BAM Federal Institute for Materials Research and Testing

in Co-operation with the

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

The Certification of Mass Fractions of Al, Ca, Co, Cr, Cu, Fe, Mn, Na, Ni, Si, Ti, Zr; $C_{(total)}$, O, N, $B_{(total)}$, $B_{(HNO_3\ soluble)}$, B_2O_3; and the Isotopic Abundance of ^{10}B in the

European Reference Material

Boron Carbide Powder (type 305F422)

ERM®–ED102

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Certification Report

Abstract

This report describes the preparation and certification of the European Reference Material ERM®–ED102, a boron carbide powder (type 305F422) with certified mass fractions of impurities and main components and the a certified amount fraction of a boron isotope carried out in the framework of ERM by Federal Institute for Materials Research and Testing (BAM) in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additionally determined data are listed below.

Certified Values

	Certified value 1)	Uncertainty 2)	
Parameter	**Mass fraction in mg/kg**		
Aluminium	157	± 5	(5)
Calcium	97	2 7 ((8 ± 8	(8)
Cobalt	0.39	± 0.09	(0.09)
Chromium	5.6	± 1.2	(1.2)
Copper	2.2	± 0.4	(0.4)
Iron	686	± 22	(21)
Manganese	10.4	± 0.5	(0.5)
Sodium	6.3	± 0.9	(0.9)
Nickel	8.0	± 1.6	(1.6)
Silicon	268	± 22	(22)
Titanium	96	± 5	(5)
Zirconium	48.9	± 2.3	(2.3)
	Mass fraction in %		
Total Carbon	21.01	± 0.28	(0.15)
Oxygen	0.1	± 0.04	(0.011)
Nitrogen	0.209	± 0.026	(0.018)
Total Boron 3)	78.47	± 0.31	(0.28)
HNO_3 Soluble Boron 4)	0.116	± 0.013	(0.012)
Boron oxide 5)	0.075	± 0.023	(0.011)
	Isotopic abundance in %		
^{10}Boron 6)	19.907	± 0.014	(0.014)

1) The certified values are the means calculated from the laboratory means of 7- 24 sets of single values (depending on the parameter) which were reported by the participating laboratories. Between 2 and 8 different analytical methods were used for the measurement of each parameter. The calibration of the methods applied for determination of element mass fractions was carried out by using pure substances of known stoichiometry or by solutions prepared from them, thus achieving traceability to the SI unit.
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. It includes contributions from sample inhomogeneity and from potential deterioration of the sample until the expiration of the validity of the certificate. Note: Values in parentheses do not include contributions from potential deterioration of the sample. These values were merely valid at the time of the measurements wich were carried out in the frame of the interlaboratory comparison for certification.
3) The recommended "Method M1" described in Appendix 1 can be used for the determination of total mass fraction of boron.
4) The recommended "Method M2" described in Appendix 2 can be used for the determination of mass fraction of in HNO_3 soluble boron.
5) The recommended "Method M3" described in Appendix 3 can be used for the determination of mass fraction of boron oxide.
6) Isotopic abundance (amount fraction) of ^{10}Boron related to total amount of Boron.

Sample description and intended use

The certified reference material ERM®-ED102 consists of a boron carbide powder (type 305F422). The material is supplied in glass bottles containing 100 g each. The reference material is intended for use in the calibration of analytical instruments or to validate or verify analytical methods to be used for the determination of the certified parameters in boron carbide. The material can also be used to calibrate analytical instruments or to validate or verify analytical methods used for the determination of the total carbon mass fraction in other materials having similar carbon contents.

Indicative values

Non certified, indicative values are given for additional analytes determined in the interlaboratory comparison by participating laboratories. They are given as indicative values, because the spread of values obtained was considerably larger than can be accepted for certified values.

	Indicative value 1)	**Uncertainty** 2)
Parameter	**Mass fraction in mg/kg**	
Magnesium	3.2	± 1.0
Tungsten	3.6	± 2.1
	Mass fraction in %	
Free Carbon 3)	0.51	± 0.12

1) Indicative values are the means of 5-18 series of results (depending on the parameter) obtained by different laboratories. Between 1 and 4 different analytical methods have been used for the measurement of each parameter. The methods applied for the determination of mass fraction were not calibrated in all cases by pure substances of known stoichiometry or by solutions prepared from them.
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. The values are quoted for information purposes.
3) The prescribed “Method M4” described in attachment shall be used for the determination of mass fraction of free carbon.

Additional Material Information

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

		Particle size in µm
Parameters characterizing particle size 1)	D_{10}	21.5
	D_{50}	33.6
	D_{90}	51.4
	D_{97}	60.4

1) The particle size distribution (volume) was determined by laser light diffraction method. Terms D_{xy} according to ISO 9276-1 [5].

European Reference Material ERM®-ED102 was certified under the responsibility of BAM Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing, Germany) in cooperation with the Committee of Chemists of the GDMB, Gesellschaft für Bergbau, Metallurgie, Rohstoff- und Umwelttechnik according to the principles laid down in the technical guidelines of the European Reference Material ERM® cooperation agreement between BAM-LGC-IRMM.
Information on these guidelines is available in the Internet (http://www.erm-crm.org)
Accepted as an ERM®, Berlin, November 18 2008.
Validity of the Certificate: Until June 30, 2015

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1 Introduction

1.1 Importance, properties and applications of boron carbide

Boron carbide is one of the hardest known materials. It ranks at third place behind diamond and cubic boron nitride. But it is the only one of these three materials produced in tonnage quantities. Boron carbide was discovered in mid of 19th century as a by-product in the production of metal borides. More detailed study of the material started only since 1930.

The main production of boron carbide is based on the reaction of carbon with B_2O_3 in an electric arc furnace by a carbo-thermal reduction or by gas phase reactions. For most commercial application B_4C materials are milled to powders and are purified by removing metallic impurities.

As for other non-oxidic ceramic materials boron carbide is difficult to sinter to the highest possible density. Therefore die or isostatic hot pressing is required to achieve high densities. Normally small mass fractions of fine carbon or silicon carbide are required as dopants when these techniques are used and temperatures of less than 2200°C are applied. An alternative to form B_4C is coating on a substrate by vapor phase reaction techniques.

Besides the extreme hardness (2900-3580 kg/mm^2, Knoop 0.1) boron carbide offers other outstanding properties, such as good chemical resistance, profitable nuclear properties and a low density of 2.52 g/cm^3.

Other typical properties of boron carbide are:

Melting Point (°C)	2445
Fracture Toughness (MPa•m^{½})	2.9 - 3.7
Young's Modulus (GPa)	450 - 470
Electrical Conductivity (at 25°C) (S)	140
Thermal Conductivity (at 25°C) (W/m·K)	30 - 42
Thermal Expansion Coeff. x10^{-6} (°C)	5
Thermal neutron capture cross section (barn)	600

One of its applications based on the high hardness of boron carbide powder is the use as an abrasive for polishing and lapping material or as an additional abrasive for cutting applications, e. g. for water jet cutting. It can also be used for sharpening diamonds or tools and sapphire slicing and polishing. Another application based on the extreme hardness of boron carbide and hence on the excellent wear and abrasion resistance is the use as material for nozzles used for grit blasting and in water jet cutters.

Additionally boron carbide has nuclear application based on its ability to absorb neutrons without forming long lived radio-nuclides. This is due to the high neutron absorption cross section of boron (760 barn at neutron velocity of 2200 m/sec). The cross section of the B^{10} isotope in boron is even considerably higher (3800 barn). Since pure boron is extremely brittle and difficult to produce in shapes (for example: control rods) boron carbide is the material of choice since it provides a high concentration of boron atoms in a strong and refractory form and it is not too difficult to be fabricated. This fact makes the material applicable as an absorbent for neutron radiation in nuclear power plants. These applications of boron carbide include shieldings and pellets for control and shut down rods.

Important is also the application of boron carbide, in conjunction with other materials, as ballistic armor material (including body or personal armor). This application is based on the combination of high hardness, high elastic modulus, and low density. Boron carbide sheets have an extraordinarily high specific stopping power to defeat high velocity projectiles.

Further applications of boron carbide are in ceramic tooling dies, in evaporating vessels for materials testing and in mortars and pestles as well as in precision tool parts.

In different fields of application lists of specification exist concerning the purity of the specific boron carbide material, because traces of impurities have negative impact to the properties aimed for.

According to the high importance of the material in many different fields of its application, the world wide production of boron carbide is steadily increasing. Many concerning facts can be seen e. g. from a special research report [1] which analyzes the worldwide market for boron carbide and provides comprehensive analytics for the US, Japan, Europe and Rest of World.

