Certification Report

Certified Reference Material

BAM-M319

AlMgSc powder

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Summary

This report describes preparation, analysis and certification of aluminium powder reference material BAM-M319.
The certified reference material (CRM) is available in the form of powder (d_{50} = 93.057 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 %	Uncertainty [2)] in %
Si	0.1043	0.0020
Fe	0.291	0.013
Cu	0.0015	0.0003
Mn	0.371	0.006
Mg	4.96	0.06
Sc	0.847	0.015
Zn	0.0073	0.0004
Ti	0.0030	0.0002
Zr	0.324	0.014

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

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

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

Three laboratories reported results for the additional elements Cr, Ga, Ni, and V and one laboratory reported results for the additional elements Bi, Cd, Pb, and Sn.

Content

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
JM	Johnson Matthey
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 (Tables 4 – 12)
EA	ETAAS (Tables 4 – 12)
I	ICP-OES, dissolution with acid (Tables 4 – 12)
-s	dissolution with acid (Tables 4 – 12)
-a	dissolution with NaOH (Tables 4 – 12)
P	spectrophotometry (Tables 4 – 12)
u_{ilc}	uncertainty contribution from inter-laboratory comparison
u_{stab}	uncertainty contribution from possible instability
u_{bb}	uncertainty contribution from possible inhomogeneity

1. Introduction

Scalmalloy® is the first aluminium alloy that has been specifically developed for additive manufacturing. With the additions of magnesium and scandium, Scalmalloy® is currently the strongest aluminium alloy that can be processed free from cracks by Additive Manufacturing.
The alloy was specifically developed by Airbus Group for the aviation and aerospace sectors. Due to its high ductility, resistance to corrosion and weldability, Scalmalloy® is used in lightweight construction, motorsport, aviation and aerospace, as well as in the automotive sector and robotics.
The idea to produce a Scalmalloy® reference material was addressed to BAM by an industrial company. Participating laboratories were recruited from the Committee of Chemists within GDMB German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB). Since all the laboratories participating in this certification project are experienced with aluminium analysis or had participated in earlier inter-laboratory comparisons, there was no preceding round robin for qualification.
Certification of reference material BAM-M319 was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2. Companies/laboratories involved

Manufacturing of the material

– TOYO ALUMINIUM K.K., Higashiyama, Japan

Test for homogeneity and stability

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

Participants in the certification inter-laboratory comparison

– ALERIS Rolled Products Germany GmbH, Koblenz, Germany
– ACL Analytisch Chemisches Labor GmbH, Hailfingen, Rottenburg Germany
– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
  Division „Inorganic Reference Materials“
  Division „Thermochemical Residues Treatment and Resource Recovery“
– Forschungsinstitut Edelmetalle & Metallchemie, Schwäbisch Gmünd (Germany)
– Fraunhofer-Institut für Silicatforschung ISC, Hanau, Germany
– Hydro Aluminium Rolled Products GmbH, R&D, Bonn, Germany
– Institut für Materialprüfung Glörfeld GmbH, Willich (Germany)
– revierlabor GmbH, Essen, Germany

Determination of particle size distribution

– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
  Division „Advanced Technical Ceramics“

Determination of tamped volume and apparent density after tamping and Hausner-factor

– Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
  Division „Ceramic Processing and Biomaterials“

Statistical evaluation of the data

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

3. Candidate material

The starting material in form of fine powder (ca. 40 kg) was taken from the normal production process within TOYO ALUMINIUM K.K., Higashiyama, Japan. The material was sieved over a 150 µm sieve, all particles above this particle size were discarded. The powder was then mixed and divided into four sub batches. From each of these sub batches three samples were taken for homogeneity testing, in total twelve bottles.

The particle size was determined by BAM using a Mastersizer 2000 laser diffraction particle size analyzer (Malvern Panalytical).

Tab. 1: Particle size distribution of BAM-M319

d 10	67.884 µm
d 50	93.057 µm
d 90	126.736 µm

In addition to the particle size distribution the tamped volume and apparent density after tamping according to ISO 787-11 was determined [4] using an Engelsmann tapped density tester STAV 2003.

Tab. 2: Determination of tamped volume, tapped density and Hausner Factor

Sample	1	2	3	Mean	Std.-dev.
m_0 in g	184.55	183.94	183.93		
m_1 in g	486.24	482.92	482.32		
bulk volume in ml	200.0	200.0	200.0		
tamped volume in mL	190.0	190.0	190.0		
tamped volume in mL/100 g	62.98	63.55	63.34	63.26	0.40
tamped density in g/mL	1.5878	1.5736	1.5788	1.5807	0.01
Hausner Factor	1.05	1.05	1.05	1.05	

A Hausner Factor between 1 and 1.11 means that the flow properties of a powder are excellent.

4. Homogeneity testing

A total of 12 samples of the candidate material were taken for homogeneity testing. From each bottle three sub-samples were analysed using ICP-OES. 0.10 g of sample was weighed and dissolved in a mixture of hydrochloric acid and 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 would be set to zero. This was not the case for any of the elements.

5. Stability testing

The material is stable. Possible phase transformations can occur if the material is stored over a longer period at temperatures above 80 °C. This is normally not the case in normal laboratory conditions.

6. Characterisation study

6.1 Analytical methods

Nine laboratories participated in the certification inter-laboratory comparison. All laboratories were experienced in the analysis of aluminium 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 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.
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.

Table 3: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Si, Zr	0.5 g	Dissolution with NaOH	Spectrophotometry, calibration with commercial solution (Merck)
	Si, Fe, Cu, Mn, Mg, Sc, Zn, Zr	0.25 g	Dissolution with NaOH	ICP-OES, calibration with commercial solution (Si, Sc, Zr, Cr, Ga, Ni, V: Merck) or pure substances (Fe: 098-1, Cu: BAM-381, Mn: 99.99% JM, Mg: 99.98% JM, Zn: 99.9999% Heraeus)
	Fe, Cu, Mn, Mg, Sc, Zn, Zr	0.1 g	Dissolution with HCl/HNO_3	ICP-OES, calibration with commercial solutions (Merck), matrix matching with Al 99.999%
	Fe, Mn, Mg, Zn	1 g	Dissolution with HCl/H_2O_2	FAAS, calibration with commercial solutions (Merck), matrix matching with Al 99.999%
	Cu	1 g	Dissolution with HCl/H_2O_2	ETAAS, calibration with commercial solution (Merck), matrix matching with Al 99.999%
	Mn		Dissolution with HCl/HNO_3	Spectrophotometry, calibration with commercial solution (Merck)
2	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr	0.5 g	Dissolution with HNO_3/HCl, addition of $LiNO_3$	ICP-OES, calibration with commercial solutions (Merck certipur)
3	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr	0.25 g	Dissolution with HCl/HNO_3,	ICP-OES, calibration with commercial solutions (Si, Fe, Cu, Mn, Mg, Zn: Merck; Sc, Zr, Ti: Sigma Aldrich)
4	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr	0.5 g	Dissolution with NaOH	ICP-OES, calibration with commercial solutions (Merck certipur)
5	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr	0.5 g	Dissolution with $HNO_3/HCl/HF/H_3BO_4$	ICP-OES, calibration with pure substances ($(NH_4)_2SiF_6$ 99.999 %, Fe_2O_3 99.998 %, Cu 99.9999 %, $MgCl_2$x6 H_2O 99.999 %, $ZrCl_4$ 99,99 %, Ti 99.99+ %, Zn 99.9999 %) or commercial mono-element solution (Sc), Alfa Aesar, matrix matching with Al 99.9999%
6	Si, Cu, Zn, Zr, Ga, Ti, V, Cr, Ni, Cd, Pb, Sn	0.25 g	Dissolution with $HNO_3/HCl/HF$	ICP-OES, calibration with commercial mono-element solutions (Merck,), matrix matching with Al 99.999%
	Fe, Mn, Mg, Sc	0.25 g	Dissolution with HCl/H_2O_2	ICP-OES, calibration with commercial solutions (Merck)
7	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr	0.5 g	Dissolution with NaOH	ICP-OES, matrix matched calibration with mono-element solutions prepared from pure substances
8	Pb, Cd, Fe, Cu, Ni, Sb	10 g	Dissolution with NaOH and H_2O_2	ICP-OES, calibration with matrix matched commercial solution standards
9	Si, Fe, Cu, Mn, Mg, Sc, Ti, Zn, Zr, Cr, Ni, Ga, V	0.5 g	Dissolution with NaOH	ICP-OES, calibration with pure substances (SiO_2 (BAM RS 1), Fe 99.9 %, Cu 99.9999 %, Mn 99.99 %, Mg 99.99 %, Sc_2O_3 99,99 %, Ti 99.9 %, Zn 99.999 %, Zr 99.9 %, $K_2Cr_2O_7$ p.A., Ni 99.99 % or commercial mono-element solution (Ga, V), Merck Certipur, matrix matching with Al 99.9995%

