN 1179 Zinc and zinc alloys - Primary zinc; German version EN 1179:2003

[2] DIN EN ISO 17034, Allgemeine Anforderungen an die Kompetenz von Referenzmaterial-herstellern, 2016

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

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

[5] ASTM B214 – 16, Standard Test Method for Sieve Analysis of Metal Powders, ASTM International, West Conshohocken, PA, 2016

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

[7] DIN 1333:1992-02 Zahlenangaben

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity

Lead:

	1	2	3
603-1	14.7836918	14.9410551	15.4099668
603-2	15.0006759	15.040836	15.358686
603-3	14.7734138	14.944562	15.347629
603-4	14.9698238	14.9383703	15.3838082
603-5	14.6520503	14.9069176	15.0641781
603-6	14.7338548	14.9737114	15.3919931
603-7	14.9307742	15.1583226	15.2783678
603-8	14.8465276	15.0136574	15.2952741
603-9	14.8813968	14.9633215	15.7294521
603-10	14.7892483	14.8256257	15.2562755
603-11	14.9774235	14.9444822	15.3411268
603-12	14.7621856	14.9012327	15.1997482
603-13	14.8272075	15.0514609	15.4099284
603-14	14.9080757	14.995756	15.3560596
603-15	15.0135349	14.8859301	15.2861347

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	45.1347137	15.0449046	0.10614362
2	3	45.4001978	15.1333993	0.03846879
3	3	45.0656048	15.0218683	0.08691297
4	3	45.2920023	15.0973341	0.0617979
5	3	44.623146	14.874382	0.04325626
6	3	45.0995593	15.0331864	0.11093946
7	3	45.3674646	15.1224882	0.03116841
8	3	45.1554591	15.0518197	0.05143561
9	3	45.5741705	15.1913902	0.21881091
10	3	44.8711495	14.9570498	0.06748282
11	3	45.2630325	15.0876775	0.04844871
12	3	44.8631666	14.9543889	0.04998443
13	3	45.2885968	15.0961989	0.08639205
14	3	45.2598914	15.0866305	0.05636602
15	3	45.1855997	15.0618666	0.0417929
			15.0543057	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.2667792	14	0.01905566	0.25999148	0.99489789	2.03742044
Within groups	2.19880172	30	0.07329339			
Total	2.46558092	44				

within-sd	0.270728	status:	homogeneous
effective n	4.00		
s_bb	0		
s_bb_min	0.068783		
u_bb	0.068783		

Contribution to combined uncertainty: 0

Silver:

	1	2	3
603-1	1.04266461	0.96210442	1.59209694
603-2	1.03155999	0.95564134	1.00669165
603-3	1.03702951	0.99711638	0.96718615
603-4	1.02098036	0.98573506	1.03482048
603-5	1.08136954	0.99068609	0.9772048
603-6	1.15472168	0.98270338	0.96017954
603-7	1.060899	0.97285992	0.95657698
603-8	1.07661941	0.98520021	0.96182086
603-9	0.96896244	0.9520668	0.95697984
603-10	1.1851405	0.96965478	0.93877289
603-11	0.97384132	0.97089113	0.96985188
603-12	0.99004367	0.95670336	0.97560934
603-13	1.19899356	1.0035938	0.96427194
603-14	1.02345529	0.9611087	0.97714863
603-15	0.99981418	1.11887901	0.95133561

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	3.59686597	1.19895532	0.11754273
2	3	2.99389298	0.99796433	0.00149803
3	3	3.00133204	1.00044401	0.00122783
4	3	3.0415359	1.0138453	0.00064053
5	3	3.04926044	1.01642015	0.00320925
6	3	3.0976046	1.03253487	0.01132404
7	3	2.9903359	0.99677863	0.00314985
8	3	3.02364049	1.00788016	0.00368046
9	3	2.87800908	0.95933636	7.5531E-05
10	3	3.09356816	1.03118939	0.01801413
11	3	2.91458434	0.97152811	4.2832E-06
12	3	2.92235638	0.97411879	0.00027956
13	3	3.16685929	1.05561976	0.01580359
14	3	2.96171262	0.98723754	0.00104811
15	3	3.07002879	1.02334293	0.0074329
			1.01781304	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.13298528	14	0.00949895	0.77047303	0.69060901	2.03742044
Within groups	0.36986168	30	0.01232872			
Total	0.50284696	44				

within-sd	0.111035			status:	homogeneous
effective n	4.00				
s_bb	0				
s_bb_min	0.02821				
u_bb	0.02821				