1.2 Certification procedure

The boron carbide powder (type 305F422) was taken from the customary production line of the producer (see 4.1) and was bottled into 320 bottles each containing 100 g of the material. From the total number 20 bottles were selected. From each of these bottles an appropriate number of vials (for most parameters 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 evaluation of the formerly carried out investigation on stability one sample bottle was distributed to each of the 35 international participants of the interlaboratory comparison for certification. The participants came from 6 different countries. Difficulties to determine some of the analytes were discussed among the members of the working group "Special Materials" of GDMB at their biannual sessions. Following to these discussions about the critical analytes, such as total Boron content (B_{total}), HNO_3 soluble Boron, adherent Boron Oxide (B_2O_3) and Free Carbon (C_{free}), 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 participating laboratory of the interlaboratory comparison 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 and asked to find out reasons for their outlying results. 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, from inhomogeneity of the material and from possible long term instability of the material.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was produced by ESK Ceramics GmbH & Co. KG,
  Kempten, Germany, and bought from there by
  Bundesanstalt für Materialforschung und –prüfung (BAM)
  Berlin (Germany)

- The material was filled into cleaned sample bottles by BAM under clean air conditions

- Sub-samples for homogeneity testing were taken from some of the bottles and additionally, a highly homogenized sample was prepared by BAM to be used to determine the repeatability of the methods used for the homogeneity investigations

2.2 Homogeneity investigation

- The analytical investigations for the homogeneity testing of the mass fractions of Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Ti and Zr were carried out by BAM, Bundesanstalt für Materialforschung und -prüfung, Germany

- The analytical investigations for the homogeneity testing of mass fractions of Na, Si, Total C, Free C, O, N, Total B, HNO_3 soluble B and B_2O_3 were carried out by ESK Ceramics GmbH & Co. KG, Germany

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

2.3 Long-term stability investigation

- The investigations of the long-term stability of a material with the same chemical and physical properties as the CRM candidate material had been carried out by ESK Ceramics GmbH & Co. KG, Germany, for the analytes Total C, Free C, O, N, Total B, HNO_3 soluble Boron and B_2O_3.
- Additional stability measurements were carried out on the CRM candidate material by BAM for the metallic analytes. In this case only measurements of the change of the net mass of selected sample bottles were carried out at different times. The values were used to assess a potential change of the analyte mass fractions of the metallic analytes during the period of validity of the certificate.
- All succeeding calculations were carried out by BAM.

2.4 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 B_4C analysis or had well known ability to analyze difficult materials by adequate analytical methods. The 35 participating laboratories of the interlaboratory comparison for certification are listed alphabetically in Tab. 1.

Tab. 1: Participating laboratories in the interlaboratory comparison for certification (arranged alphabetically)

1	Asahi Glass Ceramics Co., LTD, Development Centre, Japan
	Bundesanstalt für Materialforschung und -prüfung, Germany
2	- Division I.1
3	- Division I.4
4	Ceram Testing & Environmental Services, U.K.
5	Dunhua Zhengxing Abrasive Co., Ltd., P.R. China
6	Eagle Picher Technologies Boron Dept., USA
7	ESK Ceramics GmbH & Co. KG, Germany
8	ESK-SiC GmbH, Abteilung MQ, Germany
9	EUROPÄISCHE KOMMISSION Gemeinsame Forschungsstelle, Institut für Transurane, Germany
10	Ferro GmbH, Germany
11	Forschungszentrum Jülich GmbH, Zentralabt. für chemische Analysen, Germany
12	Framatome ANP GmbH, Abt. NGTR, Germany
	H. C. Starck GmbH & Co. KG; Germany
13	- Werk Goslar
14	- Werk Laufenburg
15	HORIBA, Ltd., Application Centre, Japan
16	Japan Analyst Corporation, Japan
17	JFE Refractories R & D Laboratory, Japan
18	Johannes Gutenberg Universität Mainz; Institut für Kernchemie, Germany
19	Krosaki Harima Co., LTD., Technical Examination Centre, Japan
18	Johannes Gutenberg Universität Mainz; Institut für Kernchemie, Germany
20	Leibnitz-Institut für Festkörper- und Werkstoffforschung, Germany
21	Max-Planck-Institut für Metallforschung, Germany
22	NSL Analytical Services, Inc., USA
23	Osram GmbH, Germany
24	Plansee AG , Werkanalyteik, Austria
25	PTB, Physikalisch Technische Bundesanstalt, Germany
26	Revierlabor Chemische Laboratorien für Industrie und Umwelt GmbH, Germany
27	Rigaku Industrial Corp., Japan
28	SGL Carbon GmbH , Laboratory Services, Germany
29	Shanghai Institute of Ceramics, Chinese Academy of Sciences, P.R. China
30	Shinagawa Refractories Co., LTD., Testing & Evaluation Centre, Japan
31	Taiko Refractories Co., LTD, Research & Development Laboratory Japan
32	Treibacher Industrie AG, Austria
33	TYK Corporation, Research & Development Centre, Japan
34	Verein für Kernverfahrenstechnik und Analytik Rossendorf e.V., Germany
35	Zhuzhou Cemented Carbide Group Corp., LTD., P.R. China

2.5 Determination of additional material data

The determination of particle size distribution was carried out by ESK Ceramics GmbH & Co. KG, Germany

2.6 Compilation and revision of the prescribed and recommended analytical methods

- Recommended Method 1 "Determination of Total Boron (B_{total}) in Boron Carbide (B_4C) by Titrimetric Method (potentiometric titration)" According to Dr. Jürgen Haßler, ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Str. 25 D-87437 Kempten, Germany

- Recommended Method 2 "Determination of HNO_3 soluble Boron in Boron Carbide (B_4C) by Titrimetric Method" According to Dr. Jürgen Haßler, ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Str. 25 D-87437 Kempten, Germany

- Recommended Method M3 "Determination of Adherent Boron Oxide (B_2O_3) in Boron Carbide (B_4C) by Titrimetric Method" According to Dr. Jürgen Haßler, ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Str. 25 D-87437 Kempten, Germany

- Prescribed Method 4 "Determination of Free Carbon (C_{free}) in Boron Carbide (B_4C) by Wet Chemical Oxidation" According to Dr. Jürgen Haßler, ESK Ceramics GmbH & Co. KG, Max-Schaidhauf-Str. 25 D-87437 Kempten, Germany

3 Abbreviations used

Tab. 2: List of abbreviations

CGHE-Coul.	Carrier gas hot extraction method with coulometric determination
CGHE-IR	Carrier gas hot extraction method with infrared detection
CGHE-TC	Carrier gas hot extraction method with thermal conductivity detection
Comb.-Coul.	Combustion of total carbon followed by coulometric determination
Comb.-Grav.	Combustion of total carbon followed by gravimetric determination
Comb.-IR	Combustion method with infrared detection
Comb.-Vol.	Combustion of total carbon followed by volumetric determination
Coul.	Coulometric determination
DC-ARC-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
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ID-ICP-MS	Isotope dilution inductively coupled plasma mass spectrometry
IPAA	Instrumental photon activation analysis
MAS	Molecular absorption spectrometry
Method M1	Recommended Method: Determination of Total Boron in Boron Carbide by Titrimetric Method (potentiometric method) (described in Appendix 1)
Method M2	Recommended Method: Determination of HNO_3 soluble Boron in Boron Carbide by Titrimetric Method (described in Appendix 2)
Method M3	Recommended Method: Determination of Adherent Boron Oxide in Boron Carbide by Titrimetric Method (described in Appendix 3)
Method M4	Prescribed Method: Determination of Free Carbon in Boron Carbide by wet Chemical Oxidation (described in Appendix 4)
SS ET AAS	Solid sampling electrothermal atomic absorption spectrometry
TIMS	Thermal ionization mass spectrometry
TITR	Titrimetry

4 Origin and homogeneity investigation of the material

4.1 Starting material

The boron carbide powder material (type 305F422) was taken from the customary production line of the producer ESK Ceramics GmbH & Co. KG, Germany. All the material had the same lot number that had been produced under the same stable working conditions. The candidate material was bottled by BAM into 320 bottles each containing 100 g of the material

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

Preliminary note: The results of the statistical homogeneity tests described below were only used to decide whether an additional procedure of homogenization of the candidate material would have been necessary or not and whether the discussed analyte could be accepted as a certified or only as an indicative one. Independent from the test results the uncertainty contribution from analyte inhomogeneity, the measured (or in some cases a potentially buried) contribution was included into the calculation of the uncertainty of the final results (see 8.2).

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 100 g of candidate material. From each of the N = 20 bottles four appropriate sample masses were filled into vials (described as “larger sub-samples”) with masses of the taken material depending on the needs of the corresponding methods used for the homogeneity investigation of different analytes. The vials were distributed to the laboratories, where the measurements for homogeneity testing were carried out. For some analytes for which the determination was very time consuming (Na, Si, Total C, Free C, O and N), only 10 of the 20 selected bottles were used from which the 4 "larger sub-samples" were filled into the vials.
- For comparison, a thoroughly homogenized sample was produced. For this purpose about 20 g of the material were highly homogenized in the “Mixer/Mill” (Spex. Ind., USA) for 10 min. (5 x 2 min.) using polypropylene vessels and balls. Partial masses of such samples were distributed to the laboratories, in which the measurements for homogeneity investigation were carried out.

4.2.2 Homogeneity investigations for the metallic traces (except Na, Co, W)

The measurements for homogeneity of most metallic traces were carried out by ICP OES. Na (see 4.2.3) was investigated by ETV-ICP OES and Co was not measured because of its very low mass fraction in the material leading to a very low precision of ICP OES. W was not measured because it was handled as an element with indicative values only. For the other 10 metallic elements the measurements were carried out by using aliquots of digestion solutions prepared from parts of the four larger sub-samples taken from each of the 20 selected bottles to be used for the investigation of homogeneity as well as from the 20 sub-samples taken from the bottle containing the highly homogenised material. An ICP OES spectrometer “IRIS-advantage Duo” (Thermo Elemental) was used for the investigation. For further details see 6.3. To minimize influences of drifts, drift corrections were made. Additionally, the solutions of the sub-samples were measured at two different days and the mean values of all interrelated pairs of results from both days of measurements were calculated and inserted into the tables of Appendix 5. To improve the precision of the measurements additionally, for some analytes more than one analytical spectral line was measured. This was done for the analytes (number of spectral lines in parentheses): Al(2), Cr(3), Fe(3), Mg(2) Mn(3), Ni(2), Ti(3), Zr(3).