6.2 Analytical results and statistical evaluation

The analytical results of the inter-laboratory certification comparison are listed in Tables 4 to 12. 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 4: Results for Si

Lab./Meth.	7/I-a	2/I-s	3/I-s	8/I-a	1/I-a	6/I-s	9/I-a	5/I-s	1/P	4/I-a		
M_i [%]	0.064	0.079	0.078	0.100	0.105	0.104	0.106	0.105	0.105	0.106		n
	0.064	0.061	0.079	0.100	0.106	0.104	0.106	0.103	0.106	0.113		7
	0.062	0.053	0.078	0.100	0.105	0.102	0.106	0.106	0.106	0.107		
	0.065	0.069	0.083	0.099	0.102	0.105	0.102	0.103	0.106	0.108		
	0.065	0.077	0.079	0.100	0.101	0.104	0.102	0.104	0.106	0.108		
	0.064	0.078	0.078	0.099	0.104	0.104	0.102	0.107	0.106	0.107		
M [%]	**0.0640**	**0.0695**	**0.0792**	**0.0997**	**0.1038**	**0.1041**	**0.1041**	**0.1047**	**0.1057**	**0.1081**		**0.1043**
s [%]	0.0011	0.0105	0.0019	0.0005	0.0019	0.0008	0.0024	0.0017	0.0004	0.0027	s_M [%]	0.0025
											$\bar{s}_i$ [%]	0.0017
s_{rel}	0.0171	0.1512	0.0245	0.0052	0.0187	0.0079	0.0226	0.0162	0.0036	0.0246		0.0242

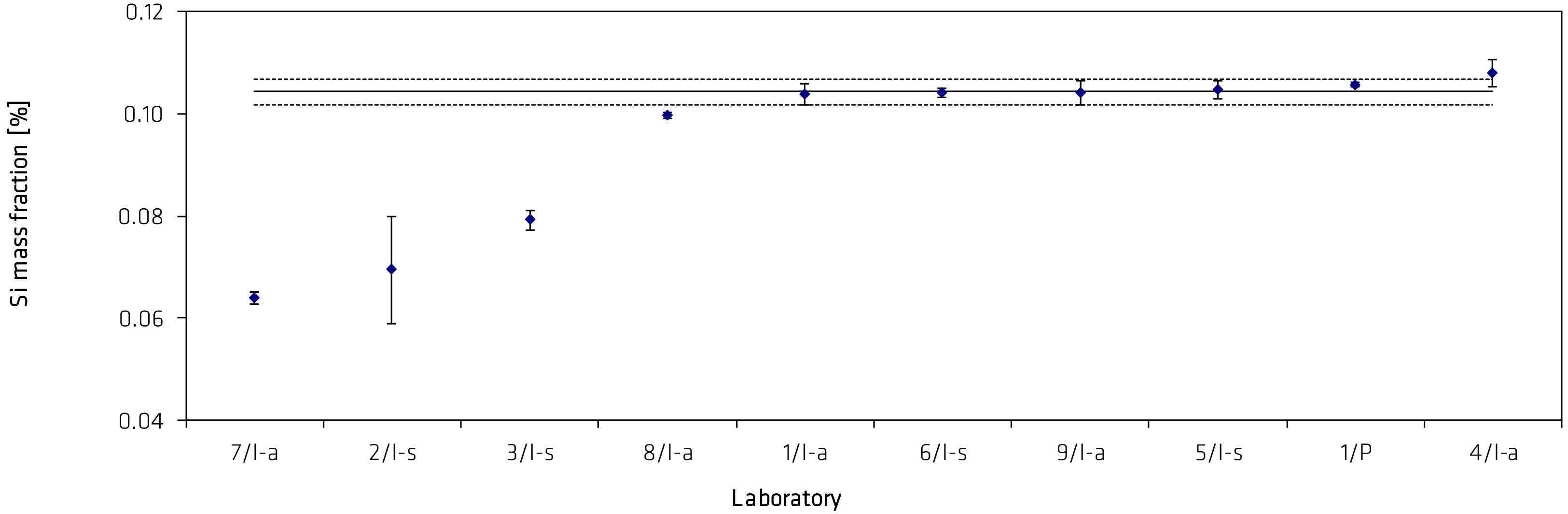

Table 5: Results for Fe

Lab./Meth.	8/I-a	1/P	1/I-s	2/I-s	4/I-a	5/I-s	1/A-s	1/I-a	6/I-s	7/I-a	3/I-s	9/I-a		
M_i [%]	0.280	0.281	0.290	0.283	0.289	0.292	0.295	0.284	0.302	0.308	0.298	0.323		n
	0.280	0.279	0.294	0.278	0.288	0.285	0.289	0.292	0.299	0.303	0.313	0.312		11
	0.280	0.280	0.297	0.285	0.288	0.294	0.291	0.291	0.298	0.302	0.305	0.314		
	0.281	0.282	0.273	0.288	0.287	0.283	0.295	0.293	0.294	0.300	0.298	0.325		
	0.281	0.283	0.269	0.283	0.286	0.298	0.297	0.311	0.300	0.293	0.298	0.317		
	0.281	0.288	0.269	0.284	0.288	0.295	0.298	0.299		0.296	0.301	0.338		
M [%]	**0.280**	**0.282**	**0.282**	**0.283**	**0.287**	**0.291**	**0.294**	**0.295**	**0.299**	**0.300**	**0.302**	**0.322**		**0.291**
s [%]	0.0006	0.0033	0.0129	0.0033	0.0013	0.0059	0.0036	0.0092	0.0028	0.0053	0.0060	0.0097	s_M [%]	0.0080
													$\bar{s}_i$ [%]	0.0060
s_{rel}	0.0021	0.0116	0.0458	0.0117	0.0044	0.0201	0.0124	0.0311	0.0093	0.0177	0.0198	0.0302		0.0275

