Federal Institute for Materials Research and Testing (BAM)

in Co-operation with the

Committee of Chemists of GDMB
Gesellschaft für Bergbau, Metallurgie, Rohstoff- und Umwelttechnik

The Certification of Mass Fractions of Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, Ti, V, Zr; $C_{(total)}$, $C_{(free)}$ and O in Silicon Carbide Powder (green micro F800)

BAM-S003

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Final certification report

Abstract

This report describes the preparation and certification of BAM reference material BAM-S003, a silicon carbide powder (green micro F 800) with certified impurity contents carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additional determined data are listed below.

Element/ Constituent	Certified Values		
	Symbols	Mass fraction 1) in mg/kg	Uncertainty 2) in mg/kg
Aluminium	Al	372	20
Boron	B	63	7
Calcium	Ca	29.4	1.8
Chromium	Cr	3.5	0.4
Copper	Cu	1.5	0.4
Iron	Fe	149	10
Magnesium	Mg	6.3	0.6
Manganese	Mn	1.44	0.17
Sodium	Na	17.7	0.8
Nickel	Ni	32.9	2.7
Titanium	Ti	79	4
Vanadium	V	41.4	2.8
Zirconium	Zr	25.2	2.0
Free Carbon 3)	C_{free}	493	79
Oxygen 5)	O	910	35
		Mass fraction 1) in %	**Uncertainty 2) in %**
Total Carbon 4)	C_{total}	29.89	0.07

1) The certified values are the means of 4-22 series of results (depending on the parameter) obtained by different laboratories. 2 up to 8 different analytical methods were used for the measurement of one parameter. The calibrations of the methods applied for determination of element mass fractions were carried out by using pure substances of definite stoichiometry or by using solutions prepared from them, thus achieving traceability to SI unit.
2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor *k* = 2. It includes contributions from sample inhomogeneity.
3) The mass fraction of carbon free is a method–depending value. It was determined by two different methods and is only related to the application of these methods, which are described as “Method M1” and “Method M2” respectively, attached to this certification report (see appendices 1 and 2).
4) The recommended “Method M3” described in attachment (appendix 3) can be used for the determination of mass fraction of carbon total.
5) The recommended “Method M4” described in attachment (appendix 4) can be used for the determination of mass fraction of oxygen.

Date of certification: 2004

Sample description

The certified reference material BAM-S003 is a silicon carbide powder (type green micro F800). The material is supplied in glass bottles containing 50 g each.

Indicative values

Not certified indicative values were determined in the interlaboratory comparison by participating laboratories.

Parameter	Indicative Values	
	Mass fraction [1) in mg/kg]	**Uncertainty [2) in mg/kg]**
Nitrogen	93	22
Silicon dioxide free	600	148
Silicon free	481	223

1) The indicative values are the means of 6-11 series of results (depending on the parameter) obtained by different laboratories. 1 up to 4 different analytical methods were used for the measurement of one parameter. The methods applied for determination of mass fractions were not always carried out by using pure substances of definite stoichiometry or by using solutions prepared from them, thus was not achieved traceability to SI units.
2) The uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor k = 2.

Additional Material Data

Additional material properties were determined by using one method, and can be used as informative values, only.

Parameter		Additional Material Data	
		Mass fraction in %	**Uncertainty in mass %**
Phases:	SiC-6H	89.2 [1)]	0.2 [2)]
	SiC-15R	6.1 [1)]	0.2 [2)]
	SiC-4H	4.7 [1)]	0.2 [2)]
Parameters of particle size		**Particle size in µm**	
	D_{10}	5.55 [3)]	
	D_{50}	10.18 [3)]	
	D_{90}	16.69 [3)]	

1) The measurements were carried out by X-ray powder diffraction using Rietveld method for evaluation.
2) The calculation of the standard uncertainty is based on a raw estimation from the evaluation of the Rietveld method.
3) The particle size distribution was determined by laser light diffraction method.

Contents

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1 Introduction

1.1 Scope

Silicon carbide is a material of extreme hardness and therefore very wear-resistant. This is because of the tight covalent bond of Si and C atoms, which is also the reason for the high thermal conductivity, high elasticity modulus, the low thermal expansion and the very high chemical durability. The high oxidation resistance is based on thin layers of oxides which are formed in some seconds on fresh surfaces after breaking or forming the material.

In the early field of application, SiC was used as abrading medium. Today SiC is of additional wide technical importance because of its outstanding properties, such as hardness, thermal conductivity, refractoriness and chemical durability as well as special semiconductor properties useful for opto- and micro-electronic applications.

Silicon carbide is normally produced from quartz sand and coke as starting materials. At temperatures above 2000°C silicon dioxide and carbon are chemically converted to SiC and carbon monoxide.

The world wide production of SiC at present is about 900,000 tons per year (t/a). The larger part (ca. 660,000 t/a) is used in metallurgy sector as aggregate, the other part (ca. 240,000 t/a) is the so-called crystalline SiC. It is used as abrading medium (ca. 96,000 t/a), as refractory ceramics (ca. 96,000 t/a) or for other applications (ca. 48.000 t/a), such as for formed components or opto- or micro-electronics components.

The purity of the material is of high importance for its practical value, especially in the high tech applications, such as power current and high frequency technology or opto- and micro electronics. This is the reason why so many traces in the material have to be routinely checked by chemical analysis and consequently have to be certified in a certified reference material for the chemical composition of silicon carbide. But also the fraction of silicon carbide itself is of high importance for the properties, the practical value and the price of the material. It is determined by measuring the total as well as the free carbon content. Another important information is the oxygen content, indicating the aging process of the material. Therefore all these parameters were certified: The prominent metallic traces (additionally boron), the content of total and of free carbon and the oxygen content. Besides these the following contents are of interest, which therefore have been determined as indicative values: Nitrogen, free silicon dioxide and free silicon. The eminent importance of the certified carbon values are additionally based on the fact, that this certified reference material can be used to validate methods and results of carbon determination in other refractory materials with high carbon content.

1.2 Certification procedure

The silicon carbide powder material (quality green micro F 800) was taken from the customary production line of the producer and was bottled into 320 bottles each containing 50g of the material. From the total number 20 bottles were selected. From each of these bottles 4 vials were filled and sent to the laboratories by which the homogeneity investigations were carried out. After positive conclusion of all homogeneity testing and of investigation on stability one sample bottle was distributed to each of the 29 international participants of the interlaboratory comparison for certification. The participants came from 8 different countries. Difficulties to determine some of the analytes were discussed among the members of the working group "Special Materials" of GDMB at its biannual sessions. In the end for the critical analytes, such as C_{total} as well as O and N, analytical methods were specified and proposed or (in case of C_{free}) prescribed to use. For the uncritical analytes a free selection of analytical methods was admitted. For the final certification, each laboratory carried out 6 independent determinations for the investigated analytes. The statistical evaluation of the results of interlaboratory comparison included some statistical tests.

Indicated outliers were discussed at the sessions of GDMB. The participants who had delivered these values were informed. After removal of all relevant outliers the mean values of the interlaboratory comparison were taken as the certified mass fractions. The certified uncertainties were calculated by taking into account the contributions from interlaboratory comparison and from inhomogeneity of the material.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was produced by Wacker Ceramics, Kempten, Germany, and bought from there by Bundesanstalt für Materialforschung und –prüfung (BAM) Berlin (Germany)

- The material was filled into sample bottles by BAM,

- Sub-samples for homogeneity testing were bottled and a highly homogenized sample was produced by BAM

2.2 Homogeneity testing

- The analytical investigations for the homogeneity testing of Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Ti, V, Zr, C_{free}, O, C_{total}, N and SiO_2 were carried out by Wacker Ceramics, Kempten, Germany.

- The analytical investigations for the homogeneity testing of B and Na were carried out by H. C. Starck GmbH & Co. KG, Goslar, Germany.

- All statistical evaluations for homogeneity testing were carried out by BAM.

2.3 Certification analysis (certified and indicative values)

To achieve a high international acceptance prominent laboratories located world wide were asked to participate. These laboratories were either involved in daily SiC analysis or had well known ability to analyze difficult materials by adequate analytical methods. The 29 participants of the interlaboratory comparison for certification are listed alphabetically in Tab. 1.

Tab. 1: Participating laboratories (arranged alphabetically)

BAM, Bundesanstalt für Materialforschung und -prüfung Berlin (Germany)
- Laboratory: Activation Analysis; Gas Analysis
- Project group: Quality Assurance and Metrological Aspects in Production of High Tech Reference materials

Chinese Academy of Sciences, Shanghai Institute of Ceramics, Analysis and Testing Center for Inorganic Materials, Shanghai (PR China)

CRB GmbH, Hardegsen (Germany)

DIFK Deutsches Institut für Feuerfest und Keramik GmbH, Bonn (Germany)

Elektroschmelzwerk Delfzijl B.V., TE Farmsum (Netherlands)

ESK-SiC GmbH, Frechen (Germany)
Forschungszentrum Jülich GmbH, Jülich (Germany)
H.C. Starck Ceramics GmbH & Co. KG; Selb (Germany)
H.C. Starck GmbH & Co. KG; Goslar (Germany)
H.C. Starck GmbH & Co. KG; Laufenburg (Germany)
Institut für Festkörper und Werkstoffforschung, Dresden (Germany)
Japan Fine Ceramics Center, Atsuta-ku Nagoya (Japan)
Johannes Gutenberg Universität, Institut für Kernchemie, Mainz (Germany)
Jožef Stefan Institute, Ljubljana (Slovenia)
Max-Plank-Institut für Metallforschung, Stuttgart (Germany)
Molab AS, Mo I Rana (Norway)
NGK Insulators, LTD., Chemical analysis materials research lab., Nagayo (Japan)
OSRAM GmbH, München (Germany)
Plansee AG, Reutte (Austria)
Saint Gobain Ceramic Materials AS, Lillesand (Norway)
Saint Gobain Industrial Ceramics and Plastics, Northboro (USA)
Saint Gobain Industriekeramik, Geschäftsbereich Feuerfesttechnik, Rödental (Germany)
Schunk Kohlenstofftechnik GmbH, Heuchelheim (Germany)
SGL Carbon GmbH, Bonn (Germany)
SGL Carbon GmbH, Meitlingen (Germany)
W.C. Heraeus GmbH, Hanau (Germany)
Wacker Ceramics, Kempten (Germany)
Zhuzhou Cemented Carbide Group Corp., LTD., Zhuzhou, Hunan (PR China)

2.4 Determination of additional material data

- The determination of phases was carried out by BAM, laboratory "X-ray structure and phase analysis".
- The particle size distribution was determined by BAM, division "Materials Technology of Advanced Ceramics and Composites".

2.5 Compilation and revision of the prescribed and recommended analytical methods

- Method M1 "Coulometric determination of free carbon (C_{free}) in silicon carbide after wet-chemical oxidation with hot chromic-sulfuric acid": According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany.

- Method M2 "Coulometric determination of free carbon content (C_{free}) in silicon carbide comprising weighing-back the sample boat": According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany

- Method M3 "Proposal for determination of total carbon mass fraction in silicon carbide powder ": Prepared by Albrecht Meyer, Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany and revised by Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany.

- Method M4 "Proposal for the determination of oxygen and nitrogen mass fraction in silicon carbide powder": According to Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany

3 Abbreviations used

Tab. 2: List of abbreviations

CGHE/comb.-IR	Carrier gas hot extraction/combustion method with infrared detection
Comb./coul.	Combustion of free carbon followed by coulometric determination
Comb.-IR	Combustion method with infrared detection
DCarc-OES	Direct current arc optical emission spectrometry
ET AAS	Atomic absorption spectrometry with electrothermal atomization
ETV-ICP OES	Inductively coupled plasma optical emission spectrometry with electrothermal vaporisation
F AAS	Flame atomic absorption spectrometry
F AES	Flame atomic emission spectrometry
GRAV	Gravimetry
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
K_0-INAA	K_0- Instrumental neutron activation analysis
MAS	Molecular absorption spectrometry
Method M1	Coulometric determination of free carbon after wet chemical oxidation with hot chromic sulfuric acid, (described in APPENDIX 1)
Method M2	Combustion of free carbon followed by coulometric determination comprising weighing back the sample boat, (described in APPENDIX 2)
SD	Standard deviation
SS ET AAS	Solid sampling electrothermal atomic absorption spectrometry
TITR	Titrimetry
Vol.	Gas volumetric determination

4 Origin and homogeneity investigation of the material

4.1 Starting material

The silicon carbide powder material (quality green micro F 800) was taken from the customary production line of the producer and was bottled into 320 bottles each containing 50g of the material with the same lot number that has been produced under the same working conditions.

4.2 Homogeneity investigations and testing (FOR DETAILS SEE APPENDIX 5)

4.2.1 Distribution of sub-samples; homogenized sample

For the homogeneity testing 20 bottles were representatively taken from the totality of 320 bottles by a combination of random access and systematic selection. Each bottle contained 50 g of candidate material. From each of the N = 20 bottles four appropriate sample masses were filled into vials (“larger sub-samples”) with masses of the taken material depending on the needs of the corresponding methods used for the homogeneity testing of different analytes. The vials were distributed to the laboratories, where the measurements for homogeneity testing were carried out.

For comparison a thoroughly homogenized sample was produced. For this purpose – 20 g of the material were highly homogenized in the “Mixer/Mill” (Spex. Ind., USA) for 15 min. (3 x 5 min.) using polypropylene vessels and balls.

Partial masses of this sample were distributed to the laboratories, in which the measurements for homogeneity testing were carried out.

4.2.2 Homogeneity investigations for the metallic traces (excluding Na)

The measurements were carried out by using an ICP OES spectrometer "IRIS-AP" (Thermo Elemental) combined with electrothermal evaporation (ETV) for the analysis of sub-samples. In house carbide powders with known trace elemental contents and in some cases aliquots of calibration solutions were used for calibration. Resulting lack of trueness of results or of metrological traceability are not relevant, because a high precision is the only necessity in case of homogeneity investigation.

A real problem was the small sub-sample mass used with ETV ICP OES. A sub-sample mass of about 2 mg only could be applied. This is much less than normally used in wet chemical analysis and is not very representative for the entire sample. On the other hand it is possible to summarize some measurements to one result, thus summarizing the sub-sample mass to a virtual value representing a higher sub-sample mass. This procedure was followed, though more practical work is involved for measurements.
For the elements Al, Ca, Fe, Mg, Ni, Ti and Zr four series of measurements were carried out at different days and seven series of measurements for the elements Cr, Cu and V. Because of the very similar distribution of Cr and Mn in the samples, as known from former studies, Mn was not measured and the results for Cr in the homogeneity test were applied to Mn, too. The results of the measurements and the homogeneity testing are listed and explained in APPENDIX 5. They are classified by elements, each element having 4 pages in the report.
Below the results of measurement data and their summary two tables are arranged for homogeneity testing. One homogeneity test (Anova, F-test) was made for comparing variances "between the bottles" and "within the bottles". By the other testing (F-test) the standard deviation within the samples was compared with the standard deviation of the homogeneous sample. All calculations and test results are explained in APPENDIX 5.
It could be concluded from the F-tests ("between" and "within") that for all 10 investigated elements no significant contribution by an inhomogeneity "between the bottles" could be found. A significant inhomogeneity contribution "within the bottles" was only found for the elements Cu, Fe and Zr. The material can be classified as sufficiently homogeneous concerning the distribution of the 10 metallic analytes investigated.

4.2.3 Homogeneity investigations for B and Na

Both analytes could not be determined by ETV ICP OES precisely enough. Therefore other methods were used. For the determination of B sub-samples of 0.5 g were weighed into the PTFE-liner of the pressure digestion system DAB II (Berghof, Germany) and digested after adding of HF (73 %) and HNO_3 (100 %, fuming) at 250 °C for 8 hours. The boron concentrations in the digested and diluted samples were measured by ICP OES ("Ultrace", Jobin Yvon). The calibration solutions were matrix adapted for acids and the concentration of Si. The values used for the homogeneity investigation are the mean values of two measurements of the same digestion solution at different days.
For the determination of Na 0.5 mg sub-samples were analysed directly by solid sampling AAS (SS ET AAS) using the spectrometer "AAS SEA solid" (Analytik Jena AG, Jena, Germany). The calibration was done by using aliquots of calibration solutions.
It was not necessary to summarize measurements from different sub-samples, as done for metallic elements. Apart from this, the structure for the documents containing the evaluation of the measurements is similar as for the metallic elements. All values and evaluations are listed and explained in APPENDIX 5. For both analytes (B and Na) no significant inhomogeneities were found within the bottles. – The same holds true for the homogeneity of the distribution of Na between the bottles, whereas for B a significant inhomogeneity between the bottles was found.

4.2.4 Homogeneity investigations of non-metallic analytes

Different methods were applied for the determination of different analytes.

The content of C_{total} was determined by two different methods. One consisted in the combustion of sub-samples of 20 – 25 mg in a high frequency furnace WC200 (LECO) in an oxygen stream. The generated CO_2 gas was collected in a C-trap and was measured by an infrared measuring cell after release. The other method consisted in the coulometric determination of CO_2 with the Coulomat 702 (Ströhlein) after combustion of the sub-samples of ca. 50 mg in an oxygen stream and using lead borate as aggregat.
C_{free} was determined by a procedure derived from DIN 51075. About 0.5 g sub-sample was handled in an oxygen stream at 850 °C. The generated CO_2 was coulometrically determined using the Coulomat 702 (Ströhlein). The sample boat was weighed before and after the chemical reaction and the partial amount of SiC which had also reacted
($SiC + 2O_2 \rightarrow SiO_2 + CO_2 \uparrow$) was taken into account (see “Method M 2” of APPENDIX 2 of certificate).
Oxygen was determined using about 80 mg sub-samples in a resistance heated furnace TC436 (LECO) in a helium carrier gas stream. CO was catalytically oxidized to CO_2. The total concentration of CO_2 was measured by an infrared measuring cell.
Homogeneity investigations were also carried out for two of the three not certified, indicative values namely for N and Si_{free}.
N was determined by carrier gas hot extraction in a resistance heated furnace TC436 (LECO) using helium as carrier gas and a thermal conductivity measuring cell. Sub-samples of about 80 mg were used.
SiO_{2free} was determined by distillation after chemical reaction. The sub-sample was treated with HF, distilled as H_2SiF_6 and determined as Si after absorption in water using ICP OES.
The structure of the documents containing the evaluation of the measurements (see APPENDIX 5) is similar as for the analytes B and Na. The only difference is, that the homogenized sample was not analyzed for the analytes C_{free}, O, N and SiO_{2free}.Therefore no homogeneity test within the bottles (comparing the "within SD" with the SD of the homogenized sample) could be carried out for these analytes. The reason for this is, that these analytes can be assumed to be distributed homogeneously within bottles, because they are tightly fixed within the volume or at the surface of the powder grains.
The homogeneity tests between the bottles had the following results:
- For C_{total}, O and N: no significant inhomogeneities,
- For C_{free} and SiO_{2free}: significant inhomogeneities.

The homogeneity test within the bottles for C_{total} showed no significant inhomogeneity.

4.2.5 Conclusion

The homogeneity investigations showed satisfying results in most cases.
But, independent from the results of the statistical tests carried out, the contributions from the between bottle standard deviations and the within-bottle standard deviations were corrected for by the standard deviation of the homogeneous samples (if determined) and both corrected contributions were (together with the contribution from the round robin test for certification) included into the calculation of the final measurement uncertainties of the certified values (see paragraph 8.2).

5 Time stability of the material

The time stability was tested by measuring the oxygen content of the material at the beginning and at the end of a period of three years (from October 2000 till September 2003). It is well known, that the material is very stable in time - and the results of the measurements do underpin this fact. The oxygen content is the most sensitive parameter to indicate the aging of the material.

In the following Tab. 3 the results of the stability measurements are listed. (They are identical with the results achieved for the homogeneity testing and the certification measurements carried out by the same laboratory).

Tab. 3: Stability test carried out with the oxygen mass fraction in the silicon carbide candidate material

Date	10/2000	09/2003
Measure-ment no.	(A) [mg/kg]	(B) [mg/kg]
1	907.3	910
2	911.4	900
3	909.1	920
4	913.9	900
5	895.5	890
6	900.1	890
7	900.6	
8	904.9	
9	906.3	
10	895.9	
mean M	904.5	901.7
standard deviation SD	6.24	11.7
95% confi-dence interv.	14.2	30.1

The mean values of both series of measurements were compared by using a t-test.
The test value is smaller than the critical t-value [95%, f=14]. That means that there is no significant difference between both measurements. A high stability of the material can be concluded.

6 Analytical methods

This chapter describes the analytical procedures and specific parameters used in the certification campaign. The methods used for homogeneity investigations were described above (see chapter 4). The method for the determination of oxygen in the frame of the stability investigation was the same as proposed by method M4 (see APPENDIX 4).

6.1 Analytical methods used for certification

In Tab. 4 the elements with certified values and the elements having indicative values are listed as well as the methods used for their determination.
In the first column the element symbols are specified. In the following column serial numbers are given. These serial numbers correspond with the related serial numbers in Tab 5. In the last column the analytical methods (abbreviations see chapter 3) are indicated belonging to the related line numbers in Tab. 5. Thus it is possible to identify which result in Tab. 5 is based on which analytical method.

Tab. 4: Analytical methods used for the determination of certified and of indicative values

Element	Serial N°. in Tab. 5	Analytical method used
Al	4, 12	DCarc-OES
	8	ET AAS
	2	ETV-ICP OES
	(1)	F AAS
	16	ICP-MS
	3, 5, 6, 7, 9, 10, 11, 13, 14, 15, 17, 18, 19	ICP OES
B	3	DCarc-OES
	1, 2, 4, 5, 7, 8, 9, 10, 11, (12), (13)	ICP OES
	6	MAS
Ca	1	ETV-ICP OES
	5, (17)	F AAS
	13	ICP-MS
	2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 15,(16)	ICP OES
Cr	2	DCarc-OES
	9, 16	ET AAS
	3	ETV-ICP OES
	8	ICP-MS
	1, 4, 6, 11, 12, 13, 14,15, (17)	ICP OES
	7, 10	INAA
	5	K_0-INAA
Cu	11	DCarc-OES
	4	ET AAS
	3	ETV-ICP OES
	9	ICP-MS
	1, 2, 5, 6, 7, 8, 10, 12, (13)	ICP OES
Fe	(1), 5	DCarc-OES
	22	ETV-ICP OES
	9	F AAS
	12	ICP-MS
	(2), 3, 4, 7, 8, 10, 11, 13, 14, 15, 16, 17, 18, 19, 20, 21	ICP OES
	23	INAA
	6	K_0-INAA
	(24)	TITR
Mg	5	DCarc-OES
	9	ET AAS
	12	ETV-ICP OES
	17	F AAS
	15	ICP-MS
	1, 2, 3, 4, 6, 7, 8, 10, 11, 13,14, 16, (18), (19)	ICP OES
Mn	15	DCarc-OES
	6, 11	ET AAS
	17	ETV-ICP OES
	9	ICP-MS
	1, 2, 4, 8, 10, 12, 13, 14, 16, (18)	ICP OES
	3, 7	INAA
	5	K_0-INAA
Na	(1)	ETV-ICP OES
	5, 7, 11, 16	F AAS
	15	F AES
	8	ICP-MS
	2, 3, 6, 10, 14, (17), (18)	ICP OES
	4, 9	INAA
	12	K_0-INAA
	13	SS ET AAS

Element	Serial N°. in Tab. 5	Analytical method used
Ni	2, 5	DCarc-OES
	7	ET AAS
	1	ETV-ICP OES
	18	F AAS
	10	ICP-MS
	3, 4, 6, 8, 9, 11, 12, 13, 14, 16, 17, 19, 20, 21, 22	ICP OES
	15	K_0-INAA
Ti	(1), 21	DCarc-OES
	4	ETV-ICP OES
	13	ICP-MS
	(2), 3, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 20	ICP OES
	19	K_0-INAA
V	2, 16	DCarc-OES
	(1)	ETV-ICP OES
	11	ICP-MS
	3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 18, 19	ICP OES
	17	K_0-INAA
Zr	15	DCarc-OES
	17	ETV-ICP OES
	10, 16	ICP-MS
	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14, 19, (20)	ICP OES
	18	INAA
	11	K_0-INAA
C_{total}	(1), 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 18	CGHE/comb.-IR
	(2)	CGHE/titr.
	6	CGHE/grav.
	12, 19	Comb./ coul.
C_{free}	(1), (2), (3), (4), (13), (14)	CGHE/comb.-IR
	(9), (10), (11), (12)	Comb./ coul.
	6, 7	Comb./coul. (Method M1)
	5, 8	wet chem. oxidation/coul. (Method M2)
O	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, (12)	CGHE
	11	CGHE/coul.
N	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	CGHE
SiO_{2free}	1	Vol.
	2, 3	MAS
	4, 5	ICP OES
	6	Grav.
Si_{free}	1	Coul.
	2, 4, 5, 6	Vol.
	3	Comb.

Line numbers in parenthesis refer to values not used in the calculation of the certified value

For the analysis of almost all analytes a variety of different methods was aspired. The only exception was the determination of the free fraction of carbon (C_{free}). After preliminary investigations only two methods were prescribed (see methods M1 and M2, APPENDIX 1 and 2).

Note: For more detailed consideration see APPENDIX 6 containing information about sample preparation used for each determination.

6.2 Methods used for the determination of additional material data

The phase analysis was carried out using X-ray powder diffraction using Rietveld method for evaluation. The particle size distribution was determined by laser light diffraction method.

6.3 Methods used for homogeneity testing

Determination of metallic traces (without Na):

An ICP OES spectrometer "IRIS-AP" (Thermo Elemental) was used in combination with electrothermal evaporation (ETV) for the analysis of sub-samples. In house carbide powders with known trace elemental contents and in some cases aliquots of calibration solutions were used for calibration. Resulting lack of trueness of results or of metrological traceability are not relevant, because a high precision is the only necessity in case of homogeneity investigation. A real problem is the small sub-sample mass used with ETV ICP OES. A sub-sample mass of about 2 mg could be merely applied. This is much less than normally used in wet chemical analysis and is not very representative for the entire sample. On the other hand it is possible to summarize some measurements at the same sample to one result, thus summarizing the sub-sample mass to a virtual value representing a higher sub-sample mass. This procedure was followed, although additional practical work is involved to perform the measurements. For more detailled information see APPENDIX 5.

Analytes B and Na:
For the determination of B 0.5 g sub-samples were weighed into the PTFE-liner of the pressure digestion system DAB II (Berghof, Germany) and digested at 250 °C for 8 hours, after adding HF (73 %) and HNO_3 (100 %, fuming). The boron concentration in the digested and diluted sample was measured by ICP OES ("Ultrace", Jobin Yvon). The calibration solutions were matrix adapted for acids and for the concentration of Si. The final values used in the homogeneity investigation are the mean values of two measurements of the same digestion solution at different days.
For the determination of Na 0.5 mg sub-samples were analysed directly by solid sampling AAS (SS ET AAS) using the spectrometer "AAS SEA solid" (Analytik Jena AG, Jena, Germany). The calibration was done by using aliquots of calibration solutions. It was not necessary to summarize measurements from different sub-samples, as done for the other metallic elements (see above).

Non-metallic analytes:
Different methods were applied for the determination of different analytes.
The content of C_{total} was determined by two different methods. One consisted in the combustion of sub-samples of 20 – 25 mg in a high frequency furnace WC200 (LECO) in an oxygen stream. The generated CO_2 gas was collected in a C-trap and was measured by an infrared measuring cell after release. The other method consisted in the coulometric determination of CO_2 with the Coulomat 702 (Ströhlein) after combustion of the sub-samples of ca. 50 mg mass in an oxygen stream and using lead borate as aggregate.
C_{free} was determined by a procedure derived from DIN 51075. About 0.5 g sub-sample was handled in an oxygen stream at 850 °C. The generated CO_2 was coulometrically determined using the Coulomat 702 (Ströhlein). The sample boat was weighed before and after the chemical reaction and the partial amount of SiC which had also reacted ($SiC \rightarrow SiO_2 + CO_2 \uparrow$) was taken into account (see "Method M 2" of appendix of certificate).
Oxygen was determined using about 80 mg sub-samples in a resistance heated furnace TC436 (LECO) in a helium carrier gas stream. CO was catalytically oxidized to CO_2. The total concentration of CO_2 was measured by an infrared measuring cell.
Homogeneity investigations were also carried out for two of the three not certified, indicative values namely for N and Si_{free}. N was determined by carrier gas hot extraction in a resistance heated furnace TC436 (LECO) using helium as carrier gas and a thermal conductivity measuring cell. Sub-samples of about 80 mg were used. SiO_{2free} was determined by

distillation after chemical reaction. The sub-sample is treated with HF, distilled as H_2SiF_6 and determined as Si after absorption in water by using ICP OES.

6.4 Method used for time stability checking

The oxygen content was measured by CGHE with infrared detection (Method M4, APPENDIX 4)

7 Results and discussion

7.1 Presentation of the data; way of statistical evaluation

As soon as all the results of the certification analyses had been submitted, they were summarized and checked by a statistical program of BCR for evaluation of results of interlaboratory comparisons for certification [2]. After this the data were technically discussed at four of the biannual meetings of the Working Group "Special Materials" of the Committee of Chemists of the GDMB, where some of the participating laboratories were represented. After the second meeting it was clear, that all the metallic analytes (and boron) had been determined in the interlaboratory comparison without noteworthy difficulties. Furthermore it was decided to take the parameters nitrogen, free silicon dioxide and free silicon as indicative parameters because of their relatively high uncertainty and in view to their secondary importance.
The remaining problems were related to the parameters "total carbon", "free carbon" and "oxygen" (and somehow also "nitrogen", in spite of being an indicative value). The uncertainties of the results for these parameters had been inadequately high in relation to their importance. This lead to the idea to formulate prescribed methods (in case of free carbon) or recommended methods (in case of the other problematic parameters). After discussion these methods were agreed upon in the GDMB working group.
In case of free carbon three methods were prescribed and all participants who had not followed one of these methods in the first interlaboratory comparison were asked to repeat their measurements by using definitely one of the prescribed three methods. In the end it was evident that only two of the three methods lead to results without a wide spreading. Only the results of these two analytical methods were accepted. Thus the certified parameter C_{free} is a method depending one.
In case of the other three critical parameters only those participants of the interlaboratory comparison were asked to repeat their measurements, who had delivered results lying far from the central distribution. To improve their new measurements some hints were given how to carry out the analyses. The hints became part of the recommended analytical methods worked out for the determination of these parameters.
After finalization of the second part of the interlaboratory comparison all the final results of the certification analyses which had been submitted, were summarized and checked with the statistical program of BCR for evaluation of results of interlaboratory comparisons for certification [2] as explained above. After this the data were technically discussed at a meeting of the Working Group "Special Materials" of the Committee of Chemists of GDMB.
In the following Tab. 5 all accepted laboratory mean values are summarized.

Tab. 5: Means of the series of measurements for the analytical procedure of one laboratory (Laboratory means)

mass fractions in mg/kg (C_{total} in mass%)

Serial Nº	**Al**	**B**	**Ca**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Ti**	**V**	**Zr**	**C_{total} (%)**	**C_{free}**	**O**	***N***	***$SiO_{2\ free}$***	***Si_{free}***
1	-	55	21.2	2.5	1.0	-	3.8	1.00	-	24.1	-	-	19.1	-	415	825	*47*	*488*	*117*
2	305	55	25.4	2.6	1.1	-	5.5	1.10	15.0	24.2	-	28.83	21.2	-	500	845	*59*	*552*	*398*
3	327	61	-	2.6	1.2	131	5.8	1.30	15.3	26.2	68	30.83	22.0	29.57	515	862	*64*	*583*	*400*
4	334	62	27.4	3.2	1.2	135	5.9	1.32	15.7	28.7	70	36.29	22.4	29.75	540	865	*80*	*608*	*468*
5	345	63	29.1	3.3	1.3	135	5.9	1.33	16.7	29.8	72	37.00	22.8	29.82		873	*89*	*632*	*550*
6	354	63	29.1	3.4	1.3	137	6.0	1.36	17.0	30.5	73	38.00	23.2	29.85		902	*89*	*733*	*950*
7	367	63	29.1	3.4	1.4	137	6.0	1.37	17.3	30.9	74	39.27	23.7	29.86		915	*94*		
8	371	65	29.5	3.5	1.4	140	6.1	1.38	17.7	31.0	77	39.67	23.7	29.87		948	*99*		
9	371	66	29.5	3.5	1.4	142	6.3	1.41	17.8	31.1	77	41.25	24.3	29.89		951	*115*		
10	373	66	29.8	3.6	1.8	143	6.3	1.42	18.0	31.3	77	41.35	25.4	29.90		988	*128*		
11	377	67	29.8	3.6	2.3	143	6.4	1.47	18.7	31.7	77	42.38	25.6	29.91		1032	*151*		
12	378	-	30.5	3.9	2.5	146	6.5	1.48	18.8	32.2	79	42.53	25.8	29.91		-			
13	381	-	32.0	4.0	-	149	6.5	1.49	19.1	32.6	79	44.38	26.0	29.92					
14	385		32.7	4.1		149	6.8	1.53	19.3	33.1	81	45.48	26.6	29.94					
15	392		35.7	4.2		149	6.9	1.72	19.4	35.2	83	45.87	27.0	29.94					
16	399		-	4.4		152	8.2	1.79	19.5	35.5	83	46.07	28.7	29.96					
17	402		-	-		154	9.0	2.03	-	36.5	84	47.49	29.1	29.96					
18	403					155	-	-	-	39.2	84	48.27	30.4	30.03					
19	415					158	-			39.4	85	49.92	31.0	30.13					
20						162				39.4	85		-						
21						164				40.5	87								
22						164				41.1									
23						173													
24						-													
M:	372	63	29.4	3.5	1.5	149	6.3	1.4	17.7	32.9	79	41	25.2	29.89	493	910	*93*	*600*	*481*
s_M:	30	5	3.4	0.6	0.5	12	1.1	0.2	1.5	5.0	6	6	3.2	0.12	55	65	*31*	*83*	*273*

The „ - “ indicates that an outlaying value has been detected by a statistical test which was withdrawn or omitted after discussion in GDMB meetings.
Values given in *italic type* are indicative values only.
Note: The serial number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means

7.2 Technical discussion

The results of table 5 are listed in more detail in Tab. 6 (Tables 6a1 ... 6s1) compiled in APPENDIX 7. These tables are based on the statistical evaluation of the interlaboratory comparison using the BCR program [2] , they are arranged alphabetically by different element symbols. Each table consists of the following three parts:

- upper part: a table containing 11 columns.
  #First column: current laboratory number ("L") in this special test
  #second column: laboratory code number in this interlaboratory comparison together with the abbreviation of the analytical method used and a number 1, 2 or 3, which is the self- declaration of the laboratory concerning their experience to determine this analyte in SiC (“1” stands for no experience; “2” stands for medium experience and “3” stands for high experience
  #third column: laboratory mean values arranged by increasing values
  #fourth and fifth column: standard deviations of laboratory single values and half width of confidence intervals of the laboratory mean values, respectively
  #following 6 columns: all single values from different sub-samples

- center-part: a table containing: range of all single values; in case of no pooling of all single values: mean of laboratory means, half width of 95% confidence interval and half width of 95% tolerance interval; in case of pooling of all single values (but statistically not allowed in all current cases): mean of all single values and half width of 95% confidence interval and half width of 95% tolerance interval. Further on there are explanations to the abbreviations of statistical tests applied and indicated in the following diagram.

- lower part: based on the specifications of the upper and center-parts of the page - a diagram showing the mean of all means of data sets (vertical line), the corresponding 95% confidence interval (C.I.) and tolerance interval (T.I.) and the means of data sets with their 95% confidence intervals (horizontal bars) arranged by increasing mean values. These bars are marked by abbreviations of four statistical tests, if results of one or more tests were positive at a significance level of 5% or even 1%. (abbreviations are given in the center part of the page).

The following explanations are based on the results from the laboratories and their statistical evaluation as described in detail in the tables 6 of APPENDIX 7. The table of APPENDIX 8 is a supplementation to APPENDIX 7, in so far as Grubbs tests applied are explained in detail. It is distinguished between single and pair tests - and all applied Grubbs tests with their results are listed as a survey. The results of APPENDIX 7 and the decisions made are shortly summarized in the following.

7.2.1 Metallic analytes

7.2.1.1 Aluminium (Tab. 6a1; 6a2)

19 Laboratories delivered their results; with one exception based on 6 separate determinations. Most laboratories used ICP OES. The lowest set of values was based on AAS measurements. It was identified as an outlier by statistical tests and was removed after discussion. In the second run of the evaluation program carried out with the remaining 18 laboratories no further serious outlier was found. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements by

ICP-MS, ET AAS, ETV-ICP OES and DC arc-OES. All remaining values lie within the tolerance interval.

7.2.1.2 **Boron** (Tab. 6b1; 6b2)

13 Laboratories delivered their results; with two exceptions based on 6 separate determinations. Most laboratories used ICP OES. Both sets of highest values were based on ICP OES measurements. They were identified as outliers by statistical tests and were removed after discussion. In the second run of the evaluation program carried out with the remaining 11 laboratories no further serious outlier was found. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements by MAS and DC arc-OES. All remaining values lie within the tolerance interval.

7.2.1.3 **Calcium** (Tab. 6c1; 6c2)

17 Laboratories delivered their results; with two exceptions based on 6 separate determinations. Most laboratories used ICP OES. The two sets of highest values were based on ICP OES and F AAS measurements, respectively. They were identified as outliers by statistical tests and were removed after discussion. Another set of values submitted by laboratory No. 27 and based on ICP OES measurements was also removed, because of the wide spreading of the two single values which only had been delivered. In the second run of the evaluation program carried out with the remaining 14 laboratories no further sets of values were removed, although two of them were statistically eye-catching. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements by F AAS, ICP-MS and ETV-ICP OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.4 **Chromium** (Tab. 6d1; 6d2)

17 Laboratories delivered their results, each of them based on 6 separate determinations. Many laboratories used ICP OES, but there was a good mixing of different methods. The set of highest values was based on ICP OES measurements. It was identified as an outlier by statistical tests and was removed after discussion. In the second run of the evaluation program carried out with the remaining 16 laboratories no further serious outlier was identified. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with INAA, K_0-INAA, ICP-MS, DC arc-OES, ETV-ICP OES and ET AAS. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.5 **Copper** (Tab. 6e1; 6e2)

13 Laboratories delivered their results, with one exception each of them was based on 6 separate determinations. Most laboratories used ICP OES. The set of highest values was based on ICP OES measurements. It was identified as an outlier by statistical tests and was removed without discussion. In the second run of the evaluation program carried out with the remaining 12 laboratories no further outlier was removed after discussion of the remaining indicated outliers. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ET AAS, ICP-MS, ETV-ICP OES and DC arc-OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.6 **Iron** (Tab. 6f1; 6f2; 6f3)

24 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used ICP OES. The set with the lowest values based on DC arc-OES measurements and the set with the highest values was based on titrimetry measurements. They were identified as outliers by statistical tests and were removed after discussion. In the second run of the evaluation program carried out with the remaining 22

laboratories the lowest set of accepted sets of values was also identified as a serious outlier and was also removed after discussions. In the third run of the evaluation program no further serious outlier was identified. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ICP-MS, K_0-INAA, INAA, DC arc-OES, F AAS and ETV-ICP OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.7 **Magnesium** (Tab. 6g1; 6g2)

19 Laboratories delivered their results, each of them based on 6 separate determinations. Many laboratories used ICP OES. The two sets with the highest values were based on ICP OES measurements. Both of them were identified as outliers by statistical tests and were removed after discussion. In the second run of the evaluation program carried out with the remaining 17 laboratories no further outlier was removed. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ET AAS, F AAS, ETV-ICP OES, DC arc-OES and ICP-MS. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.8 **Manganese** (Tab. 6h1; 6h2)

18 Laboratories delivered their results, each of them based on 6 separate determinations. Many laboratories used ICP OES. The set with the highest values was based on ICP OES measurements. This set was identified as an outlier by statistical tests, but it was mainly removed after discussion because of the wide spreading of single values. In the second run of the evaluation program carried out with the remaining 17 laboratories no further outlier was removed. The certified mean value is not only underpinned by ICP OES measurements, but also by results of measurements with INAA, K_0-INAA, ICP-MS, ET AAS, DC arc-OES and ETV-ICP OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.9 **Sodium** (Tab. 6i1; 6i2; 6i3)

18 Laboratories delivered their results, each of them based on 6 separate determinations. There was a very good mix of different methods. The set with the lowest values was based on ETV-ICP OES measurements and the set with the highest values on ICP OES measurements. The set with the lowest values was identified as an outlier by statistical tests and the set with the highest values as one with very wide spreading single values. Both sets were removed after discussion. In the second run the evaluation program was carried out with the remaining 16 laboratories. The set with the highest values in this run was identified as a further outlier and removed after discussion. The main reason for this decision was a lack of overlapping of the confidence interval of the mean value of this data set with the lower one. The certified mean value of the means of the remaining 15 laboratories is based on measurements with ICP OES, ICP-MS, INAA, F AAS, SS ET AAS, K_0-INAA and F AES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.10 **Nickel** (Tab. 6j1)

22 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used ICP OES. No set of values was identified as a serious outlier by statistical tests, therefore no set was removed and no further run of the evaluation program was carried out. The certified mean value is not only underpinned by ICP OES measurements, but also by results of measurements with ICP-MS, ET AAS, K_0-INAA, F AAS, DC arc-OES and ETV-ICP OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.11 Titanium (Tab. 6k1; 6k2)

21 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used ICP OES. The set with the lowest values was based on DCarc-OES measurements. This set was identified as an outlier by statistical tests. Also the next set with high values was removed after discussion, but this one because of the extremely wide spreading of single values. In the second run of the evaluation program carried out with the remaining 19 laboratories no further outlier was removed. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ICP-MS, K_0-INAA, ETV-ICP OES and DC arc-OES. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.12 Vanadium (Tab. 6l1; 6l2)

19 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used ICP OES. The set with the lowest values was based on ETV-ICP OES measurements. This set was removed after discussion because of the wide spreading of single values. In the second run of the evaluation program carried out with the remaining 18 laboratories no further outlier was removed. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ICP-MS, K_0-INAA, DC arc-OES.

7.2.1.13 Zirconium (Tab. 6m1; 6m2)

20 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used ICP OES. The set with the highest values was based on ICP OES measurements. This set was removed after discussion because of the wide spreading of single values and because the mean value lying at the very outer limit of the tolerance interval. In the second run of the evaluation program carried out with the remaining 19 laboratories no further outlier was removed. The certified mean value is not only underpinned by ICP OES measurements, but also by results from measurements with ICP-MS, K_0-INAA, DC arc-OES, ETV-ICP OES and INAA. All remaining laboratory mean values lie within the tolerance interval.

7.2.2 Non-metallic certified analytes

7.2.2.2 Total carbon (Tab. 6n1; 6n2)

19 Laboratories delivered their results, with one exception each of them based on 6 separate determinations. Most laboratories used CGHE/combustion method with IR detection. The set with the lowest values was based on measurements with this method and the with the next higher values set was based on measurements with CGHE and titrimetry. Both sets were identified as outliers. They were removed after discussion. In the second run of the evaluation program carried out with the remaining 17 laboratories no further outlier was removed. The certified mean value is not only underpinned CGHE/combustion measurements with IR detection, but also by two coulometric and one gravimetric measurement. All remaining laboratory mean values lie within the tolerance interval.

7.2.2.3 Free carbon (Tab. 6o1a; 6o1b, 6o1c)

14 Laboratories delivered their results, each of them based on 6 separate determinations. Most laboratories used CGHE/combustion method with IR detection or combustion method with coulometric determination. For information all results are listed and illustrated in Tab. 6o1a. The spreading of the different laboratory mean values in this interlaboratory comparison was intolerably large. Therefore after a detailed discussion of experts two methods were prescribed for use that had led to result sets positioned in the center.

Therefore both tables, Tab. 601a which summarizes all results and Tab. 6o1b which lists only results from the not prescribed methods, are for information only. The mean of the means in both tables with 519 mg/kg and 530 mg/kg, respectively, are not so far from the finally certified value basing on the application of the prescribed methods only. This certified value in table 6o1c is 493 mg/kg of free carbon in SiC. The certified value for carbon free is the only one which is method depending, because only the two prescribed methods were admitted. The reason for this proceeding was the decrease of the confidence interval when only these methods were used (from 157 mg/kg to 86 mg/kg). Thus only the results in Tab. 6o1c are relevant for certification. They are basing on two results based on method M1 and two on method M2, respectively, (APPENDIX 1 and 2). The 4 results were submitted by 3 leading expert laboratories with very high experience in this kind of analyses. Therefore the values were accepted as being trustable.

7.2.2.4 **Oxygen** (Tab. 6p1; 6p2)

12 Laboratories delivered their results, each of them based on 6 separate determinations. With one exception all laboratories used CGHE/combustion method with IR detection. The set with the highest values was based on measurements with this method. It was identified as outlier by statistical tests and was removed after discussion, also because there was no overlapping with the confidence interval with the next set of values. In the second run of the evaluation program carried out with the remaining 11 laboratories no further outlier was removed. The certified mean value is not only underpinned by CGHE/combustion measurements with IR detection, but also by one coulometric measurement. All remaining laboratory mean values lie within the tolerance interval.

7.2.3 Non-metallic not certified analytes (indicative values)

7.2.3.1 **Nitrogen** (Tab. 6q1)

11 Laboratories delivered their results, each of them based on 6 separate determinations. All laboratories used CGHE method with TC detection. Therefore this is a method-specific parameter. No serious outlier was identified by statistical tests and no set of values was removed. All laboratory mean values lie within the tolerance interval.

7.2.3.2 **Free silicon** (Tab. 6r1)

6 Laboratories delivered their results, each of them based on 6 separate determinations. Most laboratories used volumetry. The spreading of the laboratory means was extremely wide, while the spreading of the single values within the laboratories was much smaller for most sets of results. No extreme oulier was identified. The calculated mean value is based on four different methods, but the confidence interval is extremely large.

7.2.3.3 **Free silicon dioxide** (Tab. 6s1)

6 Laboratories delivered their results, each of them based on 6 separate determinations. Most laboratories used colorimetry or ICP OES. The spreading of the laboratory means was rather wide. No extreme outlier was identified. The calculated mean value is based on four different methods.

7.3 Summary of statistical evaluation

Data and results of the statistical evaluation of the interlaboratory comparison using the BCR program [2] are summarized in Tab. 7.1, 7.2 and 7.3.

Following abbreviations were used:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

7.3.1 Metallic analytes

Tab. 7.1: Summary of results of statistical evaluation

Element run of evaluation program	Al run 1	Al run 2	B run 1	B run 2	Ca run 1
Number of data sets Total number of replicate measurements	19 110	18 104	13 72	11 60	17 95
Mean of means (a) St. Dev of means (a)	362.327 47.481	371.123 28.821	71.177 22.277	62.291 4.041	33.454 12.445
Outlying or straggling mean values					
▪ Dixon test	b, c	no	b, c	c	b, c
▪ Grubbs test (single and pair test)	b, c	no	b, c	c	b, c
▪ Nalimov t-test	b, c	c	b, c	c	b, c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	no	no	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	47.858 9.031	28.819 9.266	23.040 4.647	3.911 2.804	12.794 2.548
Half-width of the 95% confidence interval (a)	22.885	14.332	13.462	2.715	6.399

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	Ca run 2	Cr run 1	Cr run 2	Cu run 1	Cu run 2
Number of data sets Total number of replicate measurements	14 81	17 102	16 96	13 77	12 71
Mean of means (a) St. Dev of means (a)	29.351 3.362	3.616 0.771	3.486 0.575	2.874 5.061	1.476 0.479
Outlying or straggling mean values					
▪ Dixon test	no	no	no	b, c	no
▪ Grubbs test (single and pair test)	c	c	no	b, c	b, c
▪ Nalimov t-test	b, c	b, c	no	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	b, c: Did not run	b, c: Did not run
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	3.139 1.078	0.746 0.480	0.548 0.422	5.080 0.827	0.427 0.541
Half-width of the 95% confidence interval (a)	1.941	0.397	0.306	3.059	0.304

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	Fe run 1	Fe run 2	Fe run 3	Mg run 1	Mg run 2
Number of data sets Total number of replicate measurements	24 140	22 128	21 122	19 114	17 102
Mean of means (a) St. Dev of means (a)	147.648 22.468	146.517 14.096	148.383 11.323	7.356 3.670	6.340 1.092
Outlying or straggling mean values					
▪ Dixon test	b, c	c	no	b, c	b, c
▪ Grubbs test (single and pair test)	b, c	c	no	b, c	c
▪ Nalimov t-test	b, c	b, c	c	b, c	b, c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	22.204 10.501	13.231 10.866	10.370 9.902	3.478 2.874	1.056 0.678
Half-width of the 95% confidence interval (a)	9.487	6.250	5.154	1.769	0.561

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	Mn run 1	Mn run 2	Na run 1	Na run 2	Na run 3
Number of data sets Total number of replicate measurements	18 108	17 102	18 108	16 96	15 90
Mean of means (a) St. Dev of means (a)	1.489 0.310	1.441 0.241	17.855 3.131	18.012 1.933	17.691 1.494
Outlying or straggling mean values					
▪ Dixon test	no	no	c	no	no
▪ Grubbs test (single and pair test)	b, c	no	c	c	no
▪ Nalimov t-test	b, c	b, c	b, c	b, c	no
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	b, c: Did not run	b, c: Did not run	no	no	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	0.292 0.254	0.235 0.129	3.044 1.803	1.896 0.914	1.455 0.832
Half-width of the 95% confidence interval (a)	0.154	0.124	1.557	1.030	0.827

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	Ni run 1	Ti run 1	Ti run 2	V run 1	V run 2
Number of data sets Total number of replicate measurements	22 129	21 122	19 110	19 111	18 105
Mean of means (a) St. Dev of means (a)	32.904 4.980	76.969 7.807	78.668 5.550	40.510 6.752	41.382 5.743
Outlying or straggling mean values					
▪ Dixon test	no	no	no	no	no
▪ Grubbs test (single and pair test)	no	b, c	no	no	no
▪ Nalimov t-test	no	b, c	c	c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	4.830 3.332	7.344 6.482	5.364 3.399	6.702 3.323	5.710 2.647
Half-width of the 95% confidence interval (a)	2.208	3.554	2.675	3.254	2.856

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	Zr run 1	Zr run 2
Number of data sets Total number of replicate measurements	20 118	19 112
Mean of means (a) St. Dev of means (a)	25.648 3.790	25.156 3.169
Outlying or straggling mean values ▪ Dixon test ▪ Grubbs test (single and pair test) ▪ Nalimov t-test Differences between labs statistically significant? ▪ Snedecor F-test Outlying or straggling variances ▪ Cochran test Variances homogeneous ▪ Bartlett test	 no no b, c b, c b, c no	 no no c b, c b, c no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	3.631 1.956	3.022 1.520
Half-width of the 95% confidence interval (a)	1.774	1.528

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

7.3.2 Non-metallic certified analytes

Tab. 7.2: Summary of results of statistical evaluation

Element run of evaluation program	C_{total} run 1	C_{total} run 2
Number of data sets Total number of replicate measurements	19 113	17 101
Mean of means (a) St. Dev of means (a)	29.835 0.212	29.894 0.118
Outlying or straggling mean values ▪ Dixon test ▪ Grubbs test (single and pair test) ▪ Nalimov t-test Differences between labs statistically significant? ▪ Snedecor F-test Outlying or straggling variances ▪ Cochran test Variances homogeneous ▪ Bartlett test	 no b, c b, c b, c b, c no	 b, c c b, c b, c b, c no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	0.207 0.113	0.110 0.106
Half-width of the 95% confidence interval (a)	0.102	0.061

Abbreviations:
(a) = Expressed in %; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

Element run of evaluation program	(C_{free}) run 1a	(C_{free}) run 1b	C_{free} run 1c	O run 1	O run 2
Number of data sets Total number of replicate measurements	14 84	10 60	4 24	12 72	11 66
Mean of means (a) St. Dev of means (a)	519 272	530 324	493 54	930 93	909 64
Outlying or straggling mean values					
▪ Dixon test	no	no	no	c	no
▪ Grubbs test (single and pair test)	no	no	no	c	no
▪ Nalimov t-test	c	no	c	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	no	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	b, c	no	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	267 121	319 142	53 24	93 24	64 24
Half-width of the 95% confidence interval (a)	157	232	86	59	43

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

7.3.3 Non-metallic indicative analytes

Tab. 7.3: Summary of results of statistical evaluation

Element run of evaluation program	N run 1	Si_{free} run 1	$SiO_{2\text{-}free}$ run 1
Number of data sets Total number of replicate measurements	11 66	6 36	6 36
Mean of means (a) St. Dev of means (a)	92 31	481 272	599 82
Outlying or straggling mean values			
▪ Dixon test	no	no	no
▪ Grubbs test (single and pair test)	no	no	no
▪ Nalimov t-test	c	c	no
Differences between labs statistically significant?			
▪ Snedecor F-test	b, c	b, c	no
Outlying or straggling variances			
▪ Cochran test	no	b, c	b, c
Variances homogeneous			
▪ Bartlett test	b	b, c: Did not run	no
St. Dev. within – laboratories (a) St. Dev. between laboratories (a)	30 7	267 135	46 167
Half-width of the 95% confidence interval (a)	21	286	86

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

8 Calculation of certified and indicative values and their uncertainties

8.1 Mass fractions

The certified (or indicative) values of mass fractions of certified the considered elements were calculated as the mean values "*M*" of all accepted means from the participating laboratories of the interlaboratory comparison (see 7.1, Tab. 5).