The results of the measurements and of the homogeneity testing are listed in form of tables in Appendix 5. They are arranged in the report by parameters (elements), each element having 4 to 6 pages containing tables and results. The pages for the elements only having one measured spectral line are in panel format the others are in landscape format. The tables of all the different elements follow one and the same arrangement: The first table contains the measured mass fractions of all samples from the 20 investigated bottles (from each bottle four sub-samples). The first column of this table contains a "line number" (one running number for each of the selected bottles used for the homogeneity investigation). The second column contains the "sample numbers" of the selected bottles, the numbers were extended by one figure for identification of the different four sub-samples. The next column contains the measured mass fraction of the analyte in each sub-sample. This column is indicated by the spectral line used. If more than one spectral line had been measured for one analyte, the intensities were separately converted to mass fractions which are listed in separate columns in the table. From them mean values were calculated. These mean mass fractions of the sub-samples ("mean over xx lines") were used for the subsequent calculation and evaluation. The next column contains the "means of the results of sub-samples 1-4" in each of the selected bottles, followed by a column which contains the standard deviations of the results of sub-samples in each bottle (SD of sub-samples 1-4). The last column contains these values expressed as relative standard deviations RSD_w. The index "w" stands for "within the bottles". Below the first table some summarizing data are given for orientation: The mean M_{ss} of the means of the mass fractions of the four sub-samples of each bottle, the standard deviation of the means of the four sub-samples of each bottle and the corresponding RSD-value. Additionally the mean of the relative standard deviations determined "within the bottles" (mean RSD_w) is given.

The second table is analogous to the first table and contains the values of the 20 sub-samples taken from the highly homogenized sample. Below the table the analogously summarized values are listed for the homogenized sample: M_{HS} - the mean value of all sub-samples of the homogeneous sample, SD_{HS} - the standard deviation of these values and RSD_{HS} (%) – the corresponding relative standard deviation.

The next two tables contain data and results of the homogeneity testing. The first table of them contains results of the homogeneity test (F-test) made for comparing variances “between the bottles” (related to single measurements) and “within the bottles”.
For this purpose the mean standard deviation within the bottles was calculated:

$$s_\mathrm{w} = \sqrt{\sum_1^{20} SD_\mathrm{wi}^2 \Big/ N} \quad ; \qquad (N = 20) \tag{1}$$

as well as the standard deviation between the bottles (related to single determinations):

$$s_\mathrm{b} = \sqrt{SD^2_\mathrm{means\ of\ \ sub-samples} \times M} \quad ; \qquad (M = 4)\ ., \tag{2}$$

furthermore the test value

$$s_\mathrm{b}^2 / s_\mathrm{w}^2 \tag{3}$$

and the critical value of the F-table

$$\mathrm{F_{value}} = \mathrm{F}_{\alpha;\ \mathrm{N-1};\ \mathrm{N} \times (\mathrm{M-1})} = \mathrm{F}_{0,05;19;60} \tag{4}$$

and finally the “characteristic number for the homogeneity testing between the samples"

$$\left(s_\mathrm{b}^2 / s_\mathrm{w}^2\right) / \mathrm{F_{value}}. \tag{5}$$

If this "characteristic number" is ≤ 1, there is no reason to assume that the distribution of the analyte between the bottles is less homogeneous than within the bottles. For a value > 1 a less homogeneous distribution of the analyte 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 last table is for homogeneity testing (F-test) within the samples. Here the mean standard deviation within the bottles s_w is compared with the standard deviation of the homogeneous sample s_{HS}.
The corresponding test value

$$s_{\mathrm{w}}^2 / s_{\mathrm{HS}}^2 \tag{6}$$

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

$$\mathrm{F}_{\mathrm{value}} = \mathrm{F}_{\alpha;\, \mathrm{N} \times (\mathrm{M}-1);\, \mathrm{N}-1} = \mathrm{F}_{0{,}05;60;19} \tag{7}$$

The resulting "characteristic number within the bottles" is

$$\left(s_{\mathrm{w}}^2 / s_{\mathrm{HS}}^2\right) / \mathrm{F}_{\mathrm{value}} \tag{8}$$

If this "characteristic number" is ≤ 1 then there is no reason to assume that the distribution of the analyte within the bottles 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.

Tab. 3a: Characteristic numbers for homogeneity within and between the bottles for the metallic analytes investigated by ICP OES (summary from tables in Appendix 5)

Element	Within the bottles	Between the bottles
Al	0.36	1.13
Ca	0.60	0.61
Cr	2.5	1.07
Cu	0.35	0.98
Fe	0.84	0.39
Mg	0.19	3.2
Mn	0.40	0.24
Ni	0.78	2.6
Ti	0.74	0.75
Zr	0.60	0.58

From Tab. 3a one can conclude that in most cases no significant inhomogeneity was found. Only one significant inhomogeneity within the bottles was detected, namely for Cr. A significant inhomogeneity between the bottles was found for Al, Cr, Mg and Ni. For Al the value of 1 was only marginally exceeded, so that a sufficient homogeneity can be stated. Mg was finally used in this certification process as an indicative element only, so that a deeper discussion for this element is not necessary. Therefore only Cr and Ni are left to be discussed.

The characteristic number of Cr between the bottles only marginally exceeded the value of 1 and can be therefore accepted. However, the corresponding value within the bottles was 2.5. The mean relative standard deviation for Cr within the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 5.9 %rel and the mean relative standard deviation for Cr between the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 8.6 %rel These values can be tolerated and accepted in view of the rather low level of mass fraction of Cr of about 5.6 mg/kg. The characteristic number of Ni within the bottles was not exceeded and can be therefore accepted. However, the corresponding value between the bottles was 2.6. The mean relative standard deviation for Ni within the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 2.4 %rel and the mean relative standard deviation for Ni between the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 7.8%rel As for Cr, these values can be tolerated and accepted in view of the rather low level of mass fraction of Ni of about 8.0 mg/kg.

From the homogeneity study and the considerations above it was concluded that no additional process of homogenization was necessary and it was not necessary to classify metallic elements aside from Mg as indicative elements instead of certified ones.

4.2.3 Homogeneity investigations for Na and Si

Both analytes could not be determined by ICP OES precisely enough. Therefore the direct solid sampling method of ETV-ICP OES was used (for details see 6.3).

The results of the measurements and of the homogeneity testing are listed in form of tables in Appendix 5. They are arranged in the report by parameters (elements), for further explanations see above in paragraph 4.2.2. The differences of the tables for Na and Si to the tables of the elements described in 4.2.2 are as follows: only 10 of the 20 bottles selected for the homogeneity investigation were used and the number of sub-samples taken from the homogenized sample was only 10 instead of 20.

As a summarizing result of the homogeneity tests, the numeric values of the "characteristic numbers" for the homogeneity within or between the samples are listed in a table (see Tab. 3b).

Tab. 3b: Characteristic numbers for homogeneity within and between the bottles for the analytes Na and Si (summary from tables in Appendix 5)

Element	Within the bottles	Between the bottles
Na	0.70	1.16
Si	0.29	0.19

From Tab. 3b one can conclude that in three cases no significant inhomogeneity was found. Only one significant inhomogeneity between the bottles was detected, namely for Na. However, the corresponding characteristic number of Na between the bottles exceeded the value of 1 only marginally and can therefore be accepted.
From the homogeneity study of both elements and the consideration above it was concluded that no additional process of homogenization was necessary.

4.2.4 Homogeneity investigations for Total C, Free C, O, N, Total B, soluble B and boron oxide

Different methods were applied for the homogeneity investigation of different non-metallic analytes. The methods are listed in 6.3 together with the sub-sample mass intake.
The results of the measurements and of the homogeneity testing are listed in form of tables in Appendix 5. They are arranged in the report by parameters in the same order as in the headline of this paragraph. For further explanations see 4.2.2. The differences of the tables for the analytes described here in this paragraph to the tables of the elements described in paragraph 4.2.2 are as follows: only 10 of the 20 bottles selected for the homogeneity investigation were used here and the number of sub-samples taken from the homogenized sample was only 6 – 17 (depending on the analyte) instead of 20 as used for the investigation described in 4.2.2.
As a summarizing result of the homogeneity tests the numeric values of the "characteristic numbers" for the homogeneity within or between the samples are listed in Tab. 3c.

Tab. 3c: Characteristic numbers for homogeneity within and between the bottles for the analytes Total C, Free C, O, N, Total B, HNO_3 soluble B and boron oxide

Element	Within the bottles	Between the bottles
C_{total}	0.49	0.81
C_{free}	0.31	0.35
O	0.30	0.89
N	1.53	0.85
B_{total}	0.58	0.50
$B_{soluble}$	0.91	0.18
B_2O_3	0.80	0.21

From Tab. 3c one can conclude that in almost all cases no significant inhomogeneity was found. Only one significant inhomogeneity was detected, namely for N within the bottles. The corresponding characteristic number for N within the bottles was calculated to 1.53. The mean relative standard deviation for N within the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 2.3 %rel and the mean relative standard deviation for N between the bottles corrected by the contribution from the method of measurement (estimated by using the homogeneous sample) was about 3.3 %rel These values can be tolerated and accepted in view of the level of mass fraction of N of about 0.21%.

From the homogeneity study of the investigated parameters and the consideration above it was concluded that no additional process of homogenization was necessary and it was not necessary to classify N as an indicative element instead of a certified one.

4.2.5 Conclusion

The homogeneity investigations showed satisfying results in most cases, i. e. the corresponding characteristic numbers were ≤ 1 or not much greater than 1. In the remaining cases, i. e. when the characteristic numbers were clearly > 1, the corresponding RSD values were considered. They were assessed in view of their acceptance for being included into the calculation of the combined uncertainty. All the potential contributions resulting from the detected inhomogenity were estimated as lower than the potential contributions to the combined uncertainty coming from the interlaboratory comparison. Based on this fact it was concluded that no additional process of homogenization had been necessary and additionally it was not necessary to classify some of the investigated elements which had been aimed to be certified merely to classify as indicative elements. This implied that only the parameters Mg, W and Free C were taken as indicative ones.