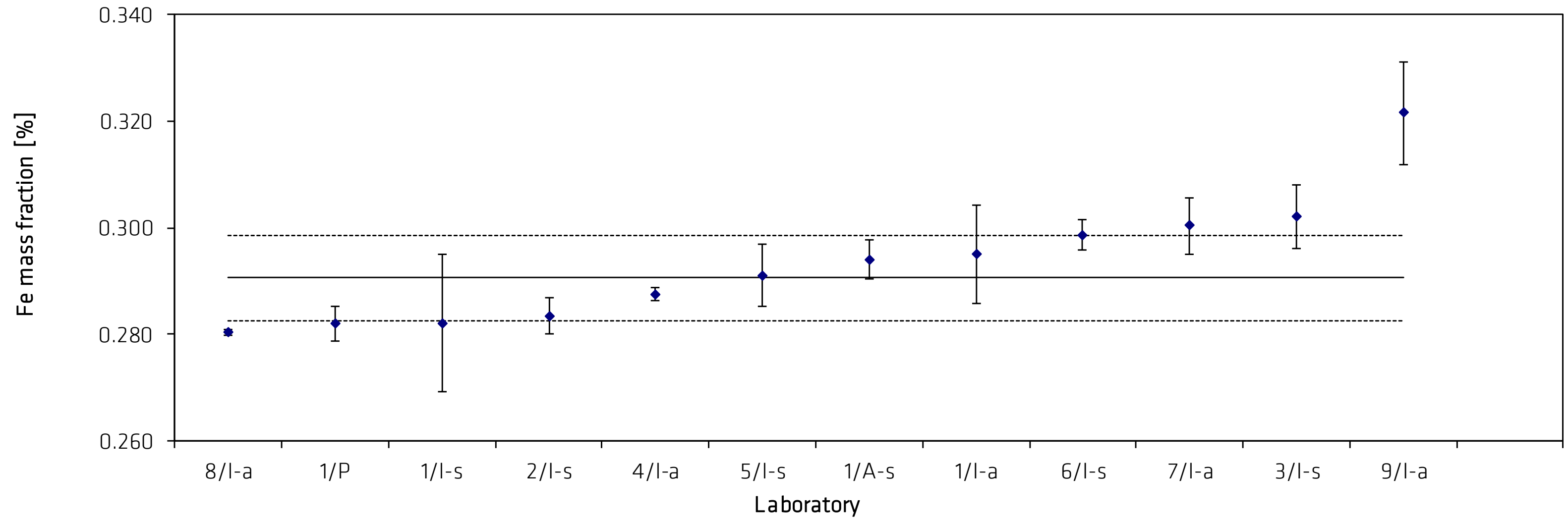

Table 6: Results for Cu

Lab./Meth.	4/I-a	2/I-s	9/I-a	3/I-s	1/I-s	6/I-s	1/EA-s	1/I-a	7/I-a		
M_i [%]	0.0011	0.0013	0.0013	0.0013	0.0015	0.0015	0.0016	0.0018	0.0019		*n*
	0.0010	0.0012	0.0013	0.0014	0.0014	0.0014	0.0016	0.0020	0.0018		9
	0.0011	0.0013	0.0013	0.0014	0.0015	0.0016	0.0016	0.0018	0.0023		
	0.0011	0.0013	0.0013	0.0015	0.0014	0.0015	0.0016	0.0020	0.0022		
	0.0010	0.0013	0.0013	0.0014	0.0014	0.0015	0.0016	0.0021	0.0019		
	0.0010	0.0014	0.0014	0.0015	0.0014		0.0016		0.0017		
M [%]	**0.0011**	**0.0013**	**0.0013**	**0.0014**	**0.0014**	**0.0015**	**0.0016**	**0.0019**	**0.0020**		**0.0015**
s [%]	0.0001	0.0000	0.0000	0.0001	0.0001	0.0001	0.0000	0.0001	0.0002	s_M [%]	0.00030
										$\bar{s}_i$ [%]	0.00010
s_{rel}	0.0522	0.0338	0.0225	0.0531	0.0375	0.0471	0.0154	0.0692	0.1189		0.1978

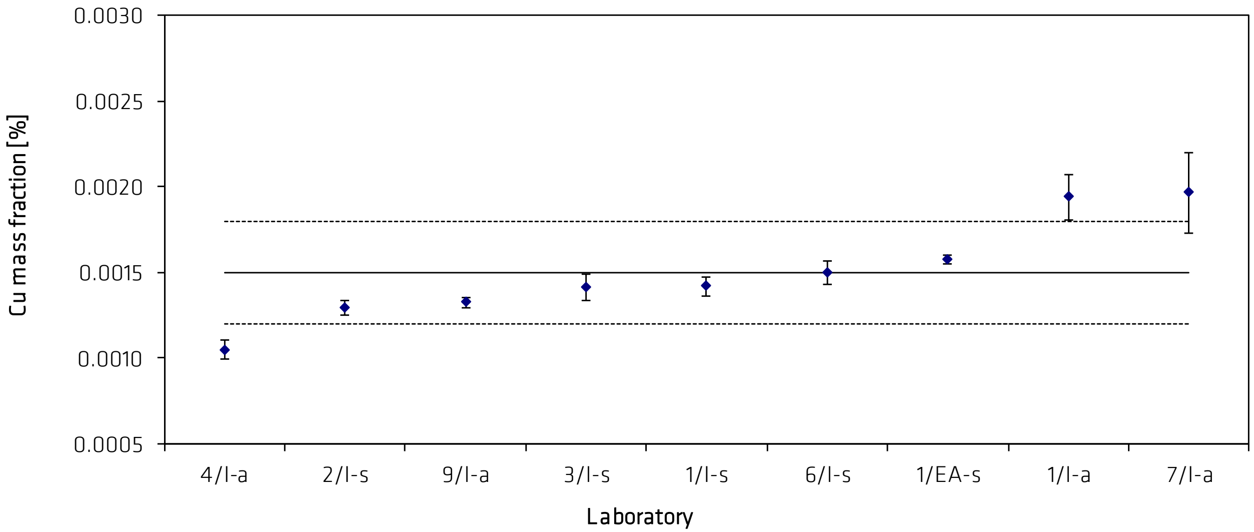

Table 7: Results for Mn

Lab./Meth.	1/I-s	7/I-a	2/I-s	9/I-a	1/I-a	6/I-s	5/I-s	1/A-s	1/P	4/I-a	3/I-s	8/I-a		
M_i [%]	0.355	0.361	0.392	0.369	0.364	0.369	0.367	0.371	0.375	0.378	0.378	0.384		*n*
	0.356	0.362	0.321	0.369	0.367	0.371	0.368	0.371	0.374	0.381	0.381	0.384		12
	0.357	0.360	0.361	0.370	0.362	0.371	0.371	0.376	0.373	0.379	0.378	0.382		
	0.359	0.361	0.345	0.365	0.365	0.369	0.367	0.373	0.373	0.380	0.384	0.384		
	0.356	0.356	0.363	0.365	0.385	0.371	0.369	0.370	0.372	0.382	0.378	0.383		
	0.360	0.361	0.407	0.367	0.373	0.369	0.380	0.367	0.374	0.378	0.386	0.385		
								0.373	0.372					
									0.372					
M [%]	**0.357**	**0.360**	**0.365**	**0.367**	**0.369**	**0.370**	**0.370**	**0.372**	**0.373**	**0.379**	**0.381**	**0.384**		**0.371**
s [%]	0.0019	0.0021	0.0309	0.0019	0.0085	0.0009	0.0051	0.0028	0.0010	0.0016	0.0035	0.0010	s_M [%]	0.00792
													$\bar{s}_i$ [%]	0.00954
s_{rel}	0.0054	0.0059	0.0847	0.0052	0.0231	0.0023	0.0138	0.0076	0.0027	0.0041	0.0092	0.0027		0.0214