8.2 Uncertainties

The combined uncertainties of the certified mass fractions were calculated independently from the results of the homogeneity tests. But the basic values of further calculations (see below) have been calculated in the context of the homogeneity investigations as described in paragraph 4.2 and as documented in detail in Appendix 5. These basic values are:

s_b = standard deviation of homogeneity investigation "between the bottles" (see APPENDIX 5) (note: it contains a contribution of the standard deviation of the analytical procedure used in homogeneity investigation)

s_w = standard deviation in homogeneity investigation "within the bottles" (see APPENDIX 5) (note: it contains a contribution of the standard deviation of the analytical procedure used in homogeneity investigation)

s_{HS} = standard deviation in homogeneity investigation of "homogeneous sample" (see APPENDIX 5). The value of s_{HS} is assumed to represent the standard deviation of the analytical procedure used for the homogeneity investigation.

Following symbols and abbreviations are used additionally:

u_c = combined uncertainty of certified mass fraction according to GUM [1] and ISO Guide 35 [3]

s_M = standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 5)

n = number of accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 5)

s_{inhom} = standard deviation resulting from inhomogeneity of the samples

whereas

$$s_{inhom} = \sqrt{\left(s_b^2 - s_{HS}^2\right) + \left(s_w^2 - s_{HS}^2\right)} \qquad (1)$$

In equation (1) from each of the variances s^2_b (between the bottles) and s^2_w (within the bottles) the variance s^2_{HS} of the homogeneous sample (=the variance of the analytical procedure) was subtracted. Thus an effective contribution of the inhomogeneity (without the contribution of the analytical procedure) was calculated.

Instead of equation (1) equation (1a) is used, if a homogeneous sample was not measured:

$$s_{inhom} = \sqrt{s_b^2 - s_w^2} \qquad (1a)$$

This follows the idea expressed in ISO guide 35 [3], that s_w can be observed as representing the standard deviation of the analytical procedure. The combined uncertainty u_c is calculated as the sum of two contributions, - on the one hand resulting from the interlaboratory comparison for certification - and on the other hand from inhomogeneity of the sample:

$$u_c = \sqrt{\frac{s_M^2}{n} + s_{inhom}^2} \qquad (2)$$

Equation (2) was used in all cases in which the variance representing the contribution of the inhomogeneity s^2_{inhom} was not less than the variance u^2_{bb} , representing the blind part of the variances (see [3]), which could be masked by the variance of the analytical procedure s^2_{HS}, i. e. when

$$s^2_{inhom} > u^2_{bb} , \qquad (3)$$

whereas

$$u_{bb} = \sqrt{\frac{s^2_{HS}}{n_{HS}}} \bullet \sqrt[4]{\frac{2}{v_{s^2_{HS}}}} \qquad (4)$$

is valid, with

n_{HS} = number of parallel measurements at homogeneous sample,

$v_{s^2_{HS}}$ = degrees of freedom for calculation of s^2_{HS} .

In cases when equation (3) was not valid , i. e. when

$$s^2_{inhom} \leq u^2_{bb} , \qquad (5)$$

the following equation was used instead of equation (2):

$$u_c = \sqrt{\frac{s^2_M}{n} + u^2_{bb}} \qquad (6)$$

In this case the combined uncertainty is consisting of the contribution of the interlaboratory comparison for certification and of a contribution (4) explained below equation (2).

If no homogeneity measurements had been carried out, the combined uncertainty was simply calculated according to:

$$u_c = \sqrt{\frac{s^2_M}{n}} \qquad (7)$$

A contribution from an uncertainty caused by the possible aging of the material was not included, because no evidence was found, that a detectable aging of the material would occur before the date of expiry (see paragraph 5).

The expanded uncertainty "*U*" (coverage factor 2) of the certified mass fraction was calculated according to GUM as

$$U = 2\ u_c\ . \qquad (8)$$

The following equations were used for the calculation of the combined uncertainties of the different analytes :

- for Al, B, Cr, Cu, Fe, (Mn), Ni, Ti : equation (2) combined with equation (1)
- for C_{free}, N, O, $SiO_{2\ free}$: equation (2) combined with equation (1a)
- for Ca, Mg, Na, V, C_{total} : equation (6) combined with equation (4)
- for Si_{free} : equation (7)

The expanded uncertainties *U* were calculated by using equation (8) (and by using a coverage factor of 2) in either case.

8.3 Certified values

Based on the calculations described in 8.1 and 8.2 the following values were certified:

Element/ Constituent	**Certified Values**		
	Symbols	**Mass fraction [1] in mg/kg**	**Uncertainty [2] in mg/kg**
Aluminium	Al	372	20
Boron	B	63	7
Calcium	Ca	29.4	1.8
Chromium	Cr	3.5	0.4
Copper	Cu	1.5	0.4
Iron	Fe	149	10
Magnesium	Mg	6.3	0.6
Manganese	Mn	1.44	0.17
Sodium	Na	17.7	0.8
Nickel	Ni	32.9	2.7
Titanium	Ti	79	4
Vanadium	V	41.4	2.8
Zirconium	Zr	25.2	2.0
Free Carbon [3]	C_{free}	493	79
Oxygen [5]	O	910	35
		Mass fraction [1] in %	**Uncertainty [2] in %**
Total Carbon [4]	C_{total}	29.89	0.07

1) The certified values are the means of 4-22 series of results (depending on the parameter) obtained by different laboratories. 2 up to 8 different analytical methods were used for the measurement of one parameter. The calibrations of the methods applied for determination of element mass fractions were carried out by using pure substances of definite stoichiometry or by using solutions prepared from them, thus achieving traceability to SI unit.
2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor *k* = 2. It includes contributions from sample inhomogeneity.
3) The mass fraction of carbon free is a method–depending value. It was determined by two different methods and is only related to the application of these methods, which are described as “Method M1” and “Method M2” respectively, attached to this certification report (see appendices 1 and 2).
4) The recommended “Method M3” described in attachment (appendix 3) can be used for the determination of mass fraction of carbon total.
5) The recommended “Method M4” described in attachment (appendix 4) can be used for the determination of mass fraction of oxygen.

8.4 Indicative values

The following not certified indicative values were also determined by using results of interlaboratory comparison and of calculations as described in 8.1 and 8.2.

Parameter	Indicative Values	
	Mass fraction [1)] in mg/kg	Uncertainty [2)] in mg/kg
Nitrogen	93	22
Silicon dioxide free	600	148
Silicon free	481	223

1) The indicative values are the means of 6-11 series of results (depending on the parameter) obtained by different laboratories. 1 up to 4 different analytical methods were used for the measurement of one parameter. The methods applied for determination of mass fractions were not always carried out by using pure substances of definite stoichiometry or by using solutions prepared from them, thus was not achieved traceability to SI units.
2) The uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor *k* = 2.

8.5 Additional material data

Additional material properties were determined by using one method, and can be used as informative values, only.

Parameter		Additional Material Data	
		mass fraction in %	Uncertainty in mass %
Phases:	SiC-6H	89.2 [1)]	0.2 [2)]
	SiC-15R	6.1 [1)]	0.2 [2)]
	SiC-4H	4.7 [1)]	0.2 [2)]
Parameters of particle size		Particle size in µm	
	D_{10}	5.55 [3)]	
	D_{50}	10.18 [3)]	
	D_{90}	16.69 [3)]	

1) The measurements were carried out by X-ray powder diffraction using Rietveld method for evaluation.
2) The calculation of the standard uncertainty is based on a raw estimation from the evaluation of the Rietveld method.
3) The particle size distribution was determined by laser light diffraction method.

9 Instructions for use
9.1 Area of application

The main area of application is checking the trueness of results when one or more of the certified parameters in silicon carbide material are determined by a laboratory. Based on own results and on certified values the uncertainty of own measurements can be calculated. The material can also be used for checking the trueness of the determination of the total carbon content in other refractory materials having similar carbon mass fractions.

9.2 Recommendations for correct sampling and sample preparation

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample.

Each sub-sample has to be taken separately. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different analytes (in paranthesis /mg): Al, Ca, Fe, Mg, Ni, Ti, Zr(8); Cr, Cu, V(14); B(500); C_{total}(25); C_{free}(500); O(80). The opening duration of the bottle should be as short as possible. The lid of the bottle containing a special sealing gasket should be locked tightly immediately after usage. Sample preparation for the determination of the analyte boron has to be carried out by using fusion technique with sodium peroxide followed by an extraction to avoid losses. For subsequent elemental analysis the sample has to be treated thermally at (135 ± 5) °C for 12 hours to achieve defined starting conditions. For the determination of metallic analytes, the required pressure digestion has to be verified concerning absence of analyte losses.

9.3 Recommendations for correct storage

The sample should be stored in a dust-free and dry environment avoiding contamination and moisture.

9.4 Expiration of certification

The date of expiry of certification is ten years after the date of certification. Before this date a new certificate will be prepared with a new date of expiry.

9.5 Safety guidelines

1. First aid measures

   In the event of contact with the skin, rinse off with water and soap. Contamination of the eyes must be treated by thorough irrigation with water, with the eyelids held open.
   If product is swallowed, induce vomiting and consult a physician. The product is not known to be toxic.

2. Accidental release measures

   Precautionary measures regarding persons: Avoid formation and deposition of dust. Ensure effective ventilation.
   Methods for cleaning up / taking up: Take up mechanically; avoid dust formation. Fill into labelled, sealable containers.

3. Handling

   Avoid formation and deposition of dust. Ensure adequate ventilation and if necessary, exhaust ventilation when handling or transferring the product.

4. Exposure restriction and personal protection

   Respiratory protection: If necessary use a respirator mask with filter typ P according to DIN EN 143
   Hand protection: protective gloves
   Eye protection: protective goggles

5. Limit values of dust concentration in air to be monitored

   Regulatory instructions concerning limit values of concentration of different particle size are to be maintained.

6. Disposal considerations

   Unused material: reuse if possible. Address manufacturer.
   Or: May be disposed of in approved special landfills provided local regulations are observed.

10 References

[1] Guide to the Expression of Uncertainty in measurement (1995)
International Organization for Standardization
ISBN 92-67-10188-9

[2] G. Bonas, M. Zervou, T. Papaeoannou and M. Lees
"SoftCRM": a new software for the Certification of Reference Materials
Accred Qual Assur, **8** (2003) 101-107

[3] ISO Guide 35 - Certification of reference materials - General and statistical principles (3rd edition, draft)

11 Regulatory information

- ANSI American National Standards Institute, Methods of chemical analysis of silicon carbide abrasive grain and abrasive crude, ANSI B74.15-1992, ANSI American National Standards Institute, 1992, pp. 20
- DIN, ISO 51079-1, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 1 Soda-Borsäure-Aufschluss
- DIN, ISO 51079-2, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 2 Säure-Druck-Aufschluss
- DIN, ISO 51079-3, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 3 Aufschluß des freien Kohlenstoffs durch naßchemische Oxidation
- DIN, ISO, 51075 - 1-5, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid, Teil 1-5
- FEPA (Féderation Européenne des Fabricants de Produits Abrasifs), Chemische Analyse von Siliciumcarbid, FEPA-Standard 45-D-1986, Fachverband Elektrokorund- und Siliziumkarbid-Hersteller e.V., Verein Deutscher Schleifmittelwerke e.V., 1986, 1-25

12 Informative references

- Kato, K.; "Atomic absorption spectrophotometric determination of total silicon in silicon carbide" in: Atomic Absorption Newsletter 15 (1976) 4-6
- Schwetz, K. A., Hassler, J.; "A wet chemical method for the determination of free carbon in boron carbide, silicon carbide and mixtures thereof" in: J. of the Less-Common Metals, Elsevier Sequoia/Netherlands, 117 (1986) 7-15
- Hunold, H., Reh, H.; "Die Hochleistungskeramik. II. Die Werkstoffe: Siliciumcarbid (SiC), ein alter Bekannter" in: Keramische Zeitschrift, (1987) 521-525
- Kriegesmann, J.; "Die Technologien der modernen Siliciumcarbidkeramiken, Teil I: Rohstoff und Formgebung" Keramische Zeitschrift (1988) 857-863
- Kriegesmann, J.; "Die Technologie der modernen Siliciumcarbidkeramiken Teil III: Eigenschaften" in: Keramische Zeitschrift (1989) 17-22
- "JIS Japanese Industrial Standard, Method for chemical analysis of silicon carbide abrasives" in: JIS R 6124-1987, Japanese Standards Association, Tokyo, Japan, (1989) 1- 51
- Broekaert, J. A. C., Graule, T., Jenett, H., Tölg, G., Tschöpel P.; "Analysis of advanced ceramics and their basis products" in: Fresenius Z. Anal. Chem. 332 (1989) 825-838

- Graule, T., Tschöpel, P.; “Analyse von hochreinen Keramikpulvern und Sinterkörpern mit der optischen Emissions- (OES) und der Atomabsoprtionsspektrometrie“ in: cfi/Ber.DKG 68 No. 1/2 (1991) 5-9
- Roßberg, A., Otto, K., Matthe, P.; “Analysenmodell zur Bestimmung von freiem Kohlenstoff in feindispersen SiC-Pulvern in Gegenwart von freiem Silizium“ in: cfi/Ber. DKG 69 No. 7/8 (1992) 251-254
- Docekal, B., Broekaert, J. A. C., Graule, T., Tschöpel, P., Tölg, G.; “Determination of impurities in silicon carbide powders” in: Fresenius J. Anal. Chem., 342 (1992) 113-117
- Záray, G., Leis, F., Kántor, T., Hassler, J., Tölg, G.; “Analysis of silicon carbide powder by ETV-ICP AES” in: Fresenius J Anal Chem, 346 (1993) 1042-1046
- Csato, I., Zaray, Gy., Gal-Solymos, K., Hassler, J.; “Direct analysis of silicon carbide powder by total reflection X-ray Fluorescence Spectrometry” in: Applied Spectroscopy 51 No. 7 (1997) 1067-1072
- Schäffer, U., Krivan, V.; “Multielement analysis of graphite and silicon carbide by inductively coupled plasma atomic emission spectrometry using solid sampling and electrothermal vaporisation” in: Anal. Chem. 71 No.4 (1999) 849-854
- Hassler, J., Förster, O.; Schwetz, K. A.; “Moderne chemische Analysenverfahren von keramischen Werkstoffen“ cfi/Ber. DKG 77 No. 7 (2000) D11-17
- Schwetz, K. A.; “Silicon carbide based hard materials” in: Handbook of Ceramic Hard Materials, R. Riedel (Ed.), Vol 2 Wiley-VCH, Weinheim, N.Y., (2000) 683-748

13 . Appendices

- Appendix 1: Method M1: Coulometric determination of free carbon (C_{free}) in silicon carbide after wet-chemical oxidation with hot chromic-sulfuric acid
- Appendix 2: Method M2: Coulometric determination of free carbon content (C_{free}) in silicon carbide comprising weighing-back the sample boat
- Appendix 3: Method M3: Proposed method for determination of total carbon mass fraction in silicon carbide powder
- Appendix 4: Method M4: Proposed Method for the determination of oxygen and nitrogen mass fraction in silicon carbide powder
- Appendix 5: Homogeneity investigations of the CRM-candidate material „Silicon Carbide Powder 1“ (SiC green micro F800)
- Appendix 6: Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003
- Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of CRM BAM-S003
- Appendix 8: Additional information to the Grubbs test carried out for the interlaboratory comparison for the certification of CRM BAM-S003

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Appendix 1: Method M1

Coulometric determination of free carbon (C_{free}) in silicon carbide after wet-chemical oxidation with hot chromic-sulfuric acid

According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany

Purpose:

C_{free}-determination in silicon carbide by wet chemical oxidation and coulometric detection

Scope:

The method is applicable preferably to very fine grain powders (grain size less than 10 µm) or low contents of free carbon (less than 0.2 % mass fraction) as well as if there are evaporable and/or easy oxidize components in the analyzed silicon carbon.
The method releases organic carbon and carbonate carbon, too (as CO_2).
The method is applicable to free carbon mass fractions of 0.01 % to 5 %. At higher concentrations incomplete recovery is possible. The method is not applicable to samples containing compounds which could adulterate the result (e.g. B_4C).

Principle

The free carbon of the sample is oxidized to carbon dioxide by of chromic sulfuric iodic acid at a temperature of 120 ºC ± 5 ºC. The inert gas carries the CO_2 to the coulometric detection system.
SiC does not react under these conditions, or only to a neglegible amount in case of very fine powders.

Apparatus

In addition to standard laboratory equipment, the following apparatus shall be used.

Coulometric detection system for determination of carbon mass fraction (e.g. coulometric system of "Coulomat 702", Ströhlein, Germany)

Analytical balance, precision ± 0,05 mg

Aluminium heating-block with temperature control to 130 ºC ± 5 ºC

Reaction vessel, with cooling device and drying trap (figure 1)

Aluminium capsules, e.g. ∅ 6 mm, L 15 mm, prepared from aluminium foil (carbon free)

External PC and plotter/printer

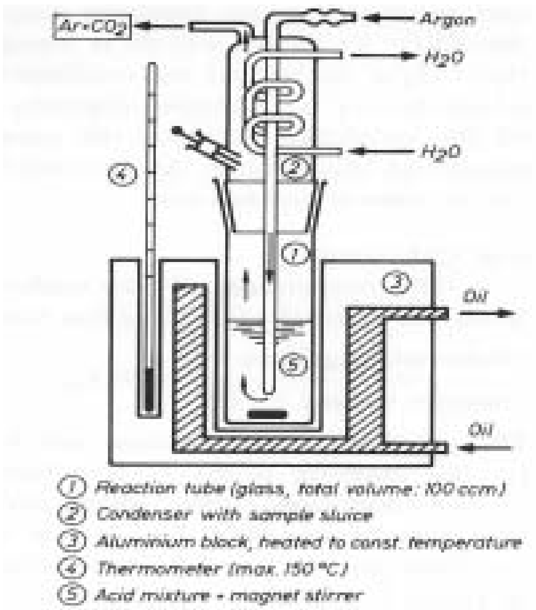

Fig.1: Aluminium heating block with reaction vessel

Reagents and auxiliary means

All reagents must be of known analytical grade. The used water shall be distilled water or water which has been fully demineralized by ion exchange (deionized water). Unless otherwise specified, solutions are aqueous solutions.

Calcium carbonate; $CaCO_3$ (dried 2h/285°C)
Barium carbonate; $BaCO_3$
Barium perchlorate; $Ba(ClO_4)_2$,
$Ba(ClO_4)_2$-solution; 20% (mass%) in H_2O
Sodium dichromate; $Na_2Cr_2O_7$ x 2 H_2O
Potassium iodate; KIO_3
Sulfuric acid H_2SO_4; ρ = 1,84 g/ml
Argon; Ar, 99,998 % pure
Chromic sulfuric acid solution: prepared by dissolving 22 g of sodium dichromate in 300 ml H_2O, and adding 700 ml sulfuric acid.
The solution is heated for 30 min at 150 ºC ± 10 ºC. After cooling the solution is stored in a glass bottle.
Little porcelain boats, not glazed
Aluminium capsules, made from aluminium foil free of carbon

Procedure

If the total dryness of sample is not assured, the sample has to be dried at 120°C ± 5 ºC for 2 hours and should be stored after cooling down in a dry surrounding (e.g. desiccator). Samples of higher grain size have to be milled to grain size ≤ 53 µm (e.g. in a steel mortar).
Use test assembly in accordance with the operating instructions.
Adjust the temperature of the heating block to 120 ºC ± 5 ºC.
Weigh ca. 0.5 g KIO_3 into the reaction vessel and pipette 30 ml of chromic sulfuric acid to it.
Insert the reaction vessel into the heating block and connect it via cooler tightly with the coulometric detection system and adjust the carrier gas with a surplus of carrier gas and a pressure compensation.
To control the tightness of the system, run a Ar-blank of about 5 min to 10 min after a heating time of 20 min.
Weigh, depending on the sample material and the expected content of free carbon 20 mg - 150 mg to the nearest 0,01 mg into an aluminium capsule.
Close the capsule with tweezers. After the chromic sulfuric acid has reached a temperature of 120°C, put the capsule in the sample insertion device in the reaction vessel and drop it into the hot acid. When the sample drops into the acid, switch on the measuring mode of the detection unit.
The total reaction time is about 60 min. The detection time depends on the chosen detection system.

Evaluation and calculation of C_{free} content

The evaluation is made graphically, counts (ordinate) versus time (abscissa).
Usually coulometric systems record add up counts for a specific time interval. Therefore it is not possible to draw running counts versus time or its first derivative.
Using a suitable interface, a measuring curve can be recorded by PC and printed out via plotter or printer.

Graphical evaluation by hand:

The slow and constant slope in the second part of the CO_2-reaction curve (system blank and negligible amount of C_{SiC}) is to be lengthened to the ordinate.
The ordinate is to shift ca. one minute before the sharp rise of the counts (moment of destruction of capsule and the start of reaction).
The stretch between the intersections of the lengthened constant line and the measuring curve (on the lower end) with the shifted ordinate corresponds to C_{free} oxidized by the hot chromic sulphuric acid attack.

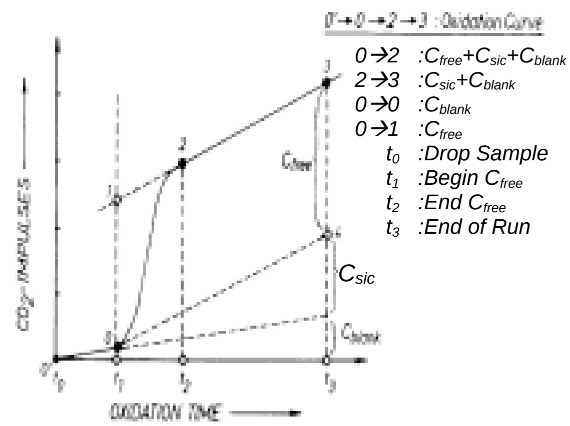

Fig. 2. Analysis of free carbon in silicon carbide: a plot of CO_2 concentration vs. time with graphical extrapolation.

The free carbon content, C_{free} shall be calculated as a percentage by mass, to the nearest 0.01 % using the following equation:

$$\% C_{free} = \frac{I * f}{m_E} * 100$$

I number of counts found for the sample by graphical evaluation
f conversion factor count → mg C (= 0.0002)
m_E sample mass, in mg

Precision:
The reproducibility of the method is: σ = ± 0.01% at a mass fraction of 0.05 – 0.50% C_{free}

Calibration:
Coulometry is an absolute method.
Use $CaCO_3$ for checking up the method and for testing assembly. The difference from theoretical value (12.00%) shall be max. ± 0.05% (absolute).
The check up is carried out daily before use.

References:

Operating instructions, Coulomat, Fa. Ströhlein
K.A.Schwetz, J.Haßler : A wet chemical method for the Determination of free carbon in boron carbide , silicon carbide and mixtures thereof, J. of the Less-Common Metals **117**, 7-15 (1986)
DIN 51079-3 Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen
Teil 3: Aufschluss des Freien Kohlenstoffs durch nasschemische Oxidation
Norm-Entwurf Okt 1997

Appendix 2: Method M2

Coulometric determination of free carbon content (C_{free}) in Silicon Carbide comprising weighing-back the sample boat

According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany

Purpose:
Indirect C_{free}-determination by weighing-back the combustion boat after direct C_{free}-determination

Scope:
To be used for SiC-powder and grains
Remark:
This method of C_{free}-determination is usable for SiC powder or grains with high proportion of fine particles (grain size < 10µm), material containing detectable quantities of β-SiC and/or material containing more than 2 % free carbon.

Principle:
Combustion of the free carbon in oxygen gas flow at 850°C followed by coulometric determination of the released carbon dioxide. The method takes into account the oxidation of silicon carbide during the combustion of the free carbon by weighing-back the sample boat (possible side reaction: $SiC \rightarrow SiO_2 + CO_2 \uparrow$) after combustion.
Comment 1:
This method is not usable if volatile components, carbonates and/or combustible impurities, such as, Fe_{met}, Si_{met} or B_{met} are contained in the sample, which can cause a significant change in weight (“met” stands for “metallic”).
Comment 2:
The method is a combination of methods described in DIN 51075 “Chemical analysis of silicon carbide”, part 2, “Direct determination of free carbon” and in DIN 51075, part 5 “Indirect determination of free carbon content in silicon carbide”.

Apparatus:
In addition to standard laboratory apparatus shall be used:
Apparatus for determination of carbon content consisting in a resistance heated tube furnace combined with a coulometric detection system (e.g. “Coulomat 702“, Ströhlein, Germany). The resistance heated furnace is equipped with ceramic tube and adjustable at (900 ± 10)°C.
Open combustion boats of unglazed ceramic material. Before use, the boats have to be heated in a laboratory furnace at (1050 ± 25)°C for 1 hour.

Reagents:
The following reagents of high purity shall be used.
Calcium carbonate; $CaCO_3$ (dried 2h/285°C),
Barium carbonate; $BaCO_3$
Barium perchlorate; $Ba(ClO_4)_2$
Absorbing-solution, dissolve about 200 g of high purity barium perchlorate, $Ba(ClO_4)_2$ in distilled or deionized water and fill up to one litre.
Oxygen, O_2: 99.99%

Procedure:
Use test assembly in accordance with the operating instructions.
Adjust the oxygen flow rate so that there is no risk of air being sucked in from outside. The measurement is carried out without splitting of gas flows.
A few reference samples of known carbon contend shall be analyzed before running the analytical sample.
Prior to series of analyses, the blank value shall be determined (with no gas volume reduction) using a precalcined boat.
Weigh to the nearest 0.01 mg, about (100 – 300) mg of the dried sample (dried at 120°C 1h) into a boat from which any carbon present has previously been removed by calcination. The mass of sample boat and the mass of sample boat plus sample (difference = weighed portion SiC) are recorded in writing.
Place the boat into the heating zone of the furnace preheated to a temperature of (850 ± 10)°C and start the measurement.
At the above temperature, the determination of free carbon takes 10 minutes. During this time the combustion gases are led to the coulometric detection system, where the coulometric current is registered and displayed.
After closing the measurement and removing the sample boat from the furnace, cool down to room temperature and weigh back the sample boat including annealed sample nearest 0.01mg.
<u>Remark:</u>
If the free carbon content is particularly high, the volume of the combustion gas can be reduced to one-tenth (1/10 gas division) using dosing pump.

Evaluation:
The content of free carbon (C_{free}) is calculated by counting the mass of additionally oxidized part of SiC.
In case of using the "Coulomat 702" the following calculation is carried out (in analogous way for other instruments):
One count corresponds to $3.212 x 10^{3}$ Coulomb or 2×10^{-4} mg C, respectively (at normal division).
The free carbon content C_{free} is calculated as a percentage by mass, to the nearest 0.01 % using the following equation:

$$C_{free} = \frac{0.6255 * C + 0.3754 * (m_1 - m_2)}{m_{SiC}} * 100$$

C = mass of carbon [mg]; determined at a temperature of (850 ± 10)°C and measuring time of about 10 min.

C = (I – I') • f
I = number of counts found for the sample
I' =number of counts in the blank value determination (mean of three repeats)
f = conversion factor count $\rightarrow$ mg C (0.0002)

m_1 = mass of sample boat + sample mass before oxidation, (mg)
m_2 = mass of sample boat + sample mass after oxidation, (mg)
m_{SiC} = sample mass (mg)

The factors used in the equations are to be calculated using the relative molar masses as follows:

$$1.6009 = \frac{\frac{SiO_2 - SiC}{C} + 1}{\frac{SiO_2 - SiC}{C}} \qquad 2.6641 = \frac{SiO_2 - SiC}{C} + 1$$

$$0.6255 = \frac{1}{1.6009} \qquad 0.3764 = \frac{1}{2.6641}$$

Precision:
The reproducibility of the method is: $\sigma = \pm$ 0.01% at 0.05-0.50% C_{free} mass fraction.

Calibration:
Use $CaCO_3$ for check up the method and test assembly. The difference from theoretical value (12.00%) should be max. ± 0.05% (absolute).
The check up is carried out daily before use.

References:
DIN 51075 Chemical analysis of silicon carbide
Operating instructions, Coulomat 702, (Ströhlein, Germany) or other instruments.

Appendix 3: Method M3

Recommended method for determination of total carbon mass fraction in silicon carbide powder

Prepared by Albrecht Meyer, Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany
Revised by Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany

Method

Oxidation in pure oxygen followed by IR-detection; (CO_2)-"Combustion method"

Preparation of measurement

- Use ceramic crucible with lid (11 mm hole). Anneal in muffle furnace at 1100°C for 8 hours in air; store in desiccator; anneal once more in a tube furnace at 1100°C in oxygen (or air) for a short time before use.
- Use purified Ni-capsules (purified with acetone in an ultrasonic bath) dried by a hair dryer.
- Use a weighed sub-sample of 25 mg (using semi-micro balance). The sub-sample mass depends on the size of Ni capsules used.
- Seal the capsule with a tong.
- Put the capsule into the crucible together with 0.5 g Fe (for reduction of carbon blank value in the iron material, the iron is heated at 950°C for 10 hours in an Ar stream before) and 1 g W as flux (sequence of putting into the crucible: Fe, sub-sample, W)

Measurement

- Put the crucible with the holed lid into the high frequency induction furnace and start the heating and the measurement cycle.
- Choose the duration of reaction to assure a total release of carbon. (Attention, it is a parameter strongly depending on the analytical instrument! A typical time is about 60 sec.)

Calibration

It is not allowed to use a certified matrix-reference material (such as steel). Use spectrographically pure graphite, a glassy carbon or powder of $CaCO_3$ introduced to Ni-capsules for calibration. In calibrating procedure a good signal adaptation is achieved with about 8 mg C or with an according mass of a (primary) pure substance such as $CaCO_3$.

Appendix 4: Method M4

Recommended method for the determination of oxygen and nitrogen mass fraction in silicon carbide powder

According to Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany

Method

Carrier gas hot extraction in inert gas atmosphere (He) with infra-red detection (CO_2) and heat conductivity measurement (N_2)

Preparation of measurement

- use pre-cleaned Ni-capsules (acetone or trichloroethylene; ultra sonic bath; dried by hair dryer)
- use a sub-sample mass dependent on capsule geometry (e.g. ∅7 X 10 mm) about 25-100 mg using semi-micro balance; carefully close capsule using tong; press capsule using a hand press; weigh back for control, if necessary

Measurement

Resistance heating oven; high temperature graphite crucibles; measurement modus – IMPULS; gas outlet and reaction temperature (usually equivalent to heating power POWER) are chosen in order to achieve a complete deliberation of the analytes (Attention: Instrument specific parameter (e.g. 5000 W / 70 sec when using LECO TC436 with EF 500)!)

Calibration

The detector is calibrated using (primary) pure substances (e.g. CO_2, N_2, KNO_3). Note, that this does not necessarily guarantee a complete deliberation of the analyte.

- In case of using solutions of salts (e.g. solution of KNO_3) dry the solution in the Ni-capsule slowly
- gas dose calibration for N is very critical, since the signal intensity ratio from sample and gas dose is about 1:100 (N_2) and for O still about 1:20 (CO_2)

Appendix 5

Homogeneity investigations of the CRM-candidate material „Silicon Carbide Powder 1“ (SiC green micro F800)

Selection of samples for homogeneity testing

For the homogeneity testing 20 bottles were representatively taken from the totality of 320 bottles by a combination of random access and systematic selection. Each bottle contained 50 g of candidate material. From each of the N = 20 bottles four appropriate sample masses were filled into vials (“larger sub-samples”) with masses of the taken material depending on the needs of the corresponding methods used for the homogeneity testing of different analytes.

The vials were distributed to the laboratories, where the measurements for homogeneity testing were carried out. For comparison a thoroughly homogenized sample was produced. For this purpose – 20 g of the material were highly homogenized in the “Mixer/Mill” (Spex. Ind., USA) for 15 min. (3 x 5 min.) using polypropylene vessels and balls.

Partial masses of this sample were distributed to the laboratories, in which the measurements for homogeneity testing were carried out.

Metallic analytes (without Na)

The measurements were carried out by ESK, Kempten (now: Wacker Ceramics, Kempten). An ICP OES spectrometer “IRIS-AP” (Thermo Elemental) was used in combination with electrothermal evaporation (ETV) for the analysis of sub-samples. In house carbide powders with known trace elemental contents and in some cases aliquots of calibration solutions were used for calibration. Resulting lack of trueness of results or of metrological traceability are not relevant, because a high precision is the only necessity in case of homogeneity investigation.

A real problem is the small sub-sample mass used with ETV ICP OES. A sub-sample mass of about 2 mg could only be applied. This is much less than normally used in wet chemical analysis and is not very representative for the entire sample. On the other hand it is possible to summarize some of the measurements to one result, thus summarizing the sub-sample masses to a virtual value representing a higher sub-sample mass. This procedure was followed, though more practical work is involved for measurements.

For the elements Al, Ca, Fe, Mg, Ni, Ti and Zr four series of measurements were carried out at different days and seven series for the elements Cr, Cu and V. Because of the very similar distribution of Cr and Mn in the samples, as known from former studies, Mn was not measured and the results for Cr in the homogeneity test were applied for Mn, too. The results of the measurement and the homogeneity testing are listed in the subsequent tables. They are classified by elements, each element filling 4 pages. On the first three pages all results are arranged, which were received from the measurements of the real small sub-samples (each was taken from one of the 4 larger sub-samples in the vials which had been representatively taken from the 20 selected bottles). They were given the "sample-number" “x/y”, with “x” = number of selected bottle and “y” = number of the larger sub-sample vial from this bottle (y = 1 … M) with (M = 4). The number “x/y” is to find in the second column of the table. In the following 4 or 7 columns, respectively, depending on the element, the single results by ETV ICP OES measurements are listed, each being calculated as mean from two different spectral lines and using sub-samples of 2 mg taken from the corresponding vials of larger sub-samples. In the following column the mean values of all the four or seven measurements for one larger sub-sample (one number “x/y”) are tabulated. These mean values represent the actual initial values of the homogeneity testing (marking: “mean”) for virtual sub-sample masses of 4 x 2 = 8 mg or 7 x 2 = 14 mg, respectively. In the subsequent column the mean of the 4 sub-sample values are tabulated; the next column contains the SD (standard deviation) of sub-samples. The values are the basis for the calculation of the “within bottle standard deviation” by quadratic averaging. The last column contains informative values of the corresponding RSD (relative standard deviation).

On the third page some results are summarized:

M_{Ss} is the mean of means of the sub-samples and $SD_{of\ mean\ of\ sub\text{-}samples}$ is the corresponding standard deviation. This value represents the deviation between the bottles. The value below is the corresponding RSD, which is not used for further calculation, the same holds true for the mean of the RSDs within the bottles "mean RSD_w".

Three tables are arranged on each one of the last page for an element. The one at the head contains the results of the measurements of the highly homogenized sample. K = 20 different sub-samples of the homogenized sample were analysed on 4 or 7 days, respectively. The mean values of the measurements from the different days are listed in the last column. Below this table the mean value of all 20 sub-samples M_{HS} is specified, together with the corresponding standard deviation SD_{HS} and the relative standard deviation RSD_{HS}.

Below these data two tables are arranged for homogeneity testing.

One homogeneity test (Anova, F-test) was made for comparing variances “between the bottles” and “within the bottles” (instead of "bottles" here was written "samples").

It contains the averaged standard deviation within the samples

$$s_w = \sqrt{\sum_{1}^{20} SD^2_{i\,\text{sub-sample}} \Big/ N} \quad ; \qquad N = 20$$

and the standard deviation between the samples (calculated for single determinations)

$$s_b = \sqrt{SD^2_{\text{means of sub-samples}} \times M} \quad ; \qquad (M = 4)$$

furthermore the test value

$$s_b^2 / s_w^2$$

and the critical value of the F-table

$$F_{\text{value}} = F_{\alpha;\, N-1;\, N \times (M-1)} = F_{0,05;19;60}$$

The “characteristic number” for the homogeneity testing between the samples is

$$\left(s_b^2 / s_w^2\right) / F_{\text{value}}.$$

If this "characteristic number" is $\leq$ 1, there is no reason to assume, that the distribution between the bottles is less homogeneous than within the bottles. For a value > 1 a less homogeneous distribution of sub-sample amounts between the bottles than within the bottles must be concluded (= “inhomogeneity between the bottles”). The extent of the “characteristic number” corresponds to the level of “inhomogeneity between the bottles”.

The other table bottom of page 4 is for homogeneity testing (F-test) within the samples. Here the standard deviation of the homogeneous sample s_{HS} is compared with the standard deviation within s_w the samples. This

$$\text{test value} = s_w^2 / s_{HS}^2$$

is compared with the critical value of the F-test-table.

$$F_{\text{value}} = F_{\alpha;\, N \times (M-1);\, K-1} = F_{0,05;60;19}$$

The resulting characteristic number within the bottles is

$$\left(s_w^2 / s_{HS}^2\right) / F_{value}$$

If this "characteristic number" is $\leq$ 1 then there is no reason to assume that the distribution within the samples is less homogeneous than in the homogenized sample. Ideally the distribution in the homogenized sample is totally homogeneous - in this case S_{HS} stands for the standard deviation of the applied analytical procedure, alone.

It can be concluded from the F-tests ("between" and "within") that for all 10 investigated elements no significant contribution to an inhomogeneity "between the bottles" could be found. A significant inhomogeneity contribution "within the bottles" was only found for the elements Cu, Fe and Zr. The material can be classified as sufficient homogeneous concerning the distribution of the 10 metallic analytes investigated.

Analytes B and Na

Both analytes could not be determined by ETV ICP OES precisely enough. Therefore other methods were used. The measurements were carried out by H.C. Starck GmbH, Goslar.

For the determination of B 0.5 g sub-samples were weighed into the PTFE-liner of the pressure digestion system DAB II (Berghof, Germany) and digested after adding of HF (73 %) and HNO_3 (100 %, fuming) at 250 °C for 8 hours. The boron concentration in the digested and diluted sample was measured by ICP OES ("Ultrace", Jobin Yvon). The calibration solutions were matrix adapted for acids and or Si. The values used for the homogeneity investigation are the mean values of two measurements of the same digestion solution at different days

For the determination of Na 0.5 mg sub-samples were analysed directly by solid sampling AAS (SS ET AAS) using the spectrometer "AAS SEA solid" (Analytik Jena AG, Jena, Germany). The calibration was done using aliquots of calibration solutions.

It was not necessary to summarize measurements from different sub-samples, as done for other metallic elements. Apart from this, the structure for the documents containing the evaluation of the measurements is similar as for the metallic elements. The table of first page of the documents for an element (B or Na) contains the results for measurements of every M = 3 sub-samples from N = 20 bottles (= column "values"). The results of every 3 sub-samples are summarized in the following columns as "mean of sub-samples 1 – 3", the corresponding standard deviations within each bottle "SD" and the derived standard deviation "RSD_W". The symbols below the table are analogous to those of the metallic elements, as well as the three tables on the next page, containing the measurement results for the homogeneous sample and the homogeneity tests between and within the bottles which are totally analogous to those for the metallic elements (see above). For both analytes (B and Na) no significant inhomogeneities were found within the bottles. – The same holds true for the homogeneity of the distribution of Na between the bottles, whereas for B a significant inhomogeneity between the bottles was found.

Non-metallic analytes

The measurements for the homogeneity investigations of these analytes were carried out by ESK, Kempten (now: Wacker Ceramics, Kempten). Different methods were applied for the determination of different analytes.

The content of C_{total} was determined by two different methods. One consisted in the combustion of sub-samples of 20 – 25 mg in a high frequency furnace WC200 (LECO) in an oxygen stream. The generated CO_2 gas was collected in a C-trap and was measured by an infrared measuring cell after release. The other method consisted in the coulometric determination of CO_2 with the Coulomat 702 (Ströhlein) after combustion of the sub-samples of ca. 50 mg in an oxygen stream and using lead borate as aggregat.

C_{free} was determined by a procedure derived from DIN 51075. About 0.5 g sub-sample was handled in an oxygen stream at 850 °C. The generated CO_2 was coulometrically determined using the Coulomat 702 (Ströhlein). The sample boat was weighed before and after the chemical reaction and the partial amount of SiC which had also reacted ($SiC \rightarrow SiO_2 + CO_2 \uparrow$) was taken into account (see “Method M 2” of appendix of certificate).

Oxygen was determined using about 80 mg sub-samples in a resistance heated furnace TC436 (LECO) in a helium carrier gas stream. CO was catalytically oxidized to CO_2. The total concentration of CO_2 was measured by an infrared measuring cell.

Homogeneity investigations were also carried out for two of the three not certified, indicative values namely for N and Si_{free}.

N was determined by carrier gas hot extraction in a resistance heated furnace TC436 (LECO) using helium as carrier gas and a thermal conductivity measuring cell. Sub-samples of about 80 mg were used.

SiO_{2free} was determined by distillation after chemical reaction. The sub-sample was treated with HF, distilled as H_2SiF_6 and determined as Si after absorption in water by using ICP OES.

The structure of the tables containing the evaluation of the measurements is similar as for the analytes B and Na. The only difference is, that the homogenized sample was not analysed for the analytes C_{free}, O, N and SiO_{2free}.Therefore no homogeneity test within the bottles could be carried out for these analytes. The reason for this is, that these analytes can be assumed to be distributed homogenously within bottles, because they are tightly fixed within the volume or at the surface of the powder grains.

The homogeneity tests between the bottles had the following results:

- For C_{total}, O and N: no significant inhomogeneities,
- For C_{free} and SiO_{2free}: significant inhomogeneities.

Conclusion:

The homogeneity investigations showed satisfying results in most cases. Independent from the results of the statistical tests carried out, the contributions from the between bottle standard deviations and the within-bottle standard deviations were corrected by the standard deviation of the homogeneous samples (if determined) and both contributions were (together with the contribution from the round robin test for certification) included into the calculation of the final measurement uncertainties of the certified values.