As explained above, it is to take note of the fact that, 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 included into the calculation of the uncertainties of the certified values. In this procedure these standard deviations were corrected with the corresponding standard deviation of the homogeneous sample. Both corrected contributions were (together with the contribution from the round robin test for certification and long term instability of the sample) included into the calculation of the final measurement uncertainties of the certified values (see paragraph 8.2).

5 Long-term stability investigation and corresponding uncertainty contributions

From theoretical considerations the B_4C material can be assumed to be stable. If at all, oxidation processes are most likely to occur and the oxygen content could be a sensitive parameter to indicate an aging of the material.

5.1 Non-metallic analytes (except Si)

5.1.1 Oxygen

A long-term stability study of the oxygen mass fraction was carried out by ESK Ceramics & Co. KG using a similar to the CRM candidate material and coming from the same production line as this material (see 6.4.2). Carrier gas hot extraction was used for the determination. The results are given in Table 4.a.

Tab. 4.a: Stability investigation carried out for the oxygen mass fraction in a material similar to the boron carbide CRM candidate material, mass fractions in %

Sub-sample	Oxygen mass fraction	
	January 1995	June 2006
1	0.172	0.178
2	0.169	0.182
3	0.177	0.177
4	0.178	
5	0.180	
Mean	**0.175**	**0.179**
SD	0.00455	0.00265
SD_{Mean}	0.00203	0.00153

A t-test carried out at these measurement results indicated no significant change of the oxygen content. Changes in the mass fraction of oxygen in this sample can be numerically transferred to the candidate material because of the high chemical and physical similarity of both types of materials, independent from the difference of the starting values of both materials. The changes in the oxygen mass fraction would mainly result from a chemical conversion of boron carbide to boron oxide according to the formula:

$$B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2$$

The long term instability contribution from change of oxygen mass fraction over the period of 10 years (120 months) was assessed by a linear interpolation from the maximum difference of the values measured at the beginning and the end of a period of 137 months:

$$u_{lts}\{w(\text{O; 120 months})\} = \Delta w_{max}(\text{O; 120 months}) = w_{max}(\text{O; 120 months}) - w_{mean}(\text{O; 0 months})\ . \qquad (9)$$

To calculate w_{max}(O; 120 months), the equation of the long term aging was formed, based on the measured values of Tab. 4.a:

$$w_{max}(\text{O; x months}) = a \cdot x + b, \text{ wheras} \qquad (10)$$

$$b = w_{mean}(\text{O; January 1995}) - SD_{Mean}\{\ w(\text{O; January 1995})\} = 0.175 - 0.00203 = 0.17297 \qquad (10a)$$

and

$$a = (1/137) \bullet [w_{\mathrm{mean}}(\mathrm{O};\ \text{June 2006}) + SD\{w_{\mathrm{mean}}(\mathrm{O};\ \text{June 2006})\} - b] = (1/137) \bullet [0.179 + 0.0153 - 0.17297] = 0.0001556 \qquad (10b)$$

from (10), (10a) and (10b) it follows that

$$w_{\mathrm{max}}(\mathrm{O};\ 120\ \text{months}) = a \bullet x + b = 0.0001556 \bullet 120 + 0.17297 = 0.191642 \qquad (11)$$

and from (9) and (11) it follows that

$$u_{\mathrm{lts}}\{w(\mathrm{O};\ 120\ \text{months})\} = 0.1916 - 0.175 = 0.0166 \qquad (12)$$

The contribution to the combined uncertainty of the oxygen mass fraction resulting from the long term instability of the samples over a period of ten years was assessed as:

$$u_{\mathrm{lts}}\{w(\mathrm{O};\ 120\ \text{months})\} = 0.0166\ \text{mass\%} \qquad (13)$$

This contribution was included into the calculation of the combined uncertainty of the certified oxygen mass fraction (see 8.2).

5.1.2 Total carbon, nitrogen, Total boron, boron oxide and Free carbon

As for oxygen, for these analytes a long-term stability study of their mass fractions was carried out by ESK Ceramics & Co. KG using a material similar to the CRM candidate material and coming from the same production line as this material. Different methods were used for the determination (see 6.4.1). The measurements were carried out at the end of a period of time, somewhat longer than the period for the study of the oxygen content. The results are given in Table 4.b.

Tab. 4.b: Stability investigations carried out for the mass fractions of five non-metallic analytes in a material similar to the boron carbide CRM candidate material, all mass fractions in %

	Total Carbon		Nitrogen		Total Boron		Boron Oxide		Free Carbon	
Sub-sample	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007
1	20.53	20.66	0.201	0.189	78.94	78.84	0.099	0.099	0.13	0.15
2	20.50	20.69	0.209	0.197	78.94	78.80	0.087	0.086	0.12	0.12
3	20.56	20.66	0.200	0.191	78.92	78.94	0.097	0.097	0.10	0.17
4	20.54	20.64	0.211	0.198	78.87	78.83	0.097	0.096	0.13	0.13
5	20.49	20.67	0.205	0.199	78.90	78.90	0.089	0.096	0.10	0.13
6	20.49	20.68	0.210	0.200	78.93		0.088	0.098		0.15
7	20.48	20.65	0.203	0.202	78.97		0.075	0.113		0.13
8	20.44	20.68	0.211	0.198	78.92		0.080	0.105		
9	20.52	20.62	0.196	0.192	78.96		0.077			
10	20.51	20.60	0.223	0.195	78.91		0.088			
11	20.55									
12	20.56									
w_{mean}	20.51417	20.65500	0.20690	0.19594	78.92600	78.86200	0.08770	0.09873	0.13100	0.13936
Δw_{mean}	+0.14083		-0.01096		-0.064		+0.01103		+0.00836	
SD	0.03630	0.02838	0.00765	0.00426	0.02914	0.05675	0.00842	0.00778	0.01553	0.01743
SD_{Mean}	0.01048	0.00897	0.00242	0.00135	0.00921	0.02538	0.00266	0.00220	0.00695	0.00659

Note: The differences Δw_{mean} of mean mass fractions in case of increased mass fractions in course of time are marked red and in case of decreased mass fractions blue. In the subsequent formulas both cases are also distinguished this way.

The change of mass fractions of the analytes over the period of 10 years (120 months) was assessed analogously as for the analyte oxygen (see above) by a linear interpolation from the maximum absolute difference of the mean values measured at the beginning and the end of a period of 151 months:

$$u_{\text{lts}}\{w(\text{analyte; 120 months})\} = \Delta w_{\text{max}}(\text{analyte; 120 months}) =$$

$$(\text{if } w_{\text{mean}}(\text{analyte; February1995}) < w_{\text{mean}}(\text{analyte; September 2007}))$$
$$= w_{\text{max}}(\text{analyte; 120 months}) - w_{\text{mean}}(\text{analyte; 0 months})\,. \quad (14a)$$

or

$$(\text{if } w_{\text{mean}}(\text{analyte; February1995}) > w_{\text{mean}}(\text{analyte; September 2007}))$$
$$= -\,w_{\text{min}}(\text{analyte; 120 months}) + w_{\text{mean}}(\text{analyte; 0 months})\,. \quad (14b)$$

To calculate w_{max}(analyte; 120 months) or w_{min}(analyte; 120 months), the equation (15) was formed, based on the measured values of Tab. 4.b:

$$w_{\text{max,min}}(\text{analyte; x months}) = a \cdot x + b, \text{ whereas,} \quad (15)$$

if w_{mean}(analyte; February1995) < w_{mean}(analyte; September 2007) :

$$b = w_{\text{mean}}(\text{analyte; February1995}) - SD_{\text{Mean}}\{w(\text{analyte; February 1995})\} \quad (15a)$$

and

$$a = (1/151) \cdot [w_{\text{mean}}(\text{analyte; September 2007}) + SD\{w_{\text{mean}}(\text{analyte; September 2007})\} - b] \quad (15a')$$

or if w_{mean}(analyte; February1995) > w_{mean}(analyte; September 2007) :

$$b = w_{\text{mean}}(\text{analyte; February1995}) + SD_{\text{Mean}}\{w(\text{analyte; February 1995})\} \quad (15b)$$

and

$$a = -\,(1/151) \cdot [-\,w_{\text{mean}}(\text{analyte; September 2007}) + SD\{w_{\text{mean}}(\text{analyte; September 2007})\} + b] \quad (15b')$$

For the calculation according to the formulas (14a) – (15b´) see Tab. 4c.

Tab. 4.c: Stability test carried out for the mass fractions of five non-metallic analytes in the boron carbide candidate material: calculation of the contribution from sample instability (according to the formulas above) to the combined uncertainties of these analytes; all mass fractions in %

Sub-sample	Total Carbon		Nitrogen		Total Boron		Boron Oxide		Free Carbon	
	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007	Febr. 1995	Sept. 2007
w_{mean}	20.51417	20.65500	0.20690	0.19594	78.92600	78.86200	0.08770	0.09873	0.13100	0.13936
SD_{Mean}	0.01048	0.00897	0.00242	0.00135	0.00921	0.02538	0.00266	0.00220	0.00695	0.00659
b	20.50369		0.20932		78.93521		0.08504		0.12405	
a	0.0010614		- 0.000097549		- 0.000652913		0.000105231		0.000145033	
$w_{\text{max, min}}$ (analyte; 120 months)	20.63098		0.197614		78.85686		0.097668		0.141454	
$u_{\text{lts}}\{w$(analyte; 120 months)$\}$	**0.116808**		**0.009286**		**0.069140**		**0.009968**		**0.010454**	

The contribution to the combined uncertainty of the mass fractions of the investigated analytes resulting from the long term instability of the samples over a period of ten years is given in the last line of Tab. 4.c. This contribution was included into the calculation of the combined uncertainties of the certified mass fractions (see 8.2).