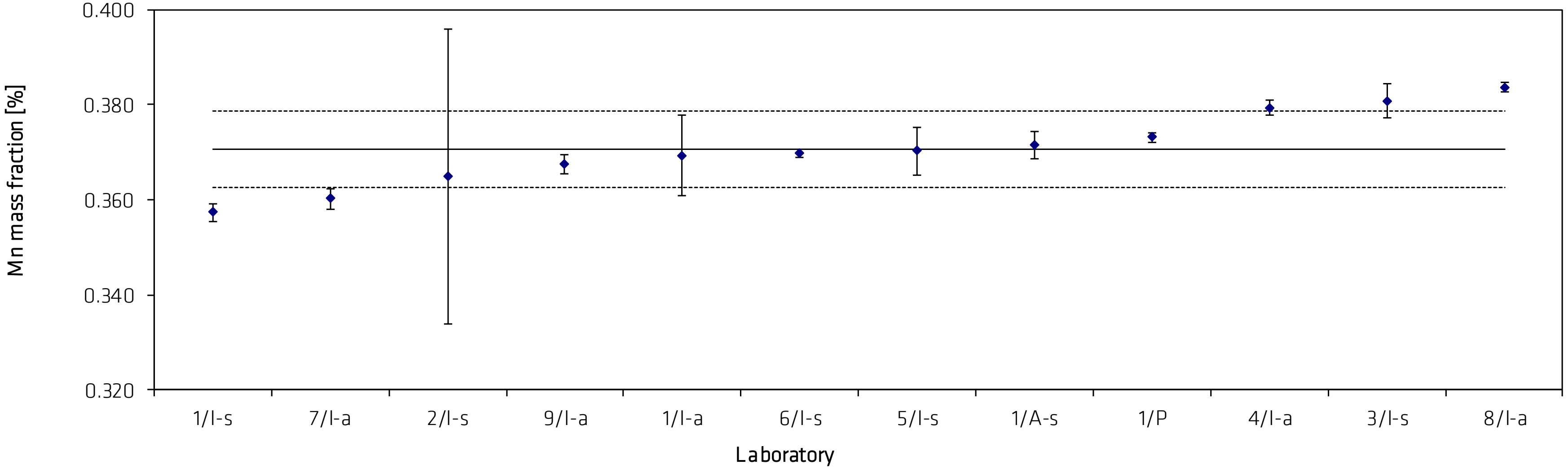

Table 8: Results for Mg

Lab./Meth.	2/I-a	1/I-s	6/I-s	9/I-a	4/I-a	5/I-s	1/I-a	8/I-a	7/I-a	1/A-s	3/I-s		
M_i [%]	4.681	4.825	4.934	4.949	4.952	4.915	4.928	5.01	5.018	4.990	5.286		n
	4.005	4.828	4.945	4.969	4.957	4.888	5.002	5.01	5.018	5.023	5.285		9
	4.538	4.826	4.940	4.971	4.923	4.991	5.028	4.99	5.019	5.009	5.284		
	4.147	4.897	4.932	4.911	4.956	4.900	5.005	5.03	5.006	5.047	5.271		
	4.522	4.829	4.932	4.926	4.931	4.922	4.950	4.94	5.000	5.008	5.321		
	4.876	4.874	4.936	4.932	4.949	5.100	4.970	5.04	5.007	5.023	5.313		
							4.987			4.994			
							4.997						
M [%]	**4.461**	**4.846**	**4.936**	**4.943**	**4.944**	**4.953**	**4.983**	**5.003**	**5.011**	**5.013**	**5.293**		**4.959**
s [%]	0.3279	0.0311	0.0050	0.0243	0.0143	0.0804	0.0324	0.0356	0.0080	0.0195	0.0193	s_M [%]	0.0524
												$\bar{s}_i$ [%]	0.0350
s_{rel}	0.0735	0.0064	0.0010	0.0049	0.0029	0.0162	0.0065	0.0071	0.0016	0.0039	0.0036		0.0106

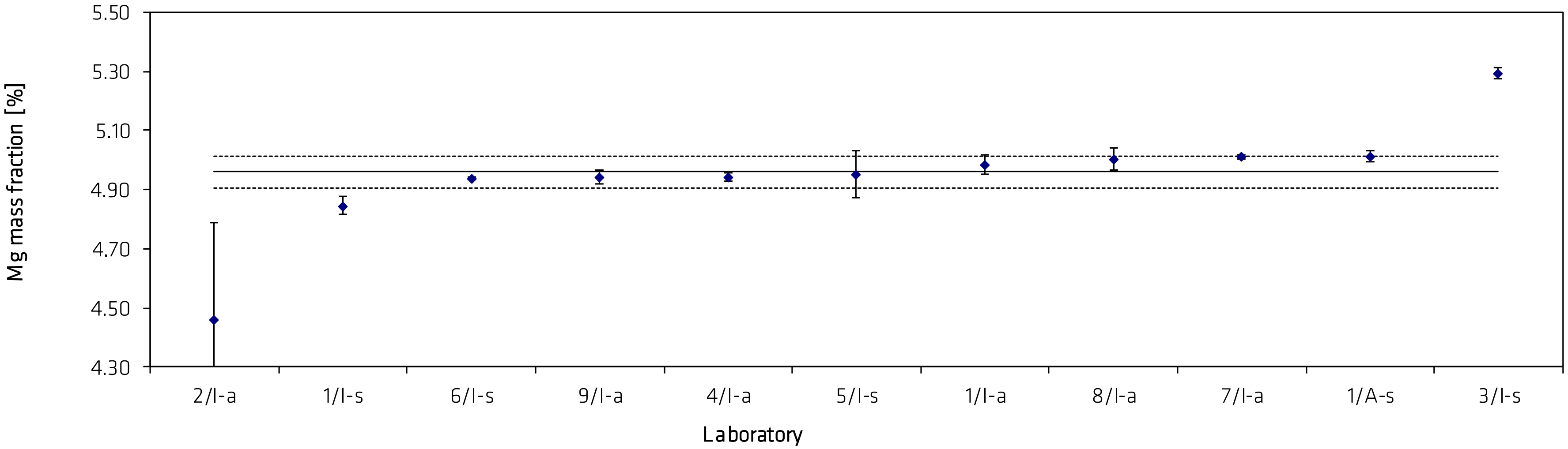

Table 9: Results for Sc

Lab./Meth.	7/I-a	8/I-a	2/I-s	1/I-a	6/I-s	9/I-a	3/I-s	4/I-a	1/I-s	5/I-s		
M_i [%]	0.816	0.815	0.887	0.822	0.850	0.859	0.856	0.873	0.871	0.855		*n*
	0.820	0.819	0.730	0.828	0.851	0.861	0.856	0.861	0.869	0.864		10
	0.815	0.821	0.821	0.822	0.851	0.861	0.859	0.849	0.869	0.870		
	0.817	0.822	0.784	0.823	0.851	0.854	0.861	0.855	0.877	0.871		
	0.802	0.822	0.827	0.849	0.849	0.857	0.861	0.870	0.865	0.880		
	0.814	0.823	0.923		0.851	0.860	0.866	0.868	0.868	0.896		
M [%]	**0.814**	**0.820**	**0.829**	**0.829**	**0.851**	**0.858**	**0.860**	**0.863**	**0.870**	**0.873**		**0.847**
s [%]	0.0062	0.0029	0.0696	0.0116	0.0007	0.0028	0.0038	0.0094	0.0040	0.0141	s_M [%]	0.0216
											$\bar{s}_i$ [%]	0.0231
s_{rel}	0.008	0.004	0.084	0.014	0.001	0.003	0.004	0.011	0.005	0.016		0.026