ETV ICP OES-results (means of two spectral lines) measured on 4 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Al

mass fraction in mg/kg

Line number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	352.949	370.906	310.255	350.430	**346.1**	**352.4**	**5.4**	**1.5**
	2/2	386.167	345.198	334.743	352.567	**354.7**			
	2/3	348.476	362.365	371.428	351.978	**358.6**			
	2/4	362.095	345.555	363.859	329.665	**350.3**			
2	29/1	368.412	348.855	383.181	350.308	**362.7**	**354.4**	**9.6**	**2.7**
	29/2	383.851	332.294	383.602	345.507	**361.3**			
	29/3	334.527	375.793	323.465	334.352	**342.0**			
	29/4	356.967	364.864	336.941	346.885	**351.4**			
3	35/1	360.794	381.766	358.433	354.476	**363.9**	**353.6**	**8.6**	**2.4**
	35/2	336.621	369.617	372.442	341.566	**355.1**			
	35/3	357.734	329.001	348.870	335.877	**342.9**			
	35/4	341.074	363.423	355.014	351.312	**352.7**			
4	56/1	374.227	371.689	347.917	347.102	**360.2**	**361.5**	**7.9**	**2.2**
	56/2	403.727	383.608	368.926	335.932	**373.0**			
	56/3	348.249	384.623	346.319	348.852	**357.0**			
	56/4	354.690	353.934	372.514	341.859	**355.7**			
5	76/1	354.875	393.698	373.662	356.530	**369.7**	**368.5**	**16.1**	**4.4**
	76/2	324.747	393.077	362.946	357.796	**359.6**			
	76/3	370.918	350.797	331.896	363.086	**354.2**			
	76/4	405.483	388.658	372.031	396.584	**390.7**			
6	90/1	373.099	360.547	398.238	355.588	**371.9**	**360.9**	**10.7**	**3.0**
	90/2	349.312	319.690	396.646	391.045	**364.2**			
	90/3	372.309	363.696	365.001	343.718	**361.2**			
	90/4	332.988	357.085	338.249	357.226	**346.4**			
7	108/1	371.413	369.700	358.373	357.501	**364.2**	**361.5**	**9.7**	**2.7**
	108/2	311.525	333.057	366.515	385.891	**349.2**			
	108/3	350.061	392.183	348.916	349.667	**360.2**			
	108/4	367.528	378.171	397.480	346.735	**372.5**			

Analyt Al

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	mean	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
8	128/1	378.667	442.141	318.504	361.038	**375.1**	**366.2**	**8.1**	**2.2**
	128/2	352.444	361.365	347.102	370.325	**357.8**			
	128/3	387.659	355.049	359.476	342.252	**361.1**			
	128/4	373.146	373.958	367.691	368.817	**370.9**			
9	132/1	365.092	397.025	329.132	369.704	**365.2**	**365.1**	**9.6**	**2.6**
	132/2	367.754	365.785	366.112	387.142	**371.7**			
	132/3	375.960	370.524	356.047	385.205	**371.9**			
	132/4	336.822	348.498	368.694	351.896	**351.5**			
10	156/1	372.554	381.774	341.129	344.043	**359.9**	**360.0**	**5.5**	**1.5**
	156/2	335.336	336.116	364.177	373.808	**352.4**			
	156/3	383.612	378.530	335.422	354.832	**363.1**			
	156/4	362.044	356.820	382.331	358.156	**364.8**			
11	164/1	353.689	432.567	353.705	351.589	**372.9**	**355.5**	**12.1**	**3.4**
	164/2	315.450	330.680	398.756	368.634	**353.4**			
	164/3	362.300	320.258	346.681	350.532	**344.9**			
	164/4	341.813	338.723	351.378	370.492	**350.6**			
12	188/1	396.318	395.686	350.294	365.871	**377.0**	**350.8**	**21.1**	**6.0**
	188/2	337.448	322.826	325.426	340.197	**331.5**			
	188/3	354.129	311.915	341.747	337.547	**336.3**			
	188/4	349.649	387.403	356.370	340.631	**358.5**			
13	195/1	347.692	381.150	358.754	356.706	**361.1**	**362.2**	**11.0**	**3.0**
	195/2	329.040	381.395	383.472	416.827	**377.7**			
	195/3	384.465	319.565	333.573	370.637	**352.1**			
	195/4	361.305	344.891	337.359	388.794	**358.1**			
14	221/1	331.108	372.018	392.735	330.534	**356.6**	**358.1**	**6.7**	**1.9**
	221/2	358.920	330.904	340.970	371.207	**350.5**			
	221/3	357.558	325.391	378.620	371.735	**358.3**			
	221/4	383.793	370.316	371.604	341.548	**366.8**			
15	229/1	391.272	403.858	374.673	350.890	**380.2**	**364.9**	**11.0**	**3.0**
	229/2	335.298	358.338	378.692	356.074	**357.1**			
	229/3	354.307	329.546	371.961	370.897	**356.7**			
	229/4	370.682	389.165	341.233	360.875	**365.5**			
16	253/1	355.072	414.507	386.593	350.008	**376.5**	**368.3**	**7.2**	**2.0**
	253/2	338.668	334.060	347.434	437.302	**364.4**			
	253/3	390.844	328.206	388.903	378.573	**371.6**			
	253/4	388.050	366.670	335.403	351.854	**360.5**			
17	264/1	388.714	360.193	352.119	332.521	**358.4**	**364.7**	**8.7**	**2.4**
	264/2	355.926	351.751	395.141	395.981	**374.7**			
	264/3	363.666	362.411	347.615	351.940	**356.4**			
	264/4	369.105	339.887	380.744	386.688	**369.1**			

Analyt Al

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
18	279/1	347.631	331.048	326.909	337.908	**335.9**	**354.7**	**17.4**	**4.9**
	279/2	408.868	339.928	345.085	362.016	**364.0**			
	279/3	358.154	350.606	329.329	342.395	**345.1**			
	279/4	397.063	355.738	382.294	360.788	**374.0**			
19	294/1	326.367	352.446	400.796	350.479	**357.5**	**360.5**	**3.7**	**1.0**
	294/2	335.120	371.518	327.441	399.449	**358.4**			
	294/3	335.719	430.366	364.327	332.682	**365.8**			
	294/4	381.380	361.626	342.350	355.848	**360.3**			
20	307/1	350.658	345.316	341.580	361.467	**349.8**	**365.4**	**11.8**	**3.2**
	307/2	324.633	399.603	367.926	361.412	**363.4**			
	307/3	347.050	349.617	396.709	413.994	**376.8**			
	307/4	418.370	396.261	327.634	344.491	**371.7**			

M_{Ss} - mean of means of the sub-samples 1-4	**360.5**
SD of means of the sub-samples 1-4	**5.4**
RSD (%)	**1.5**

mean RSD_w (%) **2.8**

Analyt Al

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**
1	HS 1	377.023	375.786	363.473	340.591	**364.2**
2	HS 2	409.853	354.320	344.315	356.633	**366.3**
3	HS 3	362.399	382.353	366.021	338.611	**362.3**
4	HS 4	334.316	394.472	361.196	338.777	**357.2**
5	HS 5	338.073	343.698	376.340	345.293	**350.9**
6	HS 6	323.128	336.456	361.785	340.248	**340.4**
7	HS 7	411.139	320.358	353.685	354.967	**360.0**
8	HS 8	360.894	372.987	368.214	391.395	**373.4**
9	HS 9	336.525	330.873	353.920	367.824	**347.3**
10	HS 10	330.724	347.927	363.606	351.729	**348.5**
11	HS 11	376.104	351.882	339.867	338.529	**351.6**
12	HS 12	348.222	375.456	368.362	411.696	**375.9**

HS = Homogeneous sample

13	HS 13	320.144	352.718	361.000	384.325	**354.5**
14	HS 14	377.707	357.339	364.779	350.302	**362.5**
15	HS 15	348.801	350.975	369.362	374.608	**360.9**
16	HS 16	386.217	361.164	355.696	347.531	**362.7**
17	HS 17	380.080	377.472	351.170	344.959	**363.4**
18	HS 18	337.797	342.003	373.163	374.335	**356.8**
19	HS 19	351.576	413.773	361.933	368.522	**374.0**
20	HS 20	380.270	377.127	351.869	377.326	**371.6**
					M_{HS} - mean of homogeneous sample	**360.2**
					SD_{HS}	**9.5**
					RSD_{HS} (%)	**2.6**

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	10.9	M_{Ss} 360.5	RSD % 1.5
standard deviation between the samples s_b	10.8	F_{value}	1.768
test value s_b^2/s_w^2	0.98	Characteristic no. for homogeneity between the samples	0.56
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample s_{HS}	9.5	M_{HS} 360.2	RSD_{HS} % 2.6
		F_{value}	1.98
test value s_w^2/s_{HS}^2	1.30	Characteristic no. for homogeneity within the samples	0.66
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of two spectral lines) measured on 4 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Ca

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	25.710	25.570	24.275	26.795	**25.59**	**25.64**	**0.3**	**1.3**
	2/2	26.693	26.075	25.584	25.653	**26.00**			
	2/3	25.148	25.712	25.886	26.318	**25.77**			
	2/4	26.842	25.212	25.546	23.216	**25.20**			
2	29/1	26.821	25.971	26.891	25.410	**26.27**	**26.01**	**0.3**	**1.2**
	29/2	24.711	26.139	25.951	26.531	**25.83**			
	29/3	25.950	25.354	25.308	28.416	**26.26**			
	29/4	26.719	26.415	24.948	24.645	**25.68**			
3	35/1	26.159	25.712	26.692	27.951	**26.63**	**26.33**	**0.5**	**2.0**
	35/2	25.224	26.264	25.762	30.278	**26.88**			
	35/3	26.553	26.115	25.767	25.935	**26.09**			
	35/4	25.227	24.897	27.152	25.550	**25.71**			
4	56/1	26.592	25.992	26.214	25.887	**26.17**	**26.19**	**0.4**	**1.5**
	56/2	25.618	26.929	26.080	25.621	**26.06**			
	56/3	25.786	27.641	26.702	26.795	**26.73**			
	56/4	25.834	26.209	26.187	24.923	**25.79**			
5	76/1	26.731	25.655	26.531	26.132	**26.26**	**26.26**	**0.2**	**1.0**
	76/2	25.396	26.555	26.591	26.442	**26.25**			
	76/3	25.320	28.865	26.190	25.945	**26.58**			
	76/4	25.456	25.942	26.523	25.953	**25.97**			
6	90/1	27.343	26.745	25.745	26.236	**26.52**	**26.27**	**0.6**	**2.4**
	90/2	26.089	25.757	23.750	26.197	**25.45**			
	90/3	27.369	25.854	28.612	25.808	**26.91**			
	90/4	26.028	27.103	26.642	25.034	**26.20**			
7	108/1	26.266	26.399	26.121	26.324	**26.28**	**26.31**	**0.2**	**0.7**
	108/2	28.111	26.177	25.752	26.292	**26.58**			
	108/3	26.008	26.666	25.461	26.955	**26.27**			
	108/4	26.183	25.386	27.188	25.697	**26.11**			
8	128/1	26.549	26.102	24.174	26.103	**25.73**	**25.76**	**0.4**	**1.6**
	128/2	25.366	26.607	25.826	27.325	**26.28**			
	128/3	25.580	25.399	24.405	25.644	**25.26**			
	128/4	25.345	25.570	27.382	24.707	**25.75**			

Analyt Ca

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	132/1	26.486	25.820	25.406	26.161	**25.97**	**25.60**	**0.4**	**1.5**
	132/2	24.995	25.574	25.352	27.666	**25.90**			
	132/3	26.324	26.467	25.681	22.403	**25.22**			
	132/4	24.763	24.992	26.044	25.428	**25.31**			
10	156/1	25.894	26.917	26.483	26.352	**26.41**	**26.15**	**0.2**	**0.7**
	156/2	25.286	26.215	25.045	28.079	**26.16**			
	156/3	26.020	25.520	26.778	25.647	**25.99**			
	156/4	26.939	26.008	25.080	26.192	**26.05**			
11	164/1	25.829	25.906	25.448	26.186	**25.84**	**26.11**	**0.2**	**0.7**
	164/2	26.379	25.642	26.283	26.706	**26.25**			
	164/3	25.862	26.347	26.113	26.552	**26.22**			
	164/4	25.572	25.004	26.169	27.829	**26.14**			
12	188/1	26.183	26.298	24.574	26.493	**25.89**	**25.82**	**0.3**	**1.3**
	188/2	26.279	25.749	24.433	26.428	**25.72**			
	188/3	24.698	25.530	26.275	25.189	**25.42**			
	188/4	26.981	26.094	26.505	25.367	**26.24**			
13	195/1	25.583	25.992	27.367	26.216	**26.29**	**25.86**	**0.5**	**1.8**
	195/2	24.794	25.710	26.075	24.923	**25.38**			
	195/3	26.698	25.791	25.971	26.490	**26.24**			
	195/4	26.121	25.683	24.304	26.034	**25.54**			
14	221/1	26.267	26.077	25.862	24.652	**25.71**	**26.09**	**0.3**	**1.3**
	221/2	25.008	25.863	26.199	28.478	**26.39**			
	221/3	25.240	25.652	26.197	26.487	**25.89**			
	221/4	27.307	25.789	26.479	25.861	**26.36**			
15	229/1	25.657	25.965	25.458	25.133	**25.55**	**25.93**	**0.3**	**1.1**
	229/2	25.511	24.829	26.751	26.444	**25.88**			
	229/3	25.761	26.493	26.030	25.975	**26.06**			
	229/4	26.406	26.388	26.083	25.951	**26.21**			
16	253/1	25.384	25.681	26.310	25.162	**25.63**	**25.91**	**0.5**	**1.8**
	253/2	26.267	26.167	25.084	24.296	**25.45**			
	253/3	26.364	26.371	26.878	26.268	**26.47**			
	253/4	26.504	26.258	25.939	25.589	**26.07**			
17	264/1	25.848	28.515	25.385	26.372	**26.53**	**26.10**	**0.6**	**2.2**
	264/2	25.168	25.863	25.764	24.453	**25.31**			
	264/3	25.820	25.452	26.868	25.946	**26.02**			
	264/4	28.347	25.920	26.616	25.286	**26.54**			

Analyt Ca

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
18	279/1	26.138	26.101	25.583	25.990	**25.95**	**25.85**	**0.3**	**1.3**
	279/2	25.064	26.795	26.279	26.865	**26.25**			
	279/3	24.586	26.714	26.347	25.382	**25.76**			
	279/4	27.162	26.488	22.809	25.348	**25.45**			
19	294/1	26.101	25.985	25.068	24.884	**25.51**	**25.78**	**0.3**	**1.2**
	294/2	25.344	26.111	26.360	26.452	**26.07**			
	294/3	25.605	26.956	26.326	25.117	**26.00**			
	294/4	26.285	25.055	25.929	24.852	**25.53**			
20	307/1	25.777	26.066	26.670	25.603	**26.03**	**26.09**	**0.6**	**2.1**
	307/2	25.955	23.936	25.585	25.935	**25.35**			
	307/3	26.799	26.034	25.772	28.105	**26.68**			
	307/4	26.646	26.543	26.088	25.903	**26.29**			

M_{Ss} - mean of means of the sub-samples 1-4	**26.00**
SD of means of the sub-samples 1-4	**0.2**
RSD (rel.%)	**0.9**

mean RSD_w (%) **1.4**

Analyt Ca

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**
1	HS 1	25.825	27.681	24.126	24.593	**25.56**
2	HS 2	25.606	25.293	26.857	26.795	**26.14**
3	HS 3	25.127	24.298	26.146	25.821	**25.35**
4	HS 4	25.535	25.924	29.671	26.033	**26.79**
5	HS 5	25.556	25.761	24.845	26.744	**25.73**
6	HS 6	25.333	26.540	26.902	25.693	**26.12**
7	HS 7	26.267	24.476	26.066	27.099	**25.98**
8	HS 8	24.657	26.688	25.349	23.445	**25.03**
9	HS 9	28.932	27.622	25.456	26.220	**27.06**
10	HS 10	25.224	25.187	25.561	29.596	**26.39**
11	HS 11	25.965	25.469	25.871	27.475	**26.20**
12	HS 12	25.838	26.515	24.708	23.883	**25.24**
13	HS 13	27.275	25.024	26.876	24.242	**25.85**

HS = Homogeneous sample

14	HS 14	26.435	26.696	26.601	26.465	**26.55**
15	HS 15	26.116	25.729	24.887	25.912	**25.66**
16	HS 16	26.461	25.254	25.398	26.112	**25.81**
17	HS 17	25.971	25.032	26.135	26.419	**25.89**
18	HS 18	25.045	25.683	27.056	25.518	**25.83**
19	HS 19	25.780	23.995	26.333	25.710	**25.45**
20	HS 20	26.160	25.852	25.724	26.374	**26.03**

M_{HS} - mean of homogeneous sample	**25.93**
SD_{HS}	**0.5**
RSD_{HS} (%)	**2.0**

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w 0.4		M_{Ss} 26.00	RSD % 0.9
standard deviation between the samples s_b 0.4		F_{value}	1.768
test value s_b^2/s_w^2	1.27	Characteristic no. for homogeneity between the samples	0.72
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.5	M_{HS} 25.93	RSD_{HS} % 2.0
		F_{value}	1.98
test value s_w^2/s_{HS}^2	0.60	Characteristic no. for homogeneity within the samples	0.30
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of 3 spectral lines) measured on 7 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Cr

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	2.952	3.068	3.110	3.376	4.094	3.162	3.478	**3.320**	**3.198**	**0.15**	**4.7**
	2/2	3.099	2.783	2.754	3.340	3.275	3.034	3.583	**3.124**			
	2/3	4.335	3.374	2.901	3.168	3.533	2.901	3.076	**3.327**			
	2/4	2.697	2.560	2.874	2.825	3.102	2.803	4.297	**3.023**			
2	29/1	2.958	2.729	3.071	3.085	3.411	2.852	3.439	**3.078**	**2.994**	**0.10**	**3.3**
	29/2	3.114	2.637	2.912	3.449	3.090	3.035	3.313	**3.079**			
	29/3	2.925	2.917	2.892	2.922	3.011	2.959	2.908	**2.933**			
	29/4	2.913	2.663	2.660	2.898	3.078	3.016	2.987	**2.888**			
3	35/1	2.858	2.569	2.980	2.974	3.132	3.162	3.376	**3.007**	**2.956**	**0.09**	**3.0**
	35/2	2.751	2.662	2.910	3.612	3.036	3.052	3.258	**3.040**			
	35/3	2.832	2.780	2.748	3.252	3.242	2.837	2.853	**2.935**			
	35/4	2.864	2.767	2.665	2.895	3.024	2.957	2.730	**2.843**			
4	56/1	2.816	2.863	2.871	3.359	3.034	3.666	3.109	**3.103**	**2.991**	**0.08**	**2.6**
	56/2	3.033	2.629	2.751	3.039	3.260	2.847	3.122	**2.954**			
	56/3	2.990	2.951	2.542	2.883	3.332	3.457	2.720	**2.982**			
	56/4	3.263	2.578	2.828	2.927	2.870	3.230	2.775	**2.925**			
5	76/1	3.117	2.715	2.752	3.292	2.832	3.349	3.386	**3.063**	**2.948**	**0.10**	**3.4**
	76/2	3.213	2.799	3.537	2.763	2.594	2.725	3.233	**2.980**			
	76/3	2.732	2.753	2.661	2.994	3.655	2.865	2.783	**2.920**			
	76/4	2.989	2.594	2.820	2.873	2.581	2.731	3.213	**2.829**			
6	90/1	2.909	2.513	2.942	3.205	3.127	2.906	3.191	**2.971**	**2.950**	**0.05**	**1.6**
	90/2	2.964	2.681	3.056	2.752	2.861	3.359	3.377	**3.007**			
	90/3	2.838	2.840	2.731	2.834	2.872	3.376	2.852	**2.906**			
	90/4	3.005	2.573	2.984	2.977	2.933	3.016	2.920	**2.915**			
7	108/1	2.726	2.768	2.681	3.246	3.091	2.980	3.215	**2.958**	**2.979**	**0.06**	**2.2**
	108/2	2.928	2.889	3.159	3.407	2.922	3.038	3.066	**3.059**			
	108/3	2.974	2.715	2.839	2.923	2.780	3.210	2.888	**2.904**			
	108/4	3.537	2.589	2.765	2.810	2.771	2.760	3.733	**2.995**			
8	128/1	2.853	2.556	2.916	3.692	3.303	3.191	3.269	**3.111**	**2.970**	**0.15**	**4.9**
	128/2	2.958	2.579	4.129	2.995	3.047	2.961	2.895	**3.081**			
	128/3	2.723	2.728	2.851	2.790	3.087	2.872	2.844	**2.842**			
	128/4	3.373	2.614	2.602	3.171	2.631	2.774	2.763	**2.847**			

Analyt Cr

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	132/1	3.039	2.679	2.675	3.737	3.367	2.685	3.327	**3.073**	**3.002**	**0.18**	**6.0**
	132/2	2.861	3.210	2.975	3.104	3.705	2.951	2.966	**3.110**			
	132/3	3.041	2.874	3.052	2.948	2.764	3.035	3.922	**3.091**			
	132/4	3.245	2.585	2.567	2.824	2.615	2.795	2.494	**2.732**			
10	156/1	2.803	2.568	2.406	3.511	3.097	3.186	3.156	**2.961**	**2.924**	**0.11**	**3.9**
	156/2	3.048	3.468	2.799	2.894	3.260	2.939	3.014	**3.060**			
	156/3	2.874	3.190	2.693	2.800	2.815	3.235	2.602	**2.887**			
	156/4	3.211	2.423	2.831	2.864	2.940	2.696	2.561	**2.789**			
11	164/1	2.867	2.703	2.369	3.230	3.269	4.225	3.522	**3.169**	**2.962**	**0.15**	**5.2**
	164/2	2.883	2.762	2.908	2.874	3.418	2.797	3.200	**2.977**			
	164/3	2.971	2.922	2.447	2.692	3.159	2.921	2.565	**2.811**			
	164/4	3.476	2.381	2.664	2.776	3.292	2.824	2.816	**2.890**			
12	188/1	2.749	2.833	2.538	3.465	3.028	3.356	3.201	**3.024**	**2.950**	**0.06**	**2.0**
	188/2	2.678	2.760	2.966	2.996	2.723	3.395	3.272	**2.970**			
	188/3	2.617	2.895	2.434	3.018	2.929	3.406	2.903	**2.886**			
	188/4	2.937	2.657	2.744	3.196	2.871	3.134	2.898	**2.920**			
13	195/1	2.752	2.693	2.306	3.308	3.045	3.264	3.221	**2.941**	**2.971**	**0.16**	**5.3**
	195/2	2.874	4.604	2.814	3.288	2.865	2.943	2.991	**3.197**			
	195/3	2.852	2.847	2.587	2.891	3.029	2.864	2.755	**2.832**			
	195/4	3.209	2.791	3.294	2.710	2.737	2.827	2.828	**2.914**			
14	221/1	2.679	3.112	2.178	3.348	3.093	3.064	3.274	**2.964**	**2.919**	**0.05**	**1.9**
	221/2	2.874	2.955	2.660	2.925	3.510	2.888	2.915	**2.961**			
	221/3	2.762	3.182	2.625	2.763	3.198	3.121	2.646	**2.899**			
	221/4	2.801	2.494	2.905	3.190	2.705	2.790	3.072	**2.851**			
15	229/1	2.735	2.886	2.582	3.500	2.892	3.366	3.097	**3.008**	**2.928**	**0.11**	**3.7**
	229/2	2.941	3.208	2.843	3.033	2.907	3.044	3.280	**3.037**			
	229/3	2.837	2.899	2.560	2.813	2.908	3.001	2.845	**2.838**			
	229/4	2.964	2.703	2.919	2.824	3.026	2.668	2.703	**2.830**			
16	253/1	2.813	2.648	2.304	3.566	2.989	3.063	3.267	**2.950**	**2.928**	**0.11**	**3.7**
	253/2	2.961	3.101	2.788	3.010	2.982	2.985	3.522	**3.050**			
	253/3	2.937	3.096	2.538	3.155	2.987	2.914	2.857	**2.926**			
	253/4	3.070	2.608	2.765	2.709	2.543	2.979	2.831	**2.786**			
17	264/1	2.763	2.801	2.895	3.109	2.986	3.132	3.395	**3.011**	**2.932**	**0.11**	**3.6**
	264/2	2.891	3.125	2.830	2.852	2.972	2.744	2.868	**2.897**			
	264/3	3.289	2.700	3.051	3.216	2.806	2.848	3.249	**3.023**			
	264/4	3.165	2.793	2.783	2.738	2.483	2.882	2.740	**2.798**			

Analyt Cr

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
18	279/1	2.818	2.717	2.933	3.226	3.623	3.174	3.485	**3.139**	**3.055**	**0.07**	**2.2**
	279/2	2.628	3.530	2.698	2.974	2.993	3.497	2.748	**3.010**			
	279/3	3.405	2.647	3.066	3.492	2.892	3.156	2.885	**3.078**			
	279/4	3.632	2.951	2.783	2.602	2.696	3.414	2.880	**2.994**			
19.000	294/1	2.738	2.523	2.845	3.537	3.255	2.860	3.841	**3.086**	**2.944**	**0.14**	**4.9**
	294/2	3.013	3.161	2.683	3.029	3.089	2.950	2.747	**2.953**			
	294/3	2.868	2.686	2.724	3.125	3.340	3.013	3.180	**2.991**			
	294/4	2.837	2.618	2.724	2.683	2.782	2.901	2.665	**2.744**			
20.000	307/1	2.701	2.812	3.078	3.634	3.260	2.990	3.082	**3.079**	**2.910**	**0.15**	**5.3**
	307/2	3.050	3.268	2.720	2.791	3.107	2.986	2.658	**2.940**			
	307/3	2.735	2.947	2.808	2.910	2.932	2.927	3.138	**2.914**			
	307/4	2.771	2.653	2.475	2.791	2.734	2.743	2.771	**2.705**			
									M_{Ss} - mean of means of the sub-samples 1-4	**2.971**		
									SD of means of the sub-samples 1-4	**0.064**		
									RSD (rel.%)	**2.143**	**mean RSD_w (%)**	**3.7**

Analyt Cr

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**
1	HS 1	3.090	2.635	3.016	3.045	2.904	3.374	3.274	**3.048**
2	HS 2	2.761	2.651	3.691	3.339	3.865	2.992	3.121	**3.203**
3	HS 3	3.191	2.623	2.579	3.315	3.263	2.976	3.331	**3.040**
4	HS 4	2.703	2.638	2.772	3.218	3.058	3.964	3.276	**3.090**
5	HS 5	2.797	3.871	2.776	3.196	3.369	3.004	3.177	**3.170**
6	HS 6	2.898	2.635	3.027	2.957	3.186	3.116	3.208	**3.004**
7	HS 7	3.074	2.694	3.222	2.780	2.758	2.979	3.085	**2.942**
8	HS 8	3.620	2.517	2.920	2.824	3.231	3.000	4.288	**3.200**
9	HS 9	2.848	3.286	2.719	2.988	3.205	2.761	3.016	**2.975**
10	HS 10	3.068	3.290	2.794	2.995	2.997	2.889	2.993	**3.004**
11	HS 11	3.157	3.195	2.700	2.724	2.904	2.768	2.774	**2.889**
12	HS 12	2.902	2.814	2.998	2.795	2.941	2.833	3.396	**2.954**
13	HS 13	2.896	3.242	2.928	3.062	3.655	3.159	3.669	**3.230**

HS = Homogeneous sample

14	HS 14	2.768	3.954	3.237	2.704	3.003	2.933	2.747	**3.049**
15	HS 15	3.279	2.795	3.399	2.761	2.955	3.112	2.670	**2.996**
16	HS 16	3.086	2.603	2.880	2.636	2.795	2.907	3.046	**2.850**
17	HS 17	3.247	2.935	2.752	3.110	3.046	2.986	2.759	**2.976**
18	HS 18	3.231	2.646	2.798	2.850	2.891	2.898	3.200	**2.931**
19	HS 19	3.100	2.629	3.910	2.576	2.989	2.619	2.741	**2.938**
20	HS 20	2.722	3.412	2.793	2.432	2.875	2.986	2.693	**2.845**
								M_{HS} - mean of homogeneous sample	**3.017**
								SD_{HS}	**0.114**
								RSD_{HS} (%)	**3.774**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.12	M_{Ss} 2.971	RSD % 2.1
standard deviation between the samples s_b	0.13	F_{value}	1.768
test value s_b^2/s_w^2	1.21	Characteristic no. for homogeneity between the samples	0.68
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.11	M_{HS} 3.017	RSD_{HS} (%) 3.8
		F_{value}	1.98
test value s_w^2/s_{HS}^2	1.03	Characteristic no. for homogeneity within the samples	0.52
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of two spectral lines) measured on 7 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Cu

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 2 lines (16.02.00)	mean calculated from 2 lines (21.02.00)	mean calculated from 2 lines (23.02.00)	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	0.933	1.055	1.141	1.034	1.058	1.100	0.967	**1.041**	**1.067**	**0.134**	**12.6**
	2/2	0.931	0.984	2.928	1.035	0.967	0.999	0.995	**1.263**			
	2/3	1.039	1.037	1.013	0.961	0.972	0.946	1.015	**0.997**			
	2/4	0.905	1.036	1.003	1.018	0.945	0.944	0.920	**0.967**			
2	29/1	0.837	0.983	1.058	1.037	1.006	1.044	1.002	**0.995**	**1.001**	**0.022**	**2.2**
	29/2	0.962	1.023	0.973	1.092	0.970	1.040	1.082	**1.021**			
	29/3	0.866	0.959	1.079	1.022	1.003	0.896	0.978	**0.972**			
	29/4	0.875	1.457	0.929	0.990	0.969	0.959	0.924	**1.015**			
3	35/1	0.931	0.919	1.010	1.037	1.006	1.044	1.002	**0.993**	**0.974**	**0.017**	**1.7**
	35/2	0.871	0.934	0.977	0.984	0.948	1.024	0.927	**0.952**			
	35/3	0.902	0.944	0.969	0.965	1.127	1.009	0.930	**0.978**			
	35/4	1.024	0.960	0.927	0.977	0.961	1.004	0.950	**0.972**			
4	56/1	0.914	0.977	0.983	1.031	0.980	1.105	0.903	**0.985**	**0.978**	**0.006**	**0.6**
	56/2	0.941	0.972	0.927	1.064	0.975	0.981	0.975	**0.976**			
	56/3	0.881	0.925	0.920	1.064	1.098	1.000	0.984	**0.982**			
	56/4	0.911	0.934	0.965	0.950	1.055	1.006	0.973	**0.971**			
5	76/1	0.858	0.933	0.994	0.999	1.010	0.940	1.024	**0.965**	**0.995**	**0.031**	**3.2**
	76/2	0.965	1.009	1.267	0.968	0.974	1.037	1.051	**1.039**			
	76/3	0.888	0.941	1.048	0.926	1.009	1.017	1.049	**0.983**			
	76/4	0.938	1.002	0.901	1.083	1.002	1.035	0.984	**0.992**			
6	90/1	0.952	1.027	1.033	1.053	0.965	1.017	0.961	**1.001**	**1.014**	**0.036**	**3.5**
	90/2	0.897	0.952	1.505	1.026	0.968	1.018	1.068	**1.062**			
	90/3	0.852	0.972	1.115	0.982	0.977	0.985	0.955	**0.977**			
	90/4	0.990	0.983	1.062	0.963	1.149	1.018	0.957	**1.017**			
7	108/1	0.868	0.978	0.970	1.000	0.998	1.004	0.971	**0.970**	**0.975**	**0.026**	**2.7**
	108/2	0.987	1.012	1.113	0.933	1.014	0.967	1.054	**1.011**			
	108/3	0.932	0.933	1.001	0.937	0.929	0.975	0.937	**0.949**			
	108/4	0.948	0.949	0.911	1.010	1.039	0.945	0.986	**0.970**			
8	128/1	0.864	0.996	1.004	1.078	1.078	1.151	1.041	**1.030**	**1.000**	**0.032**	**3.2**
	128/2	1.026	0.969	1.078	0.995	1.085	1.018	0.989	**1.023**			
	128/3	0.917	0.970	0.968	1.005	0.985	0.969	0.933	**0.964**			
	128/4	0.958	0.927	0.978	1.074	0.999	0.996	0.949	**0.983**			

Analyt Cu

Serial number	Sample number	mean calculated from 2 lines (16.02.00)	mean calculated from 2 lines (21.02.00)	mean calculated from 2 lines (23.02.00)	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD (rel.%)**
8	128/1	0.864	0.996	1.004	1.078	1.078	1.151	1.041	**1.030**	**1.000**	**0.032**	**3.2**
	128/2	1.026	0.969	1.078	0.995	1.085	1.018	0.989	**1.023**			
	128/3	0.917	0.970	0.968	1.005	0.985	0.969	0.933	**0.964**			
	128/4	0.958	0.927	0.978	1.074	0.999	0.996	0.949	**0.983**			
9	132/1	0.927	1.033	0.970	1.061	1.562	0.994	0.953	**1.072**	**1.057**	**0.085**	**8.1**
	132/2	1.016	1.391	1.595	0.952	0.792	0.918	0.979	**1.092**			
	132/3	1.028	0.950	1.867	0.930	1.023	1.003	1.104	**1.129**			
	132/4	0.834	0.950	0.930	0.922	0.980	0.986	0.936	**0.934**			
10	156/1	1.007	0.930	0.873	0.937	0.979	1.027	0.935	**0.956**	**0.976**	**0.031**	**3.1**
	156/2	0.917	1.051	1.107	0.988	0.971	0.934	1.002	**0.996**			
	156/3	0.854	1.001	1.158	0.999	1.000	1.049	0.989	**1.007**			
	156/4	0.835	0.952	0.948	0.926	0.991	0.997	0.960	**0.944**			
11	164/1	0.862	0.986	0.977	0.980	1.116	1.053	1.044	**1.003**	**0.996**	**0.035**	**3.5**
	164/2	0.890	1.020	1.004	1.005	1.003	1.063	1.078	**1.009**			
	164/3	0.910	0.957	0.918	0.975	0.954	0.958	0.957	**0.947**			
	164/4	0.973	1.229	0.933	1.004	0.969	1.012	1.073	**1.028**			
12	188/1	0.908	0.959	0.896	1.029	1.038	0.986	1.043	**0.980**	**1.002**	**0.047**	**4.6**
	188/2	0.994	1.000	1.019	1.007	0.965	1.085	1.081	**1.022**			
	188/3	0.831	0.976	0.929	1.026	0.993	0.921	0.973	**0.950**			
	188/4	0.864	1.439	0.908	1.036	1.062	0.944	1.140	**1.056**			
13	195/1	0.844	1.009	0.918	0.980	1.126	1.031	1.051	**0.994**	**1.003**	**0.014**	**1.4**
	195/2	0.949	1.240	0.996	0.981	1.050	0.978	0.943	**1.020**			
	195/3	0.993	1.005	0.940	0.997	0.964	1.071	0.959	**0.990**			
	195/4	1.025	1.107	1.047	0.928	0.948	1.022	0.993	**1.010**			
14	221/1	0.868	0.938	0.955	1.022	0.962	1.095	0.945	**0.970**	**0.980**	**0.012**	**1.2**
	221/2	0.907	0.981	0.983	0.925	1.138	0.914	0.981	**0.975**			
	221/3	0.915	0.942	1.007	1.017	1.003	0.966	0.991	**0.977**			
	221/4	1.209	0.951	0.928	0.964	0.936	1.000	0.988	**0.996**			
15	229/1	0.852	1.086	0.916	1.106	1.020	0.914	0.925	**0.974**	**0.988**	**0.032**	**3.2**
	229/2	1.015	0.958	1.033	0.980	1.059	1.050	0.974	**1.010**			
	229/3	0.943	1.012	1.045	1.059	1.041	0.963	1.058	**1.017**			
	229/4	0.913	0.956	0.922	0.981	0.964	0.925	0.983	**0.949**			
16	253/1	0.910	1.016	0.898	1.004	0.993	0.985	0.994	**0.971**	**0.993**	**0.031**	**3.1**
	253/2	1.021	1.100	0.949	0.990	0.977	0.933	0.939	**0.987**			
	253/3	0.931	0.982	0.973	1.000	0.994	0.992	0.947	**0.974**			
	253/4	0.853	1.386	0.969	1.020	1.071	0.998	0.965	**1.037**			
17	264/1	1.002	0.975	1.006	0.998	0.976	1.035	1.017	**1.001**	**0.989**	**0.019**	**1.9**
	264/2	0.954	1.005	1.010	0.905	0.948	0.991	1.002	**0.974**			
	264/3	0.846	0.950	1.043	1.024	1.000	0.946	1.000	**0.973**			
	264/4	1.003	1.046	0.980	1.005	0.943	0.989	1.093	**1.008**			

Analyt Cu

Serial number	Sample number	mean calculated from 2 lines (16.02.00)	mean calculated from 2 lines (21.02.00)	mean calculated from 2 lines (23.02.00)	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD (rel.%)**
18	279/1	0.964	0.936	0.984	1.044	0.985	1.078	1.009	**1.000**	**0.985**	**0.016**	**1.6**
	279/2	0.940	0.975	0.930	0.935	0.964	0.955	1.037	**0.962**			
	279/3	0.871	0.997	0.909	1.178	1.053	0.941	0.984	**0.990**			
	279/4	0.914	0.956	1.110	0.961	0.953	1.061	0.968	**0.989**			
19	294/1	0.998	0.988	2.922	0.945	1.001	0.994	0.982	**1.261**	**1.059**	**0.135**	**12.8**
	294/2	0.838	1.249	0.914	0.996	0.994	0.948	1.057	**0.999**			
	294/3	0.919	1.264	0.920	0.926	0.959	0.985	1.010	**0.998**			
	294/4	0.990	0.936	0.903	1.040	0.971	1.044	0.958	**0.978**			
20	307/1	0.978	1.039	1.593	0.997	0.958	0.911	1.019	**1.071**	**1.012**	**0.046**	**4.6**
	307/2	0.924	1.204	0.934	0.934	1.062	0.980	1.049	**1.012**			
	307/3	0.951	0.925	0.955	1.003	1.022	0.982	1.226	**1.009**			
	307/4	0.915	0.910	0.937	1.017	0.956	0.947	1.020	**0.957**			

M_{Ss} - mean of means of sub-samples 1-4	**1.002**
SD of means of the sub-samples 1-4	**0.028**
RSD (rel.%)	**2.790**
mean RSD_w (%)	**3.9**

Analyt Cu

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 2 lines (16.02.00)	mean calculated from 2 lines (21.02.00)	mean calculated from 2 lines (23.02.00)	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**
1	HS 1	0.956	0.968	1.024	0.986	1.012	1.035	0.902	**0.983**
2	HS 2	0.878	0.951	0.947	1.093	1.183	1.069	1.048	**1.024**
3	HS 3	0.934	0.902	1.110	1.000	0.981	1.028	0.952	**0.987**
4	HS 4	0.961	0.934	0.917	1.007	1.020	1.113	0.955	**0.987**
5	HS 5	0.848	1.105	1.014	0.970	1.003	0.966	1.002	**0.987**
6	HS 6	0.933	0.968	0.987	1.025	0.988	1.041	0.975	**0.988**
7	HS 7	0.892	0.966	1.070	0.996	0.898	0.994	0.963	**0.968**
8	HS 8	0.968	1.394	1.010	0.968	1.028	0.983	1.371	**1.103**
9	HS 9	0.999	0.976	0.979	1.076	1.030	1.018	0.939	**1.002**
10	HS 10	1.124	0.963	0.924	0.955	1.016	1.008	0.937	**0.989**
11	HS 11	0.893	1.010	0.927	0.962	0.996	0.945	0.953	**0.955**
12	HS 12	0.904	0.954	1.046	0.932	0.967	0.931	1.562	**1.042**
13	HS 13	0.863	0.952	0.909	0.965	1.168	0.987	1.224	**1.010**

HS = Homogeneous sample

14	HS 14	0.930	1.000	0.915	1.025	1.087	1.013	0.997	**0.995**
15	HS 15	0.932	1.018	0.973	0.983	0.979	1.006	1.100	**0.999**
16	HS 16	1.202	0.934	0.931	0.969	0.962	0.970	1.002	**0.996**
17	HS 17	1.521	0.989	1.045	0.933	0.995	0.964	0.948	**1.056**
18	HS 18	0.866	0.940	0.958	0.961	1.018	1.017	0.948	**0.958**
19	HS 19	0.947	0.979	1.009	0.995	0.967	0.993	1.011	**0.986**
20	HS 20	0.916	0.973	1.014	1.077	0.971	1.031	0.953	**0.991**

M_{HS} - mean of homogeneous sample	**1.000**
SD_{HS}	**0.034**
RSD_{HS} (%)	**3.4**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.05	M_{Ss} 1.002	RSD % 2.8
standard deviation between the samples s_b	0.06	F_{value}	1.768
test value s_b^2/s_w^2	1.09	Characteristic no. for homogeneity between the samples	0.61
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.03	M_{HS} 1.000	RSD_{HS} (%) 3.4
		F_{value}	1.98
test value s_w^2/s_{HS}^2	2.44	Characteristic no. for homogeneity within the samples	1.23
Homogeneity within the samples: Significant not very strong inhomogeneity			

ETV ICP OES-results (means of 3 spectral lines) measured on 4 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Fe

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD$_w$ (rel.%)**
1	2/1	171.765	164.446	163.633	160.894	**165.2**	**160.9**	**3.8**	**2.4**
	2/2	155.474	158.687	156.403	165.963	**159.1**			
	2/3	166.957	161.354	162.461	160.069	**162.7**			
	2/4	163.843	152.384	157.159	152.721	**156.5**			
2	29/1	170.087	161.300	164.764	153.908	**162.5**	**156.4**	**6.4**	**4.1**
	29/2	162.238	157.103	164.627	160.200	**161.0**			
	29/3	156.294	150.516	149.211	140.875	**149.2**			
	29/4	158.533	151.534	151.872	148.601	**152.6**			
3	35/1	158.696	160.611	171.778	163.621	**163.7**	**160.8**	**3.3**	**2.0**
	35/2	163.075	165.411	159.554	165.798	**163.5**			
	35/3	167.354	156.393	157.094	148.505	**157.3**			
	35/4	156.864	159.436	157.407	160.454	**158.5**			
4	56/1	168.424	156.648	158.125	159.040	**160.6**	**160.7**	**1.5**	**1.0**
	56/2	160.891	161.304	160.898	164.046	**161.8**			
	56/3	152.371	166.644	162.919	152.485	**158.6**			
	56/4	173.086	160.676	162.877	151.131	**161.9**			
5	76/1	166.858	166.387	156.642	157.460	**161.8**	**160.8**	**4.6**	**2.8**
	76/2	160.827	167.473	161.358	172.411	**165.5**			
	76/3	149.401	168.546	150.645	149.534	**154.5**			
	76/4	161.141	158.887	162.631	162.545	**161.3**			
6	90/1	163.652	165.131	165.399	156.511	**162.7**	**162.8**	**2.1**	**1.3**
	90/2	159.766	155.371	153.346	173.187	**160.4**			
	90/3	161.257	161.097	174.584	165.024	**165.5**			
	90/4	158.533	168.867	166.902	156.411	**162.7**			
7	108/1	162.681	163.086	164.277	162.632	**163.2**	**160.5**	**3.4**	**2.1**
	108/2	163.514	160.687	159.973	171.189	**163.8**			
	108/3	158.534	163.117	155.064	154.382	**157.8**			
	108/4	161.925	158.857	158.255	150.382	**157.4**			
8	128/1	168.840	161.968	159.993	157.275	**162.0**	**159.3**	**2.7**	**1.7**
	128/2	155.056	165.455	162.091	160.045	**160.7**			
	128/3	160.426	157.446	150.755	154.977	**155.9**			
	128/4	155.685	165.816	160.368	152.375	**158.6**			

Analyt Fe

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD (rel.%)**
7	108/1	162.681	163.086	164.277	162.632	**163.2**	**160.5**	**3.4**	**2.1**
	108/2	163.514	160.687	159.973	171.189	**163.8**			
	108/3	158.534	163.117	155.064	154.382	**157.8**			
	108/4	161.925	158.857	158.255	150.382	**157.4**			
8	128/1	168.840	161.968	159.993	157.275	**162.0**	**159.3**	**2.7**	**1.7**
	128/2	155.056	165.455	162.091	160.045	**160.7**			
	128/3	160.426	157.446	150.755	154.977	**155.9**			
	128/4	155.685	165.816	160.368	152.375	**158.6**			
9	132/1	168.415	168.944	162.079	168.995	**167.1**	**159.5**	**5.4**	**3.4**
	132/2	155.857	152.680	154.965	163.681	**156.8**			
	132/3	161.033	164.722	162.634	148.437	**159.2**			
	132/4	148.366	155.375	162.572	153.042	**154.8**			
10	156/1	156.092	166.822	156.519	162.796	**160.6**	**159.0**	**1.1**	**0.7**
	156/2	158.182	157.896	159.017	159.367	**158.6**			
	156/3	158.910	161.060	155.975	156.812	**158.2**			
	156/4	162.220	158.023	154.850	159.277	**158.6**			
11	164/1	155.986	164.487	165.033	162.904	**162.1**	**159.6**	**2.1**	**1.3**
	164/2	157.987	158.106	156.558	167.726	**160.1**			
	164/3	162.359	162.774	151.102	152.371	**157.2**			
	164/4	155.803	157.914	158.737	164.122	**159.1**			
12	188/1	149.520	165.168	155.213	165.154	**158.8**	**157.4**	**1.3**	**0.8**
	188/2	160.883	151.185	159.009	161.354	**158.1**			
	188/3	150.756	157.103	163.399	151.433	**155.7**			
	188/4	163.058	160.028	153.124	152.695	**157.2**			
13	195/1	158.311	164.582	171.242	156.668	**162.7**	**159.7**	**2.1**	**1.3**
	195/2	152.973	163.142	160.024	154.756	**157.7**			
	195/3	166.326	149.227	159.163	161.541	**159.1**			
	195/4	159.525	154.476	154.458	168.337	**159.2**			
14	221/1	156.543	164.018	169.788	151.922	**160.6**	**157.7**	**2.4**	**1.5**
	221/2	147.313	161.556	147.304	165.274	**155.4**			
	221/3	148.276	158.372	159.971	158.366	**156.2**			
	221/4	165.529	155.816	159.086	154.686	**158.8**			
15	229/1	157.750	161.082	166.947	159.270	**161.3**	**158.3**	**2.7**	**1.7**
	229/2	151.159	154.063	158.466	158.531	**155.6**			
	229/3	159.199	157.921	157.746	163.908	**159.7**			
	229/4	153.607	160.141	150.737	161.717	**156.6**			
16	253/1	156.892	160.275	167.979	153.739	**159.7**	**158.7**	**2.3**	**1.4**
	253/2	163.532	160.303	156.835	155.654	**159.1**			
	253/3	158.643	153.669	168.266	162.096	**160.7**			
	253/4	163.019	155.834	147.854	155.199	**155.5**			

Analyt Fe

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD (rel.%)**
17	264/1	167.475	163.090	164.563	168.105	**165.8**	**159.9**	**5.7**	**3.6**
	264/2	143.379	156.118	161.590	152.490	**153.4**			
	264/3	165.787	160.838	164.788	162.803	**163.6**			
	264/4	163.189	153.513	159.982	151.240	**157.0**			
18	279/1	153.819	160.964	155.767	168.635	**159.8**	**157.0**	**3.9**	**2.5**
	279/2	157.001	159.859	157.983	166.313	**160.3**			
	279/3	145.307	153.118	151.033	158.235	**151.9**			
	279/4	160.105	161.997	144.622	157.603	**156.1**			
19	294/1	161.305	155.988	155.802	157.376	**157.6**	**158.0**	**2.7**	**1.7**
	294/2	162.013	163.108	156.800	164.856	**161.7**			
	294/3	151.299	149.872	156.415	173.445	**157.8**			
	294/4	157.883	153.569	157.292	151.458	**155.1**			
20	307/1	158.471	154.360	160.587	159.453	**158.2**	**157.8**	**2.3**	**1.5**
	307/2	155.424	157.050	154.254	161.000	**156.9**			
	307/3	159.752	159.358	158.903	165.032	**160.8**			
	307/4	160.699	155.873	151.769	152.434	**155.2**			

M_{Ss} - mean of means of the sub-samples 1-4	**159.1**
SD of means of the sub-samples 1-4	**1.6**
RSD (rel.%)	**1.0**

mean RSD_w (%)	**1.9**

Analyt Fe

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**
1	HS 1	164.585	165.699	158.600	154.857	**160.9**
2	HS 2	166.950	162.163	163.785	159.090	**163.0**
3	HS 3	158.588	158.824	169.264	158.613	**161.3**
4	HS 4	154.658	163.140	165.678	158.040	**160.4**
5	HS 5	158.509	158.346	159.972	169.602	**161.6**
6	HS 6	156.396	159.127	163.222	164.399	**160.8**
7	HS 7	160.893	152.456	160.854	159.070	**158.3**
8	HS 8	157.712	167.247	150.611	156.095	**157.9**

HS = Homogeneous sample

9	HS 9	154.603	166.408	152.023	174.502	**161.9**
10	HS 10	164.460	159.821	163.169	159.632	**161.8**
11	HS 11	159.590	162.147	162.692	161.978	**161.6**
12	HS 12	151.455	161.528	155.022	159.801	**157.0**
13	HS 13	157.140	162.778	167.087	154.076	**160.3**
14	HS 14	159.493	160.262	164.100	155.766	**159.9**
15	HS 15	159.151	164.393	158.964	161.778	**161.1**
16	HS 16	158.843	160.546	160.376	151.054	**157.7**
17	HS 17	156.678	158.500	157.632	157.086	**157.5**
18	HS 18	153.736	155.120	162.041	160.137	**157.8**
19	HS 19	159.129	161.368	160.094	154.561	**158.8**
20	HS 20	157.238	157.920	154.234	157.402	**156.7**
					M_{HS} - mean of homogeneous sample	**159.8**
					SD_{HS}	**1.9**
					RSD_{HS} (%)	**1.2**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	3.4	M_{Ss} 159.1	RSD % 1.0
standard deviation between the samples s_b	3.2	F_{value}	1.768
test value s_b^2/s_w^2	0.88	Characteristic no. for homogeneity between the samples	0.50
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	1.9	M_{HS} 159.8	RSD_{HS} % 1.2
		F_{value}	1.98
test value s_w^2/s_{HS}^2	3.16	Characteristic no. for homogeneity within the samples	1.59
Homogeneity within the samples: Significant not very strong inhomogeneity			

ETV ICP OES-results (one spectral line) measured on 4 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Mg

mass fraction in mg/kg

Serial number	Sample number	1 line (02.06.01)	1 line (06.06.01)	1 line (12.06.01)	1 line (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	6.140	6.122	7.229	6.233	**6.431**	**6.101**	**0.24**	**3.9**
	2/2	6.123	6.184	6.145	5.590	**6.011**			
	2/3	5.914	6.267	6.081	6.079	**6.085**			
	2/4	5.934	5.850	6.026	5.693	**5.875**			
2	29/1	6.052	6.851	5.982	6.099	**6.246**	**5.985**	**0.18**	**3.0**
	29/2	5.713	5.908	5.988	5.787	**5.849**			
	29/3	6.102	6.064	5.688	5.869	**5.931**			
	29/4	6.077	6.045	5.762	5.765	**5.912**			
3	35/1	5.848	6.044	5.875	7.129	**6.224**	**6.041**	**0.13**	**2.1**
	35/2	5.982	6.030	5.962	5.827	**5.950**			
	35/3	5.953	6.023	5.933	6.260	**6.042**			
	35/4	6.059	5.722	6.122	5.886	**5.947**			
4	56/1	5.987	5.920	6.223	5.723	**5.963**	**6.045**	**0.11**	**1.9**
	56/2	6.013	6.049	6.055	6.048	**6.041**			
	56/3	6.043	6.503	6.122	6.167	**6.209**			
	56/4	6.100	6.068	6.084	5.615	**5.967**			
5	76/1	5.799	5.853	6.042	5.993	**5.922**	**6.000**	**0.05**	**0.9**
	76/2	5.820	5.986	6.050	6.180	**6.009**			
	76/3	5.923	6.215	6.075	5.905	**6.030**			
	76/4	6.042	6.141	5.967	6.006	**6.039**			
6	90/1	6.513	6.101	5.954	6.097	**6.166**	**6.051**	**0.08**	**1.4**
	90/2	5.974	5.953	6.118	6.047	**6.023**			
	90/3	5.895	5.873	6.231	5.901	**5.975**			
	90/4	5.970	6.096	6.202	5.883	**6.038**			
7	108/1	6.152	5.967	5.999	6.196	**6.079**	**6.069**	**0.05**	**0.8**
	108/2	5.990	6.013	6.274	6.201	**6.120**			
	108/3	5.801	6.003	6.296	5.926	**6.007**			
	108/4	5.942	5.988	6.260	6.093	**6.071**			
8	128/1	5.803	6.368	5.993	6.458	**6.155**	**6.067**	**0.07**	**1.1**
	128/2	6.020	6.051	6.030	6.184	**6.071**			
	128/3	6.039	5.977	5.785	6.192	**5.998**			
	128/4	6.007	5.891	6.378	5.899	**6.044**			

Analyt Mg

Serial number	Sample number	1 line (02.06.01)	1 line (06.06.01)	1 line (12.06.01)	1 line (30.05.01)	mean	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
9	132/1	6.306	5.977	6.185	5.965	**6.108**	**6.002**	**0.13**	**2.2**
	132/2	5.899	6.382	5.794	6.254	**6.083**			
	132/3	6.259	6.123	5.955	5.658	**5.999**			
	132/4	5.565	5.733	6.019	5.963	**5.820**			
10	156/1	5.933	6.351	6.188	5.791	**6.066**	**6.038**	**0.05**	**0.8**
	156/2	5.805	6.110	5.716	6.287	**5.980**			
	156/3	6.031	6.310	5.914	5.827	**6.020**			
	156/4	6.019	6.116	6.129	6.085	**6.087**			
11	164/1	6.017	6.033	6.355	6.078	**6.120**	**6.114**	**0.13**	**2.1**
	164/2	6.112	6.175	6.048	6.197	**6.133**			
	164/3	5.924	5.954	5.894	6.014	**5.947**			
	164/4	6.162	5.866	6.060	6.930	**6.254**			
12	188/1	6.154	5.926	5.715	6.184	**5.995**	**5.978**	**0.07**	**1.2**
	188/2	5.791	6.010	5.982	5.981	**5.941**			
	188/3	6.074	5.991	5.975	5.582	**5.906**			
	188/4	6.112	6.073	5.853	6.245	**6.071**			
13	195/1	5.991	6.027	6.177	5.696	**5.973**	**6.010**	**0.06**	**0.9**
	195/2	5.750	6.058	6.075	6.119	**6.000**			
	195/3	6.183	5.951	6.088	6.146	**6.092**			
	195/4	6.017	6.159	5.661	6.067	**5.976**			
14	221/1	6.216	5.996	6.157	5.802	**6.043**	**6.057**	**0.06**	**0.9**
	221/2	6.052	5.880	6.009	6.058	**6.000**			
	221/3	6.157	5.923	6.030	6.090	**6.050**			
	221/4	6.015	6.162	6.115	6.252	**6.136**			
15	229/1	5.969	6.000	5.769	5.780	**5.879**	**5.934**	**0.04**	**0.7**
	229/2	5.889	5.882	6.218	5.728	**5.929**			
	229/3	5.777	6.170	6.183	5.669	**5.950**			
	229/4	5.980	6.049	5.913	5.966	**5.977**			
16	253/1	6.065	5.941	6.051	5.956	**6.003**	**5.974**	**0.08**	**1.3**
	253/2	5.981	5.866	5.789	5.804	**5.860**			
	253/3	5.907	6.096	6.000	6.060	**6.016**			
	253/4	6.057	6.239	5.872	5.903	**6.018**			
17	264/1	5.779	6.143	5.771	5.678	**5.842**	**6.040**	**0.14**	**2.3**
	264/2	6.051	5.943	6.310	5.908	**6.053**			
	264/3	6.419	5.731	6.041	6.235	**6.106**			
	264/4	6.528	5.983	6.032	6.094	**6.159**			
18	279/1	6.178	5.978	5.760	5.800	**5.929**	**5.951**	**0.02**	**0.4**
	279/2	5.797	5.882	6.020	6.032	**5.932**			
	279/3	5.971	6.255	5.849	5.821	**5.974**			
	279/4	6.092	5.986	5.726	6.073	**5.969**			

Analyt Mg

Serial number	Sample number	1 line (02.06.01)	1 line (06.06.01)	1 line (12.06.01)	1 line (30.05.01)	mean	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
19	294/1	5.992	5.878	5.966	5.457	**5.823**	**5.965**	**0.13**	**2.1**
	294/2	5.810	5.979	6.285	6.339	**6.103**			
	294/3	6.148	6.111	6.026	5.835	**6.030**			
	294/4	6.079	5.796	6.122	5.614	**5.903**			
20	307/1	6.064	5.868	6.197	5.983	**6.028**	**6.043**	**0.10**	**1.7**
	307/2	5.983	5.820	5.834	6.074	**5.928**			
	307/3	5.980	6.348	6.126	6.260	**6.178**			
	307/4	5.735	6.135	6.235	6.045	**6.038**			

M_{Ss} - mean of means of the sub-samples 1-4	**6.023**
SD of means of the sub-samples 1-4	**0.049**
RSD (rel.%)	**0.8**

mean RSD_w (%) **1.6**

Analyt Mg

HS = Homogeneous sample

Serial number	Sample number	1 line (02.06.01)	1 line (06.06.01)	1 line (12.06.01)	1 line (30.05.01)	mean
1	HS 1	5.886	5.807	5.931	5.785	**5.852**
2	HS 2	5.896	5.714	5.442	6.451	**5.876**
3	HS 3	5.611	5.832	6.297	5.943	**5.921**
4	HS 4	6.240	5.837	6.655	6.011	**6.186**
5	HS 5	5.863	5.948	5.559	6.169	**5.885**
6	HS 6	5.705	5.953	5.829	5.946	**5.858**
7	HS 7	5.769	5.633	5.853	6.503	**5.940**
8	HS 8	5.947	5.978	6.068	6.947	**6.235**
9	HS 9	6.272	6.044	6.011	5.990	**6.079**
10	HS 10	5.849	5.750	5.921	6.062	**5.895**
11	HS 11	5.868	5.851	5.990	6.089	**5.950**
12	HS 12	6.226	5.859	5.571	5.793	**5.862**
13	HS 13	5.918	6.147	5.913	5.315	**5.823**
14	HS 14	6.289	6.185	6.153	5.834	**6.115**
15	HS 15	6.073	6.170	5.847	5.742	**5.958**
16	HS 16	6.143	5.811	5.695	6.170	**5.955**

HS = Homogeneous sample

17	HS 17	5.838	5.702	5.871	5.844	**5.814**
18	HS 18	5.763	5.664	6.386	5.833	**5.911**
19	HS 19	6.139	5.686	5.797	6.116	**5.934**
20	HS 20	5.939	6.018	5.912	6.115	**5.996**

M_{HS} - mean of homogeneous sample	**5.952**
SD_{HS}	**0.117**
RSD_{HS} (%)	**2.0**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.108	M_{Ss} 6.023	RSD % 0.8
standard deviation between the samples s_b	0.098	F_{value}	1.768
test value s_b^2/s_w^2	0.817	Characteristic no. for homogeneity between the samples	0.462
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.117	M_{HS} 5.952	RSD_{HS} % 2.0
		F_{value}	1.98
test value s_w^2/s_{HS}^2	0.862	Characteristic no. for homogeneity within the samples	0.435
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of 3 spectral lines) measured on 4 different days.