5.1.3 HNO_3 soluble Boron

For this parameter a stability study was carried out based on measurements carried out in the frame of an ASTM interlaboratory comparison for method validation in Februar 1995 and additionally on measurements at ESK Ceramics GmbH & Co. KG, Germany in May 2008.
The results are given in Table 4.d.

Tab. 4.d: Stability investigation carried out for the mass fraction of HNO_3 soluble Boron in the boron carbide CRM candidate material

Sub-sample	HNO_3 soluble Boron mass fraction in %	
	February 1995	May 2008
1	0.131	0.131
2	0.135	0.131
3	0.127	0.125
4	0.12	0.127
5	0.13	0.129
6	0.13	0.135
7		
8		
Mean	**0.12883**	**0.12967**
SD	0.00504	0.00350
SD_{Mean}	0.00206	0.00143

The uncertainty contribution from change of HNO_3 soluble mass fraction over the period of 10 years (120 months) was assessed by a linear extrapolation from the maximum difference of the values measured at the beginning and the end of a period of 159 months:

$$u_{lts}\{w(B_{HNO3\ sol};120\ \text{months})\} = \Delta w_{max}(B_{HNO3\ sol}\ ;\ 120\ \text{months}) = -w_{mean}(B_{HNO3\ sol};\ 0\ \text{months}) + w_{max}(B_{HNO3\ sol};\ 120\ \text{months}) \quad (16)$$

To calculate $w_{max}(B_{HNO3\ sol};\ 120\ \text{months})$, the equation of the long term aging was formed, based on the measured values of Tab. 4.1:

$$w_{max}(B_{HNO3\ sol};\ x\ \text{months}) = a \bullet x + b,\ \text{wheras} \quad (17)$$

$$b = w_{mean}(B_{HNO3\ sol};\ \text{Febr 1995}) - SD_{Mean}\{\ w(B_{HNO3\ sol};\ \text{Febr 1995})\} = 0.12883 - 0.00206 = 0.12677 \quad (17a)$$

and

$$a = (1/159) \bullet [w_{mean}(B_{HNO3\ sol};\ \text{May 2008}) + SD\{w_{mean}(B_{HNO3\ sol};\ \text{May 2008})\} - b] = (1/159) \bullet [0.12967 + 0.00143 - 0.12677] = 0.000027232 \quad (17b)$$

from (17), (17a) and (17b) it follows that

$$w_{max}(B_{HNO3\ sol};\ 120\ \text{months}) = a \bullet x + b = 0.000027232 \bullet 120 + 0.12677 = 0.13004 \quad (18)$$

and from (16) and (18) it follows that

$$u_{\mathrm{lts}}\{w(\mathrm{B}_{\mathrm{HNO3\ sol}};\ 120\ \text{months})\} = 0.13004 - 0.12883 = 0.00121 \qquad (19)$$

The contribution to the combined uncertainty of the $\mathrm{B}_{\mathrm{HNO3\ sol}}$; mass fraction resulting from the long term instability of the samples over a period of ten years was assessed as:

$$u_{\mathrm{lts}}\{\ w(\mathrm{B}_{\mathrm{HNO3\ sol}};\ 120\ \text{months})\} = 0.00121\ \text{mass\%} \qquad (19a)$$

This contribution was included into the calculation of the combined uncertainty of the certified $\mathrm{B}_{\mathrm{HNO3\ sol}}$; mass fraction (see 8.2).

5.2 Metallic analytes and Si (Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Si, Ti, W, and Zr)

For these certified or indicative analytes oxidative processes of the sample material will not lead to a change of their masses in a definite sample, because no volatile compounds could be formed under normal storage conditions of the material. Therefore not the masses of these analytes in a definite stored sample (e. g. a sample bottle) but only the mass fractions of them could be changed, according to a change of the total mass of the sample to which their masses are related.

To study this effect, the total sample masses in four selected CRM bottles were measured at different times to assess the change of the sample masses in course of time. In Tab. 4b the results of these measurements are summerized. The sample masses were determined by the difference of the masses of the filled and of the empty bottles.

Tab 4.e: Long term measurements of the sample masses in four CRM bottles (specification in g)

Bottle number	First measurement March 2004		Second measurement November 2007		Difference of measured masses
	Mass1	SD	Mass2	SD	$\Delta_{\mathrm{mass1,2}}$
035	100.3	0.05	100.2	0.05	+ 0.1
156	100.1	0.05	100.1	0.05	0.0
249	99.9	0.05	99.9	0.05	0.0
SA 321	99.9	0.05	99.9	0.05	0.0
mean		0.05		0.05	+ 0.025

The time period between both measurements in Tab. 4.e was 44 month. The validity period of the certificate shall be 10 years (120 months) from the time of the measurements in the interlaboratory comparison. Assuming a linear change of the sample mass in the course of time, the equation for the maximum change of the sample mass of a 100g sample in a period of 120 months was set up to:

$$\begin{aligned}\Delta_{\max}(\text{sample mass; 120 months}) &= (120/44) \cdot (\Delta_{\mathrm{mass1,2;\ mean}} + 2SD_{\mathrm{mean}})\\ &= 2.73 \cdot 0.125 \approx 0.34 \qquad (20)\end{aligned}$$

This value is expressed in the unit g. Because the sample mass in the bottles is about 100 g, the maximum relative change of sample mass is about 0.34 %rel. And in the same degree the maximum relative change of the mass fractions of the metallic analytes caused by an aging of the samples could be expected. Therefore this value was used as the basis to calculate the corresponding absolute values which were treated as the uncertainty contributions to the combined uncertainty and caused by a potential aging of the material:

$$u_{lts,relative}\ (\ w_{\text{metallic analytes}};\ 120\ \text{months})\ \%\text{rel} = 0.34\ \%\text{rel} \qquad (21)$$

The change to relative values of the uncertainties of the mass fractions of metallic analytes could simply be done because the measured sample mass was about 100 g and because the uncertainty (as relative value) of the change of the sample mass equals the relative uncertainty contribution to the uncertainty of mass fractions of the metallic analytes caused by the long term change of the relative sample mass.

In Tab. 4.f the relative uncertainty contribution was converted into the absolute uncertainty values based on a relative contribution of 0.34%rel.

Tab 4f: Contribution of long term instability of samples to the combined uncertainties of the certified or indicative mass fractions of the metallic analytes (and Si) based on a calculated elative uncertainty of 0.34 %rel in 10 years; all values in mg/kg

Elements	Al	Ca	Co	Cr	Cu	Fe	Mn	Na	Ni	Si	Ti	Zr	Mg	W
w (mass fraction)	157.2	96.6	0.393	5.64	2.23	686.3	10.37	6.29	8.02	267.8	95.91	48.9	3.21	3.59
u_{lts}	0.53	0.33	0.0013	0.019	0.0076	2.33	0.035	0.021	0.027	0.91	0.33	0.17	0.011	0.012

These (marginal) contributions were included into the calculation of the combined uncertainty of the certified mass fractions of the metallic analytes (see 8.2).

6 Analytical methods

This chapter describes the analytical procedures and specific parameters used in the certification campaign and for the homogeneity and stability study.

6.1 Analytical methods used for certification (certified and indicative values)

In Tab. 5 the elements having certified values and the elements having indicative values are listed as well as the methods used for their determination in the frame of the interlaboratory comparison for certification .

In the first column the element symbols are specified. In the following column "line numbers" are given. These "line numbers" are corresponding with the related "line numbers" in Tab 6. Line numbers in parenthesis belong to values which were excluded from the final run of evaluation. In the last column the analytical methods (abbreviations see chapter 3) are indicated belonging to the related line numbers (of Tab. 6). Thus it is possible to identify which result in Tab. 6 is based on which analytical method.

Tab. 5: Analytical methods used for the determination of certified and of indicative values, the result numbers are the same as in Tab. 6. Result numbers in parenthesis belong to values which were excluded from the final run of evaluation

Element	**Result No.**	**Analytical method used**
Al	(1), 9	DC-ARC-OES
	7	ET AAS
	3	ETV-ICP OES
	4, 18	ICP-MS
	2, 5, 6, 8, 10, 11, 12, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23	ICP OES
Ca	2, 15	DC-ARC-OES
	17	ETV-ICP OES
	10, 11	F AAS
	13, 22	ICP-MS
	1, 3, 4, 5, 6, 8, 9, 12, 14, 16, 18, 19, 20, 21, 23	ICP OES
	7	IPAA
Co	4	ET AAS
	2	ETV-ICP OES
	1, 5, 8	ICP-MS
	6, 7, 9, (10)	ICP OES
	3	IPAA
Cr	(18)	DC-ARC-OES
	2	ET AAS
	4	ETV-ICP OES
	1, 5, 10	ICP-MS
	3, 6, 7, 8, 9, 11, 12, 13, 14,15, 16, 17, (19)	ICP OES
Cu	3	DC-ARC-OES
	5	ET AAS
	2	ETV-ICP OES
	1, 4, 9	ICP-MS
	6, 7, 8, 10, 11, 12, 13, (14)	ICP OES
Fe	(1), 19	DC-ARC-OES
	5	ETV-ICP OES
	14, 20	F AAS
	10, 11	ICP-MS
	2, 3, 4, 7, 8, 9, 12, 13, 16, 17, 18, 21, 22, 23, 24	ICP OES
	15	IPAA
	6	MAS
Mg	17	DC-ARC-OES
	2	ET AAS
	5	ETV-ICP OES
	6, 11, 15	ICP-MS
	1, 3, 4, 7, 8, 9, 10, 12, 13, 14, 16, 18	ICP OES
Mn	1	DC-ARC-OES
	6	ET AAS
	2	ETV-ICP OES
	5, 8	ICP-MS
	3, 4, 7, 9, 10, 11, 12, 13, 14, 16, 17, (18), 19, 20, 21, 22	ICP OES
	15	IPAA
Na	2	ET AAS
	5	ETV-ICP OES
	1, 3, 6, 7, 10	F AAS
	4	ICP-MS
	8, 9, (11)	ICP OES