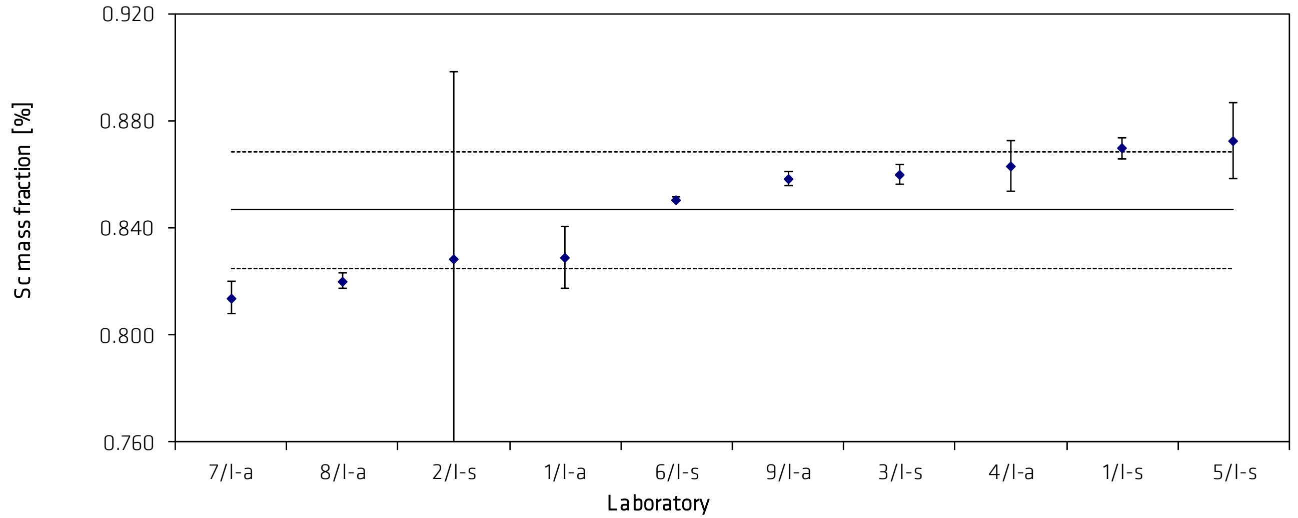

Table 10: Results for Ti

Lab./Meth.	6/I-s	7/I-a	5/I-s	3/I-s	9/I-a	1/P	1/I-s	4/I-a	2/I-s		
M_i [%]	0.0021	0.0023	0.0026	0.0028	0.0030	0.00296	0.0030	0.0030	0.0029		*n*
	0.0019	0.0023	0.0026	0.0029	0.0030	0.00299	0.0030	0.0031	0.0030		7
	0.0022	0.0024	0.0027	0.0029	0.0030	0.00301	0.0030	0.0031	0.0032		
	0.0020	0.0025	0.0027	0.0029	0.0030	0.00296	0.0030	0.0030	0.0032		
	0.0021	0.0024	0.0027	0.0029	0.0030	0.00301	0.0030	0.0030	0.0030		
		0.0024	0.0027	0.0029	0.0030	0.00299	0.0029	0.0032	0.0031		
M [%]	**0.0021**	**0.0024**	**0.0027**	**0.0029**	**0.0030**	**0.0030**	**0.0030**	**0.0031**	**0.0031**		**0.0030**
s [%]	0.00011	0.00008	0.00005	0.00004	0.00002	0.00002	0.00004	0.00008	0.00012	s_M [%]	0.00014
										$\bar{s}_i$ [%]	0.00006
s_{rel}	0.0553	0.0316	0.0194	0.0142	0.0066	0.0075	0.0133	0.0266	0.0378		0.0480

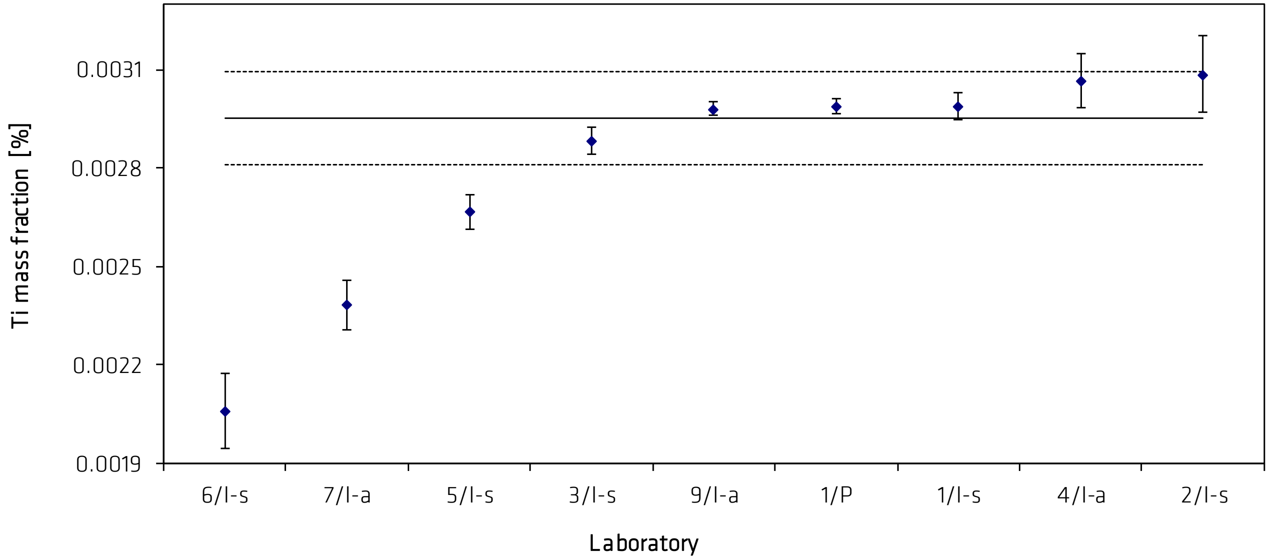

Table 11: Results for Zn

Lab./Meth.	5/I-s	1/I-a	2/I-s	9/I-a	7/I-a	3/I-s	1/A-s	6/I-s	4/I-a		
M_i [%]	0.0069	0.0072	0.0066	0.0070	0.0073	0.0073	0.0074	0.0075	0.0076		*n*
	0.0068	0.0069	0.0060	0.0070	0.0074	0.0073	0.0074	0.0075	0.0077		9
	0.0070	0.0069	0.0089	0.0070	0.0072	0.0072	0.0074	0.0077	0.0078		
	0.0068	0.0069	0.0070	0.0072	0.0072	0.0076	0.0074	0.0075	0.0078		
	0.0069	0.0072	0.0066	0.0072	0.0072	0.0073	0.0075	0.0076	0.0076		
	0.0071	0.0069	0.0069	0.0072	0.0071	0.0073	0.0075		0.0077		
							0.0074				
M [%]	**0.0069**	**0.0070**	**0.0070**	**0.0071**	**0.0072**	**0.0073**	**0.0074**	**0.0076**	**0.0077**		**0.0073**
s [%]	0.0001	0.0002	0.0010	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	s_M [%]	0.0003
										$\bar{s}_i$ [%]	0.0003
s_{rel}	0.017	0.022	0.140	0.015	0.014	0.019	0.006	0.012	0.012		0.037