Contribution to combined uncertainty: 0

Cadmium:

	1	2	3
603-1	1.22747578	1.27202213	1.26467552
603-2	1.24672028	1.25015701	1.34507898
603-3	1.2381474	1.24626539	1.28164762
603-4	1.26901531	1.28015938	1.33448122
603-5	1.24942073	1.30760869	1.28726185
603-6	1.2654886	1.30987674	1.26900664
603-7	1.28922279	1.2907518	1.27158552
603-8	1.26204715	1.31264053	1.29430657
603-9	1.21686022	1.26918695	1.29457561
603-10	1.26106211	1.2658903	1.26263078
603-11	1.2981037	1.29818217	1.27972611
603-12	1.28586723	1.22615709	1.27178184
603-13	1.22806893	1.28100343	1.30632368
603-14	1.27712044	1.29784171	1.31419417
603-15	1.30235357	1.24821205	1.2990285

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	3.76417343	1.25472448	0.00057036
2	3	3.84195627	1.28065209	0.00311607
3	3	3.76606042	1.25535347	0.00053501
4	3	3.88365591	1.29455197	0.00122681
5	3	3.84429127	1.28143042	0.00087196
6	3	3.84437198	1.28145733	0.00060884
7	3	3.8515601	1.28385337	0.00011346
8	3	3.86899424	1.28966475	0.00065608
9	3	3.78062277	1.26020759	0.00157039
10	3	3.7895832	1.2631944	6.0661E-06
11	3	3.87601198	1.29200399	0.00011306
12	3	3.78380617	1.26126872	0.00097422
13	3	3.81539604	1.27179868	0.0015945
14	3	3.88915632	1.29638544	0.00034521
15	3	3.84959413	1.28319804	0.00092078
			1.27664965	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00875291	14	0.00062521	0.70923756	0.74831321	2.03742044
Within groups	0.02644564	30	0.00088152			
Total	0.03519855	44				

within-sd	0.02969	status:	homogeneous
effective n	4.00		
s_bb	0		
s_bb_min	0.007543		
u_bb	0.007543		

Contribution to combined uncertainty: 0

Copper:

	1	2	3
603-1	3.6635424	3.6275236	3.68647797
603-2	3.70341948	3.64520928	3.78524948
603-3	3.6770794	3.68372108	3.67660609
603-4	3.54212941	3.53182524	3.69993175
603-5	3.6446718	3.60720539	3.5977587
603-6	3.59851265	3.60407407	3.62920491
603-7	3.64540539	3.56072369	3.67869554
603-8	3.61951986	3.6409348	3.59374386
603-9	3.58974757	3.51916813	3.67226065
603-10	3.61024276	3.57317246	3.5842284
603-11	3.60700885	3.52577675	3.66375656
603-12	3.69008788	3.60185293	3.61449178
603-13	3.6002119	3.59201347	3.5198452
603-14	3.6659176	3.61740769	3.57136199
603-15	3.60542703	3.62995741	3.63834986

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	10.977544	3.65918132	0.00088317
2	3	11.1338782	3.71129274	0.00494931
3	3	11.0374066	3.67913552	1.5826E-05
4	3	10.7738864	3.59129546	0.00887793
5	3	10.8496359	3.6165453	0.00061564
6	3	10.8317916	3.61059721	0.00026742
7	3	10.8848246	3.62827488	0.00369943
8	3	10.8541985	3.61806617	0.00055833
9	3	10.7811763	3.59372545	0.0058712
10	3	10.7676436	3.58921454	0.0003622
11	3	10.7965422	3.59884739	0.00480956
12	3	10.9064326	3.63547753	0.00227665
13	3	10.7120706	3.57069019	0.00195571
14	3	10.8546873	3.61822909	0.0022357
15	3	10.8737343	3.6245781	0.00029268
			3.62301006	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.05702338	14	0.0040731	1.62185466	0.13005577	2.03742044
Within groups	0.07534149	30	0.00251138			
Total	0.13236487	44				

within-sd	0.050114			status:	homogeneous
effective n	4.00				
s_bb	0.019759				
s_bb_min	0.012732				
u_bb	0.019759				