Element	**Result No.**	**Analytical method used**
Ni	15	DC-ARC-OES
	8	ET AAS
	2	ETV-ICP OES
	1, 3	ICP-MS
	4, 5, 6, 7, 9, 10, 11, 12, 13, 14	ICP OES
Si	(1), 13	DC-ARC-OES
	3	ET AAS
	14	ETV-ICP OES
	4, (16)	ICP-MS
	2, 5, 6, 9, 10, 11	ICP OES
	7, 8, 12, (15)	MAS
Ti	21	DC-ARC-OES
	18	ET AAS
	(1)	ETV-ICP OES
	9, 20	ICP-MS
	2, 3, 4, 5, 6, 7, 8, 10, 11, 13, 14, 15, 16, 17, 19, 22, 23	ICP OES
	12	IPAA
W	1, 2, 5	ICP-MS
	3, 4	ICP OES
Zr	19	DC-ARC-OES
	1	ETV-ICP OES
	5, 7	ICP-MS
	2, 3, 4, 6, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18, 20, (21)	ICP OES
	14	IPAA
C_{total}	3, 6	Comb.-Coul.
	14	Comb.-Grav.
	2, 4, 5, 7, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18, 19, 20, 21, 22	Comb.-IR
	1	Comb.-Vol.
C_{free}	4	Coul.
	1, 2, 3, 5	Wet Chem. Oxidation-Coul. (Method M4)
O	5	CGHE-Coul.
	1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12	CGHE-IR
N	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12	CGHE-TC
	10	IPAA
B_{total}	12, 16	ICP OES
	(1)	ID-ICP-MS
	2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 17	TITR (Method M1)
$B_{soluble}$	2, 4, 7	ICP OES
	1, 3, 5, 6, (8), (9)	TITR (Method M2)
B_2O_3	6, 7, 8	ICP OES
	1, 2, 3, 4, 5, 9	TITR (Method M3)
$B^{10}/(B^{10}+B^{11})$	2, 3, 4, 7, (8)	ICP-MS
	1, 5, 6	TIMS

For the analysis of almost all analytes a sufficient variety of different methods was used by the participating laboratories. This question is discussed in detail in Chapter 7.

Another important question was, which and how many different procedures had been used for the sample digestion. It is well known that also from this step of the analytical procedures systematic deviations may arise which cannot be recognized without using different digestion methods or analytical methods not needing chemical sample preparation. In Appendix 6 the different procedures of sample pre-treatment are compiled which were used by the different laboratories of the interlaboratory comparison for certification. This detailed table also contains the final methods of determination as listed in Tab. 5 and also contains information about the way how the calibration was made and it is pointed out when no direct traceability was established (i. e. use of matrix materials instead of pure calibrants). The information content of the table in Appendix 6 is very big and a detailed discussion would exceed the frame of this report. However, in the context of the discussion of the results (passages 7.2 and 7.3) several details of the table are included into the considerations.

6.2 Methods used for the determination of additional material data

The particle size distribution was determined by laser light diffraction method using the instrument Mastersizer 2000. The investigated sub-sample (100 mg) was dispersed in water. The process of dispersion was enhanced by an integrated ultrasonic device.

6.3 Methods used for homogeneity testing

- Determination of metallic traces (except Na):

The measurements for the metallic traces (except Na) were carried out by ICP OES. Co was not measured because of its very low mass fraction in the sample leading to a low precision of ICP OES. W was not measured because the element was decided to be handled as one with indicative values only. For the other 10 metallic elements an ICP OES spectrometer “IRIS-advantage Duo” (Thermo Elemental) was used for the investigation. The sub-samples were digested in a high-pressure digestion system at a temperature of 250 °C for 12 hours in a mixture of HNO_3, HF and H_2SO_4. The digestion solution was filled up to 50 mL. The calibration was carried out by using matrix matched (concerning concentrations of boron and acids) solutions containing definite concentrations of all analytes under investigation. The sub-sample mass of the boron carbide powder in the beginning of the procedure was 250 mg.

- Analytes Si and Na:

The measurements for Si and Na were carried out by the direct solid sampling method of ETV-ICP OES using the spectrometer ICP IRIS Intrepid XSP (Thermo) in combination with the ETV system ETV4000 (Sectral Systems, Fürstenfeldbruck). Analytical net signals were used for evaluation because for this kind of investigation no calibration was necessary. Additional Freon gas (dichlorodifluoromethane) was used for the determination of Na, but not for the determination of Si. The temperature in the evaporation step was 2300 °C (and therefore only marginal below the melting temperature of boron carbide). The sub-sample mass intake was 2.5 mg.

- Total C

The homogeneity of Total C distribution was determined by combustion method using oxygen flow and an inductively heated furnace. The instrument was Leco WC 200, tungsten and iron granules were added to the sub-samples. The calibration was made using $CaCO_3$ and SiC as calibration substances. The sub-sample mass was 25 mg.

- O and N

Both analytes were determined in one step by carrier gas hot extraction (CGHE) method using the instrument Leco TC 436, a resistance furnace device with graphite crucible and infrared and thermal conductivity detection cells. The calibration was carried out by using certified steel materials and an in-house B_4C standard. The sub-sample mass intake was 50 mg.

- Total Boron

The mass fractions of total boron were determined using a titration device (Metrohm). The determination was carried out after an alkaline digestion according to Blumenthal by titration with 0.1n NaOH and addition of mannitol. The calibration was carried out by using a boron standard solution (Merck). The sub-sample mass intake was 100 mg.

- HNO_3 soluble Boron

The mass fractions of HNO_3 soluble boron were determined using a titration device (Metrohm). The determination was carried out after boiling the sample in 1.6n HNO_3 with reflux condenser by using titration of the dissolved boron with 0.1n NaOH and adding mannitol. The calibration was done by using a boron standard solution (Merck). The sub-sample mass intake was 4 g.

- Free Carbon

The mass fractions of Free carbon were determined by using a device for measurement of conductivity (detector of Coulomat, Ströhlein) and an apparatus for wet chemical oxidation. The determination was carried out after wet chemical oxidation with chromo sulphuric iodic acid by coulometric titration of the released CO_2 which was absorbed in the absorption solution. The calibration was carried out by using $CaCO_3$ and a B_4C in-house standard. The sub-sample mass intake was 100 mg.

- Boron Oxide

According to the Recommended Method M3 (Appendix 3) the mass fractions of boron oxide were determined by potentiometric titration after appropriate chemical sample treatment. The sub-sample mass intake was 4 g.

6.4 Methods used for time stability investigation

6.4.1 Five non-metallic analytes (Total C, N, Total B, B_2O_3, Free C)

The measurements were carried out at the beginning (February 1995) and at the end (September 2007) of a long storage period of a material B_4C F360, M243 similar in physical and chemical properties to the candidate material B_4C 305F422. Following methods were used for the measurement of the investigated parameters:

- Total C

The total mass fraction of carbon was determined at both times of measurement by combustion method. In 1995 the instrument Ströhlein 702 was used and the final determination was carried out by coulometry. In 2007 the Instrument was a LECO WC200 and carbon was detected as CO_2 by an IR detection cell.

- Nitrogen

The mass fraction of nitrogen was determined at both times of measurement by carier gas hot extraction using the LECO instrument TC 436

- Total B

To determine the total mass fraction of boron a titration was carried out after an alkaline digestion. The instruments used were from Metrohm (in 1995 the "Titroprozessor" and in 2007 the "Titrino").

- Boron Oxide

The mass fraction of boron oxide was determined by titration after extraction with pure water. The instruments used were from Metrohm (in 1995 the "Titroprozessor" and in 2007 the "Titrino").

- Free Carbon

The mass fraction of Free carbon was determined by coulometric measurement after wet chemical oxidation. The instruments used were the Ströhlein 702 in 1995 and the Behr C30 in 2007.

6.4.2 Oxygen

As for the analytes of paragraph 6.41 the measurements were carried out at the beginning (February 1995) of a long storage period of the material B_4C F360, M243 similar in physical and chemical properties to the candidate material B_4C 305F422. The date of the second measurements deviated from that one in 6.4.1. The measurements were already carried out in June 2006. Both series of measurements were executed by carrier gas hot extraction (CGHE) method using the instrument Leco TC 436, a resistance furnace device with graphite crucible and infrared detection cell.

6.4.3 HNO_3 soluble Boron

The first series of measurements was carried out in the frame of an ASTM interlaboratory comparison for method validation in Februar 1995 using the material B_4C F360, M243 very similar to the CRM candidate material and the second series was measured at ESK Ceramics GmbH & Co. KG, Germany in May 2008 using the same material. In both cases the recommended Method M2 (see Appendix 2) with final titrimetric determination was used. The dried sub-samples (about 1.5 g) were treated with 100 mL of 1.6 n HNO_3 and boiled with a reflux condenser. For further details see Appendix 2.

6.4.4 Metallic analytes and Si

The metallic analytes and Si cannot form volatile compounds under the prescribed storage conditions. Therefore it was to assume that their masses in definite samples would not be changed by long term aging of the material. However, their mass fractions could be changed as a result of the change of the entire samle mass by chemical conversion of parts of the sample material. Therefore only measurements of the net mass of some CRM sample bottles were carried out by weighing at different times using an analytical balance having a standard deviation of single measurement of 0.05 g.