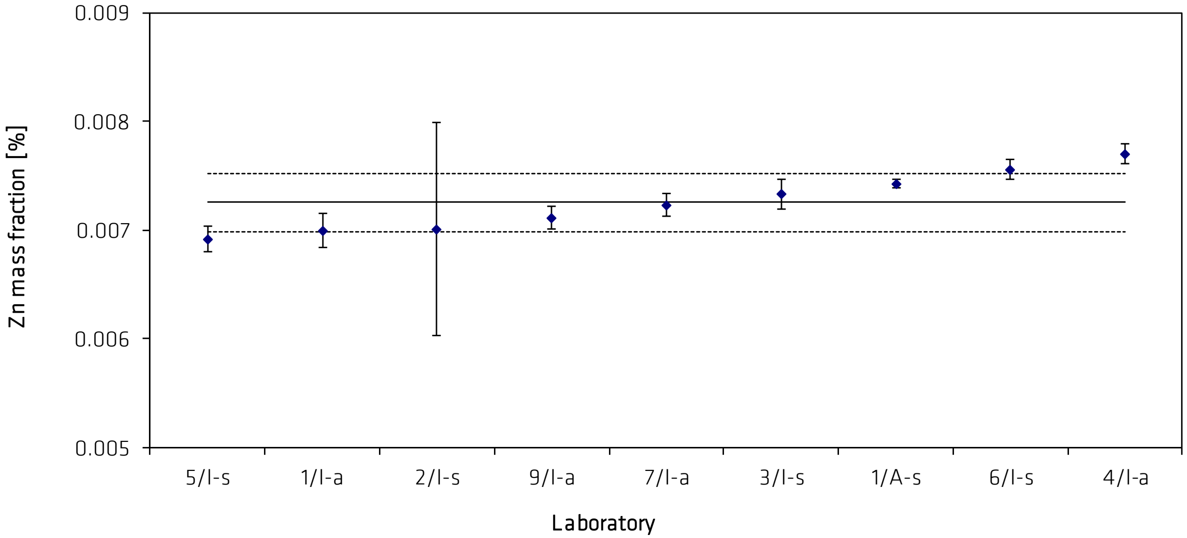

Table 12: Results for Zr

Lab./Meth.	2/I-s	1/I-a	3/I-s	6/I-s	5/I-s	1/P	9/I-a	8/I-a	7/I-a	1/I-s		
M_i [%]	0.312	0.290	0.313	0.321	0.323	0.327	0.330	0.330	0.329	0.369		*n*
	0.255	0.294	0.315	0.323	0.324	0.328	0.330	0.330	0.331	0.367		10
	0.287	0.297	0.315	0.315	0.326	0.328	0.330	0.331	0.355	0.365		
	0.273	0.300	0.318	0.322	0.325	0.329	0.328	0.332	0.330	0.364		
	0.289	0.306	0.316	0.320	0.334	0.328	0.329	0.330	0.324	0.359		
	0.324	0.292	0.319	0.321	0.336	0.331	0.330	0.331	0.336	0.362		
						0.328						
						0.329						
M [%]	**0.290**	**0.296**	**0.316**	**0.320**	**0.328**	**0.328**	**0.329**	**0.331**	**0.334**	**0.364**		**0.324**
s [%]	0.0252	0.0059	0.0022	0.0028	0.0055	0.0013	0.0010	0.0008	0.0109	0.0037	s_M [%]	0.0206
											$\bar{s}_i$ [%]	0.0092
s_{rel}	0.087	0.020	0.007	0.009	0.017	0.004	0.003	0.002	0.033	0.010		0.064

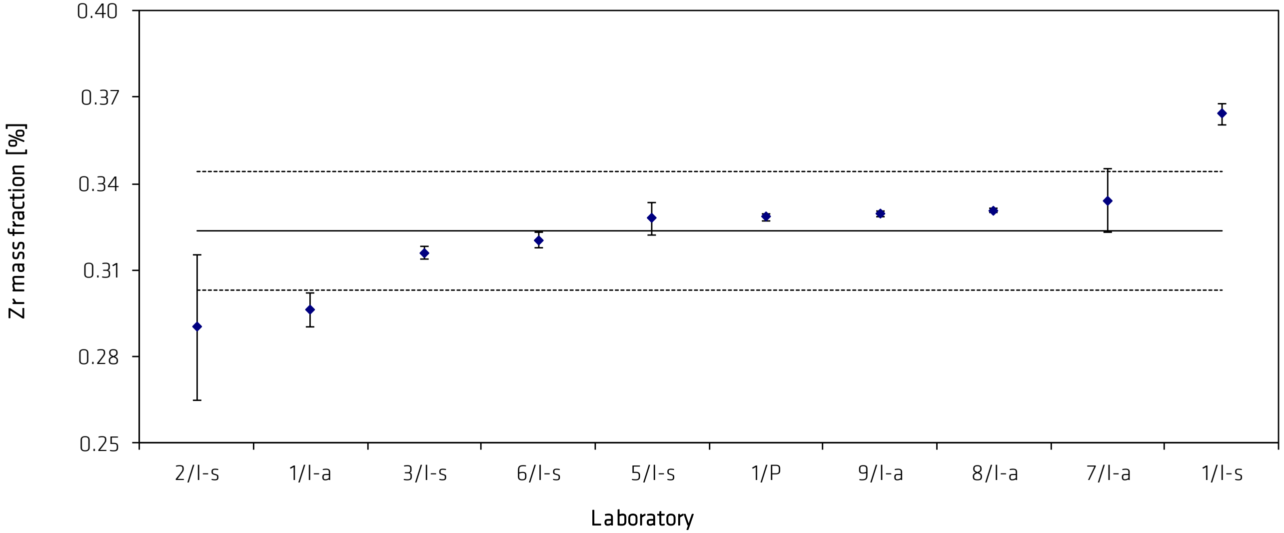

Table 13: Additional results for other elements, obtained by three laboratories

Element	Lab. 1 mass fraction in %	Lab. 2 mass fraction in %	Lab. 3 mass fraction in %
Bi	< 0.001		
Cd	< 0.0002		
Cr	0.0592	0.0566	0.0655
Ga	0.0150	0.0145	0.0153
Ni	0.0371	0.0338	0.0396
Pb	< 0.001		
Sn	< 0.001		
V	0.0108	0.0077	0.0093

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

Tab. 14: Outcome of statistical tests on the results obtained for Si (without Labs. 2, 3, and 7 which were removed as technical outliers) and Cu

	Si	Cu
Number of data sets	7	8
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 8	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The straggler (Lab. 8, Si) was not removed.

Tab. 15: Outcome of statistical tests on the results obtained for Fe

	1st run	2nd run
Number of data sets	12	11
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Lab. 9	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 9	---
Nalimov (α = 0.01)	Lab. 9	---
Grubbs (α = 0.05)	Lab. 9	---
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: not normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The outlier (Lab. 9) was removed.

Tab. 16: Outcome of statistical tests on the results obtained for Mn and Sc

	Mn	Sc
Number of data sets	12	10
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Lab. 2	Lab. 2
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The outliers (Lab. 2, Mn and Sc) were not removed.

Tab. 17: Outcome of statistical tests on the results obtained for Mg

	1st run	2nd run
Number of data sets	11	10
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. 3
Dixon (α = 0.01)	Lab. 2	Lab. 3
Nalimov (α = 0.05)	Lab. 2	Lab. 3
Nalimov (α = 0.01)	Lab. 2	Lab. 3
Grubbs (α = 0.05)	Lab. 2	Lab. 3
Grubbs (α = 0.01)	---	Lab. 3
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: not normal	Distribution: not normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: not normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: not normal	Distribution: not normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: not normal

The outliers (Labs. 2 and 3) were removed.

Tab. 18: Outcome of statistical tests on the results obtained for Zr and Zn (without "<" - results)

	Zr	Zn
Number of data sets	10	9
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 1-s	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	Lab. 2
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Distribution: normal

The outliers (Lab. 1 for Zr, Lab. 2 for Zn) were not removed.

Tab. 19: Outcome of statistical tests on the results obtained for Ti without "<" - results)

	1st run	2nd run
Number of data sets	8	6
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. 6	Lab. 2
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	Lab. 2
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	Labs. 6 and 7	---
Grubbs Pair (α = 0.01)	Labs. 6 and 7	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal	Insufficient data
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal	Insufficient data

The outliers (Labs. 6 and 7) were removed, Lab. 2 was not removed.

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.

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

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 20: Uncertainty calculation

	uncertainty contribution from							uncertainty contribution from
	M	n	s_M	u_{ilc}	u_{bb}	u (comb)	U	homogeneity test (rel. %)
	%		%	%	%	mg/kg	mg/kg	
Si	0.1043	7	0.0025	0.0009	0.00033	0.0010	0.0020	0.3210
Fe	0.291	11	0.0080	0.0024	0.00565	0.0061	0.0123	1.9446
Cu	0.0015	9	0.00030	0.0001	0.00004	0.0001	0.00021	2.5442
Mn	0.371	12	0.0079	0.0023	0.00183	0.0029	0.0059	0.4935
Mg	4.959	9	0.0524	0.0175	0.01796	0.0251	0.0501	0.3621
Zn	0.0073	9	0.00027	0.0001	0.00016	0.00018	0.00036	2.1346
Ti	0.0030	7	0.00014	0.0001	0.00001	0.00005	0.00011	0.4156
Sc	0.847	10	0.0216	0.0068	0.00203	0.0071	0.0143	0.2403
Zr	0.324	10	0.0206	0.0065	0.00228	0.0069	0.0138	0.7040

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 [5].