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Ni

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	39.820	41.526	40.575	41.553	**40.87**	**39.86**	**0.7**	**1.9**
	2/2	40.755	39.258	38.669	40.993	**39.92**			
	2/3	38.319	38.925	40.255	40.654	**39.54**			
	2/4	40.183	39.036	38.197	39.029	**39.11**			
2	29/1	40.087	40.756	38.845	38.918	**39.65**	**39.62**	**1.1**	**2.8**
	29/2	43.110	39.617	42.026	39.015	**40.94**			
	29/3	39.294	40.608	36.530	36.434	**38.22**			
	29/4	40.027	40.824	40.299	37.509	**39.66**			
3	35/1	39.969	41.992	41.355	40.277	**40.90**	**40.31**	**0.8**	**2.0**
	35/2	38.581	40.319	39.532	39.356	**39.45**			
	35/3	42.553	38.855	37.883	40.092	**39.85**			
	35/4	41.946	40.208	40.989	41.074	**41.05**			
4	56/1	38.686	39.224	40.838	37.668	**39.10**	**40.42**	**1.0**	**2.4**
	56/2	41.325	40.524	40.896	40.563	**40.83**			
	56/3	40.699	41.134	40.675	43.106	**41.40**			
	56/4	40.542	40.093	40.416	40.284	**40.33**			
5	76/1	38.452	40.216	38.863	40.457	**39.50**	**39.87**	**0.8**	**2.0**
	76/2	39.023	40.198	40.385	40.970	**40.14**			
	76/3	39.009	41.367	37.258	38.323	**38.99**			
	76/4	38.932	40.165	42.823	41.444	**40.84**			
6	90/1	39.079	41.039	40.310	39.205	**39.91**	**40.96**	**0.8**	**1.9**
	90/2	41.801	40.204	39.707	42.468	**41.05**			
	90/3	40.541	41.552	43.203	41.911	**41.80**			
	90/4	40.384	43.688	41.260	38.982	**41.08**			
7	108/1	40.481	39.261	41.993	39.936	**40.42**	**40.30**	**0.4**	**1.0**
	108/2	37.659	39.220	40.498	41.898	**39.82**			
	108/3	40.983	40.409	39.501	39.888	**40.20**			
	108/4	41.321	41.768	41.620	38.439	**40.79**			
8	128/1	40.701	39.384	38.643	41.563	**40.07**	**40.31**	**0.4**	**0.9**
	128/2	40.756	39.837	41.135	38.419	**40.04**			
	128/3	40.254	41.162	40.209	39.539	**40.29**			
	128/4	40.987	39.739	42.039	40.526	**40.82**			

Analyt Ni

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	132/1	43.099	40.671	37.817	39.583	**40.29**	**39.41**	**0.8**	**2.0**
	132/2	38.893	42.296	38.030	39.641	**39.71**			
	132/3	41.752	40.074	39.660	35.182	**39.17**			
	132/4	38.100	39.450	39.633	36.686	**38.47**			
10	156/1	39.002	40.717	39.389	39.467	**39.64**	**39.85**	**0.2**	**0.5**
	156/2	36.670	40.889	39.962	42.765	**40.07**			
	156/3	40.311	41.072	39.922	38.607	**39.98**			
	156/4	39.453	39.991	40.501	38.901	**39.71**			
11	164/1	39.951	39.078	41.713	41.475	**40.55**	**40.04**	**0.5**	**1.3**
	164/2	38.053	39.330	38.628	41.432	**39.36**			
	164/3	42.108	40.361	37.612	40.794	**40.22**			
	164/4	39.917	39.716	41.797	38.602	**40.01**			
12	188/1	37.404	39.616	40.158	40.527	**39.43**	**39.52**	**0.5**	**1.3**
	188/2	39.203	39.436	40.443	39.860	**39.74**			
	188/3	37.730	38.916	38.067	40.709	**38.86**			
	188/4	41.347	39.410	39.343	40.203	**40.08**			
13	195/1	39.589	41.775	41.942	40.838	**41.04**	**39.78**	**0.9**	**2.2**
	195/2	38.790	40.126	39.393	37.971	**39.07**			
	195/3	40.291	39.684	39.380	39.385	**39.68**			
	195/4	38.624	39.397	37.033	42.250	**39.33**			
14	221/1	40.346	37.740	40.426	37.589	**39.02**	**39.27**	**0.3**	**0.8**
	221/2	37.699	39.443	38.127	40.690	**38.99**			
	221/3	40.583	39.569	40.630	37.884	**39.67**			
	221/4	40.059	39.036	39.558	38.920	**39.39**			
15	229/1	40.227	39.285	39.054	39.756	**39.58**	**39.59**	**0.7**	**1.8**
	229/2	40.298	39.530	41.395	40.720	**40.49**			
	229/3	39.387	37.240	39.862	38.487	**38.74**			
	229/4	39.368	38.443	38.253	42.115	**39.54**			
16	253/1	40.132	40.474	41.812	39.520	**40.48**	**40.23**	**1.0**	**2.5**
	253/2	38.172	40.692	37.323	39.876	**39.02**			
	253/3	42.838	39.299	43.732	39.893	**41.44**			
	253/4	41.809	40.383	37.176	40.612	**39.99**			
17	264/1	39.183	40.443	39.999	40.100	**39.93**	**39.60**	**0.4**	**1.1**
	264/2	38.719	39.919	39.759	38.275	**39.17**			
	264/3	39.850	39.734	39.773	40.572	**39.98**			
	264/4	39.833	39.607	38.634	39.120	**39.30**			
18	279/1	41.822	42.154	37.576	37.843	**39.85**	**40.08**	**0.6**	**1.6**
	279/2	38.857	40.364	41.456	41.393	**40.52**			
	279/3	40.204	38.223	38.029	40.715	**39.29**			
	279/4	40.679	42.277	38.913	40.761	**40.66**			

Analyt Ni

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
19	294/1	41.578	40.901	36.303	43.384	**40.54**	**40.02**	**0.4**	**1.1**
	294/2	38.972	39.867	37.768	43.565	**40.04**			
	294/3	37.380	39.088	41.122	40.387	**39.49**			
	294/4	42.186	39.398	41.288	37.102	**39.99**			
20	307/1	42.275	37.944	38.463	40.973	**39.91**	**40.13**	**0.6**	**1.6**
	307/2	39.508	40.862	38.424	39.807	**39.65**			
	307/3	42.265	40.281	40.161	41.580	**41.07**			
	307/4	40.035	39.770	40.274	39.423	**39.88**			

M_{Ss} - mean of means of the sub-samples 1-4	**39.96**
SD of means of the subsamples 1-4	**0.40**
RSD (rel.%)	**1.0**
mean RSD_w (%)	**1.6**

Analyt Ni

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**
1	HS 1	40.061	38.368	43.647	38.836	**40.23**
2	HS 2	38.255	40.176	39.335	39.646	**39.35**
3	HS 3	38.961	38.419	41.885	39.441	**39.68**
4	HS 4	39.705	37.218	40.814	40.275	**39.50**
5	HS 5	40.483	37.846	38.795	41.742	**39.72**
6	HS 6	38.652	40.065	42.258	38.722	**39.92**
7	HS 7	41.758	37.915	43.086	40.729	**40.87**
8	HS 8	39.062	40.028	40.705	40.811	**40.15**
9	HS 9	38.641	41.163	39.125	40.947	**39.97**
10	HS 10	39.405	39.350	41.794	39.876	**40.11**
11	HS 11	39.236	41.106	38.622	41.933	**40.22**
12	HS 12	37.299	39.694	38.183	43.069	**39.56**
13	HS 13	40.585	42.837	41.221	37.896	**40.63**
14	HS 14	40.029	40.149	40.947	39.586	**40.18**
15	HS 15	41.167	41.486	38.212	40.679	**40.39**

HS = Homogeneous sample

16	HS 16	38.152	41.376	39.403	38.909	**39.46**
17	HS 17	39.432	42.564	40.892	39.768	**40.66**
18	HS 18	38.145	38.871	39.529	40.145	**39.17**
19	HS 19	40.209	41.008	41.435	38.806	**40.36**
20	HS 20	41.760	41.248	40.558	40.420	**41.00**
					M_{HS} - mean of homogeneous sample	**40.06**
					SD_{HS}	**0.51**
					RSD_{HS} (%)	**1.3**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.70	M_{Ss} 39.96	RSD % 1.0
standard deviation between the samples s_b	0.81	F_{value}	1.768
test value s_b^2/s_w^2	1.36	Characteristic no. for homogeneity between the samples	0.77
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.51	M_{HS} 40.06	RSD_{HS} % 1.3
		F_{value}	1.98
test value s_w^2/s_{HS}^2	1.83	Characteristic no. for homogeneity within the samples	0.93
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of 3 spectral lines) measured on 4 different days

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Ti

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	81.220	89.075	86.976	80.517	**84.45**	**81.55**	**2.9**	**3.5**
	2/2	83.663	82.245	78.011	78.871	**80.70**			
	2/3	78.164	85.894	83.925	84.679	**83.17**			
	2/4	81.937	79.912	77.663	72.088	**77.90**			
2	29/1	77.575	81.307	82.141	78.454	**79.87**	**79.33**	**0.5**	**0.7**
	29/2	76.746	80.036	79.429	81.031	**79.31**			
	29/3	81.254	80.807	78.520	77.413	**79.50**			
	29/4	79.192	81.728	77.043	76.528	**78.62**			
3	35/1	79.806	79.227	78.824	82.434	**80.07**	**80.08**	**1.4**	**1.7**
	35/2	81.941	78.916	79.516	84.859	**81.31**			
	35/3	80.880	84.479	79.117	78.502	**80.74**			
	35/4	76.598	76.559	81.728	77.871	**78.19**			
4	56/1	83.442	79.621	79.737	81.407	**81.05**	**80.49**	**0.6**	**0.7**
	56/2	77.405	80.365	82.060	80.815	**80.16**			
	56/3	80.909	81.850	79.740	80.888	**80.85**			
	56/4	79.120	79.795	80.637	79.971	**79.88**			
5	76/1	81.262	79.310	79.432	81.268	**80.32**	**80.74**	**1.5**	**1.9**
	76/2	81.997	81.880	82.144	85.315	**82.83**			
	76/3	78.939	82.184	77.560	78.291	**79.24**			
	76/4	80.523	79.976	81.492	80.257	**80.56**			
6	90/1	78.022	80.025	79.006	82.990	**80.01**	**80.25**	**0.7**	**0.9**
	90/2	81.023	79.209	77.971	82.001	**80.05**			
	90/3	79.161	77.566	82.367	79.526	**79.65**			
	90/4	81.625	82.553	81.700	79.200	**81.27**			
7	108/1	77.460	79.685	79.854	83.891	**80.22**	**79.51**	**1.2**	**1.4**
	108/2	81.079	79.105	79.059	80.333	**79.89**			
	108/3	79.172	79.073	76.963	75.991	**77.80**			
	108/4	79.733	77.404	79.044	84.388	**80.14**			
8	128/1	81.740	78.888	72.110	80.448	**78.30**	**79.64**	**1.6**	**2.0**
	128/2	80.250	84.745	79.052	82.292	**81.58**			
	128/3	78.344	78.056	75.937	81.558	**78.47**			
	128/4	80.296	80.042	81.152	79.355	**80.21**			

Analyt Ti

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
7	108/1	77.460	79.685	79.854	83.891	**80.22**	**79.51**	**1.2**	**1.4**
	108/2	81.079	79.105	79.059	80.333	**79.89**			
	108/3	79.172	79.073	76.963	75.991	**77.80**			
	108/4	79.733	77.404	79.044	84.388	**80.14**			
8	128/1	81.740	78.888	72.110	80.448	**78.30**	**79.64**	**1.6**	**2.0**
	128/2	80.250	84.745	79.052	82.292	**81.58**			
	128/3	78.344	78.056	75.937	81.558	**78.47**			
	128/4	80.296	80.042	81.152	79.355	**80.21**			
9	132/1	85.360	82.864	75.833	80.519	**81.14**	**79.78**	**2.2**	**2.7**
	132/2	80.452	83.945	79.060	79.711	**80.79**			
	132/3	81.598	81.745	81.295	77.984	**80.66**			
	132/4	75.459	76.553	78.877	75.170	**76.51**			
10	156/1	81.986	78.404	80.005	79.935	**80.08**	**79.51**	**1.2**	**1.5**
	156/2	79.604	80.539	79.191	79.716	**79.76**			
	156/3	80.305	78.664	82.153	80.545	**80.42**			
	156/4	78.374	76.024	78.478	78.165	**77.76**			
11	164/1	81.032	80.555	81.984	81.765	**81.33**	**80.14**	**1.8**	**2.2**
	164/2	80.238	82.009	81.606	84.016	**81.97**			
	164/3	79.099	78.913	79.216	78.825	**79.01**			
	164/4	78.302	77.640	78.561	78.463	**78.24**			
12	188/1	80.117	77.914	81.175	81.044	**80.06**	**80.13**	**1.0**	**1.3**
	188/2	81.604	81.157	80.885	82.620	**81.57**			
	188/3	78.811	79.590	79.239	81.605	**79.81**			
	188/4	77.668	80.526	79.858	78.324	**79.09**			
13	195/1	80.770	81.181	81.864	81.639	**81.36**	**80.77**	**1.1**	**1.3**
	195/2	81.937	83.636	79.517	78.951	**81.01**			
	195/3	78.760	80.596	79.274	78.132	**79.19**			
	195/4	83.851	79.387	82.698	80.083	**81.50**			
14	221/1	78.810	78.622	77.824	80.194	**78.86**	**79.92**	**0.7**	**0.9**
	221/2	81.467	80.410	77.741	81.838	**80.36**			
	221/3	79.919	82.007	79.454	79.699	**80.27**			
	221/4	82.478	80.347	79.616	78.219	**80.16**			
15	229/1	79.627	78.174	76.746	81.249	**78.95**	**78.84**	**0.8**	**1.0**
	229/2	78.968	77.866	80.062	78.192	**78.77**			
	229/3	79.541	79.525	78.202	81.853	**79.78**			
	229/4	75.505	77.733	79.275	78.919	**77.86**			
16	253/1	81.601	76.148	79.924	79.886	**79.39**	**79.21**	**0.8**	**1.0**
	253/2	79.855	79.131	78.714	75.402	**78.28**			
	253/3	78.347	81.875	81.792	78.794	**80.20**			
	253/4	79.532	79.565	79.469	77.278	**78.96**			

Analyt Ti

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
17	264/1	80.565	85.936	85.402	79.443	**82.84**	**80.07**	**2.2**	**2.8**
	264/2	79.262	79.452	77.169	75.596	**77.87**			
	264/3	78.582	80.896	83.102	81.023	**80.90**			
	264/4	81.318	76.486	79.542	77.276	**78.66**			
18	279/1	80.714	83.170	81.251	80.576	**81.43**	**79.82**	**1.1**	**1.4**
	279/2	78.602	79.419	81.377	79.133	**79.63**			
	279/3	81.153	76.600	79.765	78.688	**79.05**			
	279/4	80.441	78.835	80.136	77.285	**79.17**			
19	294/1	81.811	81.003	77.814	78.886	**79.88**	**79.20**	**1.4**	**1.7**
	294/2	79.818	80.186	81.985	79.216	**80.30**			
	294/3	80.289	74.808	79.019	83.582	**79.42**			
	294/4	78.198	75.970	77.398	77.231	**77.20**			
20	307/1	81.041	80.165	82.617	84.716	**82.13**	**80.01**	**1.6**	**2.0**
	307/2	79.523	78.873	80.148	78.579	**79.28**			
	307/3	81.407	78.039	81.318	79.758	**80.13**			
	307/4	77.149	79.633	78.485	78.773	**78.51**			

M_{Ss} - mean of means of the sub-samples 1-4	**79.93**
SD of means of the sub-samples 1-4	**0.63**
RSD (rel.%)	**0.8**

mean RSD_w (%)	**1.6**

Analyt Ti

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**
1	HS 1	79.885	81.093	81.993	81.393	**81.09**
2	HS 2	79.355	82.059	83.681	81.096	**81.55**
3	HS 3	78.225	81.145	79.789	80.682	**79.96**
4	HS 4	81.980	76.865	81.141	82.079	**80.52**
5	HS 5	79.249	84.156	78.206	82.832	**81.11**
6	HS 6	79.573	81.390	80.058	81.159	**80.55**
7	HS 7	79.829	76.461	81.254	80.853	**79.60**
8	HS 8	78.432	79.152	79.173	84.908	**80.42**
9	HS 9	79.989	84.838	80.768	80.904	**81.62**

HS = Homogeneous sample

10	HS 10	80.816	77.919	79.222	78.388	**79.09**
11	HS 11	77.091	80.181	80.085	80.915	**79.57**
12	HS 12	78.946	79.023	79.632	78.218	**78.95**
13	HS 13	83.624	76.839	83.408	80.070	**80.99**
14	HS 14	80.583	82.091	80.510	79.777	**80.74**
15	HS 15	79.072	80.684	80.213	77.392	**79.34**
16	HS 16	78.994	77.109	82.310	81.068	**79.87**
17	HS 17	79.088	77.980	80.837	77.003	**78.73**
18	HS 18	77.142	80.318	80.554	77.800	**78.95**
19	HS 19	78.727	81.884	82.189	80.160	**80.74**
20	HS 20	77.056	80.298	78.579	76.844	**78.19**
					M_{HS} - mean of homogeneous sample	**80.08**
					SD_{HS}	**1.00**
					RSD_{HS} (%)	**1.2**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	1.44	M_{Ss} 79.93	RSD % 0.8
standard deviation between the samples s_b	1.27	F_{value}	1.768
test value s_b^2/s_w^2	0.77	Characteristic no. for homogeneity between the samples	0.44
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	1.00	M_{HS} 80.08	RSD_{HS} % 1.2
		F_{value}	1.98
test value s_w^2/s_{HS}^2	2.08	Characteristic no. for homogeneity within the samples	1.05
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of 3 spectral lines) measured on 7 different days

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt V

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	43.920	50.128	44.676	58.364	66.511	51.280	52.204	**52.44**	**51.14**	**2.7**	**5.2**
	2/2	52.599	52.987	48.635	57.748	56.016	46.338	64.826	**54.16**			
	2/3	50.272	46.536	50.834	45.364	45.185	50.975	47.932	**48.16**			
	2/4	51.205	38.639	52.360	45.570	47.787	53.617	59.435	**49.80**			
2	29/1	47.849	51.134	46.637	53.519	57.073	45.267	47.270	**49.82**	**51.45**	**3.5**	**6.8**
	29/2	54.659	52.954	48.087	64.680	52.108	60.461	63.849	**56.69**			
	29/3	49.933	41.772	54.588	48.258	46.119	49.330	53.784	**49.11**			
	29/4	52.953	41.988	52.014	49.960	59.059	49.976	45.362	**50.19**			
3	35/1	46.790	51.401	49.447	52.498	57.545	44.266	58.850	**51.54**	**50.72**	**3.5**	**6.9**
	35/2	51.370	52.394	50.040	67.022	53.417	51.967	60.388	**55.23**			
	35/3	50.144	39.733	53.654	47.506	49.548	45.835	43.043	**47.07**			
	35/4	52.031	43.485	47.261	55.108	47.962	55.876	41.458	**49.03**			
4	56/1	44.526	51.966	46.862	62.349	54.983	44.521	54.255	**51.35**	**50.03**	**2.9**	**5.7**
	56/2	51.343	53.519	47.354	50.464	53.687	59.431	54.262	**52.87**			
	56/3	49.071	38.846	47.807	47.262	47.361	49.065	44.170	**46.23**			
	56/4	52.271	41.782	53.265	55.108	47.962	55.876	41.458	**49.67**			
5	76/1	47.898	49.878	43.440	54.765	58.965	43.330	53.029	**50.19**	**49.09**	**0.9**	**1.9**
	76/2	51.962	49.092	57.895	48.031	41.985	42.855	54.743	**49.51**			
	76/3	47.616	38.936	52.742	53.790	50.856	54.209	41.094	**48.46**			
	76/4	48.921	47.535	52.853	43.481	41.786	45.118	57.751	**48.21**			
6	90/1	48.575	50.833	46.142	55.592	57.884	54.024	63.561	**53.80**	**50.92**	**2.0**	**4.0**
	90/2	52.073	53.505	50.790	45.264	41.479	57.993	55.015	**50.87**			
	90/3	52.163	42.800	50.775	48.907	47.129	48.641	55.602	**49.43**			
	90/4	53.967	48.542	51.110	47.847	46.924	48.452	50.257	**49.59**			
7	108/1	43.865	53.537	45.797	53.916	56.616	47.644	54.886	**50.89**	**50.42**	**1.7**	**3.4**
	108/2	52.323	49.338	47.133	55.567	45.679	48.949	63.319	**51.76**			
	108/3	50.790	40.609	53.749	47.875	47.928	50.743	43.740	**47.92**			
	108/4	51.833	49.431	53.356	48.133	47.184	50.774	57.015	**51.10**			
8	128/1	50.307	51.144	45.174	55.118	66.290	43.957	54.182	**52.31**	**51.45**	**2.1**	**4.1**
	128/2	54.702	50.025	52.561	58.465	52.697	51.019	58.601	**54.01**			
	128/3	50.975	40.600	52.786	46.036	47.561	58.198	49.743	**49.41**			
	128/4	50.457	50.048	48.746	56.715	49.101	48.103	47.423	**50.08**			

Analyt V

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	132/1	49.858	53.643	40.924	50.850	49.148	52.699	58.390	**50.79**	**49.96**	**2.1**	**4.1**
	132/2	48.556	53.835	49.439	56.028	56.250	42.677	57.226	**52.00**			
	132/3	53.743	42.123	51.069	47.622	46.986	46.001	61.520	**49.87**			
	132/4	48.443	48.894	49.995	48.226	44.436	54.189	36.031	**47.17**			
10	156/1	48.936	53.791	41.627	60.597	53.502	48.532	56.352	**51.91**	**49.84**	**2.9**	**5.9**
	156/2	54.176	54.500	50.596	51.171	51.961	49.570	57.760	**52.82**			
	156/3	49.117	42.970	50.908	47.682	51.605	43.553	44.791	**47.23**			
	156/4	49.968	46.264	51.218	46.175	49.609	50.253	38.383	**47.41**			
11	164/1	49.960	56.137	41.143	53.250	63.620	52.414	54.711	**53.03**	**50.04**	**2.7**	**5.5**
	164/2	50.859	55.803	49.128	48.188	50.134	47.401	58.882	**51.48**			
	164/3	49.823	42.566	51.670	45.508	46.351	49.123	43.416	**46.92**			
	164/4	50.073	44.827	48.183	47.865	45.806	50.634	53.762	**48.74**			
12	188/1	49.808	53.763	41.141	54.707	52.283	50.498	53.625	**50.83**	**50.25**	**3.3**	**6.5**
	188/2	54.660	52.820	51.123	51.946	49.393	58.171	63.931	**54.58**			
	188/3	50.050	41.632	49.367	50.190	45.200	49.317	44.527	**47.18**			
	188/4	49.001	45.816	49.377	47.072	47.724	57.371	42.547	**48.42**			
13	195/1	48.475	54.810	39.344	62.897	54.245	56.021	57.643	**53.35**	**49.45**	**2.7**	**5.5**
	195/2	49.822	48.521	50.951	46.083	41.615	54.220	53.050	**49.18**			
	195/3	49.534	42.468	50.653	45.789	48.401	52.186	44.558	**47.66**			
	195/4	51.520	51.508	53.471	44.863	41.719	51.281	38.878	**47.61**			
14	221/1	52.913	52.626	41.604	50.689	53.649	60.898	52.937	**52.19**	**49.47**	**2.0**	**4.0**
	221/2	52.047	44.946	47.895	48.863	54.679	49.892	45.434	**49.11**			
	221/3	50.910	42.571	48.679	47.336	50.562	56.624	46.816	**49.07**			
	221/4	51.188	50.128	50.023	42.292	45.711	48.212	44.966	**47.50**			
15	229/1	53.365	55.300	42.297	58.005	53.016	52.428	61.627	**53.72**	**50.75**	**2.5**	**5.0**
	229/2	56.758	47.170	56.398	48.405	57.528	45.882	50.274	**51.77**			
	229/3	53.071	40.642	50.345	46.504	45.676	54.312	45.160	**47.96**			
	229/4	51.810	55.684	49.553	52.519	50.155	48.506	38.598	**49.55**			
16	253/1	52.462	58.004	41.019	61.348	52.943	54.275	55.317	**53.62**	**51.04**	**1.9**	**3.8**
	253/2	49.414	44.175	52.359	52.859	48.147	46.497	57.340	**50.11**			
	253/3	51.217	45.000	47.356	47.762	56.135	55.221	56.034	**51.25**			
	253/4	46.388	49.107	53.554	46.525	45.061	55.924	47.571	**49.16**			
17	264/1	48.909	48.904	47.999	47.785	48.859	54.397	64.670	**51.65**	**50.06**	**1.9**	**3.9**
	264/2	53.385	42.603	53.659	51.384	48.418	54.177	58.956	**51.80**			
	264/3	51.494	37.261	54.424	55.235	47.297	49.448	41.098	**48.04**			
	264/4	48.442	50.519	51.198	46.645	45.084	47.889	51.577	**48.76**			
18	279/1	52.672	52.007	49.933	52.209	55.173	47.254	60.436	**52.81**	**51.17**	**1.2**	**2.4**
	279/2	53.703	45.232	51.097	53.309	50.678	56.043	48.001	**51.15**			
	279/3	50.642	37.221	52.659	54.038	51.481	60.046	49.716	**50.83**			
	279/4	51.998	49.825	52.881	48.571	47.234	60.359	38.419	**49.90**			

Analyt V

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
19	294/1	52.596	46.715	48.389	59.981	53.464	60.590	67.694	**55.63**	**51.20**	**3.2**	**6.3**
	294/2	49.593	46.803	50.728	51.339	49.903	53.431	51.624	**50.49**			
	294/3	50.999	35.271	53.034	44.831	59.139	51.004	61.243	**50.79**			
	294/4	48.700	50.043	47.371	49.110	52.063	50.490	37.524	**47.90**			
20	307/1	52.505	49.574	52.591	58.977	52.842	51.497	56.909	**53.56**	**50.89**	**1.8**	**3.6**
	307/2	49.484	44.391	54.307	47.676	54.176	53.833	44.976	**49.83**			
	307/3	50.147	38.630	54.121	50.034	46.563	59.066	56.103	**50.67**			
	307/4	50.025	52.071	48.610	52.422	50.624	45.358	47.349	**49.49**			

M_{Ss} - mean of means of the sub-samples 1-4	**50.47**
SD of means of the sub-samples 1-4	**0.71**
RSD (rel.%)	**1.4**

mean RSD_w (%) **4.7**

Analyt V

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 3 lines (16.02.00)	mean calculated from 3 lines (21.02.00)	mean calculated from 3 lines (23.02.00)	mean calculated from 3 lines (02.06.01)	mean calculated from 3 lines (06.06.01)	mean calculated from 3 lines (12.06.01)	mean calculated from 3 lines (30.05.01)	**mean**
1	HS 1	48.746	56.657	47.772	55.818	57.990	55.456	62.660	**55.01**
2	HS 2	44.579	53.622	42.421	59.341	51.907	46.269	56.537	**50.67**
3	HS 3	50.531	58.052	41.704	53.805	58.699	55.891	57.191	**53.70**
4	HS 4	52.245	54.641	41.554	54.140	52.874	49.414	59.349	**52.03**
5	HS 5	51.408	56.844	45.434	54.513	56.373	49.910	56.157	**52.95**
6	HS 6	51.485	48.368	47.293	51.612	52.473	57.167	56.366	**52.11**
7	HS 7	50.960	51.210	53.125	51.660	49.936	48.825	47.226	**50.42**
8	HS 8	54.818	50.511	45.963	47.800	52.809	49.525	68.170	**52.80**
9	HS 9	52.168	44.311	53.566	46.298	50.023	48.630	57.854	**50.41**
10	HS 10	52.834	42.542	52.430	53.859	48.668	52.040	51.367	**50.53**
11	HS 11	53.331	41.383	52.258	43.267	50.980	43.748	47.785	**47.54**
12	HS 12	51.246	40.434	51.179	46.674	47.280	43.915	51.648	**47.48**
13	HS 13	50.320	43.531	49.719	48.811	59.782	51.761	60.252	**52.03**
14	HS 14	51.313	42.058	50.619	41.079	45.580	54.159	51.432	**48.03**
15	HS 15	49.662	43.798	54.764	48.405	48.237	50.365	49.251	**49.21**

HS = Homogeneous sample

16	HS 16	50.479	40.399	54.028	50.282	45.462	59.173	46.413	**49.46**
17	HS 17	53.284	51.058	48.957	48.904	58.048	50.352	51.680	**51.75**
18	HS 18	50.179	49.329	52.005	43.505	48.597	49.400	46.691	**48.53**
19	HS 19	50.213	50.615	55.021	42.851	54.976	44.568	45.798	**49.15**
20	HS 20	46.402	51.929	52.797	42.038	49.223	44.848	42.266	**47.07**
								M_{HS} - mean of homogeneous sample	**50.54**
								SD_{HS}	**2.23**
								RSD_{HS} (%)	**4.4**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	2.49	M_{Ss} 50.47	RSD % 1.4
standard deviation between the samples s_b	1.41	F_{value}	1.768
test value s_b^2/s_w^2	0.32	Characteristic no. for homogeneity between the samples	0.18
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	2.23	M_{HS} 50.54	RSD_{HS} % 4.4
		F_{value}	1.98
test value s_w^2/s_{HS}^2	1.24	Characteristic no. for homogeneity within the samples	0.62
Homogeneity within the samples: No significant inhomogeneity			

ETV ICP OES-results (means of 2 spectral lines) measured on 4 different days

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Zr

mass fraction in mg/kg

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	2/1	23.860	22.666	24.685	23.897	**23.78**	**22.17**	**1.1**	**4.9**
	2/2	22.628	22.686	21.223	20.912	**21.86**			
	2/3	20.854	22.895	22.810	19.307	**21.47**			
	2/4	22.586	21.553	23.530	18.690	**21.59**			
2	29/1	22.161	21.374	23.826	20.848	**22.05**	**21.71**	**1.0**	**4.8**
	29/2	23.913	22.669	22.379	22.710	**22.92**			
	29/3	20.857	23.660	20.735	20.372	**21.41**			
	29/4	21.602	19.663	20.936	19.632	**20.46**			
3	35/1	21.499	24.110	21.859	23.784	**22.81**	**22.19**	**0.6**	**2.6**
	35/2	19.914	22.504	21.849	23.064	**21.83**			
	35/3	21.090	21.720	21.690	21.914	**21.60**			
	35/4	21.965	21.321	22.877	23.944	**22.53**			
4	56/1	22.092	21.982	20.510	22.566	**21.79**	**21.86**	**0.3**	**1.4**
	56/2	23.267	21.236	23.272	21.446	**22.31**			
	56/3	21.850	21.461	21.170	22.670	**21.79**			
	56/4	21.685	21.273	21.913	21.440	**21.58**			
5	76/1	21.402	21.427	20.936	21.669	**21.36**	**22.08**	**0.5**	**2.3**
	76/2	22.590	22.036	22.534	22.078	**22.31**			
	76/3	21.725	23.720	20.567	22.500	**22.13**			
	76/4	23.639	21.484	22.697	22.255	**22.52**			
6	90/1	22.460	22.360	22.654	21.232	**22.18**	**22.36**	**0.3**	**1.5**
	90/2	22.444	22.821	21.248	22.119	**22.16**			
	90/3	21.931	21.880	24.224	23.385	**22.85**			
	90/4	22.799	22.455	22.469	21.295	**22.25**			
7	108/1	22.683	22.964	23.612	22.879	**23.03**	**22.14**	**0.8**	**3.5**
	108/2	24.453	22.552	22.366	20.899	**22.57**			
	108/3	22.715	22.811	20.049	20.576	**21.54**			
	108/4	23.463	22.851	21.262	18.159	**21.43**			
8	128/1	23.768	22.740	16.471	21.812	**21.20**	**21.80**	**0.5**	**2.2**
	128/2	23.790	20.387	19.615	22.836	**21.66**			
	128/3	22.633	21.419	20.709	23.290	**22.01**			
	128/4	21.906	23.507	23.280	20.589	**22.32**			

Analyt Zr

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	132/1	20.530	22.392	20.720	22.094	**21.43**	**21.98**	**0.9**	**3.9**
	132/2	21.718	25.323	22.655	23.356	**23.26**			
	132/3	22.604	22.402	23.559	17.995	**21.64**			
	132/4	21.923	21.888	21.940	20.617	**21.59**			
10	156/1	21.295	21.103	23.558	22.650	**22.15**	**22.23**	**1.0**	**4.4**
	156/2	24.497	23.194	22.722	21.265	**22.92**			
	156/3	22.167	22.802	22.796	24.180	**22.99**			
	156/4	19.991	19.687	21.913	21.866	**20.86**			
11	164/1	21.303	23.484	25.394	22.774	**23.24**	**21.97**	**1.1**	**4.9**
	164/2	21.729	21.720	22.202	23.220	**22.22**			
	164/3	20.449	20.662	23.761	22.138	**21.75**			
	164/4	21.499	20.601	21.124	19.418	**20.66**			
12	188/1	21.609	21.027	24.045	23.109	**22.45**	**22.22**	**0.3**	**1.4**
	188/2	20.581	22.704	21.941	22.352	**21.89**			
	188/3	22.841	21.665	20.517	23.013	**22.01**			
	188/4	21.690	21.565	24.875	21.941	**22.52**			
13	195/1	23.448	22.409	22.007	22.408	**22.57**	**21.88**	**0.6**	**2.6**
	195/2	21.328	22.110	22.844	21.104	**21.85**			
	195/3	19.454	21.748	21.812	21.767	**21.20**			
	195/4	23.035	21.927	20.720	22.037	**21.93**			
14	221/1	21.770	21.537	21.870	22.791	**21.99**	**22.08**	**0.9**	**3.9**
	221/2	21.923	22.593	25.146	22.394	**23.01**			
	221/3	21.162	24.209	20.810	23.198	**22.34**			
	221/4	21.710	21.175	19.778	21.160	**20.96**			
15	229/1	22.265	20.628	20.296	20.853	**21.01**	**21.50**	**0.7**	**3.0**
	229/2	21.879	22.777	21.683	22.566	**22.23**			
	229/3	20.619	21.572	23.596	21.730	**21.88**			
	229/4	21.578	20.012	21.216	20.781	**20.90**			
16	253/1	22.875	21.076	22.684	22.686	**22.33**	**22.07**	**0.5**	**2.2**
	253/2	21.251	21.425	22.839	22.582	**22.02**			
	253/3	20.324	22.231	21.818	21.198	**21.39**			
	253/4	21.956	21.718	22.454	23.978	**22.53**			
17	264/1	22.947	22.433	21.886	22.981	**22.56**	**21.68**	**0.7**	**3.1**
	264/2	23.230	21.230	23.088	19.756	**21.83**			
	264/3	19.478	23.608	21.054	20.214	**21.09**			
	264/4	21.769	20.777	20.857	21.593	**21.25**			
18	279/1	21.965	23.108	24.334	21.714	**22.78**	**22.15**	**0.5**	**2.5**
	279/2	21.160	21.166	22.952	23.206	**22.12**			
	279/3	22.658	22.300	22.426	21.552	**22.23**			
	279/4	21.910	21.211	21.240	21.420	**21.45**			

Analyt Zr

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
18	279/1	21.965	23.108	24.334	21.714	**22.78**	**22.15**	**0.5**	**2.5**
	279/2	21.160	21.166	22.952	23.206	**22.12**			
	279/3	22.658	22.300	22.426	21.552	**22.23**			
	279/4	21.910	21.211	21.240	21.420	**21.45**			
19	294/1	23.706	22.023	20.427	21.987	**22.04**	**22.33**	**0.2**	**1.0**
	294/2	21.541	21.178	22.823	23.731	**22.32**			
	294/3	21.995	25.842	20.038	21.832	**22.43**			
	294/4	23.446	25.344	21.606	19.815	**22.55**			
20	307/1	24.496	23.317	23.456	22.571	**23.46**	**22.37**	**1.2**	**5.4**
	307/2	22.651	24.339	21.317	20.415	**22.18**			
	307/3	23.306	23.030	22.929	23.098	**23.09**			
	307/4	21.938	20.148	21.534	19.429	**20.76**			

M_{Ss} - mean of means of the sub-samples 1-4	**22.02**
SD of means of the sub-samples 1-4	**0.24**
RSD (rel.%)	**1.1**

mean RSD_w (%) **3.1**

Analyt Zr

HS = Homogeneous sample

Serial number	Sample number	mean calculated from 2 lines (02.06.01)	mean calculated from 2 lines (06.06.01)	mean calculated from 2 lines (12.06.01)	mean calculated from 2 lines (30.05.01)	**mean**
1	HS 1	21.487	21.838	21.549	22.812	**21.92**
2	HS 2	20.764	22.228	20.935	23.825	**21.94**
3	HS 3	21.419	19.974	22.135	21.654	**21.30**
4	HS 4	21.814	19.124	22.528	23.510	**21.74**
5	HS 5	20.909	22.139	22.195	23.868	**22.28**
6	HS 6	22.737	21.631	23.040	22.453	**22.47**
7	HS 7	21.106	21.184	21.605	21.597	**21.37**
8	HS 8	21.685	22.954	20.428	21.872	**21.73**
9	HS 9	21.013	23.371	22.100	22.384	**22.22**
10	HS 10	22.125	20.980	20.642	22.867	**21.65**
11	HS 11	22.066	21.529	21.970	20.297	**21.47**
12	HS 12	22.890	21.802	22.331	19.712	**21.68**
13	HS 13	23.203	22.224	22.254	20.465	**22.04**
14	HS 14	22.167	20.736	21.075	22.441	**21.60**
15	HS 15	22.857	22.336	20.627	21.015	**21.71**

HS = Homogeneous sample

16	HS 16	20.949	22.269	22.810	23.536	**22.39**
17	HS 17	21.337	21.668	22.887	22.673	**22.14**
18	HS 18	21.147	21.719	23.019	21.101	**21.75**
19	HS 19	21.384	24.643	23.856	21.421	**22.83**
20	HS 20	23.228	22.015	22.929	21.507	**22.42**

M_{HS} - mean of homogeneous sample	**21.93**
SD_{HS}	**0.41**
RSD_{HS} (%)	**1.8**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.73	M_{Ss} 22.02	RSD % 1.1
standard deviation between the samples s_b	0.48	F_{value}	1.768
test value s_b^2/s_w^2	0.42	Characteristic no. for homogeneity between the samples	0.24
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.41	M_{HS} 21.93	RSD_{HS} % 1.8
		F_{value}	1.98
test value s_w^2/s_{HS}^2	3.28	Characteristic no. for homogeneity within the samples	1.66
Homogeneity within the samples: Significant not very strong inhomogeneity			

ICP OES results
Measurements, compilation of results: HC Starck GmbH & Co. KG, Goslar
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt B

mass fraction in mg/kg

Serial number	Sample number	values	mean of sub-samples 1-3	SD of sub-samples 1-3	RSD_w (rel.%)
1	**I / 1 / 2 - 1**	55.3	**56.167**	**1.3317**	**2.37**
	I / 1 / 2 - 2	55.5			
	I / 1 / 2 - 3	57.7			
2	**I / 1 / 29 - 1**	63.1	**62.800**	**0.2646**	**0.42**
	I / 1 / 29 - 2	62.7			
	I / 1 / 29 - 3	62.6			
3	**I / 1 / 35 - 1**	63.2	**62.233**	**1.2662**	**2.03**
	I / 1 / 35 - 2	62.7			
	I / 1 / 35 - 3	60.8			
4	**I / 1 / 90 - 1**	60.1	**60.100**	**0.3000**	**0.50**
	I / 1 / 90 - 2	60.4			
	I / 1 / 90 - 3	59.8			
5	**I / 1 / 108 - 1**	62.4	**61.400**	**1.4000**	**2.28**
	I / 1 / 108 - 2	62.0			
	I / 1 / 108 - 3	59.8			
6	**I / 2 / 132 - 1**	60.1	**60.300**	**1.1136**	**1.85**
	I / 2 / 132 - 2	61.5			
	I / 2 / 132 - 3	59.3			
7	**I / 2 / 164 - 1**	61.9	**60.867**	**0.9074**	**1.49**
	I / 2 / 164 - 2	60.5			
	I / 2 / 164 - 3	60.2			
8	**I / 2 / 195 - 1**	62.7	**62.633**	**0.0577**	**0.09**
	I / 2 / 195 - 2	62.6			
	I / 2 / 195 - 3	62.6			
9	**I / 2 / 253 - 1**	61.5	**60.567**	**0.8622**	**1.42**
	I / 2 / 253 - 2	60.4			
	I / 2 / 253 - 3	59.8			
10	**I / 3 / 279 -1**	59.5	**58.833**	**0.6506**	**1.11**
	I / 3 / 279 -2	58.2			
	I / 3 / 279 -3	58.8			

M_{Ss} - mean of means of the sub-samples 1-3	**60.590**
SD of means of the sub-samples 1-3	**1.9852**
RSD (%)	**3.28**

mean RSD_w (%) **1.36**

Analyt B
HS = Homogeneous sample

Serial number	Sample number	values
1	HS 1	**63.9**
2	HS 2	**62.9**
3	HS 3	**63.8**
4	HS 4	**62.4**
5	HS 5	**63.7**
6	HS 6	**61.5**
7	HS 7	**63.1**
8	HS 8	**63.2**
9	HS 9	**62.0**
10	HS 10	**62.7**

Serial number	Sample number	values
11	HS 11	**60.1**
12	HS 12	**61.7**
13	HS 13	**63.8**
14	HS 14	**60.7**
15	HS 15	**62.5**
16	HS 16	**61.6**
17	HS 17	**60.4**
18	HS 18	**60.0**
19	HS 19	**61.8**
20	HS 20	**59.6**

M_{HS} - mean of homogeneous sample	**62.07**
SD_{HS}	**1.365**
RSD_{HS} (%)	**2.20**

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.934	M_{Ss} 60.59	RSD % 3.28
standard deviation between the samples s_b	3.438	F_{value}	2.39
test value s_b^2/s_w^2	13.543	Characteristic no. for homogeneity between the samples	5.669
Homogeneity between the samples: Significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	1.365	M_{HS} 62.07	RSD % 2.20
		F_{value}	2.16
test value s_w^2/s_{HS}^2	0.468	Characteristic no. for homogeneity within the samples	0.217
Homogeneity within the samples: No significant inhomogeneity			

SS ET AAS results

Measurements, compilation of results: H.C. Starck GmbH & Co.KG, Goslar; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt Na

mass fraction in mg/kg

Serial number	Sample number	values	mean of sub-samples 1-3	SD of sub-samples 1-3	RSD_w (rel.%)
1	**I / 1 / 2 - 1**	19.0	**19.200**	**0.3464**	**1.80**
	I / 1 / 2 - 2	19.6			
	I / 1 / 2 - 2	19.0			
2	**I / 1 / 29 - 1**	18.9	**18.867**	**0.0577**	**0.31**
	I / 1 / 29 - 2	18.9			
	I / 1 / 29 - 3	18.8			
3	**I / 1 / 35 - 1**	18.3	**18.600**	**0.2646**	**1.42**
	I / 1 / 35 - 2	18.8			
	I / 1 / 35 - 3	18.7			
4	**I / 1 / 90 - 1**	19.3	**19.400**	**0.1732**	**0.89**
	I / 1 / 90 - 2	19.3			
	I / 1 / 90 - 3	19.6			
5	**I / 1 / 108 - 1**	19.4	**19.400**	**0.3000**	**1.55**
	I / 1 / 108 - 2	19.7			
	I / 1 / 108 - 3	19.1			
6	**I / 2 / 132 - 1**	19.2	**19.100**	**0.6557**	**3.43**
	I / 2 / 132 - 2	19.7			
	I / 2 / 132 -3	18.4			
7	**I / 2 / 164 - 1**	18.7	**19.033**	**0.3055**	**1.61**
	I / 2 / 164 - 2	19.3			
	I / 2 / 164 - 3	19.1			
8	**I / 2 / 195 - 1**	18.8	**18.733**	**0.4041**	**2.16**
	I / 2 / 195 - 2	18.3			
	I / 2 / 195 - 3	19.1			
9	**I / 2 / 253 - 1**	18.7	**18.800**	**0.2646**	**1.41**
	I / 2 / 253 - 2	18.6			
	I / 2 / 253 - 3	19.1			
10	**I / 3 / 279 -1**	19.6	**19.267**	**0.3055**	**1.59**
	I / 3 / 279 -2	19.2			
	I / 3 / 279 -3	19.0			

M_{Ss} - mean of means of the sub-samples 1-3	**19.040**
SD of means of the sub-samples 1-3	**0.2819**
RSD (rel.%)	**1.48**

mean RSD_w (%) **1.62**

Analyt Na

HS = Homogeneous sample

Serial number	sample number	values
1	HS 1	**19.1**
2	HS 2	**19.6**
3	HS 3	**18.8**
4	HS 4	**19.9**
5	HS 5	**19.3**
6	HS 6	**19.5**
7	HS 7	**19.6**
8	HS 8	**19.2**
9	HS 9	**19.9**
10	HS 10	**19.6**

Serial number	sample number	values
11	HS 11	**19.9**
12	HS 12	**19.1**
13	HS 13	**18.4**
14	HS 14	**19.6**
15	HS 15	**19.7**
16	HS 16	**19.8**
17	HS 17	**18.5**
18	HS 18	**20.1**
19	HS 19	**19.4**
20	HS 20	**20.1**

M_{HS} - mean of homogeneous sample	**19.46**
SD_{HS}	**0.486**
RSD_{HS} (%)	**2.50**

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.341	M_{Ss} 19.04	RSD % 1.48
standard deviation between the samples s_b	0.488	F_{value}	2.39
test value s_b^2/s_w^2	2.049	Characteristic no. for homogeneity between the samples	0.857
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.486	M_{HS} 19.46	RSD_{HS} % 2.50
		F_{value}	2.16
test value s_w^2/s_{HS}^2	0.493	Characteristic no. for homogeneity within the samples	0.228
Homogeneity within the samples: No significant inhomogeneity			