Contribution to combined uncertainty [rel. %]: 0.54538273

Iron:

	1	2	3
603-1	2.64728927	3.16747897	1.52499725
603-2	3.07407565	2.19608939	2.01280848
603-3		1.77912541	1.71507126
603-4	2.29120233	1.41428451	1.63707023
603-5		1.48026727	2.89260448
603-6		2.0284794	2.55707603
603-7	1.72046867	3.92211322	1.85855375
603-8	2.04316297		1.59291156
603-9	2.5342946	1.25804648	1.62418718
603-10	2.07640924	1.92699254	2.60482463
603-11	1.53645273	2.32609578	1.52604024
603-12	2.82554786	1.61770082	3.1150766
603-13	3.4628893	3.57304064	1.88339552
603-14	1.83752653		1.98820922
603-15	2.20218557	2.9746597	3.04505701

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	7.3397655	2.4465885	0.70464715
2	3	7.28297352	2.42765784	0.32178996
3	2	3.49419666	1.74709833	0.00205147
4	3	5.34255706	1.78085235	0.20775119
5	2	4.37287176	2.18643588	0.99734819
6	2	4.58555543	2.29277772	0.1397072
7	3	7.50113564	2.50037855	1.52076398
8	2	3.63607452	1.81803726	0.10136317
9	3	5.41652826	1.80550942	0.43186063
10	3	6.60822641	2.20274214	0.12683408
11	3	5.38858875	1.79619625	0.21062224
12	3	7.55832528	2.51944176	0.63080926
13	3	8.91932547	2.97310849	0.89363909
14	2	3.82573575	1.91286788	0.01135264
15	3	8.22190227	2.74063409	0.21868405
			2.21002176	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	5.89649726	14	0.42117838	0.89333957	0.5752499	2.11110505
Within groups	11.786626	25	0.47146504			
Total	17.6831232	39				

within-sd	0.686633	status:	homogeneous
effective n	4.00		
s_bb	0		
s_bb_min	0.182586		
u_bb	0.182586		
Contribution to combined uncertainty:	0		

Nickel:

	1	2	3
603-1	0.45914851	0.58305152	0.24533115
603-2	0.69973285	0.45725524	0.45527261
603-3		0.29451233	0.68678487
603-4	0.546732	0.28410759	0.30649407
603-5		0.27589638	0.44598447
603-6	0.3137757	0.31652465	0.29863853
603-7	0.38197806	0.99082096	0.27903061
603-8	0.50488823		0.28221518
603-9	0.40821904	0.23451034	0.28130699
603-10	0.3474397	0.30828216	0.33838241
603-11	0.27327273	0.26902244	0.24513943
603-12	0.44009191	0.27752831	0.51383547
603-13	0.82640152	0.30559651	0.37905877
603-14	0.31111761		0.3655607
603-15	0.34543364	0.51973651	0.47096431

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	1.28753119	0.42917706	0.02918748
2	3	1.6122607	0.53742023	0.01976002
3	2	0.9812972	0.4906486	0.07693887
4	3	1.13733366	0.37911122	0.02119783
5	2	0.72188084	0.36094042	0.01446498
6	3	0.92893888	0.30964629	9.2767E-05
7	3	1.65182963	0.55060988	0.1479889
8	2	0.78710341	0.3935517	0.02479164
9	3	0.92403638	0.30801213	0.00807855
10	3	0.99410428	0.33136809	0.00042023
11	3	0.7874346	0.2624782	0.00022999
12	3	1.23145569	0.41048523	0.01461768
13	3	1.5110568	0.5036856	0.07945835
14	2	0.67667831	0.33833916	0.00148202
15	3	1.33613447	0.44537816	0.00808636
			0.40339013	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.31454547	14	0.02246753	0.75286179	0.70584729	2.09394853
Within groups	0.77591384	26	0.02984284			
Total	1.09045931	40				

within-sd	0.172751		status:	homogeneous
effective n	4.00			
s_bb	0			
s_bb_min	0.045489			
u_bb	0.045489			

Contribution to combined uncertainty: 0

Antimony:

	1	2	3
603-1	0.01665756	0.0637144	0.00864561
603-2	0.02193321	0.01713919	0.01288371
603-3	0.02969051	0.0190958	0.01241805
603-4	0.01111885	0.01485184	0.01695393
603-5	0.02651487	0.01288077	0.15588546
603-6	0.02827179	0.01979	0.0135856
603-7	0.02367804	0.04357929	0.01598101
603-8	0.03484388	0.05145519	0.01233888
603-9	0.02978057	0.23572727	0.01379679
603-10	0.0266808	0.01423293	0.08468759
603-11	0.08982451	0.01970122	0.01289253
603-12	0.028322	0.03368867	0.02529902
603-13	0.02221	0.01787818	0.02790622
603-14	0.02153694	0.13905028	0.0286513
603-15	0.01736943	0.03601448	0.02632907

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	0.08901757	0.02967252	0.00088518
2	3	0.05195611	0.0173187	2.0498E-05
3	3	0.06120436	0.02040145	7.5863E-05
4	3	0.04292461	0.0143082	8.7337E-06
5	3	0.1952811	0.0650937	0.00622883
6	3	0.06164739	0.02054913	5.4353E-05
7	3	0.08323835	0.02774612	0.00020283
8	3	0.09863796	0.03287932	0.00038542
9	3	0.27930462	0.09310154	0.01532044
10	3	0.12560133	0.04186711	0.00141393
11	3	0.12241827	0.04080609	0.00181369
12	3	0.08730969	0.02910323	1.8054E-05
13	3	0.06799439	0.0226648	2.5296E-05
14	3	0.18923852	0.06307951	0.00434132
15	3	0.07971298	0.02657099	8.6953E-05
			0.03634416	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.01988953	14	0.00142068	0.69006625	0.76593077	2.03742044
Within groups	0.0617628	30	0.00205876			
Total	0.08165234	44				
within-sd	0.045374			status:	homogeneous	
effective n	4.00					
s_bb	0					
s_bb_min	0.011528					
u_bb	0.011528					

Contribution to combined uncertainty: 0

Thallium:

	1	2	3
603-1	3.66482549	3.6636487	3.71382867
603-2	3.56125374	3.6238902	3.67346016
603-3	3.52338034	3.52989282	3.64897352
603-4	3.54706365	3.5565716	3.64639188
603-5	3.45393784	3.54703677	3.57860174
603-6	3.63123584	3.67753254	3.70545532
603-7	3.5547756	3.61996137	3.63841846
603-8	3.54077514	3.57235956	3.63837664
603-9	3.52403195	3.53777681	3.6176079
603-10	3.54263445	3.53628729	3.63511248
603-11	3.64635566	3.70293044	3.71359945
603-12	3.5192432	3.5425673	3.64170318
603-13	3.51995204	3.59601366	3.68841542
603-14	3.51182365	3.55174913	3.57167759
603-15	3.53035438	3.50813397	3.62495773

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	11.0423029	3.68076762	0.00082012
2	3	10.8586041	3.6195347	0.0031618
3	3	10.7022467	3.56741556	0.00499938
4	3	10.7500271	3.58334237	0.00300403
5	3	10.5795763	3.52652545	0.00420081
6	3	11.0142237	3.6714079	0.00140527
7	3	10.8131554	3.60438514	0.001931
8	3	10.7515113	3.58383711	0.00248031
9	3	10.6794167	3.55980555	0.00255306
10	3	10.7140342	3.57134474	0.00305982
11	3	11.0628856	3.68762852	0.00130604
12	3	10.7035137	3.56783789	0.00422806
13	3	10.8043811	3.60146037	0.00711723
14	3	10.6352504	3.54508346	0.00092895
15	3	10.6634461	3.55448202	0.00384856
			3.59499056	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.10465682	14	0.00747549	2.4893713	0.0176768	2.03742044
Within groups	0.09008886	30	0.00300296			
Total	0.19474567	44				

within-sd	0.054799		status:	inhomogeneous
effective n	4.00			
s_bb	0.033438			
s_bb_min	0.013923			
u_bb	0.033438			

Contribution to combined uncertainty [rel. %]: 0.9301407

Bismuth:

	1	2	3
603-1	0.0957987	0.09531659	0.17672275
603-2	0.14373142	0.07745933	0.07872286
603-3	0.07249139	0.07925708	0.10744127
603-4	0.14551801	0.07376878	0.1406387
603-5	0.14349551	0.11018905	0.07701115
603-6	0.0729571	0.07535941	0.15088356
603-7	0.10544932	0.07521551	0.10406651
603-8	0.13631529	0.07881258	0.10191226
603-9	0.10380829	0.14514837	0.1185599
603-10	0.07535322	0.09175984	0.08095523
603-11	0.0946874	0.09425163	0.09666569
603-12	0.07245515	0.09750665	0.07939621
603-13	0.13035754	0.12196369	0.10458498
603-14	0.11213144	0.09257106	0.1105968
603-15	0.09134776	0.08682176	0.11916561

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	0.36783803	0.12261268	0.00219598
2	3	0.29991361	0.0999712	0.00143662
3	3	0.25918975	0.08639658	0.0003436
4	3	0.35992549	0.11997516	0.00160722
5	3	0.33069571	0.1102319	0.00110504
6	3	0.29920006	0.09973335	0.0019637
7	3	0.28473133	0.09491044	0.0002914
8	3	0.31704013	0.10568004	0.00083729
9	3	0.36751656	0.12250552	0.00043893
10	3	0.24806828	0.08268943	6.955E-05
11	3	0.28560472	0.09520157	1.6552E-06
12	3	0.24935801	0.08311934	0.00016729
13	3	0.3569062	0.11896873	0.00017278
14	3	0.3152993	0.10509977	0.00011832
15	3	0.29733513	0.09911171	0.00030674
			0.1030805	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00785018	14	0.00056073	0.76074717	0.69987411	2.03742044
Within groups	0.02211223	30	0.00073707			
Total	0.02996241	44				

within-sd	0.027149			status:	homogeneous
effective n	4.00				
s_bb	0				
s_bb_min	0.006898				
u_bb	0.006898				

Contribution to combined uncertainty: 0

Cobalt:

	1	2	3
603-1	0.04168381	0.04436165	0.03820285
603-2	0.04224407	0.03794271	0.03953527
603-3	0.04274222	0.03974967	0.04062967
603-4	0.04222882	0.03857188	0.04196084
603-5	0.0413699	0.04043464	0.03981146
603-6	0.03842189	0.04114737	0.03953129
603-7	0.03959513	0.04009234	0.04087184
603-8	0.03810101	0.04111654	0.03978305
603-9	0.04040482	0.03805293	0.03775766
603-10	0.03993063	0.04087401	0.04087938
603-11	0.03993396	0.03924837	0.03856181
603-12	0.04325771	0.03841336	0.0413948
603-13	0.03979537	0.04013191	0.04033948
603-14	0.03949196	0.04033071	0.04160485
603-15	0.04050478	0.04468323	0.04194216

Bottle	*Number*	*Sum*	*Mean*	*Variance*
1	3	0.12424831	0.0414161	9.5364E-06
2	3	0.11972205	0.03990735	4.7293E-06
3	2	0.12312155	0.04104052	2.3654E-06
4	3	0.12276154	0.04092051	4.155E-06
5	2	0.121616	0.04053867	6.153E-07
6	2	0.11910055	0.03970018	1.8784E-06
7	3	0.12055931	0.04018644	4.1414E-07
8	2	0.11900059	0.03966686	2.2835E-06
9	3	0.11621541	0.03873847	2.1043E-06
10	3	0.12168403	0.04056134	2.9835E-07
11	3	0.11774413	0.03924804	4.707E-07
12	3	0.12306587	0.04102196	5.9712E-06
13	3	0.12026677	0.04008892	7.5401E-08
14	2	0.12142751	0.04047584	1.1319E-06
15	3	0.12713017	0.04237672	4.5065E-06
			0.04039253	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3.4674E-05	14	2.4767E-06	0.91649869	0.55223879	2.03742044
Within groups	8.1072E-05	30	2.7024E-06			
Total	0.00011575	44				

within-sd	0.001644		status:	homogeneous

effective n	4.00
s_bb	0
s_bb_min	0.000418
u_bb	0.000418

Contribution to combined uncertainty: 0