7. Instructions for users

The certified reference material BAM-M319 is intended for the development, validation and quality control of analytical methods and procedures for the determination of trace components in samples of similar matrix.
For wet chemical analysis, a minimum sample intake of 0.1 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 internally checked commercial calibration solutions.

9. Information on and purchase of the CRM

Certified reference material BAM-M319 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-M319 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 ISO 17034, General requirements for the competence of reference material producers, 2016

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

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

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

[5] DIN 1333:1992-02 Zahlenangaben

Annex 1: Calculation of uncertainty contribution of potential inhomogeneity

Silicon:

	1	2	3	4
1-1	0.1018	0.0991	0.1036	
1-2	0.102		0.1029	0.1022
2-1	0.1023	0.1024	0.1023	0.1033
2-2	0.1006	0.1011	0.1015	0.1025
3-1	0.1015	0.1029	0.1014	0.1013
3-2	0.1014		0.1005	0.1028

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	0.3045	0.1015	5.13E-06
1-2	3	0.3071	0.102366667	2.2333E-07
1-3	4	0.4103	0.102575	2.3583E-07
2-1	4	0.4057	0.101425	6.4917E-07
2-2	4	0.4071	0.101775	5.6917E-07
2-3	3	0.3047	0.101566667	1.3433E-06
			0.1019	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	4.24226E-06	5	8.48452E-07	0.71676646	0.62068518	2.90129454
Within groups	1.77558E-05	15	1.18372E-06			
Total	2.19981E-05	20				

within-sd	0.00108799	
effective n	5.00	
s_bb	0	
s_bb_min	0.00029402	
u_bb	0.00029402	0.2940184
u_bb(rel.)	0.288626741	

Iron:

	1	2
1-1	0.303	0.2999
1-2	0.2936	0.2963
1-3	0.3035	0.2982
2-1	0.2981	0.3002
2-2	0.3009	0.2976
2-3	0.3007	0.3044
3-1	0.3998	0.2996
3-2	0.2953	0.2991
3-3	0.2933	0.3001
4-1	0.3001	0.2964
4-2	0.2976	0.2964
4-3	0.2976	0.2959

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	2	0.6029	0.3015	4.805E-06
1-2	2	0.5899	0.2950	3.645E-06
1-3	2	0.6017	0.3009	1.4045E-05
2-1	2	0.5983	0.2992	2.205E-06
2-2	2	0.5985	0.2993	5.445E-06
2-3	2	0.6051	0.3026	6.845E-06
3-1	2	0.6994	0.3497	0.00502002
3-2	2	0.5944	0.2972	7.22E-06
3-3	2	0.5934	0.2967	2.312E-05
4-1	2	0.5965	0.2983	6.845E-06
4-2	2	0.5940	0.2970	7.2E-07
4-3	2	0.5935	0.2968	1.445E-06
			0.3028	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.004904713	11	0.000445883	1.04988587	0.46439325	2.71733144
Within groups	0.00509636	12	0.000424697			
Total	0.010001073	23				

within-sd	0.02060817	
effective n	5.00	
s_bb	0.00205846	
s_bb_min	0.00588866	
u_bb	0.00588866	5.8886618
u_bb(rel.)	1.944629353	

Copper:

	1	2	3
1-1	0.0018	0.00146	0.00141
1-2	0.00144	0.00154	0.00146
1-3	0.00141	0.00141	0.00139
2-1	0.00129	0.0013	0.00128
2-2	0.00141	0.00154	0.00133
2-3	0.00141	0.00137	0.00132
3-1	0.00208	0.0013	0.00135
3-2	0.0013	0.00132	0.00134
3-3	0.00146	0.00143	0.00148
4-1	0.00135	0.00144	0.00136
4-2	0.00138	0.00133	0.00131
4-3	0.00134	0.00138	0.00136

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	0.00431	0.00144	6.33333E-10
1-2	3	0.00444	0.00148	2.8E-09
1-3	3	0.00421	0.00140	1.33333E-10
2-1	3	0.00387	0.00129	1E-10
2-2	3	0.00428	0.00143	1.12333E-08
2-3	3	0.00410	0.00137	2.03333E-09
3-1	3	0.00398	0.00133	6.33333E-10
3-2	3	0.00396	0.00132	4E-10
3-3	3	0.00437	0.00146	6.33333E-10
4-1	3	0.00415	0.00138	2.43333E-09
4-2	3	0.00402	0.00134	1.3E-09
4-3	3	0.00408	0.00136	4E-10
			0.00138	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between grc	2.67133E-07	11	2.42848E-08	1.133334905	0.37999871	2.21630865
Within grouŗ	5.14267E-07	24	2.14278E-08			
Total	7.814E-07	35				
within-sc	0.000146382					
effective	5.00					
s_bb	2.39043E-05					
s_bb_min	3.51729E-05					
u_bb	3.51729E-05	0.03517291				
u_bb(rel.	2.544152343					

Manganese:

	1	2	3
1-1	0.35996	0.36019	0.36008
1-2	0.3584	0.35858	0.36031
1-3	0.35971	0.35757	0.35999
2-1	0.35592	0.35534	0.35235
2-2	0.35621	0.34839	0.35394
2-3	0.35485	0.35625	0.35736
3-1	0.35937	0.35627	0.3598
3-2	0.36093	0.35639	0.36016
3-3	0.36083	0.36269	0.36108
4-1	0.35997	0.3593	0.36013
4-2	0.36157	0.3584	0.3599
4-3	0.35867	0.36189	0.35764

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	1.0802	0.3601	1.32333E-08
1-2	3	1.0773	0.3591	1.11223E-06
1-3	3	1.0773	0.3591	1.7524E-06
2-1	3	1.0636	0.3545	3.67023E-06
2-2	3	1.0585	0.3528	1.61846E-05
2-3	3	1.0685	0.3562	1.58203E-06
3-1	3	1.0754	0.3585	3.7093E-06
3-2	3	1.0775	0.3592	5.9029E-06
3-3	3	1.0846	0.3615	1.01903E-06
4-1	3	1.0794	0.3598	1.939E-07
4-2	3	1.0799	0.3600	2.51463E-06
4-3	3	1.0782	0.3594	4.9153E-06
			0.3583	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between gro	0.000210998	11	1.91816E-05	5.407101913	0.00027361	2.21630865
Within grou	8.51397E-05	24	3.54749E-06			
Total	0.000296137	35				

within-s	0.001883477	
effective	5.00	
s_bb	0.001768284	
s_bb_min	0.000452564	
u_bb	0.001768284	1.76828351
u_bb(rel.	0.493459549	

Magnesium:

	1	2	3
1-1	4.86607	4.91029	4.88035
1-2	4.84746	4.86676	4.86994
1-3	4.89032	4.83077	4.85344
2-1	4.82469	4.82343	4.81295
2-2	4.82029	4.78604	4.81684
2-3	4.82464	4.82845	4.82566
3-1	4.89665	4.8286	4.87409
3-2	4.86706	4.81599	4.86424
3-3	4.91891	4.87146	4.84471
4-1	4.87641	4.87214	4.90471
4-2	4.88605	4.86365	4.89329
4-3	4.86987	4.85924	4.85487