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt: C_{total}

mass fraction in mass %

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	O/8/1	29.838	29.819	29.829	**29.903**	**0.056**	**0.19**
	O/8/3	29.902	29.915	29.909			
	O/8/5	29.972	29.958	29.965			
	O/8/7	29.900	29.921	29.911			
2	O/56/1	29.868	29.819	29.844	**29.886**	**0.042**	**0.14**
	O/56/3	29.865	29.939	29.902			
	O/56/5	29.872	29.848	29.860			
	O/56/7	29.904	29.971	29.938			
3	O/76/1	29.936	29.890	29.913	**29.881**	**0.035**	**0.12**
	O/76/3	29.915	29.894	29.905			
	O/76/5	29.815	29.857	29.836			
	O/76/7	29.851	29.889	29.870			
4	O/128/1	29.917	29.992	29.955	**29.935**	**0.035**	**0.12**
	O/128/3	29.967	29.966	29.967			
	O/128/5	29.902	29.870	29.886			
	O/128/7	29.913	29.956	29.935			
5	O/143/1	29.895	29.900	29.898	**29.883**	**0.026**	**0.09**
	O/143/3	29.961	29.858	29.910			
	O/143/5	29.873	29.873	29.873			
	O/143/7	29.828	29.875	29.852			
6	O/188/1	29.994	29.898	29.946	**29.901**	**0.041**	**0.14**
	O/188/3	29.948	29.900	29.924			
	O/188/5	29.875	29.840	29.858			
	O/188/7	29.888	29.865	29.877			
7	O/203/1	29.905	29.806	29.856	29.893	0.054	0.18
	O/203/3	29.937	29.963	29.950			
	O/203/5	29.886	29.968	29.927			
	O/203/7	29.834	29.842	29.838			
8	O/229/1	29.896	29.972	29.934	29.931	0.025	0.08
	O/229/3	29.957	29.934	29.946			
	O/229/5	29.920	29.868	29.894			
	O/229/7	29.955	29.942	29.949			

Analyt: C_{total}

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
9	O/286/1	29.885	29.935	29.910	29.909	0.066	0.22
	O/286/3	29.864	29.939	29.902			
	O/286/5	29.812	29.853	29.833			
	O/286/7	29.994	29.993	29.994			
10	O/294/1	29.859	29.842	29.851	29.885	0.069	0.23
	O/294/3	29.811	29.810	29.811			
	O/294/5	29.976	29.964	29.970			
	O/294/7	29.977	29.838	29.908			

M_{Ss} - mean of means of the sub-samples	29.901
SD of means of the sub-samples	0.020
RSD (rel.%)	0.07

mean RSD (%) 0.15

Analyt: C_{total}

HS = Homogeneous sample

Serial number	Sample number	1. measurement
1	HS 1	30.04
2	HS 2	29.9
3	HS 3	30.02
4	HS 4	29.89
5	HS 5	29.91
6	HS 6	30.01
7	HS 7	30.01
8	HS 8	30.01
9	HS 9	30.04
10	HS 10	30.04
11	HS 11	30.02

M_{HS} - mean of homogeneous sample	29.99
SD_{HS}	0.059
RSD_{HS} (%)	0.20

Analyt C_{total}

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.047	M_{Ss} 29.90	RSD % 0.07
standard deviation between the samples s_b	0.039	F_{value}	2.21
test value s_b^2/s_w^2	0.676	Characteristic no. for homogeneity between the samples	0.306
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample s_{HS}	0.059	M_{HS} 29.99	RSD_{HS} % 0.20
		F_{value}	2.70
test value s_w^2/s_{HS}^2	0.635	Characteristic no. for homogeneity within the samples	0.235
Homogeneity within the samples: No significant inhomogeneity			

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt: C_{free}

mass fraction in mg/kg

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	C/8/1	610	590	600	610.00	14.720	2.41
	C/8/3	630	610	620			
	C/8/5	620	630	625			
	C/8/7	600	590	595			
2	C/56/1	630	620	625	612.50	11.902	1.94
	C/56/3	600	610	605			
	C/56/5	600	600	600			
	C/56/7	620	620	620			
3	C/76/1	620	580	600	617.50	14.434	2.34
	C/76/3	600	630	615			
	C/76/5	640	630	635			
	C/76/7	620	620	620			
4	C/128/1	610	600	605	608.75	7.500	1.23
	C/128/3	610	600	605			
	C/128/5	620	620	620			
	C/128/7	590	620	605			
5	C/143/1	620	620	620	631.25	19.311	3.06
	C/143/3	650	640	645			
	C/143/5	600	620	610			
	C/143/7	650	650	650			
6	C/188/1	600	590	595	602.50	8.660	1.44
	C/188/3	640	580	610			
	C/188/5	630	590	610			
	C/188/7	590	600	595			
7	C/203/1	610	620	615	623.75	16.520	2.65
	C/203/3	620	590	605			
	C/203/5	640	640	640			
	C/203/7	630	640	635			
8	C/229/1	630	650	640	643.75	11.087	1.72
	C/229/3	590	670	630			
	C/229/5	670	630	650			
	C/229/7	640	670	655			

Analyt C_{free}

9	C/286/1	570	610	590	625.00	33.417	5.35
	C/286/3	620	610	615			
	C/286/5	610	640	625			
	C/286/7	670	670	670			
10	C/294/1	640	640	640	655.00	20.412	3.12
	C/294/3	630	640	635			
	C/294/5	670	680	675			
	C/294/7	670	670	670			

M_{Ss} - mean of means of the sub-samples 1-4	623.000
SD of means of the sub-samples 1-4	16.53
RSD (rel.%)	2.65

mean RSD_w (%) 2.53

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	17.32	M_{Ss} 623.0	RSD % 2.65
standard deviation between the samples s_b	33.07	F_{value}	2.21
test value s_b^2/s_w^2	3.644	Characteristic no. for homogeneity between the samples	1.649
Homogeneity between the samples: Significant not very strong inhomogeneity			

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt: O

mass fraction in mg/kg

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	008/2	912	919	916	907.25	5.909	0.65
	008/4	909	894	902			
	008/6	913	898	906			
	008/8	903	910	907			
2	056/2	905	926	916	911.38	9.437	1.04
	056/4	899	904	902			
	056/6	908	937	923			
	056/8	900	912	906			
3	076/2	919	894	907	909.13	8.702	0.96
	076/4	912	898	905			
	076/6	930	914	922			
	076/8	891	915	903			
4	128/2	897	895	896	913.88	13.098	1.43
	128/4	910	923	917			
	128/6	929	926	928			
	128/8	925	906	916			
5	143/2	890	917	904	895.50	8.689	0.97
	143/4	894	888	891			
	143/6	900	904	902			
	143/8	889	882	886			
6	188/2	894	924	909	900.13	9.508	1.06
	188/4	908	906	907			
	188/6	895	896	896			
	188/8	882	896	889			
7	203/2	889	897	893	900.63	10.045	1.12
	203/4	885	904	895			
	203/6	911	919	915			
	203/8	898	902	900			
8	229/2	903	895	899	904.88	6.033	0.67
	229/4	921	883	902			
	229/6	918	908	913			
	229/8	921	890	906			

Analyt: O

9	286/2	884	930	907	906.25	6.982	0.77
	286/4	905	912	909			
	286/6	914	912	913			
	286/8	894	899	897			
10	294/2	904	901	903	895.88	4.715	0.53
	294/4	890	898	894			
	294/6	895	896	896			
	294/8	899	884	892			

M_{Ss} - mean of means of the sub-samples 1-4	904.49
SD of means of the sub-samples 1-4	6.297
RSD (rel.%)	0.70

mean RSD_w (%) 0.92

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	8.634	M_{Ss} 904.4900	RSD % 0.70
standard deviation between the samples s_b	12.594	F_{value}	2.21
test value s_b^2/s_w^2	2.128	Characteristic no. for homogeneity between the samples	0.963
Homogeneity between the samples: No significant inhomogeneity			

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt: N

mass fraction in mg/kg

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	008/2	51	46	48.5	56.375	7.532	13.36
	008/4	57	56	56.5			
	008/6	54	54	54.0			
	008/8	88	45	66.5			
2	056/2	49	60	54.5	51.625	3.966	7.68
	056/4	49	49	49.0			
	056/6	40	55	47.5			
	056/8	49	62	55.5			
3	076/2	44	50	47.0	49.750	5.838	11.73
	076/4	48	46	47.0			
	076/6	71	46	58.5			
	076/8	39	54	46.5			
4	128/2	59	56	57.5	55.250	3.969	7.18
	128/4	51	49	50.0			
	128/6	68	50	59.0			
	128/8	51	58	54.5			
5	143/2	47	45	46.0	45.750	6.410	14.01
	143/4	39	40	39.5			
	143/6	47	62	54.5			
	143/8	40	46	43.0			
6	188/2	45	53	49.0	47.625	3.794	7.97
	188/4	44	51	47.5			
	188/6	44	59	51.5			
	188/8	42	43	42.5			
7	203/2	54	42	48.0	53.750	5.752	10.70
	203/4	45	66	55.5			
	203/6	79	43	61.0			
	203/8	41	60	50.5			
8	229/2	42	53	47.5	56.375	7.075	12.55
	229/4	82	46	64.0			
	229/6	52	57	54.5			
	229/8	71	48	59.5			

Analyt: N

9	286/2	51	42	46.5	54.875	8.606	15.68
	286/4	49	83	66.0			
	286/6	52	62	57.0			
	286/8	54	46	50.0			
10	294/2	50	58	54.0	48.375	4.535	9.37
	294/4	42	46	44.0			
	294/6	50	50	50.0			
	294/8	52	39	45.5			

M_{Ss} - mean of means of the sub-samples 1-4	51.975
SD of means of the sub-samples 1-4	3.897
RSD (rel.%)	7.50

mean RSD_w (%) 11.02

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	5.963	M_{Ss} 51.9750	RSD % 7.50
standard deviation between the samples s_b	7.795	F_{value}	2.21
test value s_b^2/s_w^2	1.709	Characteristic no. for homogeneity between the samples	0.773
Homogeneity between the samples: No significant inhomogeneity			

Measurements, compilation of results: ESK, Ceramics GmbH & Co.KG, Kempten; Germany
Final evaluation: BAM, Federal Institute for Materials and Testing (Division I.1)

Analyt: SiO_2 free

mass fraction in mg/kg

Serial number	Sample number	1. measurement	2. measurement	**mean**	**mean of sub-samples 1-4**	**SD of sub-samples 1-4**	**RSD_w (rel.%)**
1	O/8/2	680	660	670	661.25	31.46	4.76
	O/8/4	680	670	675			
	O/8/6	660	710	685			
	O/8/8	630	600	615			
2	O/56/2	680	660	670	647.50	21.02	3.25
	O/56/4	640	630	635			
	O/56/6	640	680	660			
	O/56/8	650	600	625			
3	O/76/2	690	670	680	666.25	13.15	1.97
	O/76/4	660	650	655			
	O/76/6	660	690	675			
	O/76/8	680	630	655			
4	O/128/2	680	660	670	657.50	31.75	4.83
	O/128/4	690	660	675			
	O/128/6	670	680	675			
	O/128/8	620	600	610			
5	O/143/2	680	660	670	648.75	30.10	4.64
	O/143/4	670	610	640			
	O/143/6	650	700	675			
	O/143/8	630	590	610			
6	O/188/2	570	510	540	587.50	45.55	7.75
	O/188/4	630	570	600			
	O/188/6	620	670	645			
	O/188/8	590	540	565			
7	O/203/2	600	600	600	591.25	35.68	6.03
	O/203/4	600	560	580			
	O/203/6	630	640	635			
	O/203/8	560	540	550			
8	O/229/2	640	660	650	645.0000	13.54	2.10
	O/229/4	650	600	625			
	O/229/6	620	690	655			
	O/229/8	630	670	650			

Analyt: $SiO_{2\ free}$

9	O/286/2	570	600	585	578.75	17.02	2.94
	O/286/4	610	580	595			
	O/286/6	560	600	580			
	O/286/8	570	540	555			
10	O/294/2	590	580	585	590.00	20.41	3.46
	O/294/4	600	560	580			
	O/294/6	620	620	620			
	O/294/8	550	600	575			

M_{Ss} - mean of means of the sub-samples 1-4	627.38
SD of means of the sub-samples 1-4	35.58
RSD (rel.%)	5.67

mean RSD_w (%) 4.17

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	27.85	M_{Ss} 627.3800	RSD % 5.67
standard deviation between the samples s_b	71.17	F_{value}	2.21
test value s_b^2/s_w^2	6.530	Characteristic no. for homogeneous between the samples	2.955
Homogeneity between the samples: Significant inhomogeneity			

Appendix 6 for CRM BAM-S003

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Aluminium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
4	without sample preparation	Merck-Al-standard solution 1000 mg/L	ETV-ICP OES
6	M: 0.5 g Decomposition with Na_2CO_3 in Pt-crucible	Al-stock-solution 1000 mg/L	F AAS
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Al stock solution 1 g/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	Al-metal 1000 mg/L in 5% HCl calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel	Spex standard solution	ICP OES
19	M: 0.25 g; $HF-HNO_3-H_2SO_4$. HP 250°C 18h → 50 ml flask	Al metal; digestion reagent HCl	ICP OES
20	M: 0.1 g Micro wave decomposition with $HF-HNO_3-H_2SO_4$. 260°C	Al metal (5N); digestion reagent H_2SO_4	ICP OES
22	M: 0.25 g; decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel (16h-250°C) → 50 ml flask	Al metal (5N J&M) digestion reagent HCl	ET AAS
24	M: 0.25 g; decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3101a/ NIST checked with Merck 1000 mg/L Al	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation	Al_2O_3 Merck addition method: pure SiC + addition Al_20_3	DCarc-OES
26	M: 0.5 g; decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with $HF-HNO_3-H_2SO_4$ in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; $HF-HNO_3-H_2SO_4$ → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1004 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with $HF-HNO_3-H_2SO_4$. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Al	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Boron			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: B stock solution 1 g/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
18	SW 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex standard solution	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	H_3BO_3. digestion reagent water	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
25	M: 0.005 g sample mixing; without sample preparation	B powder Merck addition method: pure SiC + addition B	DCarc-OES
26	decomposition with $NaKCO_3$ in Pt-crucible	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 –H_3PO_4 → 250°C 16h → H_3PO_4 → H_2SO_4 fume → 100 ml flask	JCSS – Kanto Co. 1007 mg/L	ICP OES
33	M: 0.125 g; fusion decomposition in Pt-vessel with Na_2CO_3. then evaporate with HCl → Filtration → 100 ml flask → with precipitate fusion decomposition rerun	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF-HNO_3-H_2SO_4	Kraft 1 g/L B	ICP OES (a)
	M: 1 g; fusion decomposition in Zr-crucible with 2.5 g $NaKCO_3$ and /.5 g Na_2O_2. Transferred into 100 ml flask. Aliquot of 25 ml has been used to separate BF_4-complex. (J.W. Maeck et.al. Anal. Chem. 35. (1963). 62-65)	Kraft 1 g/L B	ICP OES (d)
	M: 1 g; fusion decomposition in Zr-crucible with 2.5 g $NaKCO_3$ and /.5 g Na_2O_2. Transferred into 200 ml calibrated flask.	Kraft 1 g/L B close matrix matching with $NaCO_3$/K_2CO_3	ICP OES (e)
	M: 1 g; sample + 10 g $NaKCO_3$ in Pt-crucible leach out. Transferred into 100 ml plastic flask. (U. de la Chevallierie-Haaf et.al. Fres. Z. Anal. Chem. (1986) 323:266-270	no information	MAS

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Calcium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
4	without sample preparation	Merck-Ca-standard solution 1000 mg/L	ETV-ICP OES
6	M: 0.5 g; Decomposition with Na_2CO_3 in Pt-crucible	Ca-stock-solution 1000 mg/L	F AAS
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Ca stock solution 1 g/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	CaO. digestion reagent HNO_3	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	source $CaCO_3$. digestion reagent HCl	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	$CaCO_3$ (5N J&M) digestion reagent HNO_3	F AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3109a. NIST checked with Merck 1000 mg/L Ca	ICP-MS
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1007 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Ca	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Chromium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
1	M: 0.5 g; no sample digestion	K_2CrO_4	INAA
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Cr-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ET AAS
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	Bought from the reference material and calibration solution provider. calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Cr digestion reagent water	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Cr metal (4N) digestion reagent HNO_3	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Cr metal (99.995% J&M) digestion reagent HCl	ET AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3112a. NIST checked with Merck 1000 mg/L Cr	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation; (not results delivered)	Cr_2O_3 Merck addition method: pure SiC + addition Cr_2O_3	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Wako Co. 100.3 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
35	M: 0.08-0.11 g; no sample digestion	Cr-metal 4N8	INAA
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Copper			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
4	without sample preparation	Merck-Cu-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Cu stock solution 1 g/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Cu metal; digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Cu metal (6N J&M) digestion reagent HNO_3	ET AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	BAM A- Primary Cu 1 metal checked with Merck 1000 mg/L Cu	ICP-MS
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 100.0 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Cu	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Iron			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
1	M: 0.5 g; no sample digestion	$K_3Fe(CN)_6$	INAA
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Fe-standard solution 1000 mg/L	ETV-ICP OES
6	M: 0.5 g; Decomposition with Na_2CO_3 in Pt-crucible. Titration with $TiCl_3$	1 mg Fe_2O_3.Titration with $TiCl_3$	Titrimetry
8	M: 50 mg; fused with Lithium borate (Spektromelt) in a platinum crucible.	Merck. multielement stock solution 1000 mg/l	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Fe stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	Fe-metal 1000 mg/L in 5% HCl calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Fe metal digestion reagent HNO_3	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Fe metal (99.9985%. J&M). digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Fe metal (3N J&M) digestion reagent HNO_3/HCl	F AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3126a. NIST checked with BAM A-Primary Fe	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation	Fe_2O_3 powder Merck addition method: pure SiC + addition Fe_2O_3	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.003 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Fe	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Magnesium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
4	without sample preparation	Merck-Mg-standard solution 1000 mg/L	ETV-ICP OES
6	M: 0.5 g; Decomposition with Na_2CO_3 in Pt-crucible	Mg-stock-solution 1000 mg/L	F AAS
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Mg stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	MgO. digestion reagent HNO_3	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Mg metal (99.95%. J&M). digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Mg metal (m3N8 J&M) digestion reagent HCl	ET AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3131a. NIST checked with Alfa JM 1000 mg/L Mg	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation (not results delivered)	MgO powder Merck addition method: pure SiC + addition MgO	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.008 g/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Mg	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Manganese			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
1	M: 0.150 g; no sample digestion	$MnSO_4 * 4 H_2O$	INAA
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Mn-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Mn stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ET AAS
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml	Merck: standard solution 1000 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Mn. metal digestion reagent HCl	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Mn metal (99.9%. J&M). digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Mn metal (4N J&M) digestion reagent HCl	ET AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Mn - pure metal 99.99%. Alfa JM checked with Merck 1000 mg/L Mn	ICP-MS
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Wako Co. 100.6 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
35	M: 0.08 – 0.11 g; no sample digestion	self made 0.9700 mg/g	INAA
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Mn	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Sodium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
1	M: 0.150 g; no sample digestion	Na_2CO_3	INAA
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Na-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Na stock solution 1 g/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml	Merck: standard solution 1000 mg/L	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	NaCl. digestion reagent water	F AES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Na_2CO_3 (99.9%. Merck. waterfree). digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	NaCl (5N J&M) digestion reagent HCl	F AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3152a. NIST checked with Merck 1000 mg/L Na	ICP-MS
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	F AAS
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.005 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
35	M: 0.08 – 0.11 g; no sample digestion	NaCl self made 0.7202 mg/g	INAA
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Na	ICP OES
	M: 0.5 mg; no sample digestion	Kraft 1 g/L Na	S AAS

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Nickel			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Ni-standard solution 1000 mg/L	ETV-ICP OES
6	M: 0.5 g Decomposition with Na_2CO_3 in Pt-crucible	Ni-stock-solution 1000 mg/L	F AAS
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Ni stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	NiO 1000 mg/L in 1% HNO_3 calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Ni metal; digestion reagent HNO_3	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Ni metal (99.998%. J&M). digestion reagent HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
23	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Ni metal (4N J&M) digestion reagent HNO_3	ET AAS
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Ni- Powder. 5N Purity. Alfa JM checked with Merck 1000 mg/L Ni	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation	Ni powder Merck addition method: pure SiC + addition Ni	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 100.8 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: a) Aldrich. Wako 1000 mg/L b) Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Ni	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Titanium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Ti-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: Ti stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	TiO_2 1000 mg/L in 5% HCl calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Ti metal digestion reagent H_2SO_4	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Ti metal (99.9%. Koch Light). digestion reagent HF/HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3162a. NIST checked with Spectrascan 1312-2. 100 mg/L Ti	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation	TiO_2 powder Merck addition method: pure SiC + addition TiO_2	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck Titrisol 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.006 g/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Ti	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Vanadium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-V-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Merck: V stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP OES
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	Bought from the reference materials and calibration solution provider. calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel	Spex high purity 10 mg/L	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	V_2O_5. digestion reagent NaOH. H_2SO_4	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	V (99.9%. Ventron). digestion reagent HF/HNO_3	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	SRM 3165. NIST checked with Merck 1000 mg/L V	ICP-MS
25	M: 0.005 g sample mixing; without sample preparation	V_2O_5 powder Merck addition method: pure SiC + addition V_2O_5	DCarc-OES
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.005 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L V	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Zirconium			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
1	M: 0.5 g; no sample digestion	$ZrOCl_4$*8H_2O	INAA
2	no sample digestion		K_0-INAA
4	without sample preparation	Merck-Zr-standard solution 1000 mg/L	ETV-ICP OES
8	M: 50 mg; Decomposition with 1 g KOH at 400°C in a crucible of glassy carbon	Merck multi element stock solution 1000 mg/L	ICP OES
11	M: 5.0 g; Decomposition with H_2SO_4. HF. HNO_3 HCl. described in ISO 9286. 1997. Part 3.5.4	Titrisol 1000 mg/L	ICP OES
12	M: 0.5 g HF(70%) + HNO_3 (100%) 24 h by 220°C pressure digestion system → 50 ml flask	Kraft: Zr stock solution 1 g/L	ICP OES
13	M: 0.25 g; Micro wave decomposition with HCl- HNO_3-H_2SO_4	Merck standard solution 1000 mg/L	ICP-MS
14	M: 0.5 g; dissolve in HNO_3/HCl. filtering; → 250 ml flask	Merck: standard solution 1000 mg/L	ICP OES
16	M: 0.1 g; sample mixed with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7$, heat with a gas burner for 60-75 min, leach out with water, add 10 ml HCl → dilute to 100 ml	Bought from the reference material and calibration solution provider. 1000 mg/L in 10% HCl calibration: 0-2-5 mg/L matrix matching: HCl, Na_2CO_3 and $Na_2B_4O_7$, were added.	ICP OES
18	M: 0.2 g; Decomposition with HF-HNO3-H2SO4 in a high pressure vessel	Spex high purity 10 ppm	ICP OES
19	M: 0.25 g; HF-HNO_3-H_2SO_4 . HP 250°C 18h → 50 ml flask	Zr metal digestion reagent H_2SO_4	ICP OES
20	M: 0.1 g Micro wave decomposition with HF-HNO_3-H_2SO_4. 260°C	Zr metal (99.95%. J&M). digestion reagent H_2SO_4/H_2O_2	ICP OES
22	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Merck 1 g/L checked with self prepared standard and ICP-IV Merck standard	ICP OES
24	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (16h-250°C) → 50 ml flask	Zr foil. Alfa JM checked with Spectrascan 1312-2. 100 mg/L Zr	ICP-MS
26	M: 0.5 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-250°C)	standard solution: a) Merck 1000 mg/L b) Fluka 1000 mg/L	ICP OES
27	M: 0.1 g; melting with $Li_2B_4O_7$ (1100°C 1h) dissolve in HCl → 250 ml flask	Merck CERTIPUR 1000 mg/L	ICP OES
28	M: 0.25 g; decomposition with HF-HNO_3-H_2SO_4 in a high pressure vessel (12h-240°C) → 25 ml flask	Merck CERTIPUR 1000 mg/L; Baker Atomic absorption standard 1000 mg/L	ICP OES
31	M: 0.5 g; HF-HNO_3-H_2SO_4 → 230°C 16h → dryness → dissolve (HCl) → 100 ml flask	JCSS – Kanto Co. 1.006 mg/L	ICP OES
33	M: 0.5 g; SiC in Pt-crucible with HF-HNO_3-H_2SO_4. then pressure decomposition – 250°C. 72h → evaporate the H_2SO_4 → dissolve in HCl → 100 ml flask	standard solution: Spex 1000 mg/L	ICP OES
36	M: 0.5 g; pressure decomposition with HF (73%)-HNO_3 (100%) DAB-II 250°C, 8h	Kraft 1 g/L Zr	ICP OES
	M: 0.08 g; pressing in graphite electrode	synthetic mixed oxide	DCarc OES

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Total carbon			
Lab-code	**Sample preparation (M = mass of sub-samples)**	**Calibration**	**Final determination**
5	40 mg combustion in oxygen atmosphere. Temp.1450°C	$CaCO_3$	CGHE/comb.-IR
6	M:50 mg; combustion	calibration with $CaCO_3$ BAM Pure Substance No. 3	CGHE/comb.-IR
7	1.5 g Cu-(pieces of wire) at first in a crucible, than the sample in a folded Al-ship and mulch with W as additional charge; crucible cover with a lid.	$CaCO_3$	CGHE/comb.-IR
8	M: 35 mg; coulometric determination with gas split	Calibrated by a SiC-Standard (ESK- Standard No.1. SiC-dkl. F180), traced back via $CaCO_3$ (Riedel de Haen, p.a., 6 measurements)	CGHE/coul.
9	M: 67-106 mg; combustion	Calibrated by a SiC-standard (ESK- Standard No. 1) traced back via $CaCO_3$ (Merck 12.0002% C, 5 measurements)	CGHE/comb.-IR
11	M: 40 mg combustion (1050°C) with lead borate. IR-detection of CO_2	$CaCO_3$	CGHE/comb.-IR
12	M: 60 mg combustion → Cu addition	Calibration: Na_2CO_3 (Merck, suprapur, dried 11.332% C) and $BaCO_3$ (Riedel de Haen, 31142, dried 6.086% C) checked against BCS CRM 352	CGHE/comb.-TC
13	M: 50 mg; Carrier gas hot extraction in reactive atmosphere (Oxygen_"combustion") with IR-detection (EMIA 820)	$CaCO_3$	CGHE/comb.-IR
16	M: 10 mg; sample mixed with 0.25 g Pb_3O_4, heat at 1200°C in oxygen (150 ml/min), the CO_2 was absorbed with a solution (500 ml N,N-dimethylformamide + 25 ml $NH_2CH_2CH_2OH$, then titrate with tetrabutyl ammonium hydroxide solution		CGHE/titr.
18	M: 10 mg sample was combusted by using Fe-chips as analyst	Matrix Reference Material: LECO Part# 501-024 ; (C and S in white iron) **No traceability!**	CGHE/comb.-IR
19	M: 200 mg 1. copper powder + SiC agitate together. then mulch SiC with copper powder	Traceability by primary method gravimetry checked by an WC_SRM (6.100 ± 0.005% C)	Comb./grav.
20	M: 25 mg; combustion with Ni-shuck. Fe + W-additional charge. crucible + cup by 1200°C glowed in O_2 gas flow	Ringsdorf spectral-pure Carbon calibration used empty crucible and additional charge and 0.24 % C-standard	CGHE/comb.-IR
21	M: 18 mg (sample 1-3) for day 1 M: 33 mg (sample 4-6) for day 2	$CaCO_3$ (BAM RS 3) for day 1 Ba CO_3 Merck for day 2	CGHE/comb.-IR
25	M: 40 mg; digestion with leadborate; direct powder analysis (1050°C – 3 min)	$CaCO_3$	CGHE/coul.
26	M: 22 – 33 mg; combustion in oxygen atmosphere. IR-detection of CO_2	NIST 112b. SiC and $CaCO_3$	CGHE/comb.-IR
27	M: 50.0 – 51.5 mg; - determination time 50 s;	M: 109 – 111 mg $BaCO_3$ p.A. (6.08% C), Riedel de Haen, LOT No. 12250	CGHE/comb.-IR
28	M: 30 mg; additional charge: 1 g Lecocel II HP; 1 g high pure Iron ships	NBS-Standard 112b; target: 29.43 ± 0.08% C-total **No traceability!** **Participant withdrew his values**	CGHE/comb.-IR
29	M: 200 mg; combustion analysis	BAM standard, steel sample 228-1/1133 (2.05%C); **No traceability!**	CGHE/comb.
31	M: 100 mg additional charge 2 g Sn (1350°C. 70 s)	$CaCO_3$ (99.99%) 0.25 g additional charge 2 g Sn	CGHE/comb.-IR
32	furnace temp. 1050 ± 30°C decomposition with $Pb(BO_3)_2$	$CaCO_3$	CGHE/coul.
33	M: 100 mg; additional charge 2 g Sn (1350°C 5 min) under O_2 gas flow	$CaCO_3$ Merck Standard Reference Material of NIST	CGHE/comb.-IR
36	M: 20 mg; additional charge W. Cu	WC – traceable to $CaCO_3$ ZRM BAM	CGHE/Comb.-TC after absorption

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Free carbon			
Lab-code	**Sample preparation (M = mass of sub-samples)**	**Calibration**	**Final determination**
5	combustion in oxygen atmosphere Temp. 800°C	$CaCO_3$	CGHE/comb.-IR
6	M:200 mg; combustion	PRE Standard 82 – 15 **No traceability;** **Participant withdrew his values**	CGHE/comb.-IR
8	M: 200-300mg; coulometric determination	$CaCO_3$	Comb./coul.
9	no information	$CaCO_3$	CGHE/comb.-IR
11	M: 0.5 g; combustion in oxygen atmosphere. IR-detection of CO_2	$CaCO_3$ (12% C)	CGHE/comb.-IR
13	M: 200 mg; “combustion” with IR-detection at 850°C	$CaCO_3$ oxidation correction Roßberg et al in DKG 69(1992) 251	CGHE/comb.-IR
15	M: 0.4 –0.7 g;	no calibration;	Comb./coul.
16	M: 10 mg; sample mixed with 0.25 g Pb_3O_4, heat at 1200°C in oxygen (150 ml/min), the CO_2 was absorbed with a solution (500 ml N,N-dimethylformamide + 25 ml $NH_2CH_2CH_2OH$, then titrate with tetrabutyl ammonium hydroxide solution		CGHE/titr.
18	M: 0.25 g Combustion in quartz boat	NIST 112 b **No traceability;**	CGHE/comb.
19	M: 0.5 g t: 750°C. coulometric determination of carbon	pure iron (SRM 0.061% ±0.002%)	Comb./coul.
25	M: 0.1 g; no sample digestion (1050°C – 5 min)	$CaCO_3$	Comb./coul.
26	M: 0.5 g; combustion → 850°C and weighting return from chip	$CaCO_3$	Comb./coul. (Appendix 2, method M2)
	M: 0.05 – 0.12 g wet chemical oxidation → coulometric determination;	$CaCO_3$	Wet chemical oxidation/coul. (Appendix 1, method M1)
28	M: 0.1 g	gas calibration with CO_2. target: 0.3883%C	CGHE/comb.-IR
31	M: 0.5 g (850°C. 10 min)	$CaCO_3$ (99.99%) 0.25 g	CGHE/comb.-IR
32	furnace temp. 850 ± 20°C. 10 min DIN 51075 -2. DIN 51075- 4	$CaCO_3$	Comb./coul. (appendix 2, method M2)
33	M: 0.5 g; (850°C 10 min) under O_2 gas flow	$CaCO_3$ Merck Standard Reference Material of NIST	CGHE/comb.-IR
36	M: 920 mg; wet chemical oxidation → coulometric determination;	$CaCO_3$ (BAM ZRM RS 3)	Wet chemical oxidation/coul. (appendix 1, method M1)

Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S003

Oxygen			
Lab-code	**Sample preparation (M = mass of sub-samples)**	**Calibration**	**Final determination**
7	M: 30 - 70 mg; sample into a Pt-capsule (1 g) 1000A	Gas / $CaCO_3$	CGHE-IR
12	M: 25 mg; used high temperature graphite crucibles, pre-cleaned Ni-Pins, Sn-capsules, Power: 5000 W	300 mg KNO_3 solved in 100 ml Water; 100 µg solution weighted in Sn-capsules, dried at 105°C (6 calibration samples)	CGHE-IR
13	M: 40 mg;	KNO_3	CGHE-IR
15	M: 200 mg; combustion	LECO STEEL STD. **No traceability!**	CGHE-IR
18	M: 88 mg; oxygen combustion used sample plaed in Ni-basket + Sn	Steel **No traceability!**	CGHE-IR
19	M: 50 mg; with pulse coulometric apparatus for determination of oxygen; -heat power:750A,5.5V -Ar carrier gas flow rate: 150 ml/min; heat time: 20 s; -flux: Ni-Sn; -determination time 100 s	Nb powder (0.50%±0.02%) internal standard Traceability to pure primary substance was checked	CGHE/coul.
20	M: 30-50 mg; SiC into Ni shuck with Sn as additional charge	ZrO_2 (pure 99.99%) by 1000°C glowed	CGHE-IR
21	M: 330 mg into Ni capsules and Ni capsules as a tong	Fe_2O_3 1 mg to obtain some signal intensity	CGHE-IR
26	M: 50 – 100 mg; (ever 3 samples on a day) He-carrier gas T_{max} > 2500°C	$CaCO_3$ for 1 day CuO for 2 day	CGHE-IR
27	M: 88 – 92 mg;	M: 0.41 – 0.45 mg CeO_2 (18.59 % O) Sigma Aldrich, LOT No. 91K3572	CGHE-IR
28	M: 50 mg; in Pt- capsule	gas calibration with CO_2. target: 0.0214%C	CGHE-IR
29	M: 200 mg;	LECO steel standard, Part No. 501-553 **No traceability!**	CGHE-IR
31	M: 0.05 g additional charge 0 g Sn; Ni capsule 0.4 g	Y_2O_3 (99.99%) 0.01 g	CGHE-IR
33	M: 30 mg additional charge 0.7 g Sn. 2500 – 3000 °C in an induction furnace. oxygen is evaporated as CO gas in He carrier gas	JCRM Si_3N_4 Sample R005 (Ceramic Society of Japan) **No traceability!**	CGHE-IR
35	M: 18 – 27 mg;	Fe_2O_3, suprapur	CGHE-IR
36	M: 0.05 g; Ni/Sn as flux	0.5 g steel pin Part 501-553 LECO **No traceability!**	CGHE-IR
37	M: 90 mg; (ever 3 samples on a day) instrument parameter: 5300W/27 s; Sn-capsules	KNO_3 solution	CGHE-IR

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Nitrogen			
Lab-code	**Sample preparation (M = mass of sub-samples)**	**Calibration**	**Final determination**
7	M: 30 - 70 mg; sample into a Pt-capsule 1000A	Gas / company-internal standard (10 µg/g N)	CGHE-TC
12	M: 100 mg; carrier heat gas extraction	Leco standard 501 - 552	CGHE-TC
13	M: 40 mg;	KNO_3	CGHE-TC
19	M: 0.5 g; heat power: 5.0 KW/ 70 s; integral time 45 s; flux Ni	primary KNO_3	CGHE-TC
21	M: 0.55 g Sn shuck and 800 mg Cu as additional charge	KNO_3	CGHE-TC
26	M: 50 – 100 mg; (ever 3 samples on a day) He-carrier gas T_{max} > 2500°C	$NaNO_3$ – solution ; dried in capsule 1 g / 100 ml	CGHE-TC
28	M: 1 g in Pt capsule	gas calibration with N_2. target: 0.0.0458% N_2	CGHE-TC
29	M: 200 mg;	LECO steel standard, Part No. 501-553 (0.0620% N) **No traceability!**	CGHE-TC
35	M: 18 – 27 mg; (ever 3 samples on a day) He-carrier gas	KNO_3 suprapur	CGHE-TC
36	M: 0.05 g; Ni/Sn as flux	0.5 g steel pin Part 501-553 Leco 622 ppm N traceable to NIST SRM 885 steel 0.037% N **No traceability!**	CGHE-TC
37	M: 90 mg; (ever 3 samples on a day) instrument parameter: 5300W/27 s; Sn-capsules	KNO_3 solution	CGHE-TC

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Free silicon			
Lab-code	**Sample preparation**	**Calibration**	**Final determination**
6	M: 2 g; (DIN 51075/4)		volumetry
8	M: 4.0 g (DIN 51075/4)	ESK standard No. 1. SiC-dkl. F180	volumetry
9	not detected (DIN 51075/4)		volumetry
11	M: 3.0 g; liberation of hydrogen resulting from the attack on silicon by a boiling sodium hydroxide solution		volumetry
15	*ANSI B74.15 – 1992 R 2000*	no information	combustion
16	M: 0.2 g; added 1 ml 10% $NaNO_3$, 2ml HNO_3 (1+1) and 2 ml HF (1+1). Heat at 80-90 °C for 15 min, add 12 ml 45% $AlCl_3$ after cooling, then dilute to 100 ml and filter. Take 10 ml clear solution add 50 ml H_2O, 0.1 ml 0.2% p-nitrophenol as indicator, add NH_3. H_2O till it turns yellow, then add 5 ml HCl (1+4), add 5ml 10% $(NH_4)_6Mo_7O_{24}$ x $4H_2O$, after 10 min add 5 ml 10% tartaric acid 1 ml 10% Na_2SO_3, dilute to 100 ml, then measure. the result should substract the SiO_2 (convent to Si)	0.5 mg/ml SiO_2 prepare: 0.5 g SiO_2 mixed with 5 g Na_2CO_3, fused at 880 °C for 20 min, leach out with H_2O and dilute to 1000 ml	MAS
26	M: 5g	SiC – in house standard	volumetry
32	DIN ISO 9286: 1998-01		volumetry
33	M: 1 g; in glass syringe with NaOH → heat 90 min → hydrogen gas is washed and moved in another syringe → the volume is measured	NaOH 250 g/l special grade (Kanto)	volumetry

Free silicon dioxide			
Lab-code	**Sample preparation**	**Calibration**	**Final determination**
6	M: 1.0g; fuming with HF after than anneal at 400°C		gravimetry
8	M:1.7 g; HF-destillation	Merck Si-standard solution	ICP OES
9	not detected		titrimetry (S.-Hinrichs)
16	M: 0.2 g; added 1 ml 10% NaCl, 2 ml HCl (1+1) and 2 ml HF (1+1). Heat at 80-90 °C for 15 min, add 12 ml 45% $AlCl_3$ after cooling, then dilute to 100 ml and filter. Take 10 ml clear solution add 50 ml H_2O, 0.1 ml 0.2% p-nitrophenol as indicator, add NH_3. H_2O till it turns yellow, then add 5 ml HCl (1+4), add 5 ml 10% $(NH_4)_6Mo_7O_{24}$ x $4H_2O$, after 10 min add 5 ml 10% tartaric acid 1 ml 10% Na_2SO_3, dilute to 100 ml	0.5 mg/ml SiO_2 prepare: 0.5 g SiO_2 mixed with 5 g Na_2CO_3, fused at 880 °C for 20 min, leach out with H_2O and dilute to 1000 ml	MAS
26	M:1 g; HF-destillation. SiF_4 absorb in diluted NaOH	Certipur Si standard Merck. Si-standard solution Merck	ICP OES
32	DIN ISO 9286: 1998-01		volumetry
33	M: 0.2 g; acid decomposition with NaCl-HCl-HF → with $AlCl_3$ to 100 ml → 10 ml + HCl + H2O + 7-molybdic acid 6-ammonium → 10 min → tartaric acid + ascorbic acid → 100 ml → absorbance 650 nm	standard solution: a) Aldrich 1000 mg/L b) Spex 1000 mg/L	MAS

Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of CRM BAM-S003

Tab. 6a1: Aluminium evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	6 F AAS 2,3	204,000	2,757	2,893	205,000	203,000	207,000	199,000	205,000	205,000
L 2	4 ETV-ICP OES 2	305,267	10,768	11,300	315,900	312,400	303,000	314,400	296,400	289,500
L 3	8 ICP OES 3	327,167	15,420	16,182	320,000	306,000	326,000	352,000	324,000	335,000
L 4	25 DCarc-OES 3	334,000	12,215	12,819	352,000	344,000	321,000	331,000	322,000	334,000
L 5	19 ICP OES 1	345,333	4,676	4,907	343,000	344,000	354,000	347,000	343,000	341,000
L 6	26 ICP OES 3	354,267	3,000	3,149	355,300	356,900	356,800	355,500	349,700	351,400
L 7	28 ICP OES 1	367,250	2,476	2,598	370,100	364,800	367,500	365,800	370,300	365,000
L 8	23 ET AAS 2	371,000	14,085	14,782	384,000	375,000	390,000	361,000	356,000	360,000
L 9	31 ICP OES 3	371,333	4,926	5,170	366,000	375,000	369,000	366,000	377,000	375,000
L 10	33 ICP OES 3	373,217	2,674	2,806	369,100	372,800	372,200	377,100	374,800	373,300
L 11	22 ICP OES 3	376,765	2,316	2,431	372,840	376,607	378,321	375,575	379,195	378,049
L 12	36 DCarc-OES 3	377,500	16,837	17,670	374,000	397,000	371,000	355,000	370,000	398,000
L 13	16 ICP OES 3	380,500	10,968	11,510	389,000	370,000	371,000	388,000	371,000	394,000
L 14	36 ICP OES 3	385,000	4,000	4,198	388,000	384,000	391,000	382,000	380,000	385,000
L 15	27 ICP OES	392,000	15,556	139,768	403,000	381,000				
L 16	24 ICP-MS 2	399,483	5,110	5,258	395,000	392,500	402,700	398,400	406,000	402,300
L 17	20 ICP OES 3	402,167	7,705	8,086	399,000	397,000	393,000	404,000	405,000	415,000
L 18	12 ICP OES (2)	402,623	1,959	2,056	400,510	404,340	405,530	401,700	402,610	401,050
L 19	18 ICP OES 3	415,333	12,044	12,640	405,000	416,000	413,000	423,000	434,000	401,000

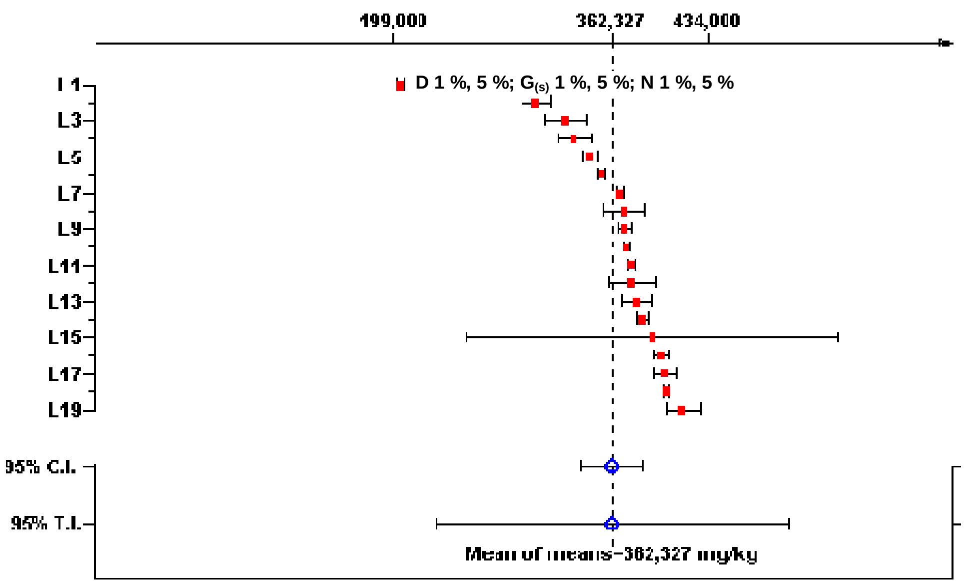
Range [min..max]	[199,000 .. 434,000]
	Case of No Pooling
Mean of means	362,327
95% H.W. Confidence Interval	22,885
95% H.W. Tolerance Interval	132,188
	Case of Pooling
Mean of All	361,248
95% H.W. Confidence Interval	9,000
95% H.W. Tolerance Interval	105,639

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test (single test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6a1)



Tab. 6a2: Aluminium accepted results in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	305,267	10,768	11,300	315,900	312,400	303,000	314,400	296,400	289,500
L 2	8 ICP OES 3	327,167	15,420	16,182	320,000	306,000	326,000	352,000	324,000	335,000
L 3	25 DCarc-OES 3	334,000	12,215	12,819	352,000	344,000	321,000	331,000	322,000	334,000
L 4	19 ICP OES 1	345,333	4,676	4,907	343,000	344,000	354,000	347,000	343,000	341,000
L 5	26 ICP OES 3	354,267	3,000	3,149	355,300	356,900	356,800	355,500	349,700	351,400
L 6	28 ICP OES 1	367,250	2,476	2,598	370,100	364,800	367,500	365,800	370,300	365,000
L 7	23 ET AAS 2	371,000	14,085	14,782	384,000	375,000	390,000	361,000	356,000	360,000
L 8	31 ICP OES 3	371,333	4,926	5,170	366,000	375,000	369,000	366,000	377,000	375,000
L 9	33 ICP OES 3	373,217	2,674	2,806	369,100	372,800	372,200	377,100	374,800	373,300
L 10	22 ICP OES 3	376,765	2,316	2,431	372,840	376,607	378,321	375,575	379,195	378,049
L 11	36 DCarc-OES 3	377,500	16,837	17,670	374,000	397,000	371,000	355,000	370,000	398,000
L 12	16 ICP OES 3	380,500	10,968	11,510	389,000	370,000	371,000	388,000	371,000	394,000
L 13	36 ICP OES 3	385,000	4,000	4,198	388,000	384,000	391,000	382,000	380,000	385,000
L 14	27 ICP OES	392,000	15,556	139,768	403,000	381,000				
L 15	24 ICP-MS 2	399,483	5,114	5,258	395,000	392,500	402,700	398,400	406,000	402,300
L 16	20 ICP OES 3	402,167	7,705	8,086	399,000	397,000	393,000	404,000	405,000	415,000
L 17	12 ICP OES (2)	402,623	1,959	2,056	400,510	404,340	405,530	401,700	402,610	401,050
L 18	18 ICP OES 3	415,333	12,044	12,640	405,000	416,000	413,000	423,000	434,000	401,000

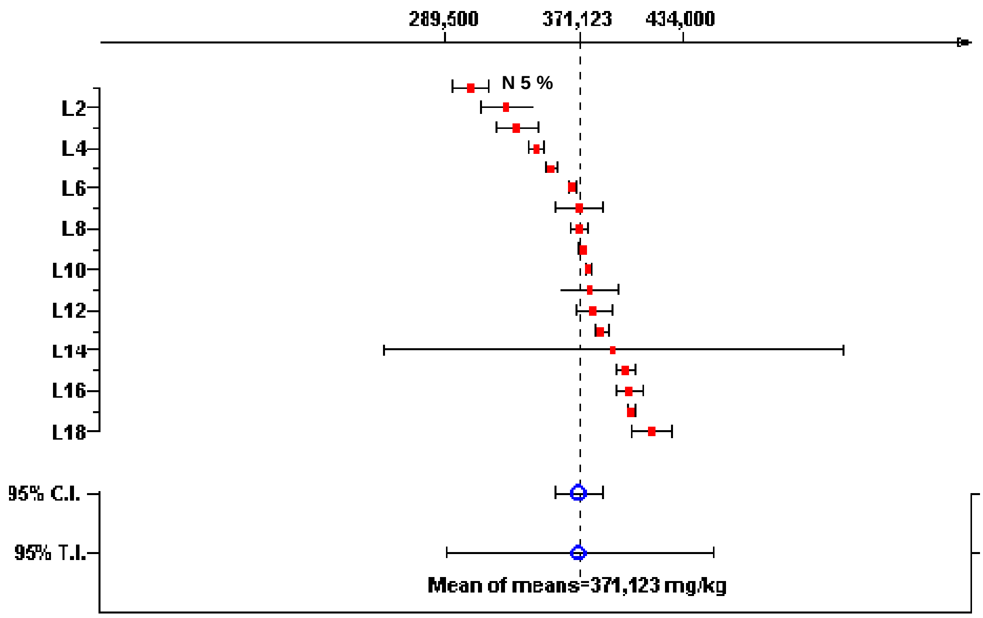
Range [min..max]	[289,500 .. 434,000]
	Case of No Pooling
Mean of means	371,123
95% H.W. Confidence Interval	14,332
95% H.W. Tolerance Interval	81,245
	Case of Pooling
Mean of All	370,320
95% H.W. Confidence Interval	5,758
95% H.W. Tolerance Interval	65,938

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6a2)



Tab. 6b1: Boron evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES 1	54,550	0,729	0,765	55,600	54,100	55,300	54,100	53,800	54,400
L 2	26 ICP OES 3	55,350	2,971	3,118	53,800	57,100	56,200	52,700	52,300	60,000
L 3	25 DCarc-OES 2	61,167	2,317	2,431	64,000	58,000	59,000	62,000	63,000	61,000
L 4	12 ICP OES (2)	62,038	5,813	6,101	70,790	66,560	57,950	62,900	58,430	55,600
L 5	18 ICP OES	62,667	3,386	3,554	57,000	63,000	61,000	64,000	64,000	67,000
L 6	36c MAS 3	62,750	3,948	6,281	61,000	58,000	66,000	66,000		
L 7	31 ICP OES 3	63,383	0,703	0,737	63,000	64,400	63,100	62,600	63,100	64,100
L 8	36a ICP OES 3	64,633	1,294	1,358	66,800	64,300	65,400	63,200	64,400	63,700
L 9	36d ICP OES 3	65,750	1,258	2,002	64,000	66,000	67,000	66,000		
L 10	22 ICP OES 3	66,162	0,231	0,242	65,781	66,108	66,368	66,046	66,377	66,289
L 11	36e ICP OES 3	66,750	2,754	4,382	65,000	64,000	70,000	68,000		
L 12	8 ICP OES 3	111,500	11,811	12,395	125,000	103,000	116,000	124,000	97,000	104,000
L 13	33 ICP OES 3	128,600	6,184	6,489	131,200	121,800	139,200	125,300	129,300	124,800