7 Results and discussion of the interlaboratory comparison

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 three of the biannual meetings of the Working Group "Special Materials" of the Committee of Chemists of the GDMB, where some of the participating laboratories of the interlaboratory comparison were present. At the sessions it was decided to take the parameters Mg, W and Free carbon as indicative parameters because of their relatively high uncertainty and in view of their minor importance.

For the determination of the parameters "total boron", "HNO_3 soluble boron" and "boron oxide" methods were discussed and agreed as recommended methods, although these parameters were not decided to be observed as method depending parameters in opposite to the parameter "Free carbon" (an “indicative parameter") for which a method of determination was prescribed. The documents containing the four methods are part of the certificate as attachments and part of this certification report as Appendices 1-4.

In the following Tab. 6 all accepted laboratory mean values are summarized.

*Tab 6: Results *) = Means of the series of independent measurements of the laboratories (Laboratory means)*

Tab. 6, Part 1

mass fractions – *arranged in increasing value*

Result no.	Al [mg/kg]	Ca [mg/kg]	Co [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Fe [mg/kg]	Mn [mg/kg]	Na [mg/kg]	Ni [mg/kg]	Si [mg/kg]	Ti [mg/kg]
1	-	61	0.28	4.0	1.4	-	8.1	5.3	6.2	-	-
2	141	62	0.30	4.5	1.5	599	9.4	5.4	6.2	205	90
3	143	83	0.31	4.7	1.6	630	9.6	5.6	6.4	216	90
4	145	87	0.39	4.7	1.7	646	9.7	5.7	6.6	227	90
5	152	89	0.41	4.7	1.7	646	9.7	5.9	7.1	238	91
6	152	90	0.42	5.2	2.0	650	9.9	6.4	7.2	264	92
7	153	91	0.45	5.2	2.3	665	10.0	6.8	7.4	265	92
8	153	91	0.45	5.4	2.3	666	10.1	7.0	7.5	275	93
9	154	92	0.53	5.4	2.7	669	10.2	7.1	7.8	281	93
10	155	93	-	5.4	2.8	669	10.3	7.6	7.8	292	94
11	155	93	-	5.5	2.8	673	10.4	-	8.3	295	95
12	156	94		5.7	3.0	679	10.6		10.0	295	95
13	158	96		5.7	3.2	687	10.8		10.1	304	96
14	158	96		5.7	-	689	10.8		10.6	323	96
15	159	97		6.9		689	10.9		11.1	-	97
16	159	99		7.8		692	11.0			-	97
17	160	103		9.3		692	11.0				97
18	163	105		-		695	-				98
19	163	107		-		696	11.4				101
20	164	110				709	11.7				102
21	168	115				720	11.9				104
22	173	135				763	12.7				104
23	177	135				771					105
24						792					
25											
M:	157	97	0.39	5.6	2.2	686	10.4	6.3	8.0	268	96
s_M:	9	18	0.09	1.3	0.7	45	1.0	0.8	1.7	37	5

*) Some laboratories delivered more than one set of results coming from different methods applied

The ‘ - ‘ indicates that an outlying value had been detected by a statistical test which was withdrawn or omitted after discussion with the delivering laboratory and at GDMB meetings.

Note: The result number does not relate to the laboratory code number
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means (rounded up)

Tab. 6, Part 2

Mass fractions and isotopic abundance(for $^{10}B/(^{10}B+^{11}B)$) *arranged in increasing value*

Result*) no..	Zr [mg/kg]	C_{total} [%]	O [%]	N [%]	B_{total} [%]	$B_{soluble}$ [%]	B_2O_3 [%]	$^{10}B/(^{10}B+^{11}B)$ **) [%]	*Mg* [mg/kg]	*W* [mg/kg]	C_{free} [%]
1	37.3	20.5	0.067	0.172	-	0.098	0.056	19.880	*1.3*	*1.1*	*0.39*
2	44.7	20.6	0.080	0.186	78.09	0.112	0.057	19.897	*1.4*	*1.2*	*0.44*
3	44.8	20.8	0.081	0.187	78.11	0.113	0.066	19.901	*1.4*	*5.0*	*0.45*
4	45.5	20.8	0.083	0.200	78.16	0.117	0.067	19.905	*1.7*	*5.1*	*0.60*
5	47.2	20.9	0.089	0.204	78.17	0.118	0.073	19.908	*1.7*	*5.6*	*0.66*
6	47.5	20.9	0.091	0.206	78.23	0.121	0.078	19.922	*1.7*		
7	47.7	20.9	0.100	0.219	78.25	0.137	0.082	19.938	*1.7*		
8	48.0	20.9	0.106	0.221	78.25	-	0.084	-	*2.2*		
9	48.7	20.9	0.109	0.224	78.25	-	0.108		*2.3*		
10	49.2	20.9	0.114	0.226	78.38				*2.6*		
11	49.5	21.0	0.118	0.230	78.46				*2.8*		
12	50.0	21.0	0.122	0.233	78.68				*2.9*		
13	50.3	21.0			78.76				*3.5*		
14	50.4	21.0			78.80				*4.7*		
15	50.7	21.0			78.81				*5.6*		
16	51.3	21.0			78.99				*6.3*		
17	51.4	21.1			79.06				*6.7*		
18	54.1	21.2							*7.3*		
19	54.5	21.2									
20	55.4	21.3									
21	-	21.5									
22		21.6									
23											
24											
25											
M:	48.9	21.0	0.097	0.209	78.47	0.116	0.075	19.907	*3.2*	*3.6*	*0.51*
s_M:	4.0	0.3	0.018	0.020	0.33	0.012	0.017	0.019	*2.0*	*2.3*	*0.12*

*) Some laboratories delivered more than one set of results coming from different methods applied

The ‘ - ‘ indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion with the delivering laboratory and at GDMB meetings.

Values given in *italic type* are indicative values only.

Note: The result number does not relate to the laboratory code number

**): Isotopic abundance (amount fraction) of ^{10}Boron related to total amount of Boron

M: Arithmetic mean of the laboratory means

s_M: Standard deviation of the laboratory means (rounded up)

7.2 Technical discussion

The results of table 6 are listed in more detail in tables 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 the 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 (=analyte, run of evaluation)
  #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 self-declaration of own 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
  #subsequent 6 columns: all single values from different sub-samples
- central 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 this was 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. Furthermore there are explanations to the abbreviations of statistical tests applied and indicated in the following diagram of the lower part.

- lower part: based on the specifications of the upper and centre-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 the means of data sets of the laboratories 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 central 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 of Appendix 7.

The results of Appendix 7 and the decisions concluded are shortly summarized in the following.

7.2.1 Metallic certified analytes and Si

7.2.1.1 Aluminium (Tab. Xa1 and Xa2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used. The remaining 23 laboratories delivered their results all based on 6 separate determinations. Most laboratories used ICP OES, but also other methods were used: DC-ARC-OES (2x), ET AAS (1x), ETV-ICP OES (1x) and ICP-MS (2x). The lowest value coming from a determination with DC-ARC-OES was identified as a clear outlier and was removed after the first run. In the second run of evaluation no severe outlier was identified. Two sets of values were indicated by Cochan test but not removed. All confidence intervals were overlapping in the second run. A problem was the dominating number of results from ICP OES method combined with an acid sample digestion under high pressure. But 3 of the accepted values came from ICP OES combined with a decomposition by fusion followed by an acid digestion and two results came from ICP-MS and one from ET AAS, all with acid digestion, furthermore two results came from the direct solid sampling methods DC-ARC-OES and ETV-ICP

OES. From this variety of different analytical procedures applied by the laboratories was concluded that the analytical basis was sufficient to accept the mean of the laboratory means of the second run as the certified value. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.2 **Calcium** (Tab. Xb1)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used. The remaining 23 laboratories delivered their results all based on 6 separate determinations. Most laboratories used ICP OES, but also other methods were used: DC-ARC-OES (2x), IPAA (1x), F AAS (2x), ETV-ICP OES (1x) and ICP-MS (2x). No value was identified as outlier at 1% level by Grubbs or Nalimov test. Some of the values were identified at 5% level by Grubbs test, but no value was removed even though the both lowest values did not overlap with the next higher one. But this one had an extremely small confidence interval. The problem of the dominating number of results from ICP OES method combined with an acid sample digestion under high pressure was assessed as not being problematic because two of the values came from ICP OES combined with a decomposition by fusion followed by an acid digestion and furthermore two results came from ICP-MS and two from F AAS, all with acid digestion and further 4 results came from the direct solid sampling methods IPAA, DC-ARC-OES and ETV-ICP OES. From this variety of different analytical procedures applied by the laboratories was concluded that the analytical basis was good enough to accept the mean of the laboratory means of the first run as the certified value. With one exception all laboratory mean values lie within the tolerance interval. The exception is the highest value, lying very near to the upper limit of the tolerance interval.

7.2.1.3 **Cobalt** (Tab. Xc1 and Xc2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of 5 laboratories were excluded, because it were "less than" values. Only 10 laboratories remained which had delivered their results for this element having the lowest certified mass fraction. All results were based on 6 separate determinations. The highest value was identified as an clear outlier by Dixon, Grubbs and Nalimov test at 1% level. Different methods were used for establishing of the remaining values taken for the second run of evaluation: ICP OES (3x), ICP MS (3x), ET AAS (1x) (they all with acid decomposition under pressure applied to the samples) and the direct solid sampling methods IPAA (1x) and ETV-ICP OES (1x). Three sets of values were identified in the second run by Cochan test at 1% level but not removed. Not all confidence intervals were overlapping: there was a gap between the third and the fourth value in the second run, but the confidence interval of the fourth value was extremely low. A problem was the rather low number of results most of them coming from methods combined with an acid sample digestion under high pressure. But the two results of the direct solid sampling methods lie not too far from the mean of the laboratory means. From this fact was concluded that the analytical basis would be sufficient to accept the mean of the laboratory means of the second run as the certified value. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.4 **Chromium** (Tab. Xd1; Xd2; Xd3)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of another laboratory were excluded, because it were "less than" values. The remaining 19 laboratories delivered their results, each of them based on 6 separate determinations. Most laboratories used ICP OES. In the first run the highest value was identified as an extreme outlier which was excluded from the second run. But the remaining highest value was also removed after it had been identified as a clear outlier by Grubbs and Nalimov test at 1% level. The remaining 17 values of the third run were all accepted although both highest values had been identified as outliers by Grubbs pair test at 1% level. 12 of the accepted values came from determination by ICP OES, 10 of them with acid digestion and two with fusion digestion followed by acid digestion. One result was determined by ICP-MS, one by ET AAS and one came from the direct solid sampling ETV-ICP OES. It was concluded that the analytical basis would be sufficient to accept the mean of the laboratory means of the third run as the certified value All remaining laboratory mean values are overlapping and lie within the tolerance interval.