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	14.6567	4.8856	0.000509288
1-2	3	14.5842	4.8614	0.000147992
1-3	3	14.5745	4.8582	0.000903378
2-1	3	14.4611	4.8204	4.15409E-05
2-2	3	14.4232	4.8077	0.000355601
2-3	3	14.4788	4.8263	3.8901E-06
3-1	3	14.5993	4.8664	0.001201516
3-2	3	14.5473	4.8491	0.000824027
3-3	3	14.6351	4.8784	0.001412118
4-1	3	14.6533	4.8844	0.000313321
4-2	3	14.6430	4.8810	0.000238785
4-3	3	14.5840	4.8613	5.95156E-05
			4.8567	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between gro	0.022519397	11	0.002047218	4.086962415	0.00190757	2.21630865
Within group	0.012021943	24	0.000500914			
Total	0.034541341	35				

within-s	0.022381115	
effective	5.00	
s_bb	0.01758581	
s_bb_min	0.00537776	
u_bb	0.01758581	17.5858104
u_bb(rel.	0.362095618	

Scandium:

	1	2	3
1-1	0.87557	0.87988	0.87284
1-2	0.86977	0.87586	0.87551
1-3	0.87778	0.87256	0.87489
2-1	0.86853	0.86919	0.86445
2-2	0.86861	0.86082	0.86848
2-3	0.87093	0.86891	0.86896
3-1	0.87704	0.86539	0.86764
3-2	0.87451	0.86854	0.87
3-3	0.87428	0.86572	0.87109
4-1	0.87678	0.87538	0.87751
4-2	0.87312	0.869	0.87595
4-3	0.87472	0.87193	0.87415

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	2.6283	0.8761	1.2598E-05
1-2	3	2.6211	0.8737	1.1693E-05
1-3	3	2.6252	0.8751	6.8382E-06
2-1	3	2.6022	0.8674	6.5916E-06
2-2	3	2.5979	0.8660	1.9896E-05
2-3	3	2.6088	0.8696	1.3273E-06
3-1	3	2.6101	0.8700	3.8191E-05
3-2	3	2.6131	0.8710	9.6854E-06
3-3	3	2.6111	0.8704	1.8714E-05
4-1	3	2.6297	0.8766	1.1716E-06
4-2	3	2.6181	0.8727	1.2214E-05
4-3	3	2.6208	0.8736	2.1729E-06
			0.8718	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.000370822	11	3.37111E-05	2.86711258	0.0149858	2.21630865
Within groups	0.000282188	24	1.17579E-05			
Total	0.00065301	35				

within-sd	0.00342897	
effective n	5.00	
s_bb	0.00209539	
s_bb_min	0.00082392	
u_bb	0.00209539	2.0953871
u_bb(rel.)	0.240340399	

Zinc:

	1	2	3
1-1	0.00407	0.00392	0.00388
1-2	0.00394	0.00407	0.00386
1-3	0.00429	0.00395	0.00385
2-1	0.00375	0.00395	0.00378
2-2	0.00407	*0.00415*	0.0042
2-3	0.00417	0.00396	0.00384
3-1	0.00407	0.00387	0.00395
3-2	0.00434	0.00419	0.0041
3-3	0.00443	0.00412	0.00435
4-1	0.00401	0.00391	0.00398
4-2	0.00412	0.00395	0.00388
4-3	0.00458	0.00409	0.00404

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	0.01187	0.00396	1.0033E-08
1-2	3	0.01187	0.00396	1.1233E-08
1-3	3	0.01209	0.00403	5.32E-08
2-1	3	0.01148	0.00383	1.1633E-08
2-2	3	0.01242	0.00414	4.3E-09
2-3	3	0.01197	0.00399	2.79E-08
3-1	3	0.01189	0.00396	1.0133E-08
3-2	3	0.01263	0.00421	1.47E-08
3-3	3	0.01290	0.00430	2.59E-08
4-1	3	0.01190	0.00397	2.6333E-09
4-2	3	0.01195	0.00398	1.5233E-08
4-3	3	0.01271	0.00424	8.9033E-08
			0.0040	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.63333E-07	11	6.0303E-08	2.62250434	0.02339405	2.21630865
Within groups	5.51867E-07	24	2.29944E-08			
Total	1.2152E-06	35				

within-sd	0.00015164	
effective n	5.00	
s_bb	8.6381E-05	
s_bb_min	3.6436E-05	
u_bb	8.6381E-05	0.0863812
u_bb(rel.)	2.13462681	

Titanium:

	1	2	3
1-1	0.00313	0.00299	0.00301
1-2	0.00298	0.00305	0.00301
1-3	0.00295	0.00303	0.00295
2-1	0.003	0.00305	0.00302
2-2	0.00302	0.00295	0.00303
2-3	0.00303	0.00298	0.00303
3-1	0.003	0.00296	0.00293
3-2	0.00297	0.00298	0.003
3-3	0.00294	0.003	0.00303
4-1	0.00299	0.00306	0.00306
4-2	0.00302	0.00304	0.00302
4-3	0.00306	0.00306	0.00303

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	0.00913	0.00304	5.73333E-09
1-2	3	0.00904	0.00301	1.23333E-09
1-3	3	0.00893	0.00298	2.13333E-09
2-1	3	0.00907	0.00302	6.33333E-10
2-2	3	0.00900	0.00300	1.9E-09
2-3	3	0.00904	0.00301	8.33333E-10
3-1	3	0.00889	0.00296	1.23333E-09
3-2	3	0.00895	0.00298	2.33333E-10
3-3	3	0.00897	0.00299	2.1E-09
4-1	3	0.00911	0.00304	1.63333E-09
4-2	3	0.00908	0.00303	1.33333E-10
4-3	3	0.00915	0.00305	3E-10
			0.0030	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between gro	2.52E-08	11	2.29091E-09	1.518834756	0.18887178	2.21630865
Within grou	3.62E-08	24	1.50833E-09			
Total	6.14E-08	35				

within-s	3.88373E-05	
effective	5.00	
s_bb	1.25106E-05	
s_bb_min	9.33186E-06	
u_bb	1.25106E-05	0.0125106
u_bb(rel.	0.415634603	

Zirconium:

	1	2	3
1-1	0.36942	0.36928	0.36828
1-2	0.36728	0.36906	0.37122
1-3	0.37153	0.37021	0.37175
2-1	0.36822	0.36821	0.36464
2-2	0.36878	0.36137	0.36767
2-3	0.3693	0.36659	0.36504
3-1	0.3638	0.35888	0.36177
3-2	0.36326	0.35937	0.36253
3-3	0.36252	0.36612	0.3646
4-1	0.36472	0.36155	0.3618
4-2	0.36346	0.36184	0.36141
4-3	0.3609	0.36226	0.35818

Sample	*Number*	*Sum*	*Mean*	*Variance*
1-1	3	1.1070	0.3690	3.86533E-07
1-2	3	1.1076	0.3692	3.89293E-06
1-3	3	1.1135	0.3712	6.93733E-07
2-1	3	1.1011	0.3670	4.26023E-06
2-2	3	1.0978	0.3659	1.59717E-05
2-3	3	1.1009	0.3670	4.64903E-06
3-1	3	1.0845	0.3615	6.11323E-06
3-2	3	1.0852	0.3617	4.2751E-06
3-3	3	1.0932	0.3644	3.26613E-06
4-1	3	1.0881	0.3627	3.1063E-06
4-2	3	1.0867	0.3622	1.16863E-06
4-3	3	1.0813	0.3604	4.31573E-06
			0.3652	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between gro	0.00041127	11	3.73882E-05	8.611601075	6.2929E-06	2.21630865
Within grou	0.000104199	24	4.34161E-06			
Total	0.000515469	35				

within-s	0.002083653	
effective	5.00	
s_bb	0.002570859	
s_bb_min	0.000500662	
u_bb	0.002570859	2.57085941
u_bb(rel.	0.703979662	