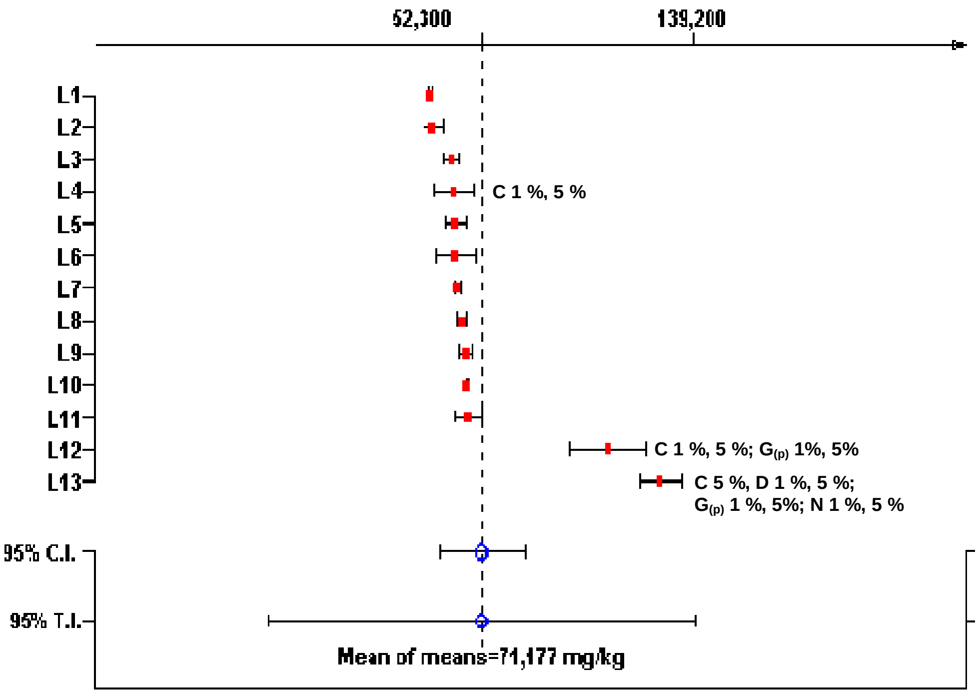
Range [min..max]	[52,300 .. 139,200]
	Case of No Pooling
Mean of means	71,177
95% H.W. Confidence Interval	13,462
95% H.W. Tolerance Interval	68,636
	Case of Pooling
Mean of All	71,685
95% H.W. Confidence Interval	5,346
95% H.W. Tolerance Interval	52,175

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(p)}$ = Grubbs test (pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6b1)



Tab. 6b2: Boron accepted results in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES 1	54,550	0,729	0,765	55,600	54,100	55,300	54,100	53,800	54,400
L 2	26 ICP OES 3	55,350	2,971	3,118	53,800	57,100	56,200	52,700	52,300	60,000
L 3	25 DCarc-OES 2	61,167	2,317	2,431	64,000	58,000	59,000	62,000	63,000	61,000
L 4	12 ICP OES (2)	62,038	5,813	6,101	70,790	66,560	57,950	62,900	58,430	55,600
L 5	18 ICP OES	62,667	3,386	3,554	57,000	63,000	61,000	64,000	64,000	67,000
L 6	36c MAS 3	62,750	3,948	6,281	61,000	58,000	66,000	66,000		
L 7	31 ICP OES 3	63,383	0,703	0,737	63,000	64,400	63,100	62,600	63,100	64,100
L 8	36a ICP OES 3	64,633	1,294	1,358	66,800	64,300	65,400	63,200	64,400	63,700
L 9	36d ICP OES 3	65,750	1,258	2,002	64,000	66,000	67,000	66,000		
L 10	22 ICP OES 3	66,162	0,231	0,242	65,781	66,108	66,368	66,046	66,377	66,289
L 11	36e ICP OES 3	66,750	2,754	4,382	65,000	64,000	70,000	68,000		

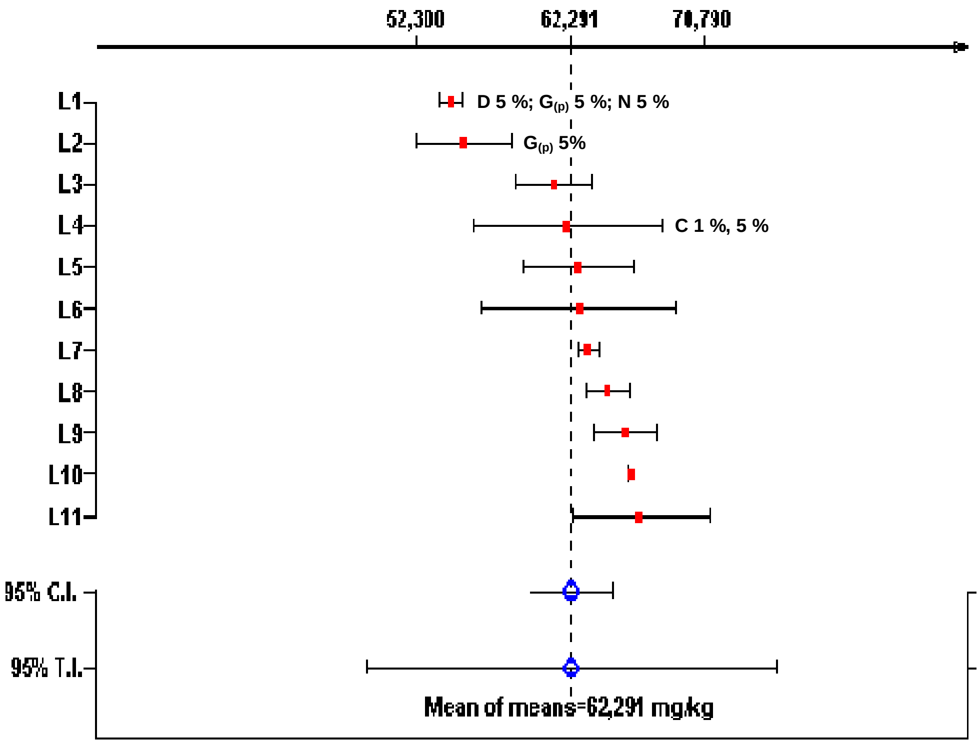
Range [min..max]	[52,300 .. 70,790]
	Case of No Pooling
Mean of means	62,291
95% H.W. Confidence Interval	2,715
95% H.W. Tolerance Interval	13,169
	Case of Pooling
Mean of All	62,012
95% H.W. Confidence Interval	1,211
95% H.W. Tolerance Interval	10,935,200

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(p)}$ = Grubbs test (pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6b2)



Tab. 6c1: Calcium evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	21,183	1,030	1,081	22,700	21,400	21,200	19,500	20,900	21,400
L 2	26 ICP OES 3	25,433	0,922	0,968	24,800	26,800	24,100	25,800	25,700	25,400
L 3	27 ICP OES	27,350	4,879	43,836	23,900	30,800				
L 4	28 ICP OES 1	27,360	0,676	0,709	28,300	26,700	26,990	27,140	26,910	28,120
L 5	23 F AAS 2	29,117	1,212	1,272	26,900	28,600	29,700	30,000	30,100	29,400
L 6	19 ICP OES 1	29,133	1,236	1,297	29,400	30,100	30,400	29,600	28,100	27,200
L 7	36 ICP OES 3	29,133	0,937	0,984	29,800	29,600	29,100	30,200	27,700	28,400
L 8	31 ICP OES 3	29,467	0,480	0,504	29,300	30,200	29,200	28,800	29,600	29,700
L 9	12 ICP OES (2)	29,493	0,670	0,704	28,950	29,050	30,260	28,750	30,250	29,700
L 10	33 ICP OES 3	29,780	0,908	0,952	29,360	29,630	28,520	31,290	29,920	29,960
L 11	11 ICP OES (2)	29,833	1,329	1,395	30,000	29,000	32,000	30,000	28,000	30,000
L 12	22 ICP OES 3	30,544	0,139	0,146	30,385	30,579	30,708	30,369	30,651	30,572
L 13	24 ICP-MS 2	32,033	0,816	0,857	30,600	32,000	32,300	31,800	33,000	32,500
L 14	18 ICP OES	32,667	0,516	0,542	32,000	33,000	33,000	32,000	33,000	33,000
L 15	20 ICP OES 2,3	35,733	3,573	8,875	34,300		33,100		39,800	
L 16	8 ICP OES 3	60,783	8,618	9,044	56,900	53,400	51,500	66,600	74,200	62,100
L 17	6 F AAS 2,3	69,667	2,582	2,710	72,000	67,000	72,000	72,000	67,000	68,000

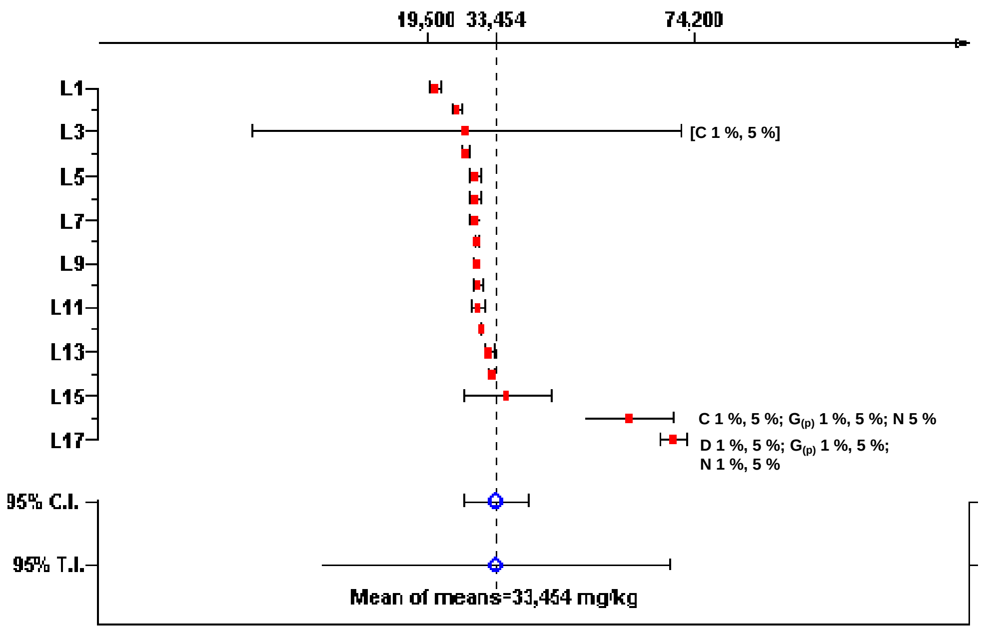
Range [min..max]	[19,500 .. 74,200]
	Case of No Pooling
Mean of means	33,454
95% H.W. Confidence Interval	6,399
95% H.W. Tolerance Interval	35,569
	Case of Pooling
Mean of All	33,639
95% H.W. Confidence Interval	2,591
95% H.W. Tolerance Interval	28,504

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(p)}$ = Grubbs test (pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6c1)



Tab. 6c2: Calcium accepted results in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg(kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	21,183	1,030	1,081	22,700	21,400	21,200	19,500	20,900	21,400
L 2	26 ICP OES 3	25,433	0,922	0,968	24,800	26,800	24,100	25,800	25,700	25,400
L 3	28 ICP OES 1	27,360	0,676	0,709	28,300	26,700	26,990	27,140	26,910	28,120
L 4	23 F AAS 2	29,117	1,212	1,272	26,900	28,600	29,700	30,000	30,100	29,400
L 5	19 ICP OES 1	29,133	1,236	1,297	29,400	30,100	30,400	29,600	28,100	27,200
L 6	36 ICP OES 3	29,133	0,937	0,984	29,800	29,600	29,100	30,200	27,700	28,400
L 7	31 ICP OES 3	29,467	0,480	0,504	29,300	30,200	29,200	28,800	29,600	29,700
L 8	12 ICP OES 2	29,493	0,670	0,704	28,950	29,050	30,260	28,750	30,250	29,700
L 9	33 ICP OES 3	29,780	0,908	0,952	29,360	29,630	28,520	31,290	29,920	29,960
L 10	11 ICP OES (2)	29,833	1,329	1,395	30,000	29,000	32,000	30,000	28,000	30,000
L 11	22 ICP OES 3	30,544	0,139	0,146	30,385	30,579	30,708	30,369	30,651	30,572
L 12	24 ICP-MS 2	32,033	0,816	0,857	30,600	32,000	32,300	31,800	33,000	32,500
L 13	18 ICP OES	32,667	0,516	0,542	32,000	33,000	33,000	32,000	33,000	33,000
L 14	20 ICP OES 2,3	35,733	3,573	8,875	34,300		33,100		39,800	

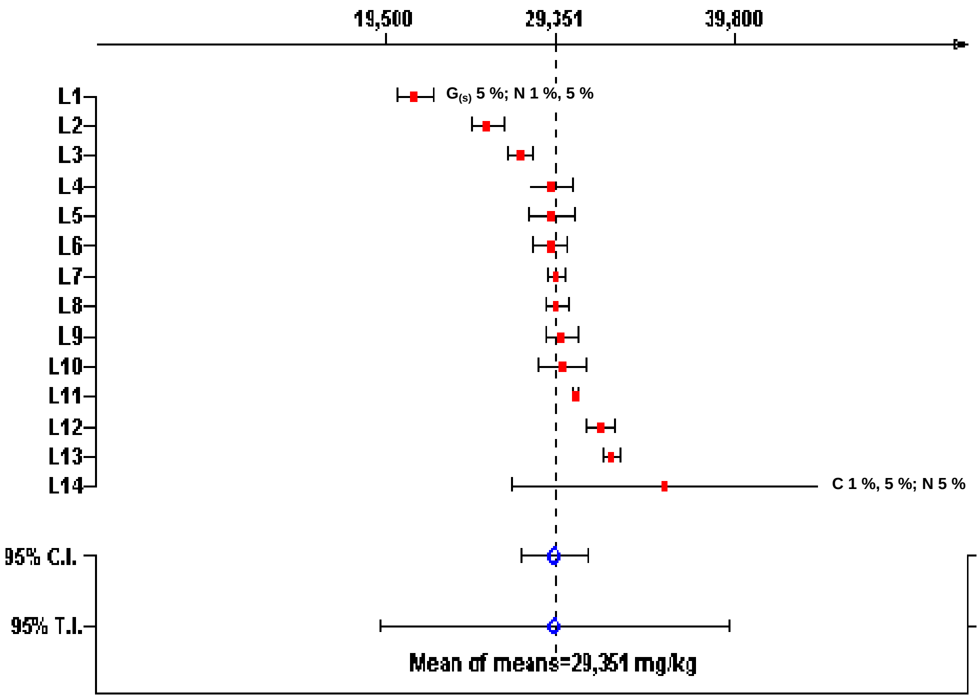
Range [min..max]	[19,500 .. 39,800]
	Case of No Pooling
Mean of means	29,351
95% H.W. Confidence Interval	1,941
95% H.W. Tolerance Interval	10,127
	Case of Pooling
Mean of All	29,114
95% H.W. Confidence Interval	713
95% H.W. Tolerance Interval	7,324

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6c2)



Tab. 6d1: Chromium evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	2,500	0,837	0,878	3,000	3,000	3,000	3,000	1,000	2,000
L 2	36 DCarc-OES 3	2,550	0,771	0,809	1,600	2,500	2,800	3,400	1,700	3,300
L 3	4 ETV-ICP OES 2	2,567	0,969	1,017	4,320	2,860	2,430	1,860	2,350	1,580
L 4	20 ICP OES 2	3,238	0,300	0,314	3,580	3,260	3,570	3,070	3,140	2,810
L 5	2 K_0-INNA 3	3,348	0,076	0,080	3,454	3,386	3,222	3,331	3,345	3,348
L 6	16 ICP OES (3)	3,400	0,276	0,289	3,500	3,100	3,200	3,800	3,200	3,600
L 7	35 INAA 2	3,418	0,066	0,070	3,350	3,360	3,380	3,440	3,460	3,520
L 8	24 ICP-MS 2	3,478	0,073	0,077	3,390	3,420	3,440	3,510	3,530	3,580
L 9	23 ET AAS 2	3,495	0,136	0,142	3,430	3,400	3,480	3,340	3,670	3,650
L 10	1 INAA (2)	3,573	0,073	0,077	3,585	3,672	3,491	3,637	3,496	3,558
L 11	33 ICP OES 3	3,628	0,277	0,291	3,350	3,310	4,050	3,660	3,610	3,790
L 12	31 ICP OES 3	3,948	0,215	0,225	3,890	4,020	3,830	4,220	3,620	4,110
L 13	36 ICP OES 3	3,950	0,105	0,110	4,000	3,800	3,900	4,000	3,900	4,100
L 14	26 ICP OES 3	4,077	0,379	0,397	4,700	4,360	3,990	3,850	3,700	3,860
L 15	28 ICP OES 1	4,190	0,253	0,265	3,910	4,347	4,393	3,881	4,468	4,141
L 16	13 ET AAS 1	4,418	0,270	0,283	4,460	4,770	4,360	4,140	4,670	4,110
L 17	19 ICP OES 1	5,688	1,033	1,084	5,010	4,860	7,040	6,210	4,500	6,510

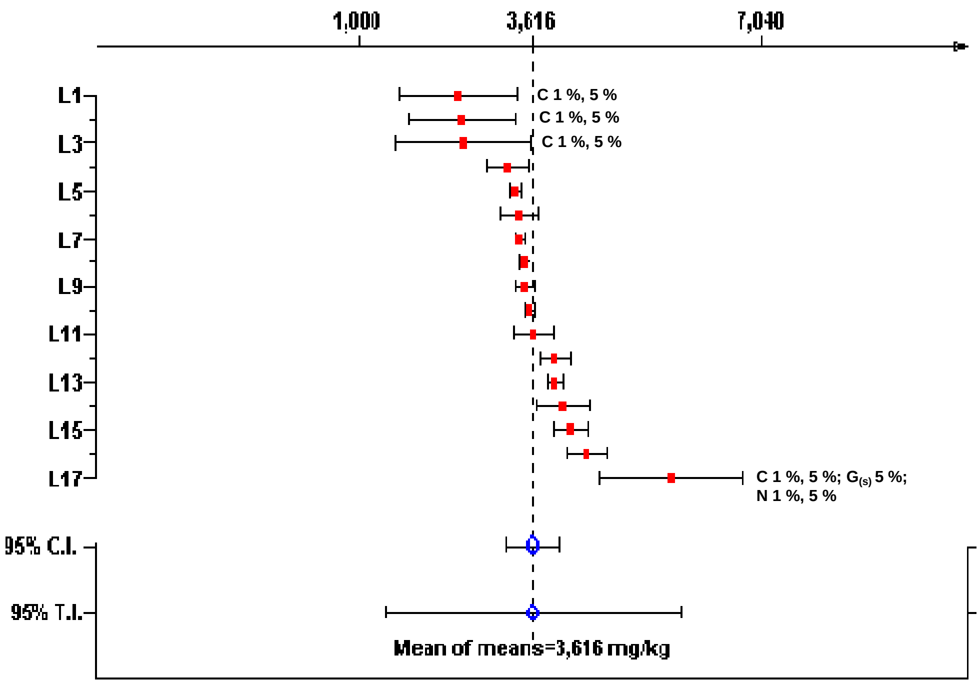
Range [min..max]	[1,000 .. 7,040]
	Case of No Pooling
Mean of means	3,616
95% H.W. Confidence Interval	0,397
95% H.W. Tolerance Interval	2,205
	Case of Pooling
Mean of All	3,616
95% H.W. Confidence Interval	0,171
95% H.W. Tolerance Interval	1,944

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test (single test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6d1)



Tab. 6d2: Chromium accepted results in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	2,500	0,837	0,878	3,000	3,000	3,000	3,000	1,000	2,000
L 2	36 DCarc-OES 3	2,550	0,771	0,809	1,600	2,500	2,800	3,400	1,700	3,300
L 3	4 ETV-ICP OES 2	2,567	0,969	1,017	4,320	2,860	2,430	1,860	2,350	1,580
L 4	20 ICP OES 2	3,238	0,300	0,314	3,580	3,260	3,570	3,070	3,140	2,810
L 5	2 K_0-INNA 3	3,348	0,076	0,080	3,454	3,386	3,222	3,331	3,345	3,348
L 6	16 ICP OES (3)	3,400	0,276	0,289	3,500	3,100	3,200	3,800	3,200	3,600
L 7	35 INAA 2	3,418	0,066	0,070	3,350	3,360	3,380	3,440	3,460	3,520
L 8	24 ICP-MS 2	3,478	0,073	0,077	3,390	3,420	3,440	3,510	3,530	3,580
L 9	23 ET AAS 2	3,495	0,136	0,142	3,430	3,400	3,480	3,340	3,670	3,650
L 10	1 INAA (2)	3,573	0,073	0,077	3,585	3,672	3,491	3,637	3,496	3,558
L 11	33 ICP OES 3	3,628	0,277	0,291	3,350	3,310	4,050	3,660	3,610	3,790
L 12	31 ICP OES 3	3,948	0,215	0,225	3,890	4,020	3,830	4,220	3,620	4,110
L 13	36 ICP OES 3	3,950	0,105	0,110	4,000	3,800	3,900	4,000	3,900	4,100
L 14	26 ICP OES 3	4,077	0,379	0,397	4,700	4,360	3,990	3,850	3,700	3,860
L 15	28 ICP OES 1	4,190	0,253	0,265	3,910	4,347	4,393	3,881	4,468	4,141
L 16	13 ET AAS 1	4,418	0,270	0,283	4,460	4,770	4,360	4,140	4,670	4,110

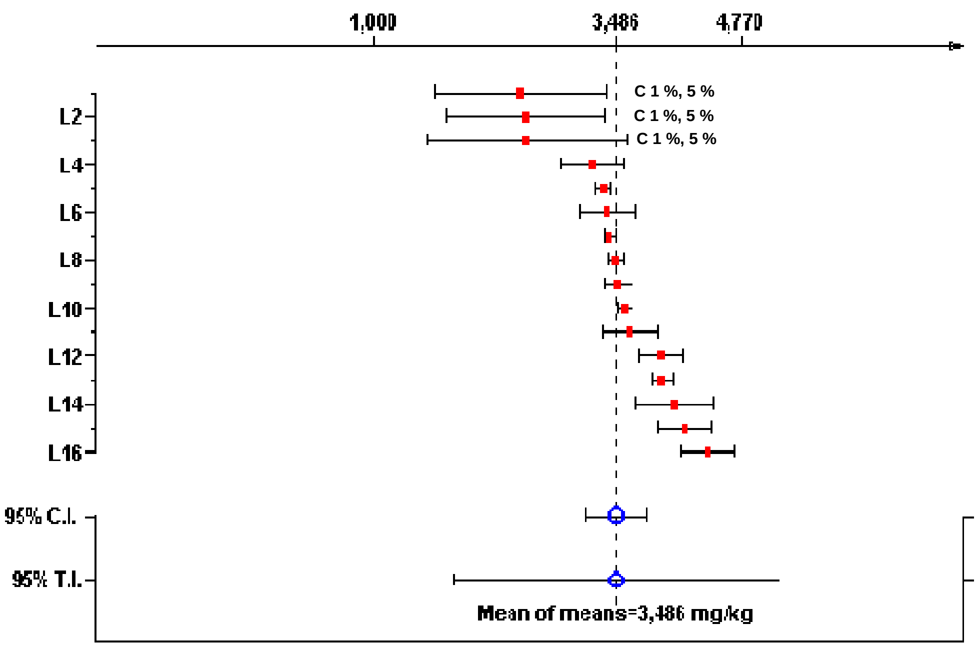
Range [min..max]	[1,000 .. 4,770]
	Case of No Pooling
Mean of means	3,486
95% H.W. Confidence Interval	0,306
95% H.W. Tolerance Interval	1,669
	Case of Pooling
Mean of All	3,486
95% H.W. Confidence Interval	0,138
95% H.W. Tolerance Interval	1,524

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6d2)



Tab. 6e1: Copper evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES 1	0,978	0,134	0,140	0,930	0,800	1,100	1,030	1,140	0,870
L 2	22 ICP OES 3	1,057	0,033	0,035	1,055	1,018	1,074	1,050	1,112	1,033
L 3	4 ETV-ICP OES 2	1,170	0,199	0,209	1,430	1,200	1,270	0,900	1,250	0,970
L 4	23 ET AAS 2	1,238	0,028	0,029	1,260	1,240	1,270	1,250	1,200	1,210
L 5	28 ICP OES 1	1,265	0,042	0,044	1,318	1,219	1,310	1,274	1,233	1,236
L 6	12 ICP OES (2)	1,282	0,140	0,174	1,150	1,320	1,390	1,430		1,120
L 7	26 ICP OES 3	1,353	0,183	0,193	1,530	1,090	1,370	1,570	1,350	1,210
L 8	33 ICP OES 3	1,378	0,122	0,128	1,430	1,440	1,310	1,310	1,560	1,220
L 9	24 ICP-MS 2	1,385	0,014	0,014	1,390	1,400	1,380	1,370	1,400	1,370
L 10	31 ICP OES 3	1,803	0,471	0,494	2,010	1,370	2,420	1,390	1,410	2,220
L 11	36 DCarc-OES 3	2,300	0,110	0,115	2,300	2,300	2,300	2,400	2,100	2,400
L 12	11 ICP OES (1)	2,500	1,761	1,848	3,000	1,000	1,000	4,000	5,000	1,000
L 13	8 ICP OES 3	19,650	2,300	2,414	20,200	20,300	17,200	20,700	22,800	16,700

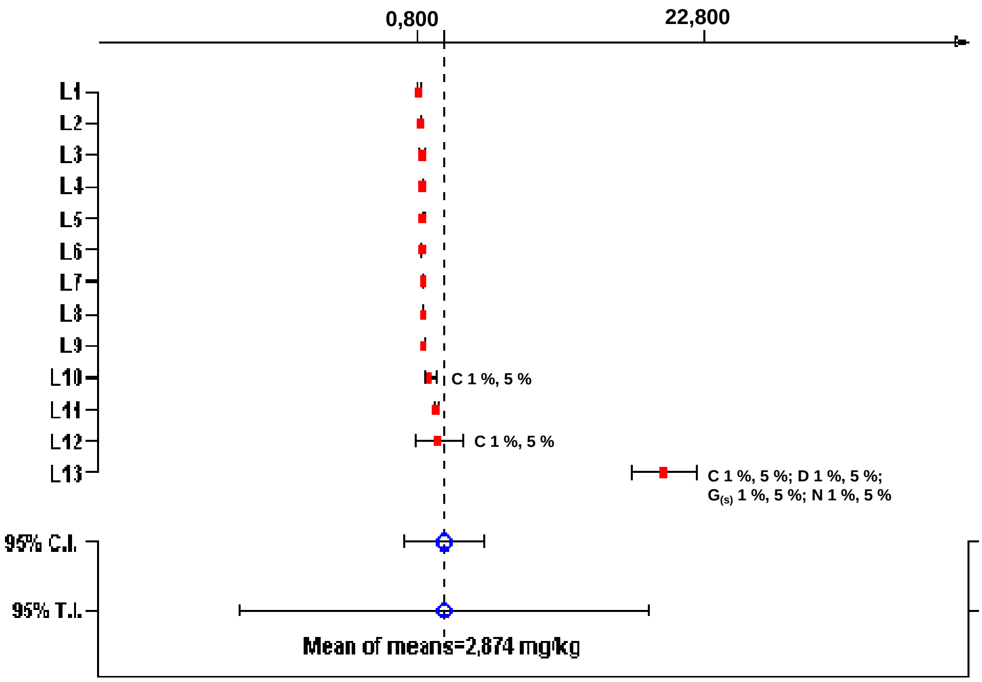
Range [min..max]	[0,800 .. 22,800]
	Case of No Pooling
Mean of means	2,874
95% H.W. Confidence Interval	3,059
95% H.W. Tolerance Interval	15,594
	Case of Pooling
Mean of All	2,895
95% H.W. Confidence Interval	1,131
95% H.W. Tolerance Interval	11,356

next page:
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6e1)



Tab. 6e2: Copper accepted results in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES 1	0,978	0,134	0,140	0,930	0,800	1,100	1,030	1,140	0,870
L 2	22 ICP OES 3	1,057	0,033	0,035	1,055	1,018	1,074	1,050	1,112	1,033
L 3	4 ETV-ICP OES 2	1,170	0,199	0,209	1,430	1,200	1,270	0,900	1,250	0,970
L 4	23 ET AAS 2	1,238	0,028	0,029	1,260	1,240	1,270	1,250	1,200	1,210
L 5	28 ICP OES 1	1,265	0,042	0,044	1,318	1,219	1,310	1,274	1,233	1,236
L 6	12 ICP OES (2)	1,282	0,140	0,174	1,150	1,320	1,390	1,430		1,120
L 7	26 ICP OES 3	1,353	0,183	0,193	1,530	1,090	1,370	1,570	1,350	1,210
L 8	33 ICP OES 3	1,378	0,122	0,128	1,430	1,440	1,310	1,310	1,560	1,220
L 9	24 ICP-MS 2	1,385	0,014	0,014	1,390	1,400	1,380	1,370	1,400	1,370
L 10	31 ICP OES 3	1,803	0,471	0,494	2,010	1,370	2,420	1,390	1,410	2,220
L 11	36 DCarc-OES 3	2,300	0,110	0,115	2,300	2,300	2,300	2,400	2,100	2,400
L 12	11 ICP OES (1)	2,500	1,761	1,848	3,000	1,000	1,000	4,000	5,000	1,000

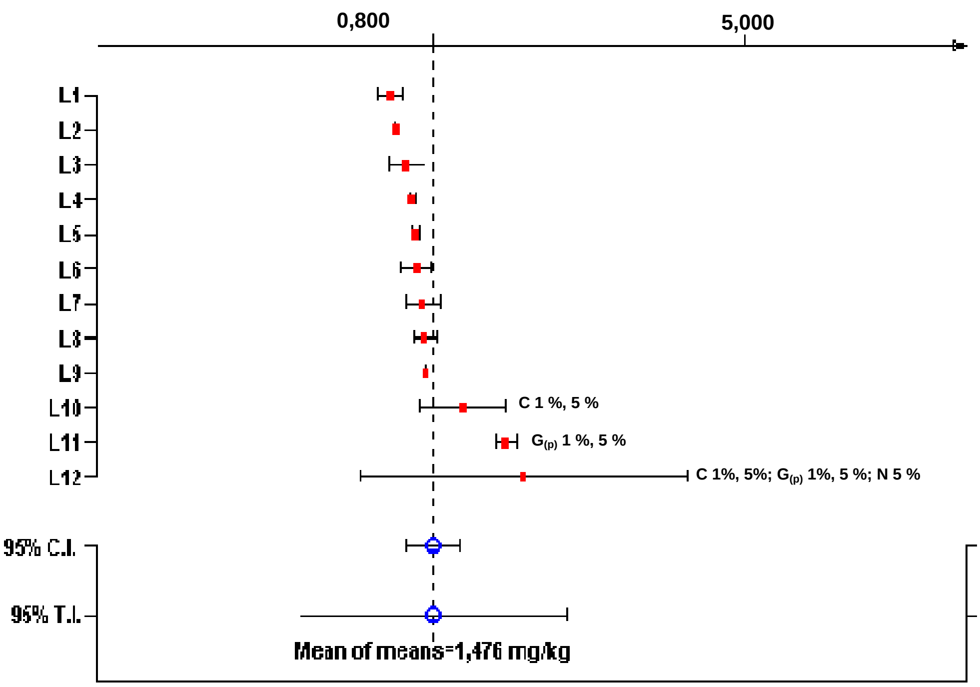
Range [min..max]	[0,800 .. 5,000]
	Case of No Pooling
Mean of means	1,476
95% H.W. Confidence Interval	0,304
95% H.W. Tolerance Interval	1,514
	Case of Pooling
Mean of All	1,479
95% H.W. Confidence Interval	0,161
95% H.W. Tolerance Interval	1,562

next page:
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(p)}$ = Grubbs test (pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6e2)



Tab. 6f1: Iron evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	25 DCarc-OES 3	100,500	4,764	5,000	94,000	99,000	105,000	98,000	107,000	100,000
L 2	14 ICP OES 2	107,333	22,853	23,983	115,000	113,000	147,000	91,000	87,000	91,000
L 3	22 ICP OES 3	130,766	1,739	1,825	131,055	129,162	133,910	129,774	131,136	129,559
L 4	28 ICP OES 1	135,000	2,880	3,022	137,000	135,500	138,900	132,000	131,400	135,200
L 5	36 DCarc-OES 3	135,333	6,282	6,593	135,000	134,000	141,000	144,000	131,000	127,000
L 6	2 K_0-INNA 3	136,500	1,589	1,667	136,800	136,400	133,700	138,500	136,300	137,300
L 7	11 ICP OES (2)	136,500	4,416	4,634	130,000	133,000	140,000	137,000	142,000	137,000
L 8	31 ICP OES 3	140,000	2,757	2,893	137,000	139,000	139,000	139,000	141,000	145,000
L 9	23 F AAS 2	142,167	7,333	7,695	132,000	134,000	145,000	146,000	150,000	146,000
L 10	19 ICP OES 1	142,833	14,261	14,966	143,000	129,000	134,000	151,000	167,000	133,000
L 11	16 ICP OES 3	143,167	7,705	8,086	150,000	154,000	138,000	145,000	136,000	136,000
L 12	24 ICP-MS 2	146,083	2,282	2,394	143,500	144,100	145,000	147,000	147,400	149,500
L 13	33 ICP OES 3	148,767	2,994	3,142	146,500	145,300	152,600	152,200	148,100	147,900
L 14	26 ICP OES 3	148,817	2,490	2,613	149,200	147,100	150,600	149,000	152,000	145,000
L 15	36 ICP OES 3	149,167	1,329	1,395	150,000	148,000	151,000	148,000	148,000	150,000
L 16	20 ICP OES 3	151,833	4,167	4,373	155,000	148,000	146,000	153,000	152,000	157,000
L 17	13 ICP OES 2	154,000	4,690	4,922	153,000	161,000	155,000	157,000	149,000	149,000
L 18	18 ICP OES	154,667	8,548	8,970	146,000	151,000	155,000	153,000	152,000	171,000
L 19	8 ICP OES 3	157,667	9,543	10,015	140,000	165,000	158,000	165,000	163,000	155,000
L 20	12 ICP OES (2)	161,855	29,681	31,148	132,750	138,310	161,670	155,340	167,040	216,020
L 21	27 ICP OES	163,500	4,950	44,472	160,000	167,000				
L 22	4 ETV-ICPOES 2	164,050	21,266	22,317	203,400	160,400	159,900	144,300	168,700	147,600
L 23	1 INAA (2)	173,371	4,472	4,693	177,331	169,762	178,928	175,189	167,603	171,413
L 24	6 Titrimetry 2,3	219,667	5,715	5,998	222,000	222,000	222,000	222,000	222,000	208,000

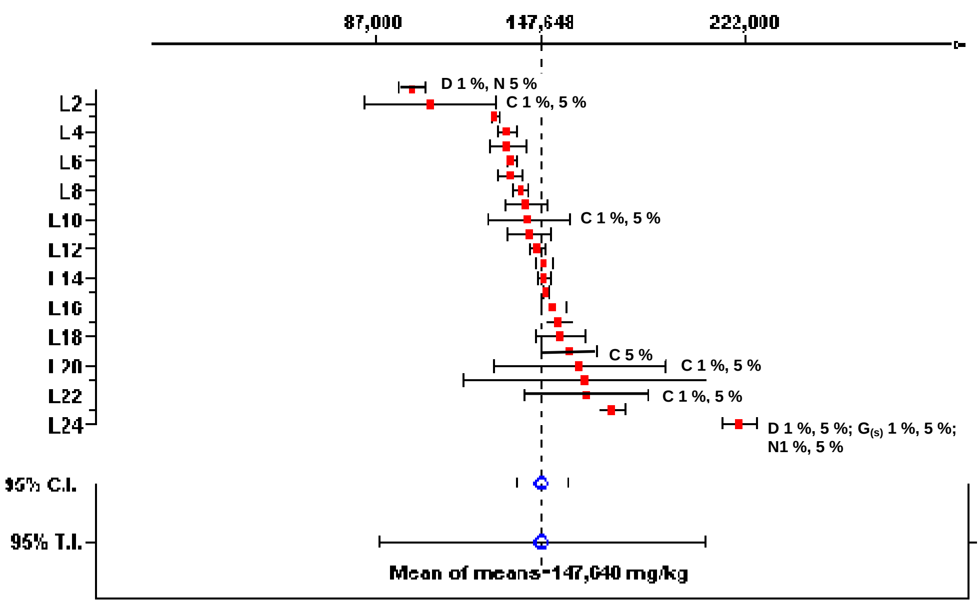
Range [min..max]	[87,000 .. 222,000]
	Case of No Pooling
Mean of means	147,648
95% H.W. Confidence Interval	9,487
95% H.W. Tolerance Interval	59,562
	Case of Pooling
Mean of All	147,195
95% H.W. Confidence Interval	4,044
95% H.W. Tolerance Interval	52,858

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test (single test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6f1)



Tab. 6f2 : Iron evaluation in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	14 ICP OES 2	107,333	22,853	23,983	115,000	113,000	147,000	91,000	87,000	91,000
L 2	22 ICP OES 3	130,766	1,739	1,825	131,055	129,162	133,910	129,774	131,136	129,559
L 3	28 ICP OES 1	135,000	2,880	3,022	137,000	135,500	138,900	132,000	131,400	135,200
L 4	36 DCarc-OES 3	135,333	6,282	6,593	135,000	134,000	141,000	144,000	131,000	127,000
L 5	2 K_0-INNA 3	136,500	1,589	1,667	136,800	136,400	133,700	138,500	136,300	137,300
L 6	11 ICP OES (2)	136,500	4,416	4,634	130,000	133,000	140,000	137,000	142,000	137,000
L 7	31 ICP OES 3	140,000	2,757	2,893	137,000	139,000	139,000	139,000	141,000	145,000
L 8	23 F AAS 2	142,167	7,333	7,695	132,000	134,000	145,000	146,000	150,000	146,000
L 9	19 ICP OES 1	142,833	14,261	14,966	143,000	129,000	134,000	151,000	167,000	133,000
L 10	16 ICP OES 3	143,167	7,705	8,086	150,000	154,000	138,000	145,000	136,000	136,000
L 11	24 ICP-MS 2	146,083	2,282	2,394	143,500	144,100	145,000	147,000	147,400	149,500
L 12	33 ICP OES 3	148,767	2,994	3,142	146,500	145,300	152,600	152,200	148,100	147,900
L 13	26 ICP OES 3	148,817	2,490	2,613	149,200	147,100	150,600	149,000	152,000	145,000
L 14	36 ICP OES 3	149,167	1,329	1,395	150,000	148,000	151,000	148,000	148,000	150,000
L 15	20 ICP OES 3	151,833	4,167	4,373	155,000	148,000	146,000	153,000	152,000	157,000
L 16	13 ICP OES 2	154,000	4,690	4,922	153,000	161,000	155,000	157,000	149,000	149,000
L 17	18 ICP OES	154,667	8,548	8,970	146,000	151,000	155,000	153,000	152,000	171,000
L 18	8 ICP OES 3	157,667	9,543	10,015	140,000	165,000	158,000	165,000	163,000	155,000
L 19	12 ICP OES (2)	161,855	29,681	31,148	132,750	138,310	161,670	155,340	167,040	216,020
L 20	27 ICP OES	163,500	4,950	44,472	160,000	167,000				
L 21	4 ETV-ICP OES 2	164,050	21,266	22,317	203,400	160,400	159,900	144,300	168,700	147,600
L 22	1 INAA (2)	173,371	4,472	4,693	177,331	169,762	178,928	175,189	167,603	171,413

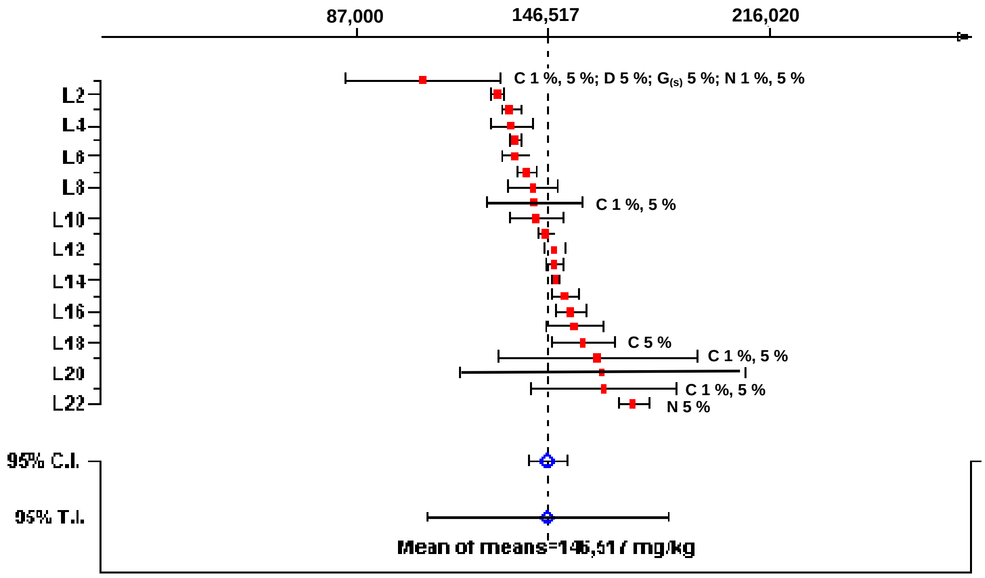
Range [min..max]	[87,000 .. 216,020]
	Case of No Pooling
Mean of means	146,517
95% H.W. Confidence Interval	6,250
95% H.W. Tolerance Interval	38,018
	Case of Pooling
Mean of All	145,986
95% H.W. Confidence Interval	2,960
95% H.W. Tolerance Interval	37,161

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6f2)



Tab. 6f3: Iron accepted results in run 3 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	22 ICP OES 3	130,766	1,739	1,825	131,055	129,162	133,910	129,774	131,136	129,559
L 2	28 ICP OES 1	135,000	2,880	3,022	137,000	135,500	138,900	132,000	131,400	135,200
L 3	36 DCarc-OES 3	135,333	6,282	6,593	135,000	134,000	141,000	144,000	131,000	127,000
L 4	2 K_0-INNA 3	136,500	1,589	1,667	136,800	136,400	133,700	138,500	136,300	137,300
L 5	11 ICP OES (2)	136,500	4,416	4,634	130,000	133,000	140,000	137,000	142,000	137,000
L 6	31 ICP OES 3	140,000	2,757	2,893	137,000	139,000	139,000	139,000	141,000	145,000
L 7	23 F AAS 2	142,167	7,333	7,695	132,000	134,000	145,000	146,000	150,000	146,000
L 8	19 ICP OES 1	142,833	14,261	14,966	143,000	129,000	134,000	151,000	167,000	133,000
L 9	16 ICP OES 3	143,167	7,705	8,086	150,000	154,000	138,000	145,000	136,000	136,000
L 10	24 ICP-MS 2	146,083	2,282	2,394	143,500	144,100	145,000	147,000	147,400	149,500
L 11	33 ICP OES 3	148,767	2,994	3,142	146,500	145,300	152,600	152,200	148,100	147,900
L 12	26 ICP OES 3	148,817	2,490	2,613	149,200	147,100	150,600	149,000	152,000	145,000
L 13	36 ICP OES 3	149,167	1,329	1,395	150,000	148,000	151,000	148,000	148,000	150,000
L 14	20 ICP OES 3	151,833	4,167	4,373	155,000	148,000	146,000	153,000	152,000	157,000
L 15	13 ICP OES 2	154,000	4,690	4,922	153,000	161,000	155,000	157,000	149,000	149,000
L 16	18 ICP OES	154,667	8,548	8,970	146,000	151,000	155,000	153,000	152,000	171,000
L 17	8 ICP OES 3	157,667	9,543	10,015	140,000	165,000	158,000	165,000	163,000	155,000
L 18	12 ICP OES (2)	161,855	29,681	31,148	132,750	138,310	161,670	155,340	167,040	216,020
L 19	27 ICP OES	163,500	4,950	44,472	160,000	167,000				
L 20	4 ETV-ICP OES 2	164,050	21,266	22,317	203,400	160,400	159,900	144,300	168,700	147,600
L 21	1 INAA (2)	173,371	4,472	4,693	177,331	169,762	178,928	175,189	167,603	171,413

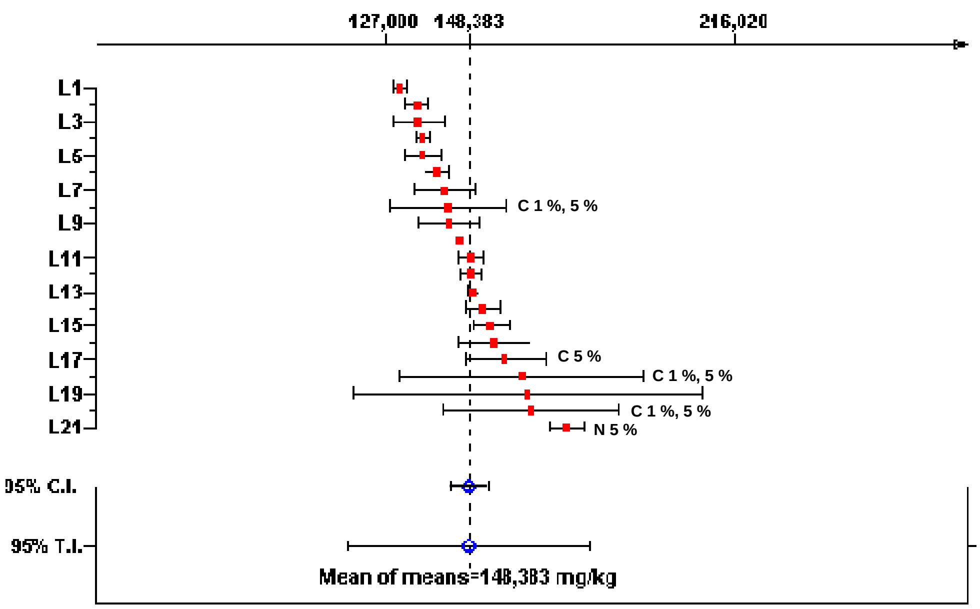
Range [min..max]	[127,000 .. 216,020]
	Case of No Pooling
Mean of means	148,383
95% H.W. Confidence Interval	5,154
95% H.W. Tolerance Interval	30,833
	Case of Pooling
Mean of All	147,887
95% H.W. Confidence Interval	2,542
95% H.W. Tolerance Interval	31,246

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
nedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6f3)



Tab. 6g1: Magnesium evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	3,833	0,753	0,790	4,000	5,000	3,000	4,000	4,000	3,000
L 2	19 ICP OES 1	5,512	0,895	0,939	7,170	4,930	5,740	4,750	4,980	5,500
L 3	28 ICP OES 1	5,807	0,171	0,180	6,012	5,632	6,016	5,643	5,779	5,758
L 4	26 ICP OES 3	5,873	0,195	0,204	5,860	5,950	5,560	6,160	5,820	5,890
L 5	36 DCarc-OES 3	5,883	0,519	0,545	5,300	6,200	5,200	6,400	6,300	5,900
L 6	13 ICP OES 2	6,000	0,443	0,465	6,400	6,400	5,800	6,300	5,300	5,800
L 7	31 ICP OES 3	6,013	0,074	0,078	5,910	6,090	5,990	5,950	6,080	6,060
L 8	22 ICP OES 3	6,079	0,146	0,153	6,268	6,228	6,026	5,963	6,086	5,900
L 9	23 ET AAS 2	6,278	0,141	0,148	6,090	6,410	6,360	6,400	6,120	6,290
L 10	36 ICP OES 3	6,283	0,488	0,512	5,900	7,100	6,200	6,400	5,700	6,400
L 11	33 ICP OES 3	6,433	0,476	0,499	6,020	6,060	6,260	6,500	6,440	7,320
L 12	4 ETV-ICP OES 2	6,463	0,481	0,505	7,270	5,930	6,470	6,700	6,080	6,330
L 13	18 ICP OES	6,467	0,186	0,195	6,200	6,300	6,500	6,500	6,600	6,700
L 14	12 ICP OES (2)	6,755	0,132	0,138	6,650	6,830	6,770	6,590	6,730	6,960
L 15	24 ICP-MS 2	6,877	0,460	0,483	7,430	6,780	6,290	6,410	7,140	7,210
L 16	20 ICP OES 2	8,218	2,028	2,128	7,170	7,140	5,170	9,730	10,100	10,000
L 17	6 F AAS 2,3	9,000	0,894	0,939	10,000	8,000	9,000	9,000	8,000	10,000
L 18	14 ICP OES 2	10,667	12,028	12,622	11,000	10,000	34,000	2,000	3,000	4,000
L 19	8 ICP OES 3	21,317	2,122	2,227	20,400	20,200	20,300	24,500	23,400	19,100

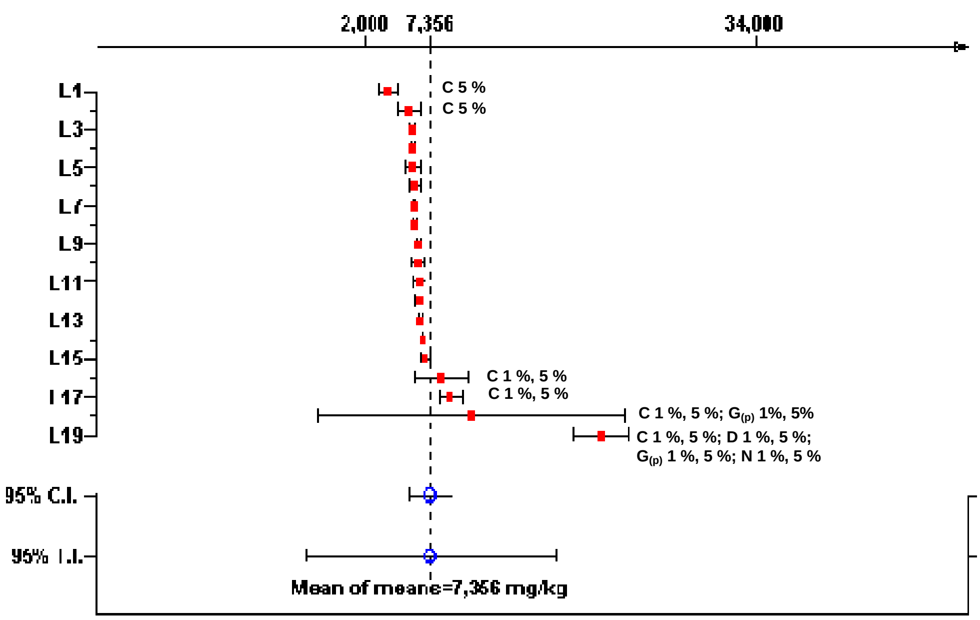
Range [min..max]	[2,000 .. 34,000]
	Case of No Pooling
Mean of means	7,356
95% H.W. Confidence Interval	1,769
95% H.W. Tolerance Interval	10,219
	Case of Pooling
Mean of All	7,356
95% H.W. Confidence Interval	0,826
95% H.W. Tolerance Interval	9,852

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(p)}$ = Grubbs test (pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6g1)



Tab. 6g2: Magnesium accepted results in run 2 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	3,833	0,753	0,790	4,000	5,000	3,000	4,000	4,000	3,000
L 2	19 ICP OES 1	5,512	0,895	0,939	7,170	4,930	5,740	4,750	4,980	5,500
L 3	28 ICP OES 1	5,807	0,171	0,180	6,012	5,632	6,016	5,643	5,779	5,758
L 4	26 ICP OES 3	5,873	0,195	0,204	5,860	5,950	5,560	6,160	5,820	5,890
L 5	36 DCarc-OES 3	5,883	0,519	0,545	5,300	6,200	5,200	6,400	6,300	5,900
L 6	13 ICP OES 2	6,000	0,443	0,465	6,400	6,400	5,800	6,300	5,300	5,800
L 7	31 ICP OES 3	6,013	0,074	0,078	5,910	6,090	5,990	5,950	6,080	6,060
L 8	22 ICP OES 3	6,079	0,146	0,153	6,268	6,228	6,026	5,963	6,086	5,900
L 9	23 ET AAS 2	6,278	0,141	0,148	6,090	6,410	6,360	6,400	6,120	6,290
L 10	36 ICP OES 3	6,283	0,488	0,512	5,900	7,100	6,200	6,400	5,700	6,400
L 11	33 ICP OES 3	6,433	0,476	0,499	6,020	6,060	6,260	6,500	6,440	7,320
L 12	4 ETV-ICP OES 2	6,463	0,481	0,505	7,270	5,930	6,470	6,700	6,080	6,330
L 13	18 ICP OES	6,467	0,186	0,195	6,200	6,300	6,500	6,500	6,600	6,700
L 14	12 ICP OES (2)	6,755	0,132	0,138	6,650	6,830	6,770	6,590	6,730	6,960
L 15	24 ICP-MS 2	6,877	0,460	0,483	7,430	6,780	6,290	6,410	7,140	7,210
L 16	20 ICP OES 2	8,218	2,028	2,128	7,170	7,140	5,170	9,730	10,100	10,000
L 17	6 F AAS 2,3	9,000	0,894	0,939	10,000	8,000	9,000	9,000	8,000	10,000

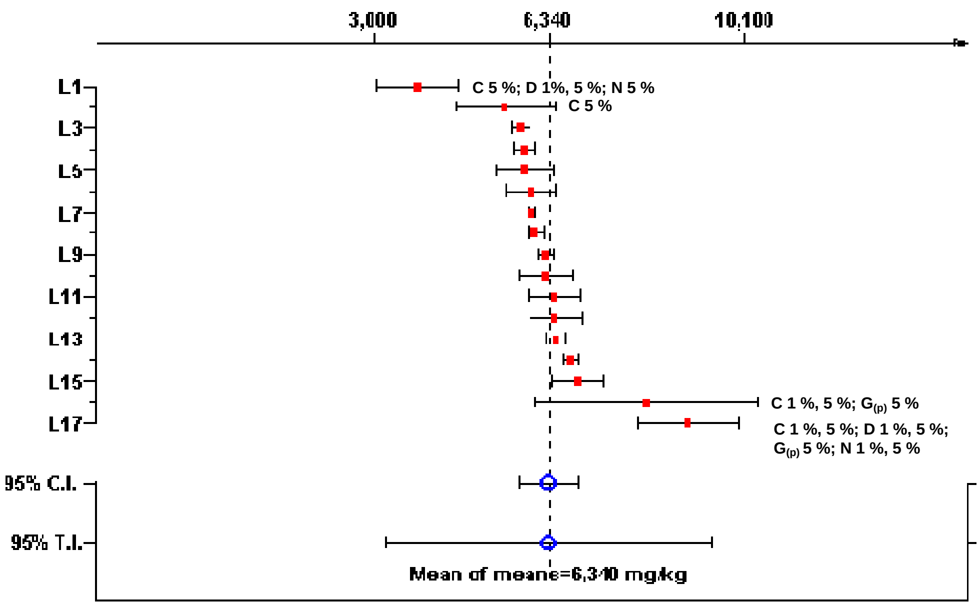
Range [min..max]	[3,000 .. 10,100]
	Case of No Pooling
Mean of means	6,340
95% H.W. Confidence Interval	0,561
95% H.W. Tolerance Interval	3,121
	Case of Pooling
Mean of All	6,340
95% H.W. Confidence Interval	0,242
95% H.W. Tolerance Interval	2,750

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(p)}$ = Grubbs test (pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6g2)



Tab. 6h1: Manganese evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	1,000	0	0	1,000	1,000	1,000	1,000	1,000	1,000
L 2	26 ICP OES 3	1,095	0,126	0,132	1,020	1,040	1,060	1,000	1,110	1,340
L 3	1 INAA 2	1,298	0,017	0,018	1,302	1,287	1,283	1,324	1,283	1,311
L 4	28 ICP OES 1	1,321	0,062	0,065	1,357	1,280	1,431	1,272	1,283	1,300
L 5	2 K_0-INNA 3	1,332	0,066	0,069	1,274	1,410	1,296	1,419	1,276	1,316
L 6	23 ET AAS 2	1,362	0,029	0,031	1,320	1,370	1,330	1,390	1,380	1,380
L 7	35 INAA 1	1,373	0,037	0,039	1,390	1,360	1,350	1,360	1,340	1,440
L 8	33 ICP OES 3	1,383	0,056	0,059	1,420	1,400	1,460	1,380	1,330	1,310
L 9	24 ICP-MS 2	1,407	0,010	0,011	1,410	1,400	1,390	1,410	1,420	1,410
L 10	36 ICP OES 3	1,417	0,306	0,321	1,600	1,600	0,800	1,500	1,500	1,500
L 11	13 ET AAS 1	1,472	0,053	0,056	1,410	1,470	1,500	1,460	1,430	1,560
L 12	20 ICP OES 3	1,482	0,272	0,285	1,790	1,470	1,650	1,540	0,990	1,450
L 13	31 ICP OES 3	1,490	0,023	0,024	1,490	1,480	1,490	1,460	1,490	1,530
L 14	22 ICP OES 3	1,530	0,034	0,036	1,582	1,557	1,531	1,506	1,516	1,490
L 15	36 DCarc-OES 3	1,717	0,214	0,224	1,900	1,600	1,500	1,500	2,000	1,800
L 16	19 ICP OES 1	1,788	0,140	0,147	1,990	1,690	1,700	1,620	1,850	1,880
L 17	4 ETV-ICP OES 2	2,027	0,126	0,132	2,150	2,030	2,200	1,980	1,900	1,900
L 18	12 ICP OES (2)	2,302	0,937	0,984	1,500	1,650	1,870	1,850	3,150	3,790

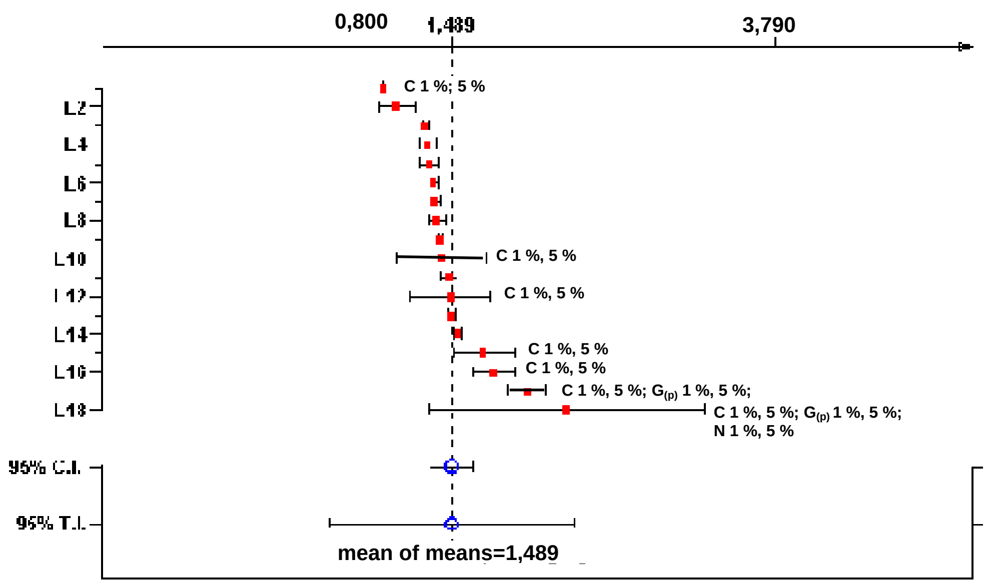
Range [min..max]	[0,800 .. 3,790]
	Case of No Pooling
Mean of means	1,489
95% H.W. Confidence Interval	0,154
95% H.W. Tolerance Interval	0,873
	Case of Pooling
Mean of All	1,489
95% H.W. Confidence Interval	0,073
95% H.W. Tolerance Interval	0,848

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(p)}$ = Grubbs test (pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6h1)



Tab. 6h2: Manganese accepted results in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	1,000	0	0	1,000	1,000	1,000	1,000	1,000	1,000
L 2	26 ICP OES 3	1,095	0,126	0,132	1,020	1,040	1,060	1,000	1,110	1,340
L 3	1 INAA 2	1,298	0,017	0,018	1,302	1,287	1,283	1,324	1,283	1,311
L 4	28 ICP OES 1	1,321	0,062	0,065	1,357	1,280	1,431	1,272	1,283	1,300
L 5	2 K_0-INNA 3	1,332	0,066	0,069	1,274	1,410	1,296	1,419	1,276	1,316
L 6	23 ET AAS 2	1,362	0,029	0,031	1,320	1,370	1,330	1,390	1,380	1,380
L 7	35 INAA 1	1,373	0,037	0,039	1,390	1,360	1,350	1,360	1,340	1,440
L 8	33 ICP OES 3	1,383	0,056	0,059	1,420	1,400	1,460	1,380	1,330	1,310
L 9	24 ICP-MS 2	1,407	0,010	0,011	1,410	1,400	1,390	1,410	1,420	1,410
L 10	36 ICP OES 3	1,417	0,306	0,321	1,600	1,600	0,800	1,500	1,500	1,500
L 11	13 ET AAS 1	1,472	0,053	0,056	1,410	1,470	1,500	1,460	1,430	1,560
L 12	20 ICP OES 3	1,482	0,272	0,285	1,790	1,470	1,650	1,540	0,990	1,450
L 13	31 ICP OES 3	1,490	0,023	0,024	1,490	1,480	1,490	1,460	1,490	1,530
L 14	22 ICP OES 3	1,530	0,034	0,036	1,582	1,557	1,531	1,506	1,516	1,490
L 15	36 DCarc-OES 3	1,717	0,214	0,224	1,900	1,600	1,500	1,500	2,000	1,800
L 16	19 ICP OES 1	1,788	0,140	0,147	1,990	1,690	1,700	1,620	1,850	1,880
L 17	4 ETV-ICP OES 2	2,027	0,126	0,132	2,150	2,030	2,200	1,980	1,900	1,900

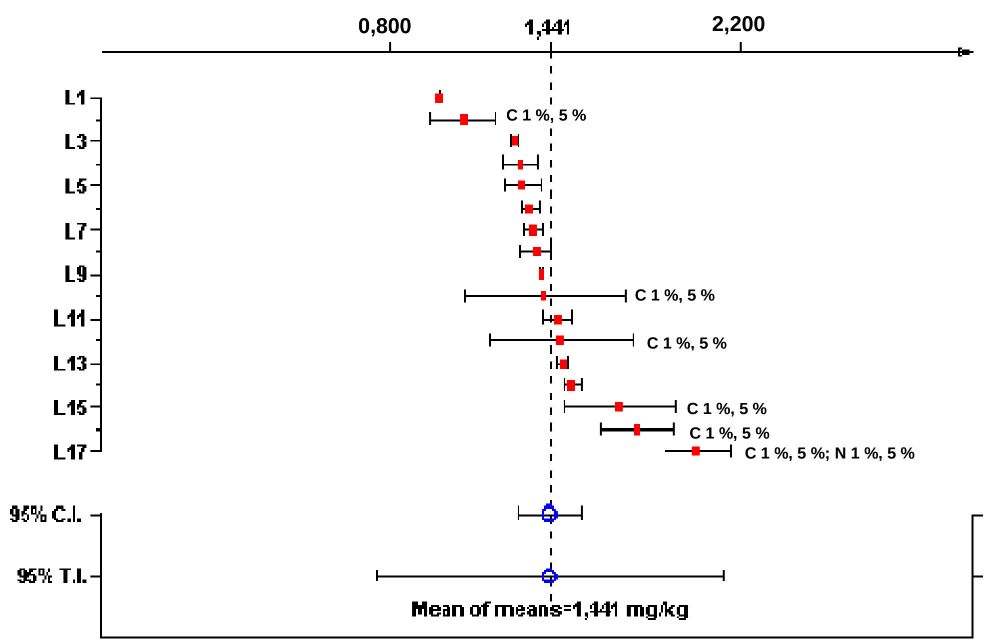
Range [min..max]	[0,800 .. 2,200]
	Case of No Pooling
Mean of means	1,441
95% H.W. Confidence Interval	0,124
95% H.W. Tolerance Interval	0,689
	Case of Pooling
Mean of All	1,441
95% H.W. Confidence Interval	0,052
95% H.W. Tolerance Interval	0,587

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(p)}$ = Grubbs test (pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6h2)



Tab. 6i1: Sodium evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	9,282	2,448	2,570	7,900	11,980	12,370	6,060	8,400	8,980
L 2	31 ICP OES 3	15,000	1,548	1,624	13,400	13,800	13,800	15,700	17,200	16,100
L 3	22 ICP OES 3	15,308	0,519	0,545	15,558	15,848	15,493	14,382	15,508	15,058
L 4	1 INAA 2	15,746	0,197	0,207	15,848	15,783	15,567	15,591	15,613	16,076
L 5	23 F AAS 2	16,717	0,674	0,707	16,300	17,400	17,200	17,100	15,600	16,700
L 6	28 ICP OES 1	17,032	0,293	0,307	17,550	17,010	17,090	16,660	16,920	16,960
L 7	26 F AAS 3	17,317	0,760	0,798	18,300	17,300	16,300	16,900	18,100	17,000
L 8	24 ICP-MS 2	17,667	0,476	0,500	17,500	17,600	17,300	17,200	18,500	17,900
L 9	35 INAA 2	17,800	0,486	0,510	18,100	17,300	17,400	17,600	17,800	18,600
L 10	33 ICP OES 3	18,032	0,446	0,468	17,770	17,620	17,770	18,850	18,010	18,170
L 11	36 F AAS (3)	18,717	1,689	1,773	17,400	18,500	20,200	21,300	17,000	17,900
L 12	2 K_0-INNA 3	18,765	0,518	0,543	18,105	19,410	18,505	19,313	18,832	18,424
L 13	36 SS ET AAS (3)	19,067	0,418	0,439	19,400	19,000	18,900	19,100	19,600	18,400
L 14	18 ICP OES	19,267	0,836	0,877	18,300	18,700	18,600	19,700	20,300	20,000
L 15	19 F AES 1	19,417	0,665	0,697	19,000	19,500	20,500	19,500	19,500	18,500
L 16	12 F AAS (2)	19,517	1,214	1,274	18,100	18,000	20,500	20,900	19,900	19,700
L 17	11 ICP OES (1)	22,833	1,722	1,808	23,000	23,000	22,000	22,000	26,000	21,000
L 18	20 ICP OES 2	23,917	6,256	6,566	15,400	21,900	27,900	18,400	29,900	30,000

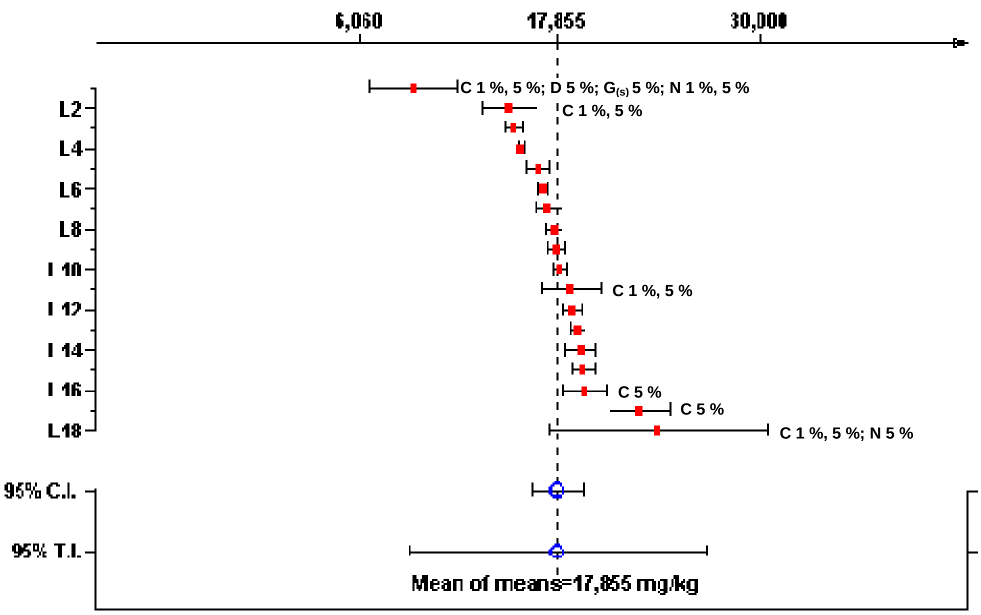
Range [min..max]	[6,060 .. 30,000]
	Case of No Pooling
Mean of means	17,855
95% H.W. Confidence Interval	1,557
95% H.W. Tolerance Interval	8,827
	Case of Pooling
Mean of All	17,855
95% H.W. Confidence Interval	0,663
95% H.W. Tolerance Interval	7,719

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6i1)



Tab. 6i2 : Sodium evaluation in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	31 ICP OES 3	15,000	1,548	1,624	13,400	13,800	13,800	15,700	17,200	16,100
L 2	22 ICP OES 3	15,308	0,519	0,545	15,558	15,848	15,493	14,382	15,508	15,058
L 3	1 INAA 2	15,746	0,197	0,207	15,848	15,783	15,567	15,591	15,613	16,076
L 4	23 F AAS 2	16,717	0,674	0,707	16,300	17,400	17,200	17,100	15,600	16,700
L 5	28 ICP OES 1	17,032	0,293	0,307	17,550	17,010	17,090	16,660	16,920	16,960
L 6	26 F AAS 3	17,317	0,760	0,798	18,300	17,300	16,300	16,900	18,100	17,000
L 7	24 ICP-MS 2	17,667	0,476	0,500	17,500	17,600	17,300	17,200	18,500	17,900
L 8	35 INAA 2	17,800	0,486	0,510	18,100	17,300	17,400	17,600	17,800	18,600
L 9	33 ICP OES 3	18,032	0,446	0,468	17,770	17,620	17,770	18,850	18,010	18,170
L 10	36 F AAS (3)	18,717	1,689	1,773	17,400	18,500	20,200	21,300	17,000	17,900
L 11	2 K_0-INNA 3	18,765	0,518	0,543	18,105	19,410	18,505	19,313	18,832	18,424
L 12	36 SS ET AAS (3)	19,067	0,418	0,439	19,400	19,000	18,900	19,100	19,600	18,400
L 13	18 ICP OES	19,267	0,836	0,877	18,300	18,700	18,600	19,700	20,300	20,000
L 14	19 F AES 1	19,417	0,665	0,697	19,000	19,500	20,500	19,500	19,500	18,500
L 15	12 F AAS (2)	19,517	1,214	1,274	18,100	18,000	20,500	20,900	19,900	19,700
L 16	11 ICP OES (1)	22,833	1,722	1,808	23,000	23,000	22,000	22,000	26,000	21,000

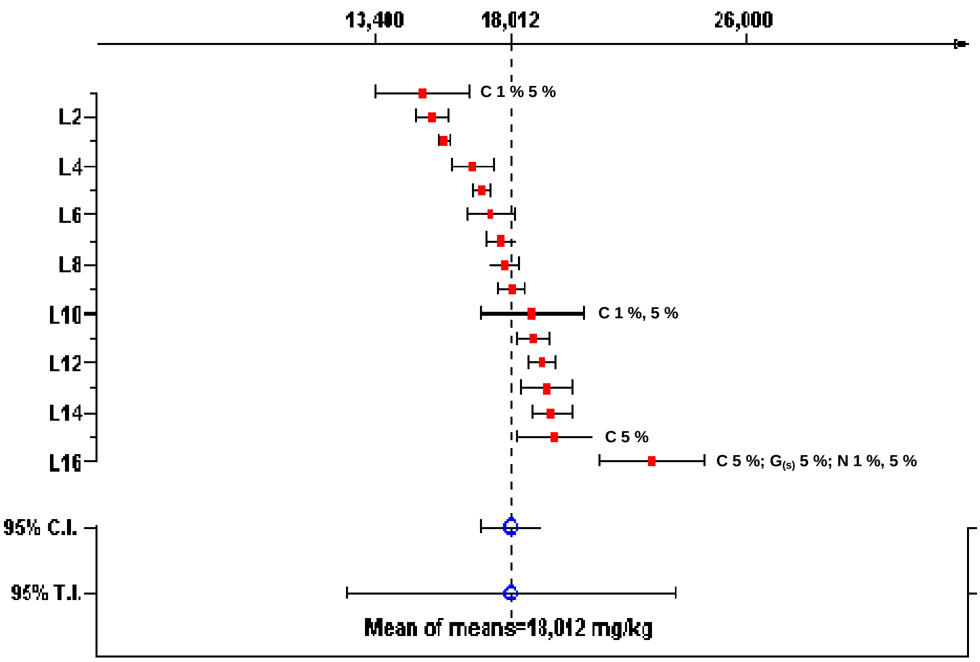
Range [min..max]	[13,400 .. 26,000]
	Case of No Pooling
Mean of means	18,012
95% H.W. Confidence Interval	1,030
95% H.W. Tolerance Interval	5,611
	Case of Pooling
Mean of All	18,012
95% H.W. Confidence Interval	0,417
95% H.W. Tolerance Interval	4,612

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6i2)



Tab. 6i3: Sodium accepted results in run 3 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	31 ICP OES 3	15,000	1,548	1,624	13,400	13,800	13,800	15,700	17,200	16,100
L 2	22 ICP OES 3	15,308	0,519	0,545	15,558	15,848	15,493	14,382	15,508	15,058
L 3	1 INAA 2	15,746	0,197	0,207	15,848	15,783	15,567	15,591	15,613	16,076
L 4	23 F AAS 2	16,717	0,674	0,707	16,300	17,400	17,200	17,100	15,600	16,700
L 5	28 ICP OES 1	17,032	0,293	0,307	17,550	17,010	17,090	16,660	16,920	16,960
L 6	26 F AAS 3	17,317	0,760	0,798	18,300	17,300	16,300	16,900	18,100	17,000
L 7	24 ICP-MS 2	17,667	0,476	0,500	17,500	17,600	17,300	17,200	18,500	17,900
L 8	35 INAA 2	17,800	0,486	0,510	18,100	17,300	17,400	17,600	17,800	18,600
L 9	33 ICP OES 3	18,032	0,446	0,468	17,770	17,620	17,770	18,850	18,010	18,170
L 10	36 F AAS (3)	18,717	1,689	1,773	17,400	18,500	20,200	21,300	17,000	17,900
L 11	2 K_0-INNA 3	18,765	0,518	0,543	18,105	19,410	18,505	19,313	18,832	18,424
L 12	36 SS ET AAS (3)	19,067	0,418	0,439	19,400	19,000	18,900	19,100	19,600	18,400
L 13	18 ICP OES	19,267	0,836	0,877	18,300	18,700	18,600	19,700	20,300	20,000
L 14	19 F AES 1	19,417	0,665	0,697	19,000	19,500	20,500	19,500	19,500	18,500
L 15	12 F AAS (2)	19,517	1,214	1,274	18,100	18,000	20,500	20,900	19,900	19,700

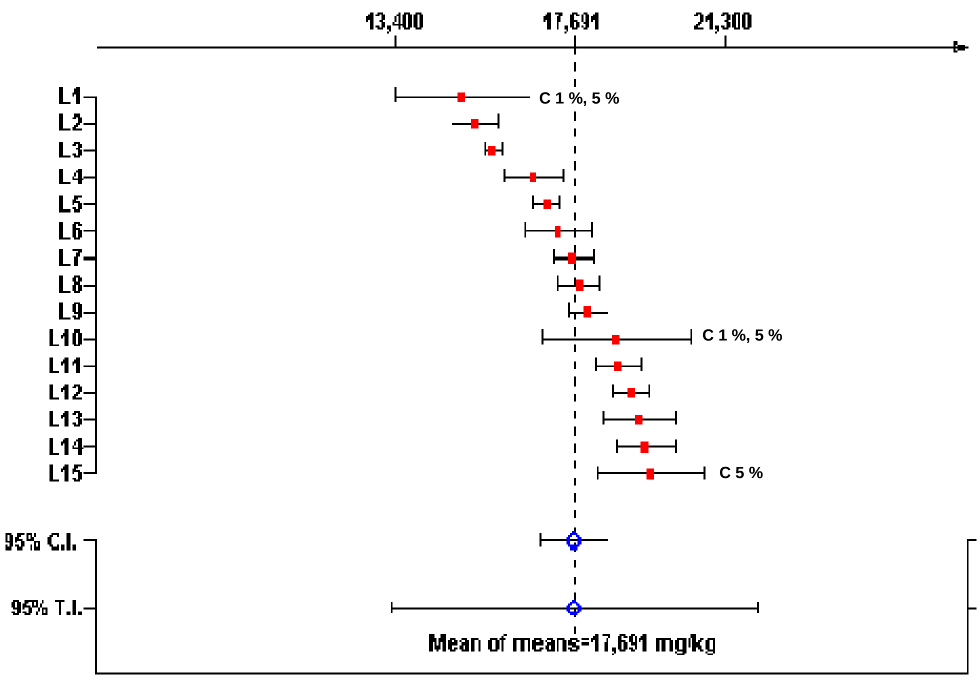
Range [min..max]	[13,400 .. 21,300]
	Case of No Pooling
Mean of means	17,691
95% H.W. Confidence Interval	0,827
95% H.W. Tolerance Interval	4,413
	Case of Pooling
Mean of All	17,691
95% H.W. Confidence Interval	0,344
95% H.W. Tolerance Interval	3,692

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6i3)



Tab. 6j1 : Nickel accepted results in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	24,100	6,466	6,785	34,000	24,600	25,400	15,400	26,400	18,800
L 2	25 DCarc-OES 3	24,167	0,753	0,790	25,000	24,000	23,000	24,000	24,000	25,000
L 3	11 ICP OES (1)	26,167	1,329	1,395	25,000	25,000	27,000	28,000	27,000	25,000
L 4	31 ICP OES 3	28,717	0,861	0,904	28,000	27,700	28,300	28,900	29,800	29,600
L 5	36 DCarc-OES 3	29,750	1,237	1,299	28,300	29,400	30,600	31,700	29,700	28,800
L 6	20 ICP OES 3	30,483	0,685	0,719	31,200	30,100	30,000	30,200	29,900	31,500
L 7	23 ET AAS 2	30,933	0,497	0,521	31,600	30,200	31,000	31,300	30,900	30,600
L 8	19 ICP OES 1	30,983	2,101	2,205	28,200	33,600	31,400	29,100	32,900	30,700
L 9	33 ICP OES 3	31,115	0,237	0,249	31,240	30,920	31,530	31,090	30,910	31,000
L 10	24 ICP-MS 2	31,250	0,524	0,550	32,100	30,600	31,000	31,100	31,600	31,100
L 11	22 ICP OES 3	31,673	0,422	0,443	31,684	31,677	31,981	30,884	32,087	31,724
L 12	16 ICP OES 3	32,167	3,251	3,411	35,000	29,000	37,000	32,000	31,000	29,000
L 13	36 ICP OES 3	32,617	0,549	0,576	32,700	32,000	33,400	32,300	32,200	33,100
L 14	13 ICP OES (1)	33,083	2,462	2,584	35,600	33,100	36,500	31,600	30,600	31,100
L 15	2 K_0-INNA (3)	35,185	4,266	4,477	33,660	37,300	33,350	37,540	28,520	40,740
L 16	27 ICP OES	35,467	4,302	10,686	31,100	35,600	39,700			
L 17	18 ICP OES	36,517	4,635	4,864	29,800	35,200	39,800	40,500	32,800	41,000
L 18	6 F AAS 2,3	39,167	2,401	2,520	37,000	37,000	39,000	41,000	38,000	43,000
L 19	28 ICP OES 1	39,398	8,528	8,950	28,990	32,780	41,700	34,860	49,240	48,820
L 20	26 ICP OES 3	39,417	1,216	1,276	39,600	40,900	40,800	38,500	38,600	38,100
L 21	8 ICP OES 3	40,450	5,871	6,161	41,400	47,400	41,800	36,900	44,400	30,800
L 22	12 ICP OES (2)	41,082	2,647	2,778	37,770	38,510	40,830	42,030	42,440	44,910

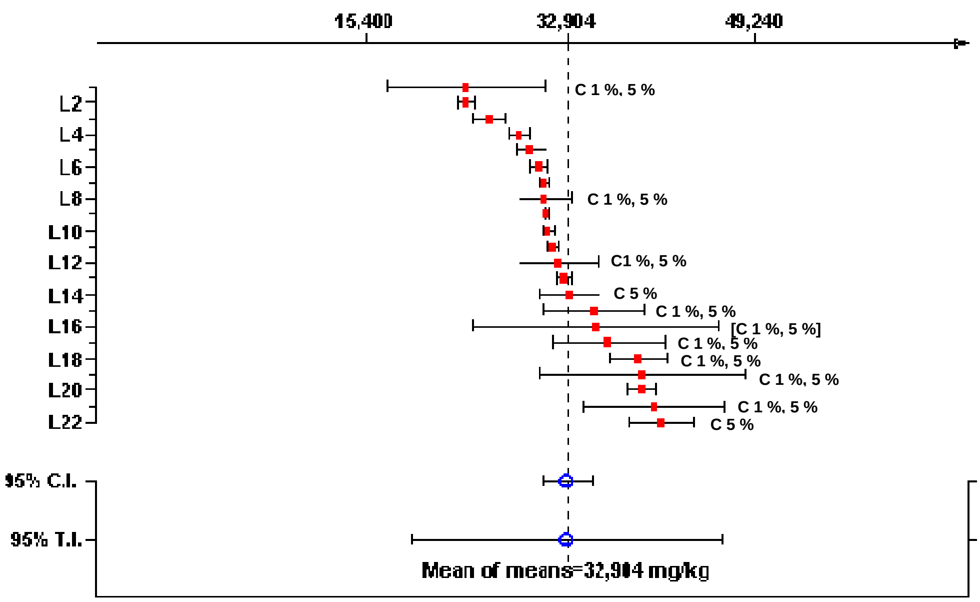
Range [min..max]	[15,400 .. 49,240]
	Case of No Pooling
Mean of means	32,904
95% H.W. Confidence Interval	2,208
95% H.W. Tolerance Interval	13,430
	Case of Pooling
Mean of All	32,844
95% H.W. Confidence Interval	1,009
95% H.W. Tolerance Interval	12,711

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6j1)



Tab. 6k1 : Titanium evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	25 DCarc-OES 3	54,167	5,269	5,530	59,000	62,000	51,000	50,000	49,000	54,000
L 2	14 ICP OES 2	67,500	24,712	25,934	44,000	43,000	48,000	90,000	89,000	91,000
L 3	11 ICP OES (1)	67,667	1,966	2,064	71,000	67,000	67,000	69,000	66,000	66,000
L 4	4 ETV-ICP OES 2	69,567	4,709	4,942	71,100	66,700	63,600	66,700	76,200	73,100
L 5	19 ICP OES 1	72,133	1,167	1,225	71,300	71,000	71,500	74,200	72,500	72,300
L 6	8 ICP OES 3	72,700	0,869	0,912	73,100	73,500	71,400	72,800	73,500	71,900
L 7	28 ICP OES 1	74,470	0,400	0,420	74,560	74,070	74,490	75,150	74,060	74,490
L 8	26 ICP OES 3	76,500	1,324	1,389	75,800	76,700	74,200	77,800	77,500	77,000
L 9	22 ICP OES 3	77,342	0,939	0,986	75,903	76,957	78,719	77,100	77,719	77,652
L 10	13 ICP OES 2	77,450	2,185	2,293	80,200	77,100	79,600	77,600	74,600	75,600
L 11	12 ICP OES (2)	77,462	4,468	4,689	74,990	75,580	73,580	84,050	82,180	74,390
L 12	31 ICP OES 3	78,550	0,880	0,924	77,600	79,600	78,600	77,400	78,900	79,200
L 13	24 ICP-MS 2	79,433	1,138	1,194	78,700	78,500	79,000	79,700	79,100	81,600
L 14	33 ICP OES 3	80,947	0,546	0,573	80,900	81,060	81,940	80,730	80,730	80,320
L 15	16 ICP OES 3	82,500	2,811	2,950	86,000	80,000	80,000	81,000	82,000	86,000
L 16	18 ICP OES	83,000	1,265	1,327	81,000	83,000	83,000	83,000	85,000	83,000
L 17	36 ICP OES 3	83,750	0,774	0,812	84,500	83,800	84,800	82,800	83,200	83,400
L 18	27 ICP OES	84,150	0,071	0,635	84,200	84,100				
L 19	2 K_0-INNA 3	85,070	7,910	8,301	74,140	91,030	81,860	94,230	90,200	78,960
L 20	20 ICP OES 2	85,100	1,586	1,665	85,500	83,600	83,300	85,500	85,000	87,700
L 21	36 DCarc-OES 3	86,900	8,776	9,210	83,200	90,100	73,500	83,000	93,800	97,800

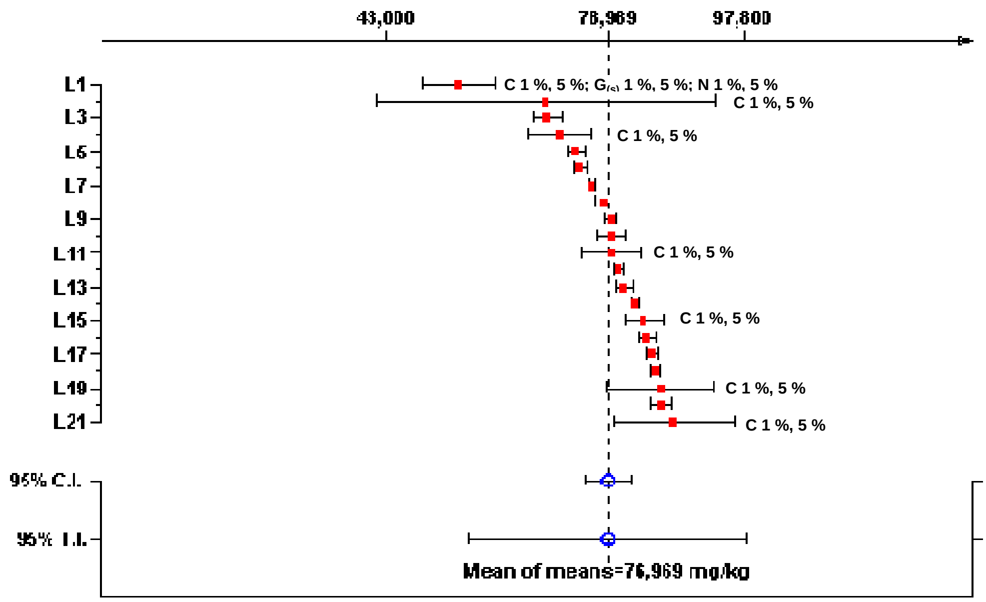
Range [min..max]	[43,000 .. 97,800]
	Case of No Pooling
Mean of means	76,969
95% H.W. Confidence Interval	3,554
95% H.W. Tolerance Interval	21,258
	Case of Pooling
Mean of All	76,734
95% H.W. Confidence Interval	1,736
95% H.W. Tolerance Interval	21,329

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test (single test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6k1)



Tab. 6k2 : Titanium accepted results in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	11 ICP OES (1)	67,667	1,966	2,064	71,000	67,000	67,000	69,000	66,000	66,000
L 2	4 ETV-ICP OES 2	69,567	4,709	4,942	71,100	66,700	63,600	66,700	76,200	73,100
L 3	19 ICP OES 1	72,133	1,167	1,225	71,300	71,000	71,500	74,200	72,500	72,300
L 4	8 ICP OES 3	72,700	0,869	0,912	73,100	73,500	71,400	72,800	73,500	71,900
L 5	28 ICP OES 1	74,470	0,400	0,420	74,560	74,070	74,490	75,150	74,060	74,490
L 6	26 ICP OES 3	76,500	1,324	1,389	75,800	76,700	74,200	77,800	77,500	77,000
L 7	22 ICP OES 3	77,342	0,939	0,986	75,903	76,957	78,719	77,100	77,719	77,652
L 8	13 ICP OES 2	77,450	2,185	2,293	80,200	77,100	79,600	77,600	74,600	75,600
L 9	12 ICP OES (2)	77,462	4,468	4,689	74,990	75,580	73,580	84,050	82,180	74,390
L 10	31 ICP OES 3	78,550	0,880	0,924	77,600	79,600	78,600	77,400	78,900	79,200
L 11	24 ICP-MS 2	79,433	1,138	1,194	78,700	78,500	79,000	79,700	79,100	81,600
L 12	33 ICP OES 3	80,947	0,546	0,573	80,900	81,060	81,940	80,730	80,730	80,320
L 13	16 ICP OES 3	82,500	2,811	2,950	86,000	80,000	80,000	81,000	82,000	86,000
L 14	18 ICP OES	83,000	1,265	1,327	81,000	83,000	83,000	83,000	85,000	83,000
L 15	36 ICP OES 3	83,750	0,774	0,812	84,500	83,800	84,800	82,800	83,200	83,400
L 16	27 ICP OES	84,150	0,071	0,635	84,200	84,100				
L 17	2 K_0-INNA 3	85,070	7,910	8,301	74,140	91,030	81,860	94,230	90,200	78,960
L 18	20 ICP OES 2	85,100	1,586	1,665	85,500	83,600	83,300	85,500	85,000	87,700
L 19	36 DCarc-OES 3	86,900	8,776	9,210	83,200	90,100	73,500	83,000	93,800	97,800

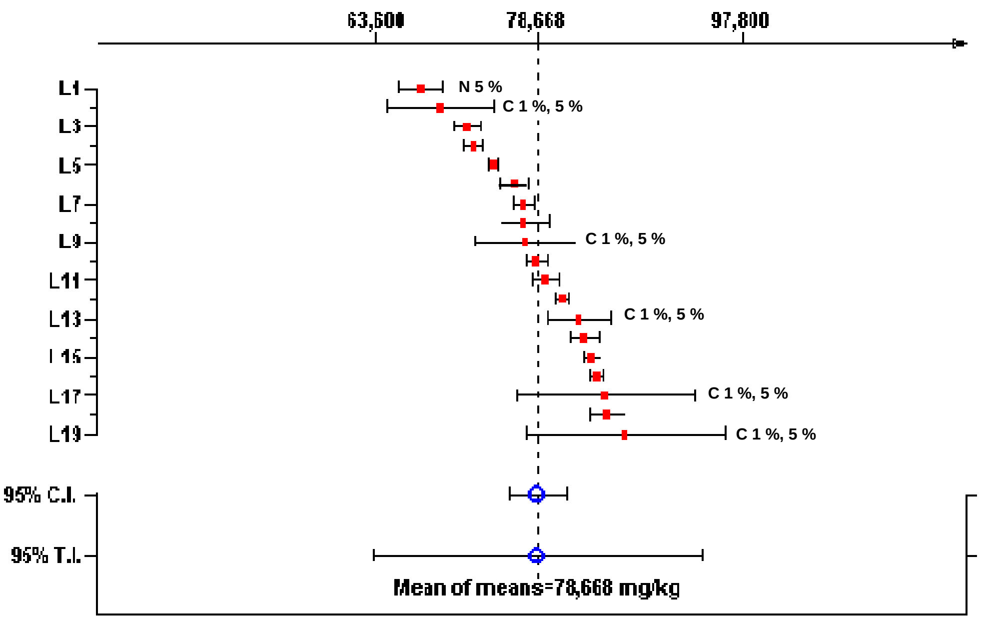
Range [min..max]	[63,600 .. 97,800]
	Case of No Pooling
Mean of means	78,668
95% H.W. Confidence Interval	2,675
95% H.W. Tolerance Interval	15,451
	Case of Pooling
Mean of All	78,469
95% H.W. Confidence Interval	1,180
95% H.W. Tolerance Interval	13,855

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6k2)



Tab. 6l1: Vanadium evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ETV-ICP OES 2	24,817	9,015	9,461	21,400	40,100	16,700	15,800	27,300	27,600
L 2	25 DCarc-OES 3	28,833	1,472	1,545	31,000	28,000	28,000	30,000	27,000	29,000
L 3	13 ICP OES (1)	30,833	1,080	1,134	32,500	31,000	31,500	30,500	29,500	30,000
L 4	16 ICP OES 3	36,287	1,109	1,163	34,720	35,000	37,000	37,000	37,000	37,000
L 5	8 ICP OES 3	37,000	5,707	5,989	44,300	43,700	33,900	30,200	34,500	35,400
L 6	11 ICP OES (1)	38,000	1,265	1,327	38,000	39,000	39,000	39,000	36,000	37,000
L 7	27 ICP OES	39,267	3,907	9,705	38,500	35,800	43,500			
L 8	18 ICP OES	39,667	4,965	5,211	32,300	43,000	35,400	45,000	39,300	43,000
L 9	19 ICP OES 1	41,250	2,471	2,593	38,600	38,900	44,200	44,100	41,500	40,200
L 10	28 ICP OES 1	41,348	5,026	5,275	48,250	44,900	36,050	43,850	36,420	38,620
L 11	24 ICP-MS 2	42,383	0,722	0,758	42,400	43,000	42,900	41,000	42,600	42,400
L 12	12 ICP OES (2)	42,532	1,585	1,663	43,990	42,590	43,830	43,390	41,490	39,900
L 13	26 ICP OES 3	44,383	0,458	0,481	44,500	43,900	43,900	45,100	44,300	44,600
L 14	36 ICP OES 3	45,483	1,339	1,405	45,400	44,400	47,400	44,100	44,800	46,800
L 15	31 ICP OES 3	45,867	1,742	1,828	48,400	46,900	43,700	45,700	44,200	46,300
L 16	36 DCarc-OES 3	46,067	2,760	2,897	47,300	48,100	43,100	42,000	47,900	48,000
L 17	2 K_0-INNA 3	47,485	0,925	0,971	46,080	48,110	48,180	48,490	47,000	47,050
L 18	20 ICP OES 2	48,267	1,031	1,082	47,600	49,400	47,100	47,600	48,300	49,600
L 19	22 ICP OES 3	49,925	1,846	1,937	48,966	52,036	48,011	51,327	47,897	51,311

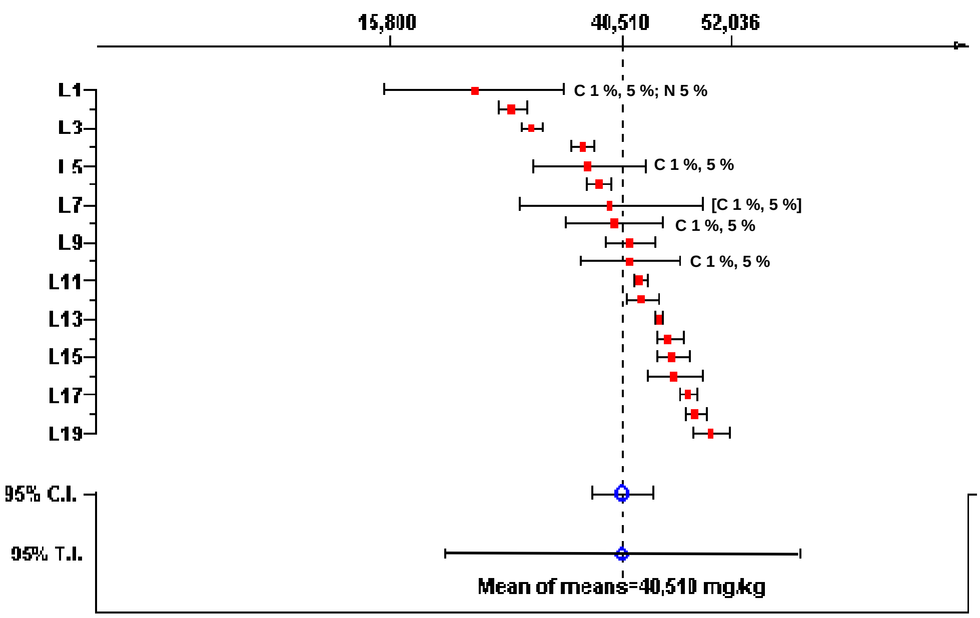
Range [min..max]	[15,800 .. 52,036]
	Case of No Pooling
Mean of means	40,510
95% H.W. Confidence Interval	3,254
95% H.W. Tolerance Interval	18,797
	Case of Pooling
Mean of All	40,544
95% H.W. Confidence Interval	1,382
95% H.W. Tolerance Interval	16,282

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6l1)



Tab. 6l2: Vanadium accepted results in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	25 DCarc-OES 3	28,833	1,472	1,545	31,000	28,000	28,000	30,000	27,000	29,000
L 2	13 ICP OES (1)	30,833	1,080	1,134	32,500	31,000	31,500	30,500	29,500	30,000
L 3	16 ICP OES 3	36,287	1,109	1,163	34,720	35,000	37,000	37,000	37,000	37,000
L 4	8 ICP OES 3	37,000	5,707	5,989	44,300	43,700	33,900	30,200	34,500	35,400
L 5	11 ICP OES (1)	38,000	1,265	1,327	38,000	39,000	39,000	39,000	36,000	37,000
L 6	27 ICP OES	39,267	3,907	9,705	38,500	35,800	43,500			
L 7	18 ICP OES	39,667	4,965	5,211	32,300	43,000	35,400	45,000	39,300	43,000
L 8	19 ICP OES 1	41,250	2,471	2,593	38,600	38,900	44,200	44,100	41,500	40,200
L 9	28 ICP OES 1	41,348	5,026	5,275	48,250	44,900	36,050	43,850	36,420	38,620
L 10	24 ICP-MS 2	42,383	0,722	0,758	42,400	43,000	42,900	41,000	42,600	42,400
L 11	12 ICP OES (2)	42,532	1,585	1,663	43,990	42,590	43,830	43,390	41,490	39,900
L 12	26 ICP OES 3	44,383	0,458	0,481	44,500	43,900	43,900	45,100	44,300	44,600
L 13	36 ICP OES 3	45,483	1,339	1,405	45,400	44,400	47,400	44,100	44,800	46,800
L 14	31 ICP OES 3	45,867	1,742	1,828	48,400	46,900	43,700	45,700	44,200	46,300
L 15	36 DCarc-OES 3	46,067	2,760	2,897	47,300	48,100	43,100	42,000	47,900	48,000
L 16	2 K_0-INNA 3	47,485	0,925	0,971	46,080	48,110	48,180	48,490	47,000	47,050
L 17	20 ICP OES 2	48,267	1,031	1,082	47,600	49,400	47,100	47,600	48,300	49,600
L 18	22 ICP OES 3	49,925	1,846	1,937	48,966	52,036	48,011	51,327	47,897	51,311

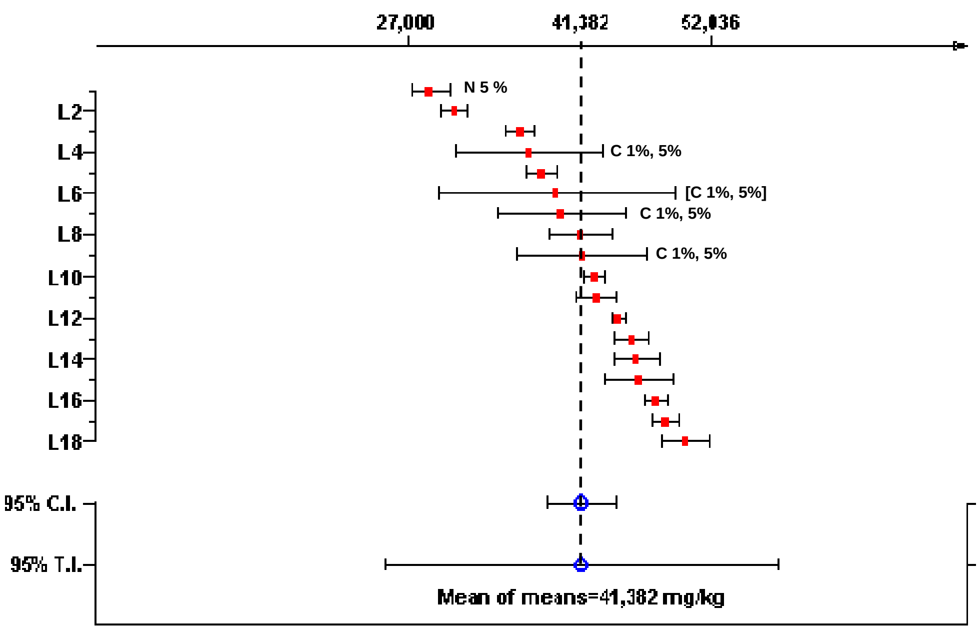
Range [min..max]	[27,000 .. 52,036]
	Case of No Pooling
Mean of means	41,382
95% H.W. Confidence Interval	2,856
95% H.W. Tolerance Interval	16,188
	Case of Pooling
Mean of All	41,442
95% H.W. Confidence Interval	1,194
95% H.W. Tolerance Interval	13,732

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6l2)



Tab. 6m1: Zirconium evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	27 ICP OES	19,100	1,602	2,549	17,000	18,800	20,700	19,900		
L 2	19 ICP OES 1	21,200	0,696	0,730	21,000	21,200	20,600	21,500	20,500	22,400
L 3	11 ICP OES (1)	22,000	0,894	0,939	22,000	22,000	23,000	23,000	21,000	21,000
L 4	18 ICP OES	22,400	1,166	1,224	20,900	21,700	21,600	23,000	23,300	23,900
L 5	26 ICP OES 3	22,833	0,432	0,453	23,600	22,700	22,400	22,800	22,500	23,000
L 6	28 ICP OES 1	23,175	0,250	0,263	22,930	23,100	23,470	23,440	23,230	22,880
L 7	22 ICP OES 3	23,686	0,237	0,249	23,286	23,553	23,946	23,693	23,837	23,798
L 8	12 ICP OES (2)	23,703	1,403	1,472	22,460	22,200	23,560	23,200	25,390	25,410
L 9	31 ICP OES 3	24,317	0,560	0,588	24,500	25,000	23,900	23,700	23,900	24,900
L 10	24 ICP-MS 2	25,433	0,207	0,217	25,300	25,800	25,200	25,500	25,400	25,400
L 11	2 K_0-INNA 3	25,553	0,711	0,746	26,660	25,210	26,090	24,920	25,590	24,850
L 12	33 ICP OES 3	25,763	0,357	0,374	25,920	26,280	25,790	25,870	25,420	25,300
L 13	36 ICP OES 3	25,950	0,266	0,280	26,200	25,800	26,300	25,600	25,800	26,000
L 14	20 ICP OES 2	26,633	0,680	0,714	26,600	26,000	25,900	27,100	26,500	27,700
L 15	36 DCarc-OES 3	27,000	1,927	2,022	23,900	27,700	25,500	29,100	28,200	27,600
L 16	13 ICP-MS	28,683	1,151	1,208	29,100	27,500	29,600	30,100	28,600	27,200
L 17	4 ETV-ICP OES 2	29,133	3,121	3,275	34,400	28,800	30,800	25,800	26,600	28,400
L 18	1 INAA	30,410	2,672	2,804	32,386	28,175	29,036	27,053	32,129	33,678
L 19	8 ICP OES 3	30,983	3,618	3,797	37,100	33,300	29,700	29,900	28,800	27,100
L 20	16 ICP OES 3	35,000	5,657	5,936	44,000	32,000	34,000	28,000	33,000	39,000

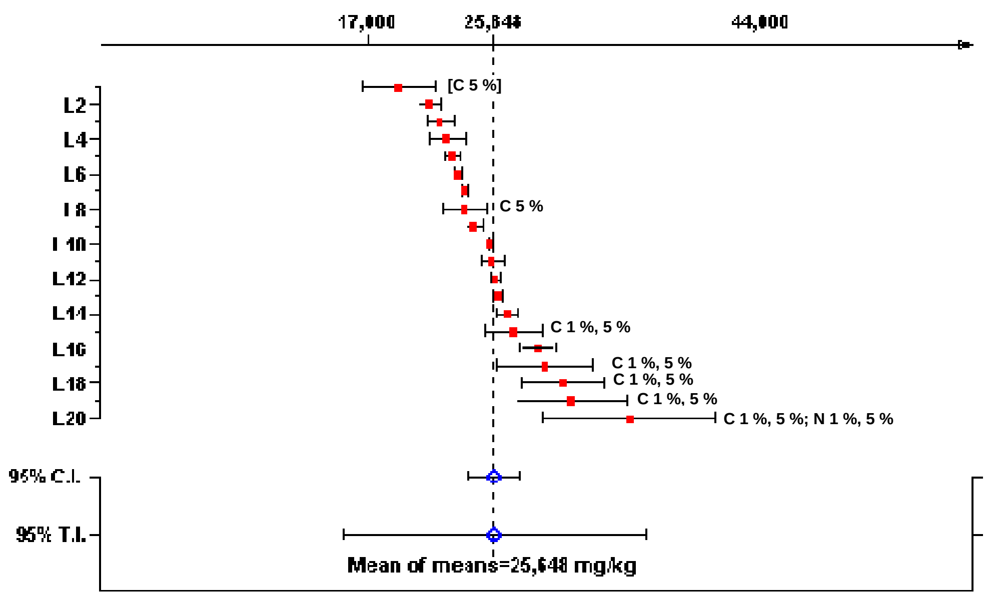
Range [min..max]	[17,000 .. 44,000]
	Case of No Pooling
Mean of means	25,648
95% H.W. Confidence Interval	1,774
95% H.W. Tolerance Interval	10,429
	Case of Pooling
Mean of All	25,759
95% H.W. Confidence Interval	0,740
95% H.W. Tolerance Interval	8,955

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6m1)



Tab. 6m2: Zirconium accepted results in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	27 ICP OES	19,100	1,602	2,549	17,000	18,800	20,700	19,900		
L 2	19 ICP OES 1	21,200	0,696	0,730	21,000	21,200	20,600	21,500	20,500	22,400
L 3	11 ICP OES (1)	22,000	0,894	0,939	22,000	22,000	23,000	23,000	21,000	21,000
L 4	18 ICP OES	22,400	1,166	1,224	20,900	21,700	21,600	23,000	23,300	23,900
L 5	26 ICP OES 3	22,833	0,432	0,453	23,600	22,700	22,400	22,800	22,500	23,000
L 6	28 ICP OES 1	23,175	0,250	0,263	22,930	23,100	23,470	23,440	23,230	22,880
L 7	22 ICP OES 3	23,686	0,237	0,249	23,286	23,553	23,946	23,693	23,837	23,798
L 8	12 ICP OES (2)	23,703	1,403	1,472	22,460	22,200	23,560	23,200	25,390	25,410
L 9	31 ICP OES 3	24,317	0,560	0,588	24,500	25,000	23,900	23,700	23,900	24,900
L 10	24 ICP-MS 2	25,433	0,207	0,217	25,300	25,800	25,200	25,500	25,400	25,400
L 11	2 K_0-INNA 3	25,553	0,711	0,746	26,660	25,210	26,090	24,920	25,590	24,850
L 12	33 ICP OES 3	25,763	0,357	0,374	25,920	26,280	25,790	25,870	25,420	25,300
L 13	36 ICP OES 3	25,950	0,266	0,280	26,200	25,800	26,300	25,600	25,800	26,000
L 14	20 ICP OES 2	26,633	0,680	0,714	26,600	26,000	25,900	27,100	26,500	27,700
L 15	36 DCarc-OES 3	27,000	1,927	2,022	23,900	27,700	25,500	29,100	28,200	27,600
L 16	13 ICP-MS	28,683	1,151	1,208	29,100	27,500	29,600	30,100	28,600	27,200
L 17	4 ETV-ICP OES 2	29,133	3,121	3,275	34,400	28,800	30,800	25,800	26,600	28,400
L 18	1 INAA	30,410	2,672	2,804	32,386	28,175	29,036	27,053	32,129	33,678
L 19	8 ICP OES 3	30,983	3,618	3,797	37,100	33,300	29,700	29,900	28,800	27,100

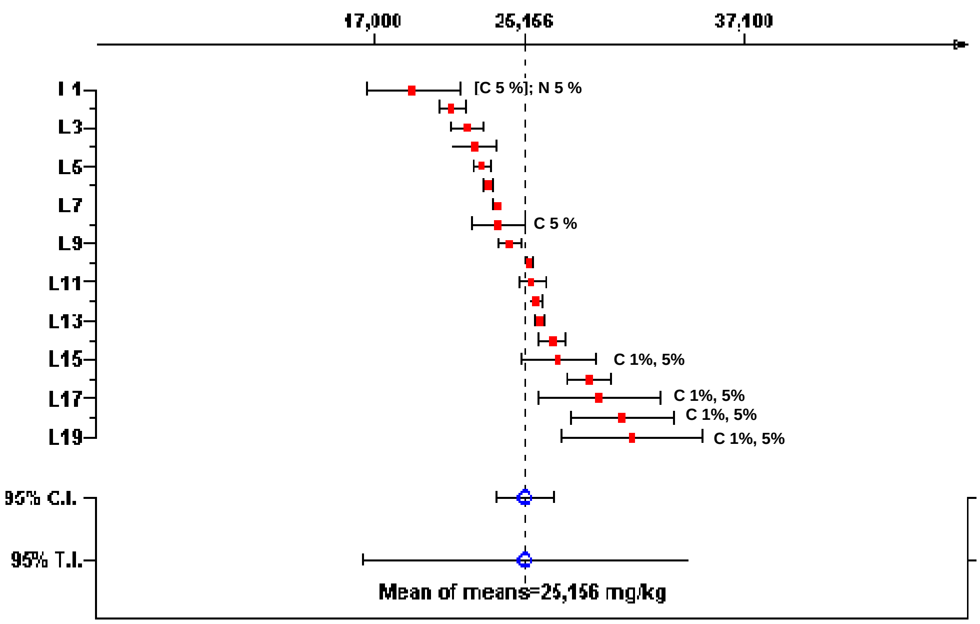
Range [min..max]	[17,000 .. 37,100]
	Case of No Pooling
Mean of means	25,156
95% H.W. Confidence Interval	1,528
95% H.W. Tolerance Interval	8,824
	Case of Pooling
Mean of All	25,264
95% H.W. Confidence Interval	0,622
95% H.W. Tolerance Interval	7,360

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6m2)



Tab. 6n1 : Total carbon evaluation in run 1 (values in %)

Current Lab number	Lab Abbreviation	Mean (%)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	27 CGHE/comb.-IR	29,283	0,117	0,123	29,300	29,200	29,400	29,300	29,400	29,100
L 2	16 CGHE/titr. 3	29,367	0,197	0,206	29,300	29,300	29,200	29,500	29,200	29,700
L 3	6 CGHE/comb.-IR 3	29,573	0,043	0,045	29,600	29,580	29,620	29,520	29,600	29,520
L 4	7 CGHE/comb.-IR	29,746	0,022	0,023	29,725	29,716	29,744	29,764	29,771	29,753
L 5	31 CGHE/comb.-IR 3	29,817	0,041	0,043	29,900	29,800	29,800	29,800	29,800	29,800
L 6	19 Comb,/grav. 1	29,853	0,057	0,059	29,803	29,868	29,954	29,865	29,815	29,814
L 7	9 CGHE/comb.-IR 3	29,863	0,042	0,044	29,890	29,830	29,890	29,800	29,910	29,860
L 8	13 CGHE/comb.-IR 2	29,865	0,279	0,293	30,150	30,110	30,020	29,640	29,450	29,820
L 9	32 CGHE/comb.-IR 3	29,892	0,048	0,051	29,971	29,864	29,903	29,827	29,906	29,879
L 10	5 CGHE/comb.-IR 3	29,898	0,122	0,128	29,850	29,790	30,100	29,800	29,860	29,990
L 11	26 CGHE/comb.-IR 3	29,912	0,021	0,022	29,880	29,910	29,940	29,930	29,900	29,910
L 12	8 Coul. 3	29,913	0,064	0,068	29,860	29,850	29,860	29,940	29,980	29,990
L 13	36 CGHE/comb.-TC 3	29,920	0,035	0,037	29,950	29,950	29,900	29,940	29,860	29,920
L 14	21 CGHE/comb.-IR 2	29,937	0,258	0,271	30,060	30,120	30,180	30,040	29,600	29,620
L 15	20 CGHE/comb.-IR 3	29,943	0,045	0,047	29,880	29,980	29,900	29,980	29,940	29,980
L 16	12 CGHE/comb.-TC (2)	29,955	0,047	0,050	29,880	30,000	29,930	30,000	29,980	29,940
L 17	11 CGHE/comb.-IR (2)	29,956	0,047	0,058	29,890	29,950	30,020	29,970	29,950	
L 18	33 CGHE/comb.-IR 3	30,033	0,067	0,071	29,960	29,980	30,030	30,110	30,000	30,120
L 19	25 Coul. 3	30,130	0,036	0,038	30,090	30,130	30,110	30,150	30,110	30,190

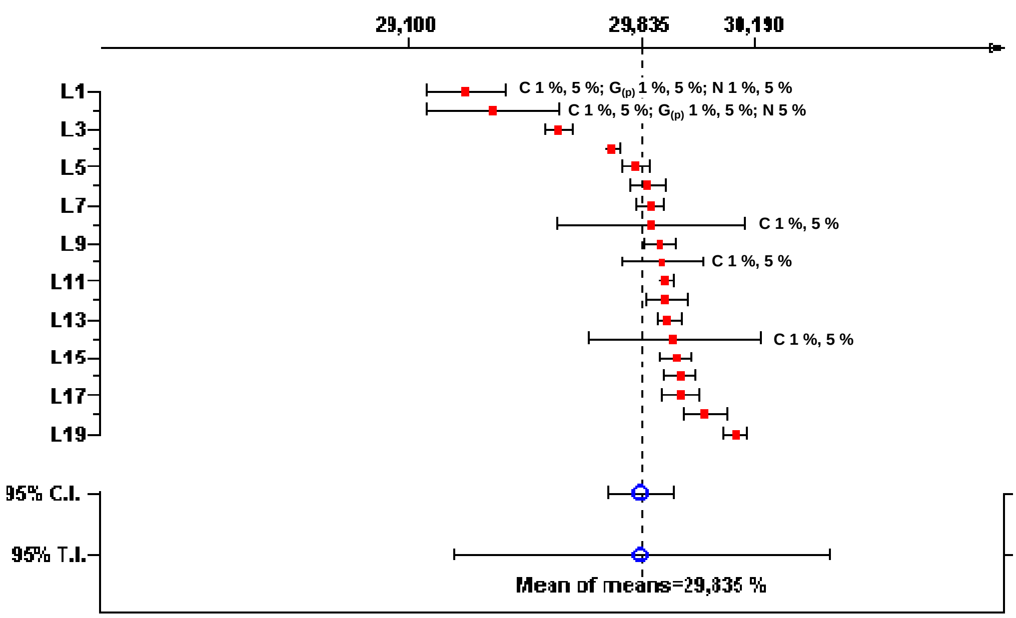
Range [min..max]	[29,100 .. 30,190]
	Case of No Pooling
Mean of means	29,835
95% H.W. Confidence Interval	0,102
95% H.W. Tolerance Interval	0,589
	Case of Pooling
Mean of All	29,833
95% H.W. Confidence Interval	0,043
95% H.W. Tolerance Interval	0,514

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(p)}$ = Grubbs test (pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6n1)



Tab. 6n2: Total carbon accepted results in run 2 (values in %)

Current Lab number	Lab Abbreviation	Mean (%)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	6 CGHE/comb.-IR 3	29,573	0,043	0,045	29,600	29,580	29,620	29,520	29,600	29,520
L 2	7 CGHE/comb.-IR	29,746	0,022	0,023	29,725	29,716	29,744	29,764	29,771	29,753
L 3	31 CGHE/comb.-IR 3	29,817	0,041	0,043	29,900	29,800	29,800	29,800	29,800	29,800
L 4	19 comb,/grav. 1	29,853	0,057	0,059	29,803	29,868	29,954	29,865	29,815	29,814
L 5	9 CGHE/comb.-IR 3	29,863	0,042	0,044	29,890	29,830	29,890	29,800	29,910	29,860
L 6	13 CGHE/comb.-IR 2	29,865	0,279	0,293	30,150	30,110	30,020	29,640	29,450	29,820
L 7	32 CGHE/comb.-IR 3	29,892	0,048	0,051	29,971	29,864	29,903	29,827	29,906	29,879
L 8	5 CGHE/comb.-IR 3	29,898	0,122	0,128	29,850	29,790	30,100	29,800	29,860	29,990
L 9	26 CGHE/comb.-IR 3	29,912	0,021	0,022	29,880	29,910	29,940	29,930	29,900	29,910
L 10	8 Comb./coul. 3	29,913	0,064	0,068	29,860	29,850	29,860	29,940	29,980	29,990
L 11	36 CGHE/comb.-TC 3	29,920	0,035	0,037	29,950	29,950	29,900	29,940	29,860	29,920
L 12	21 CGHE/comb.-IR 2	29,937	0,258	0,271	30,060	30,120	30,180	30,040	29,600	29,620
L 13	20 CGHE/comb.-IR 3	29,943	0,045	0,047	29,880	29,980	29,900	29,980	29,940	29,980
L 14	12 CGHE/comb.-TC (2)	29,955	0,047	0,050	29,880	30,000	29,930	30,000	29,980	29,940
L 15	11 CGHE/comb.-IR (2)	29,956	0,047	0,058	29,890	29,950	30,020	29,970	29,950	
L 16	33 CGHE/comb.-IR 3	30,033	0,067	0,071	29,960	29,980	30,030	30,110	30,000	30,120
L 17	25 Comb./coul. 3	30,130	0,036	0,038	30,090	30,130	30,110	30,150	30,110	30,190

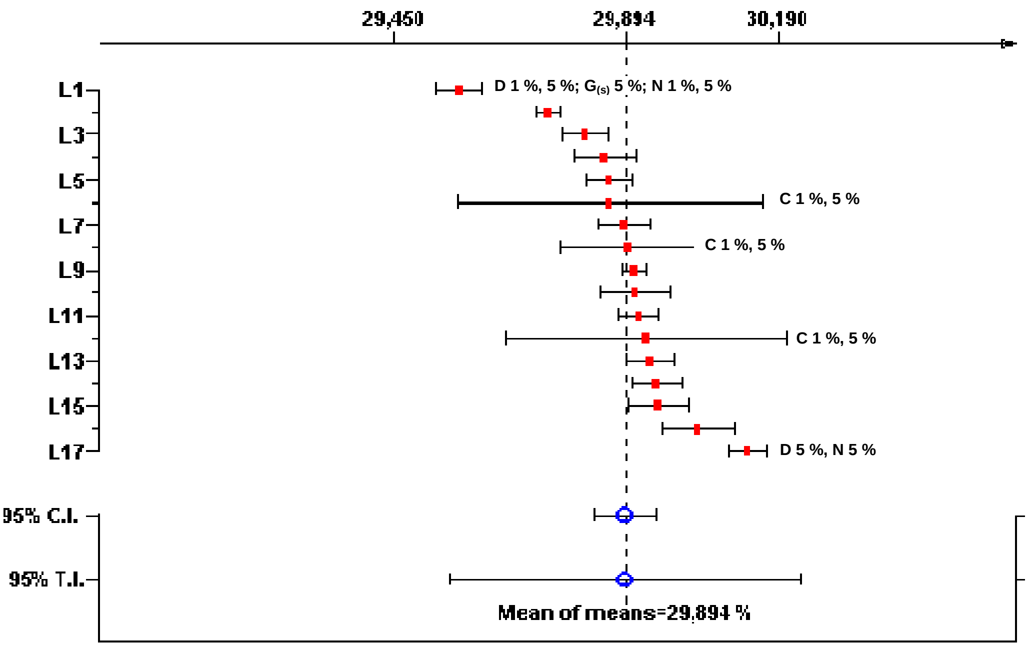
Range [min..max]	[29,450 .. 30,190]
	Case of No Pooling
Mean of means	29,894
95% H.W. Confidence Interval	0,061
95% H.W. Tolerance Interval	0,337
	Case of Pooling
Mean of All	29,894
95% H.W. Confidence Interval	0,030
95% H.W. Tolerance Interval	0,336

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test (single test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **<u>pooling is: Not Allowed</u>**

Diagram of means and 95% confidence intervals (to Tab. 6n2)



Tab. 6o1a : Free carbon evaluation in run 1 (values in mg/kg)

(for information only)

Evaluation with all delivered results based on prescribed and non-prescribed methods.

Current Lab number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 CGHE/comb-IR	125	29	30	110	130	160	120	80	150
L 2	31 CGHE/comb.-IR 3	159	22	23	135	167	161	182	131	178
L 3	33 CGHE/comb.-IR3	206	59	62	187	187	164	178	192	325
L 4	13 CGHE/comb.-IR3	255	55	57	322	282	215	283	169	258
L 5	36 wet chemical oxidation/coul. 3	415	10	11	420	410	400	410	430	420
L 6	26a comb./coul. 3 *)	500	27	28	520	510	490	520	450	510
L 7	32 comb./coul. 3 *)	515	26	27	490	510	490	520	560	520
L 8	26b wet chemical oxidation/coul. 3	540	28	30	510	530	540	590	520	550
L 9	19 comb./coul. 1 **)	608	33	35	590	570	650	620	580	640
L 10	25 comb./coul. 3 **)	617	75	79	700	600	600	500	700	600
L 11	15 comb./coul. 3 **)	643	60	62	660	670	580	740	590	620
L 12	8 comb./coul. **)	812	59	62	840	840	773	860	850	710
L 13	9 CGHE/comb.-IR3	817	397	417	1300	500	1000	1000	200	900
L 14	11 CGHE/comb.-IR 2	1055	153	160	1260	1000	1150	1130	950	840

*) by method M1 **) not by method M1

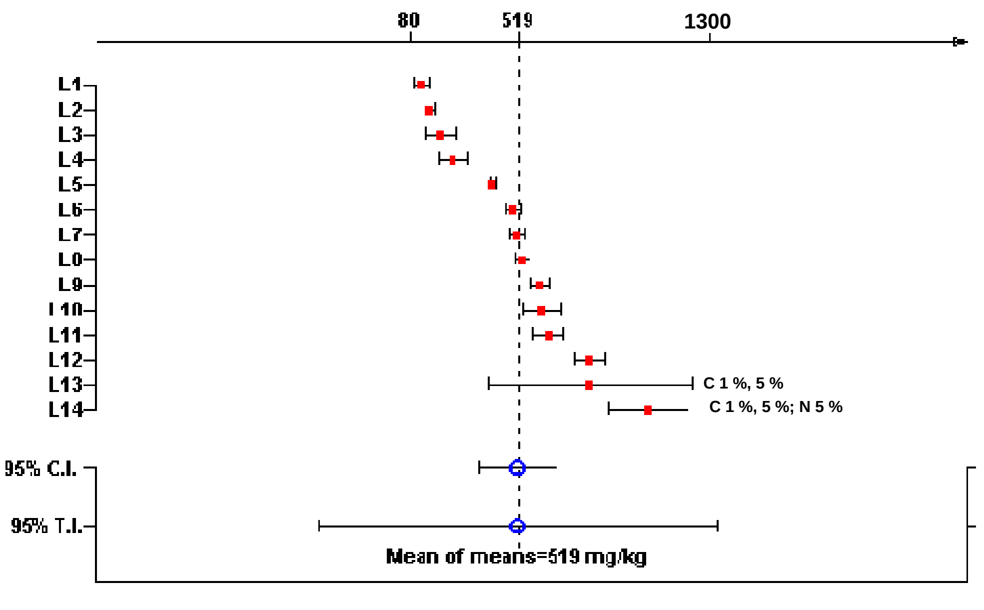
Range [min..max]	[80 .. 1300]
	Case of No Pooling
Mean of means	519
95% H.W. Confidence Interval	157
95% H.W. Tolerance Interval	818
	Case of Pooling
Mean of All	519
95% H.W. Confidence Interval	62
95% H.W. Tolerance Interval	647

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6o1)



Tab. 6o1b: Free carbon evaluation in run 1 (values in mg/kg)
(for information only)
Evaluation of results based on non-prescribed methods.

Current Lab number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 CGHE/comb-IR	125	29	30	110	130	160	120	80	150
L 2	31 CGHE/comb.-IR 3	159	22	23	135	167	161	182	131	178
L 3	33 CGHE/comb.-IR 3	206	59	62	187	187	164	178	192	325
L 4	13 CGHE/comb.-IR 3	255	55	57	322	282	215	283	169	258
L 5	19 comb./coul. 1	608	33	35	590	570	650	620	580	640
L 6	25 comb./coul. 3	617	75	79	700	600	600	500	700	600
L 7	15 comb./coul. 3	643	60	62	660	670	580	740	590	620
L 8	8 comb./coul..	812	59	62	840	840	773	860	850	710
L 9	9 CGHE/comb.-IR 3	817	397	417	1300	500	1000	1000	200	900
L 10	11 CGHE/comb.-IR 2	1055	153	160	1260	1000	1150	1130	950	840

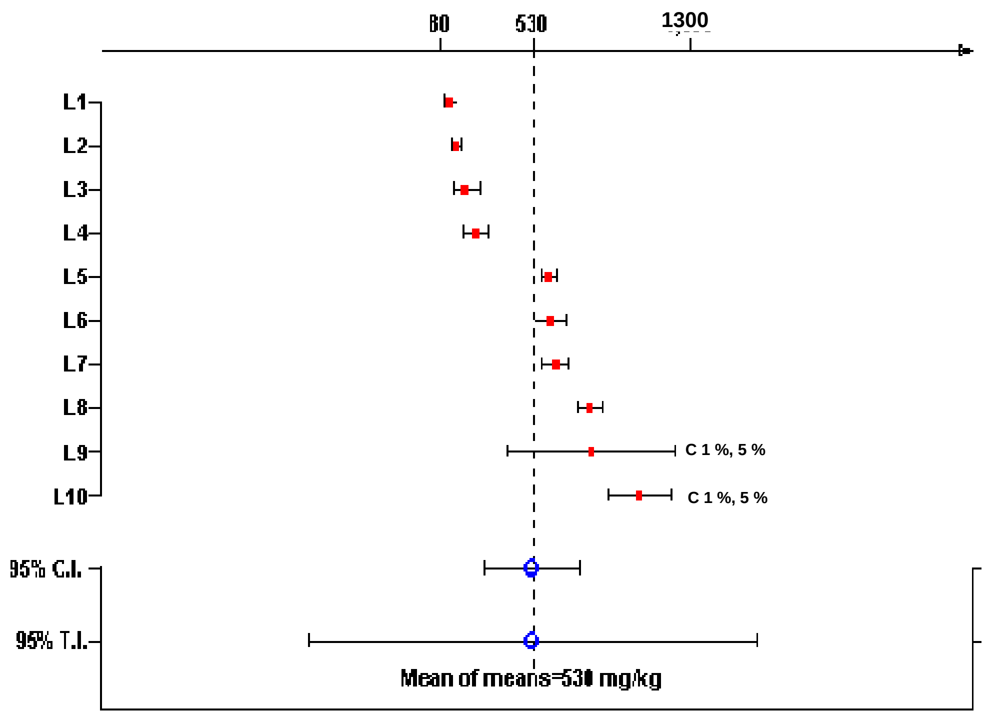
Range [min..max]	[80 .. 1300]
	Case of No Pooling
Mean of means	530
95% H.W. Confidence Interval	232
95% H.W. Tolerance Interval	1096
	Case of Pooling
Mean of All	530
95% H.W. Confidence Interval	87
95% H.W. Tolerance Interval	785,761

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6o1a)



Tab. 6o1c: Free carbon accepted results in run 1 (values in mg/kg) (accepted results)

Determined by the prescribed methods only:

*) Coulometric determination of free carbon content (C_{free}) in silicon carbide comprising weighing-back the sample boat = Method M2 (APPENDIX 2)

**) Coulometric determination of free carbon (C_{free}) in silicon carbide by wet-chemical oxidation with hot chromic-sulfuric acid = Method M1 (APPENDIX 1)

Current Lab number	Lab Abbreviation	Mean mg/kg	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	36 oxidation / coul. 3 **)	415	10	11	420	410	400	410	430	420
L 2	26a comb,/coul. 3 *)	500	27	28	520	510	490	520	450	510
L 3	32 comb,/coul. 3 *)	515	26	27	490	510	490	520	560	520
L 4	26b oxidation / coul. 3 **)	540	28	30	510	530	540	590	520	550

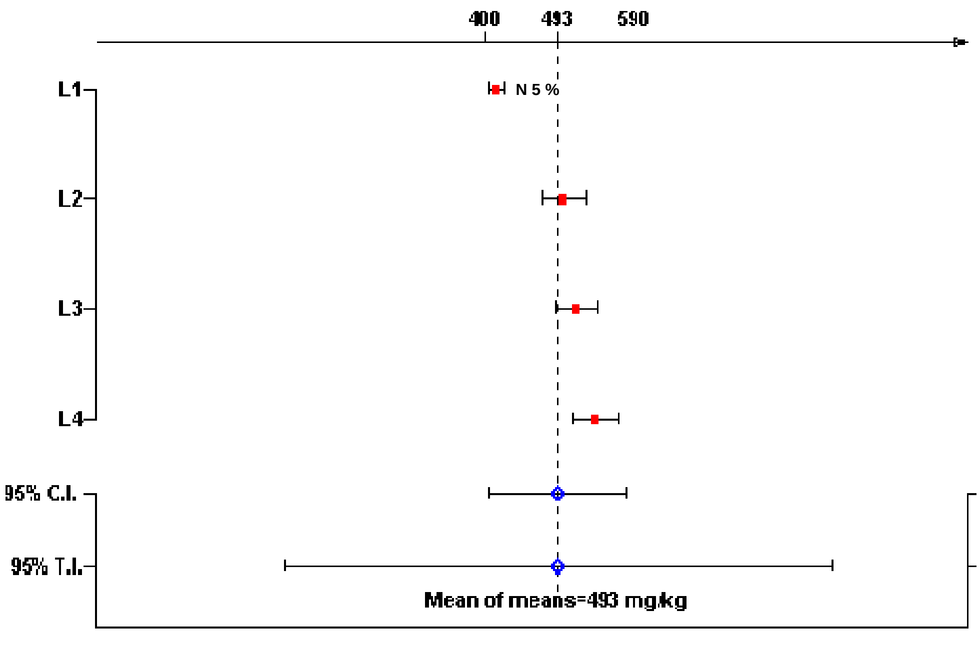
Range [min..max]	[400 .. 590]
	Case of No Pooling
Mean of means	493
95% H.W. Confidence Interval	86
95% H.W. Tolerance Interval	345
	Case of Pooling
Mean of All	493
95% H.W. Confidence Interval	22
95% H.W. Tolerance Interval	140

next page:
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6o1)



Tab. 6p1: Oxygen evaluation in run 1 (values in mg/kg)

Current Lab number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	27 CGHE-IR	825	16	17	820	820	810	810	850	840
L 2	12 CGHE-IR2	845	23	24	815	877	836	857	826	857
L 3	7 CGHE-IR	862	1	1	861	862	861	863	862	863
L 4	21 CGHE-IR2	865	18	19	837	871	866	877	887	849
L 5	13 CGHE-IR3	873	19	20	880	849	871	895	890	851
L 6	26 CGHE-IR3	902	12	12	910	900	920	900	890	890
L 7	31 CGHE-IR3	915	11	12	919	926	916	907	924	896
L 8	28 CGHE-IR1	948	3	3	950	950	946	948	950	942
L 9	37 CGHE-IR3	951	27	29	993	935	968	919	958	932
L 10	35 CGHE-IR1	988	37	39	1034	932	1007	1008	987	961
L 11	19 CGHE-coul 1	1032	52	54	980	1000	1120	1000	1030	1060
L 12	20 CGHE-IR2	1153	18	18	1160	1130	1180	1160	1150	1140

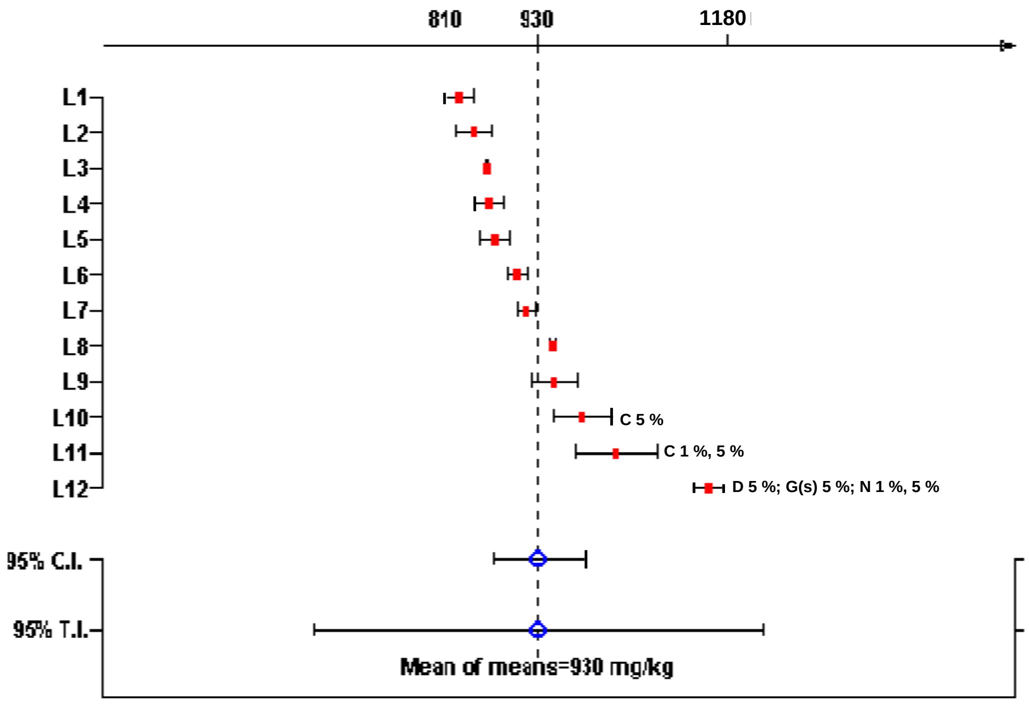
Range [min..max]	[810 .. 1180]
	Case of No Pooling
Mean of means	930
95% H.W. Confidence Interval	59
95% H.W. Tolerance Interval	295
	Case of Pooling
Mean of All	930
95% H.W. Confidence Interval	22
95% H.W. Tolerance Interval	213

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
$G_{(s)}$ = Grubbs test (single test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6p1)



Tab. 6p2: Oxygen accepted results in run 2 (values in mg/kg)

Current Lab number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	27 CGHE-IR	825	16	17	820	820	810	810	850	840
L 2	12 CGHE-IR 2	845	23	24	815	877	836	857	826	857
L 3	7 CGHE-IR	862	1	1	861	862	861	863	862	863
L 4	21 CGHE-IR 2	865	18	19	837	871	866	877	887	849
L 5	13 CGHE-IR 3	873	19	20	880	849	871	895	890	851
L 6	26 CGHE-IR 3	902	12	12	910	900	920	900	890	890
L 7	31 CGHE-IR 3	915	11	12	919	926	916	907	924	896
L 8	28 CGHE-IR 1	948	3	3	950	950	946	948	950	942
L 9	37 CGHE-IR 3	951	27	29	993	935	968	919	958	932
L 11	35 CGHE-IR 1	988	37	39	1034	932	1007	1008	987	961
L 12	19 CGHE/coul. 1	1032	52	54	980	1000	1120	1000	1030	1060

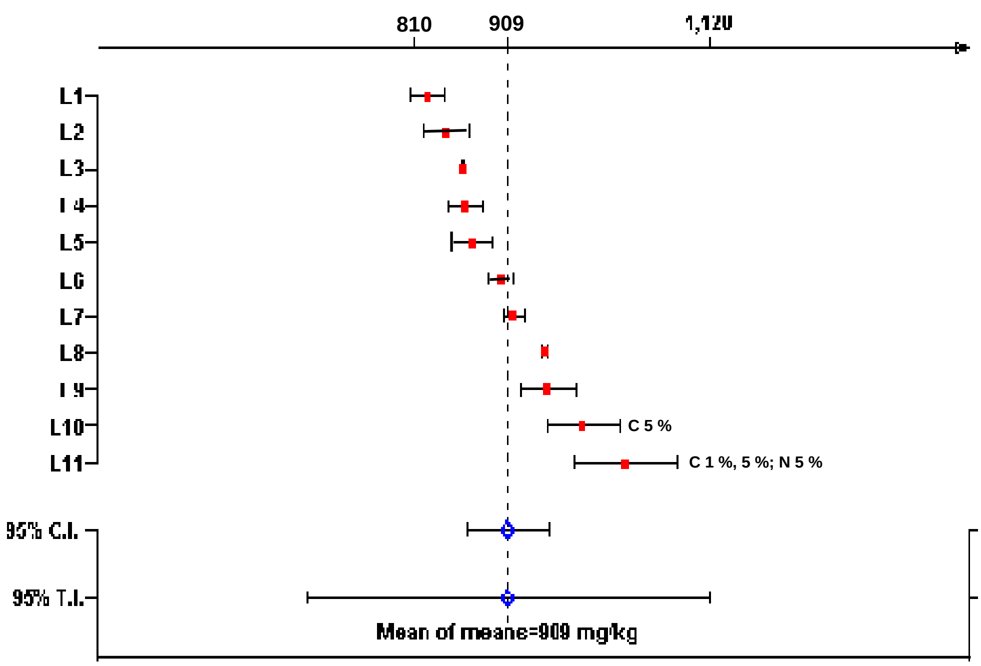
Range [min..max]	[810 .. 1120]
	Case of No Pooling
Mean of means	916
95% H.W. Confidence Interval	41
95% H.W. Tolerance Interval	205
	Case of Pooling
Mean of All	916
95% H.W. Confidence Interval	16
95% H.W. Tolerance Interval	153

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6p2)



Tab. 6q1: Nitrogen accepted results in run 1 (values in mg/kg)

Current Lab number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	37 CGHE-TC	47	6	6	42	46	43	55	52	42
L 2	26 CGHE-TC	59	8	8	55	64	67	67	52	50
L 3	21 CGHE-TC 2	64	4	4	61	60	68	61	68	68
L 4	12 CGHE-TC 2	80	11	11	70	70	80	80	80	100
L 5	7 CGHE-TC	89	4	5	84	93	88	88	95	85
L 6	29 CGHE-TC	89	4	4	93	84	86	92	91	89
L 7	36 CGHE-TC 3	94	6	7	95	98	103	88	86	93
L 8	19 CGHE-TC	99	5	6	95	95	106	105	94	99
L 9	28 CGHE-TC 1	115	3	3	111	116	117	112	118	113
L 10	13 CGHE-TC	128	5	5	134	128	132	122	124	127
L 11	35 CGHE-TC	151	12	12	135	146	162	142	156	164

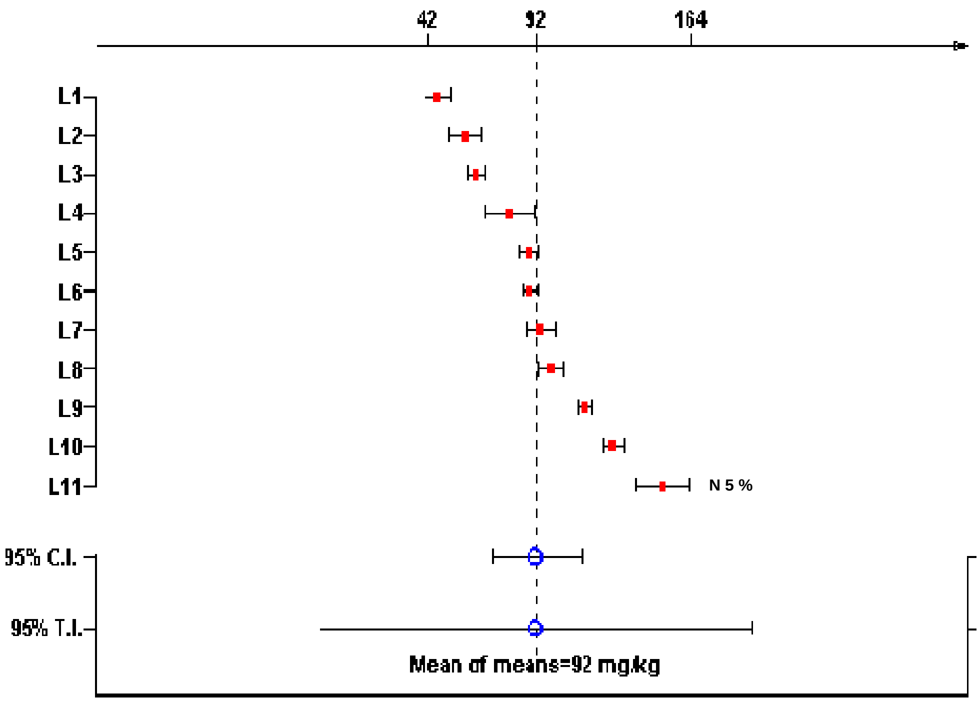
Range [min..max]	[42 .. 164]
	Case of No Pooling
Mean of means	92
95% H.W. Confidence Interval	21
95% H.W. Tolerance Interval	100
	Case of Pooling
Mean of All	92
95% H.W. Confidence Interval	7
95% H.W. Tolerance Interval	69

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6q1)



Tab. 6r1: Free silicon accepted results in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	16 coulorimetry 3	117	19	20	120	120	130	100	89	140
L 2	26 gas-volumetry 3	398	33	34	410	420	340	380	420	420
L 3	15 combustion 3	400	0	0	400	400	400	400	400	400
L 4	32 volumetry 3	468	39	41	450	470	530	470	480	410
L 5	6 volumetry	550	315	330	500	500	800	1000	400	100
L 6	11 volumetry 2	950	84	88	900	1000	900	900	900	1100

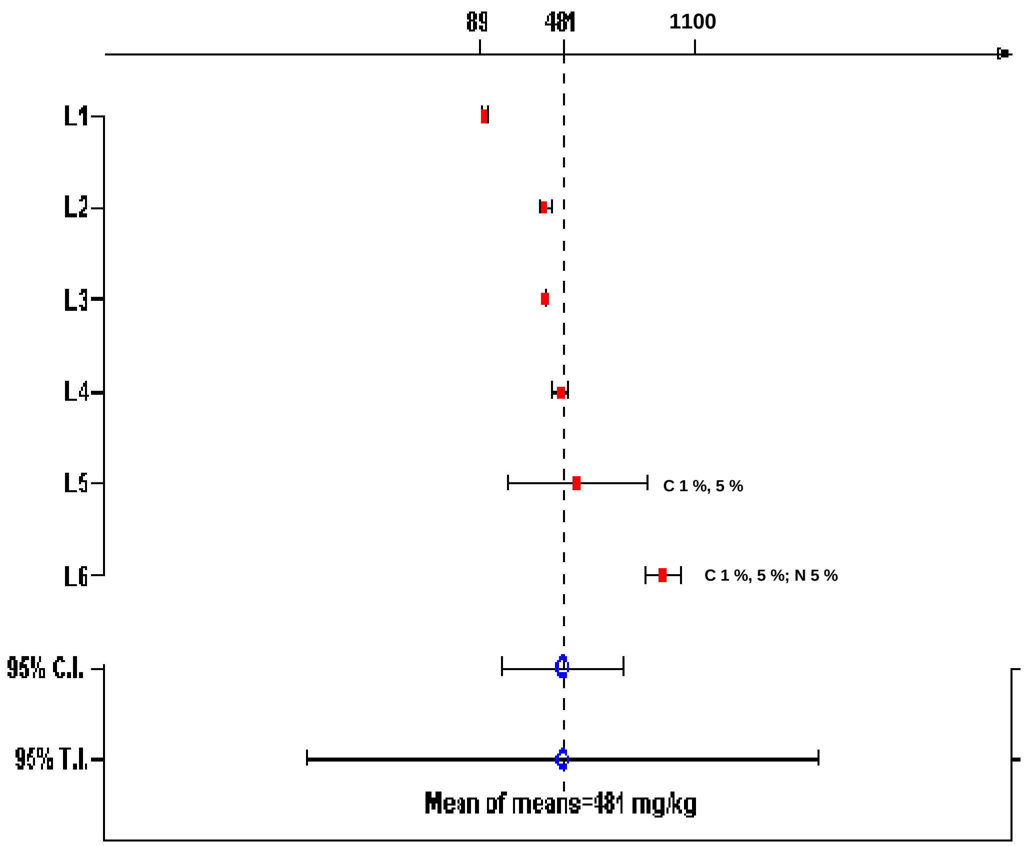
Range [min..max]	[89 .. 1100]
	Case of No Pooling
Mean of means	481
95% H.W. Confidence Interval	286
95% H.W. Tolerance Interval	1203
	Case of Pooling
Mean of All	481
95% H.W. Confidence Interval	95
95% H.W. Tolerance Interval	698

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- G = Grubbs test (single and pair test)
- N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Tab. 6r1)



Tab. 6s1: Free silicon dioxide accepted results in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sampl e #1	Sampl e #2	Sampl e #3	Sampl e #4	Sampl e #5	Sampl e #6
L 1	32 volumetry 3	488	101	106	530	390	630	480	540	360
L 2	33 colorimetry 3	552	44	46	540	520	540	640	530	540
L 3	16 colorimetry 3	583	27	29	590	570	630	590	550	570
L 4	8 ICP OES 3	608	38	39	650	570	590	600	580	660
L 5	26 ICP OES 3	632	49	51	670	670	650	580	560	660
L 6	6 gravimetry 3	733	388	407	400	500	1400	1000	500	600

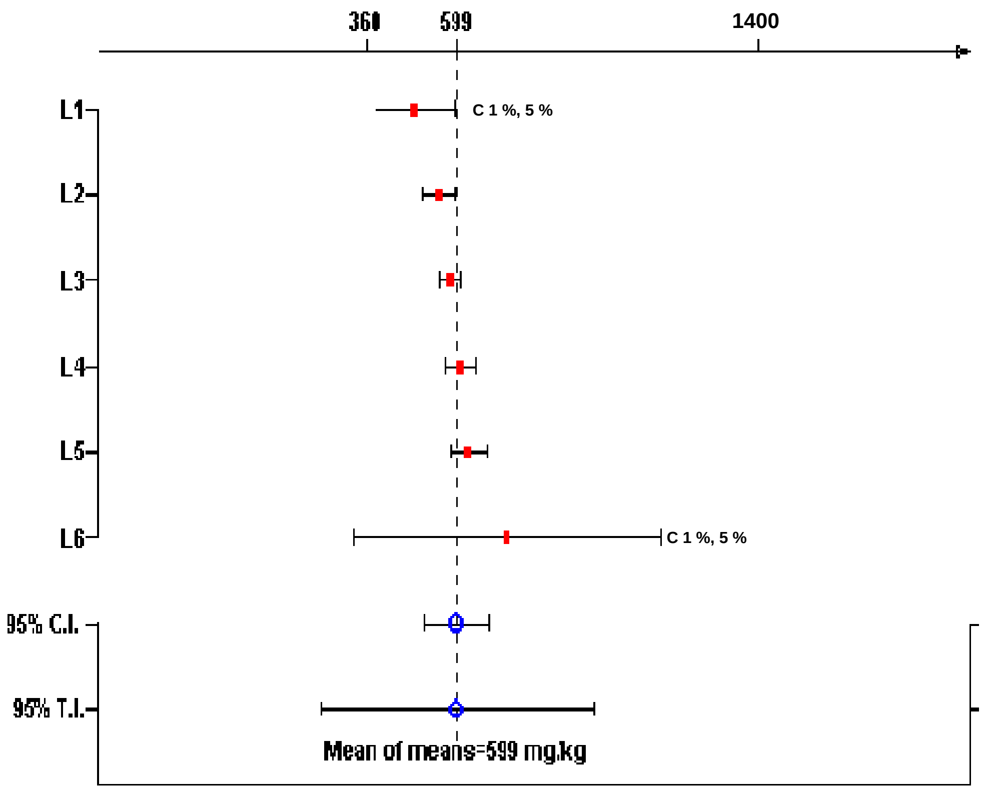
Range [min..max]	[360 .. 1400]
	Case of No Pooling
Mean of means	599
95% H.W. Confidence Interval	86
95% H.W. Tolerance Interval	364
	Case of Pooling
Mean of All	599
95% H.W. Confidence Interval	58
95% H.W. Tolerance Interval	428

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **<u>pooling is: Not Allowed</u>**

Diagram of means and 95% confidence intervals (to Tab. 6s1)



Appendix 8: Additional information to the Grubbs tests carried out for the interlaboratory comparison for the certification of CRM BAM-S003

Parameter	Evaluation	test	Comments
Al	run 1	single test	L1, → outlier at 1%, 5% level
		pair test	no pair test calculated
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L 17, L 18 → outlier NOT detected
B	run 1	single test	L13 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L12, L13 → outlier at 1% and 5% level
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier at 5% level
Ca	run 1	single test	L17 → outlier at 1% and 5% level
		pair test	L1, L2 → outlier NOT detected L16, L17 → outlier at 1% and 5% level
	run 2	single test	L1 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L14, L15 → outlier NOT detected
Cr	run 1	single test	L17 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L16, L17 → outlier at 5% level
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L15, L16 → outlier NOT detected
Cu	run 1	single test	L13 → outlier at 1%, 5% level
		pair test	no pair test calculated
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L11, L12 → outlier at 1% and 5% level
Fe	run 1	single test	L24 → outlier at 1%, 5% level
		pair test	no pair test calculated
	run 2	single test	L1 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L21, L22 → outlier NOT detected
	run 3	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L20, L21 → outlier NOT detected
Mg	run 1	single test	L19 → outlier at 1% and 5% level
		pair test	L1, L2 → outlier NOT detected L18, L19 → outlier at 1% and 5% level
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L16, L17 → outlier at 5% level
Mn	run 1	single test	L18 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L17, L18 → outlier at 1% and 5% level
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L16, L17 → outlier NOT detected
Na	run 1	single test	L1 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L17, L18 → outlier NOT detected
	run 2	single test	L16 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L15, L16 → outlier NOT detected
	run 3	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L13, L14 → outlier NOT detected

Parameter	Evaluation	test	Comments
Ni	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L21, L22 → outlier NOT detected
Ti	run 1	single test	L1 → outlier at 1% and 5% level
		pair test	no pair test calculated
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L18, L19 → outlier NOT detected
V	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L18, L19 → outlier NOT detected
V	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L17, L18 → outlier NOT detected
Zr	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L19, L20 → outlier NOT detected
	run 2	single test pair test	outlier NOT detected L1, L2 → outlier NOT detected L18, L19 → outlier NOT detected
C_{total}	run 1	single test	L1 → outlier at 5% level
		pair test	L1, L2 → outlier at 1% and 5% level L18, L19 → outlier NOT detected
	run 2	single test pair test	L1 → outlier at 5% level L1, L2 → outlier at 1% and 5% level L16, L17 → outlier NOT detected
C_{free} with all results	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L3, L4 → outlier NOT detected
C_{free} without Lab. of experts	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L3, L4 → outlier NOT detected
C_{free} Lab. of experts	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L3, L4 → outlier NOT detected
O	run 1	single test	L12 → outlier at 5% level
		pair test	L1, L2 → outlier NOT detected L11, L12 → outlier at 5% level
	run 2	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L10, L11 → outlier NOT detected
N	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L10, L11 → outlier NOT detected
Si_{free}	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L5, L6 → outlier NOT detected
SiO_2-free	run 1	single test	outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L5, L6 → outlier NOT detected