7.2.1.5 **Copper** (Tab. Xe1; Xe2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of three other laboratories were excluded, because it were "less than" values. The delivered results of the remaining 14 laboratories were all based on 6 separate determinations. Most laboratories used ICP OES. The set of highest values was also based on ICP OES measurements. It was identified as an outlier by statistical tests and was removed. The corresponding laboratory had declared their experience for this task of analysis as low (number "1"). In the second run of the evaluation program carried out with the remaining 13 laboratories no further outlier was found. The remaining 13 sets of results came mainly from measurements by ICP OES(7x) after acid digestion, others from ICP-MS(3x), ET AAS(1x) and from direct solid sampling methods ETV-ICP OES(1x) or DC-ARC-OES(1x). It was concluded that the analytical basis would be sufficient to accept the mean of the laboratory means of the second run as the certified value. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.6 **Iron** (Tab. Xf1; Xf2)

In the beginning the results of one laboratory were excluded, because a semi quantitative XRF method had been used. The remaining 24 Laboratories delivered their results based on 6 separate determinations. Most laboratories used ICP OES. The set with the lowest values based on DC arc-OES measurements was identified as very clear outlier by statistical tests and was removed. In the second run of the evaluation program carried out with the remaining 23 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 ICP-MS(2x), MAS(1x), F AAS (2x) as well as from measurements with the three direct solid sampling methods IPAA(1x), DC arc-OES(1x) and ETV-ICP OES(1x). For most wet chemical methods direct acid digestion was used whereas in case of MAS and in case of 3 analytical procedures with ICP OES wet chemical digestion was used after fusion digestion. Thus a very solid basis of different methods and digestion procedures was contained in the certification of this analyte. It was concluded that the analytical basis would be sufficient to accept the mean of the laboratory means of the second run as the certified value. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.7 **Manganese** (Tab. Xh1; Xh2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of another laboratory were excluded, because it were "less than" values. The remaining 22 laboratories delivered their results, each of them based on 6 separate determinations. Most laboratories used ICP OES. One of these laboratory sets having an extremely large spreading of the single values was excluded after the first run. In the second run of the evaluation program carried out with the remaining 21 laboratories no further outlier was removed although the lowest value was identified as an outlier by Nalimov test at 1% level and was not overlapping with the next higher values. The distribution of the values is not S-shaped and having no clear plateau. On the other hand the distribution of the mean values ranges from about 8 mg/kg to about 13 mg/kg, which can be very well tolerated. The certified mean value is not only underpinned by ICP OES measurements with acid digestion (one after fusion digestion), but also by results of measurements with ICP-MS (2x) and ET AAS(1x) and by measurements with the direct solid sampling methods IPAA(1x), DC arc-OES(1x) and ETV-ICP OES(1x). All accepted laboratory mean values lie within the tolerance interval.

7.2.1.8 **Sodium** (Tab. Xi1; Xi2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because it were "less than" values. Only 11 laboratories remained which had delivered their results, 10 of them based on 6 separate determinations, one on 4 separate measurements. There was a good mix of different methods. The set of one laboratory with the highest values based on ICP OES measurements was identified as a clear outlier by statistical tests. This set was removed after the first run. In the second run the evaluation program was carried out with the remaining 10 laboratories and no outlier was identified. The certified mean value of the means of the remaining 10 laboratories is based on measurements with ICP OES(2x), ICP-MS(1x), F AAS or ET AAS (together 6x) and the direct solid sampling method of ETV-ICP OES, the result of which is lying near to the centre of the distribution of laboratory mean values. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.9 **Nickel** (Tab. Xj1)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of two laboratories were excluded, because it were "less than" values. The remaining 15 laboratories delivered their results, all of them based on 6 separate determinations. Ten laboratories used ICP OES (one of them combined with fusion digestion before final dissolution of the samples). 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 distribution of values is not S-shaped and has no clear plateau in the centre. Another negative fact is that the interval of the accepted laboratory mean values is rather large reaching from about 6 mg/kg to about 11 mg/kg. On the other hand the certified mean value is not only underpinned by ICP OES measurements, but also by results of measurements with ICP-MS(2x), ET AAS(1x) and by those of the two direct solid sampling methods DC arc-OES and ETV-ICP OES the results of which are lying at the lowest and highest ends of the distribution of values. All laboratory mean values lie within the tolerance interval.

7.2.1.10 **Silicon** (Tab. Xk1; Xk2; Xk3; Xk4)

In the beginning the results of one laboratory were excluded, because a semi quantitative XRF method had been used. 14 of the remaining 16 laboratories delivered their results based on 6 separate determinations, the other two laboratories delivered 5 single values each. The different applied methods were well mixed. The set of one laboratory with the highest values was based on ICP-MS measurements. This set was identified as an very clear outlier by statistical tests in the first run and was therefore excluded. In the second run the lowest sets of values based on measurements with DC-ARC-OES was identified as a clear outlier and removed. In the third run the highest sets of values based on MAS measurements was identified as a clear outlier and removed. The remaining 13 sets of values of the fourth run were well overlapping. The distribution of laboratory mean values reached over a rather wide range from about 200 mg/kg to about 320 mg/kg. However, the certified mean value of the laboratory means is underpinned by application of a variety of different methods: ICP OES(6x), ICP-MS(1x), MAS(3x) and the direct solid sampling methods ETV-ICP OES and DC arc-OES. The results of these both methods are the highest of the distribution of values. But this negative fact may be compensated that the other methods were combined with acid digestion as well as with fusion digestion in about equally large parts. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.11 **Titanium** (Tab. Xl1; Xl2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of another laboratory were excluded, because it were "less than" values. The remaining 23 laboratories delivered their results, 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. In the first run this set was identified as a clear outlier by statistical tests and was removed. In the second run of the evaluation program carried out with the remaining 22 laboratories no further outlier was found. The certified mean value is not only underpinned by ICP OES measurements (three of them combined with fusion digestion before wet chemical digestion), but also by results from measurements with ICP-MS(2x), ET AAS(1x) and the direct solid sampling methods IPAA(1x) and DC arc-OES(1x). The results from IPAA are very near to the mean of the laboratory means. All remaining laboratory mean values lie within the tolerance interval.

7.2.1.12 **Zirconium** (Tab. Xn1; Xn2)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of another laboratory were excluded, because it were "less than" values. The remaining 20 laboratories delivered their results each 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 because of the wide spreading of single values and because the mean value was lying out of the limit of the tolerance interval and being identified as a clear outlier at 1% level by 3 different tests. In the second run of the evaluation program carried out with the remaining 20 laboratories no further value was removed although the lowest one had been identified as an outlier. The certified mean value of all means is not only underpinned by ICP OES measurements (two of them combined with fusion digestion followed by wet chemical digestion), but also by results from measurements with ICP-MS (2x), and from measurements with the three direct solid sampling methods DC arc-OES, ETV-ICP OES and IPAA. The result of IPAA lies very near to the mean of the means. The remaining laboratory mean values lie, with exception of the lowest one, within the tolerance interval.

7.2.2 Non-metallic certified analytes

7.2.2.1 **Total Carbon** (Tab. Xo1)

In the beginning of the discussion of the delivered values the results of three laboratories were excluded, because their calibrations were based on the use of matrix materials instead of pure substances having a definite stoichiometry. The remaining 22 laboratories delivered their results each based on 6 separate determinations. Most laboratories used combustion method with IR detection. Even though the distribution of the laboratory mean values was not ideal and the lowest both values were not overlapping, no clear outlier was identified and no value was removed after the first run of the evaluation program. The certified mean value is underpinned by results from combustion method combined with other detection methods than IR dtection: two with coulometric, one with gravimetric and one with volumetric measurement. All laboratory mean values lie within the tolerance interval.

7.2.2.2 **Oxygen** (Tab. Xq1)

In the beginning of the discussion of the delivered values the results of six laboratories were excluded, because their calibration was based on the use of matrix materials instead of pure substances having a definite stoichiometry. The remaining 12 Laboratories delivered their results each based on 6 separate determinations. With one exception all laboratories used CGHE method with IR detection. One laboratory used CGHE method with coulometric detection and delivered results lying near to the mean of the laboratory means. Although the set with the lowest values did not overlap with other results, the set was not identified as outlier by statistical tests and was not removed. The interval of the distribution of all mean values is wide. All the same the results reflect the state of the art of this kind of analytical problem and therefore the mean of the means was accepted as the certified value having a rather large uncertainty. All laboratory mean values lie within the tolerance interval.

7.2.2.3 **Nitrogen** (Tab. Xr1)

In the beginning of the discussion of the delivered values the results of eight laboratories were excluded, because their calibrations were based on the use of matrix materials instead of pure substances having a definite stoichiometry. The remaining 12 laboratories delivered their results each based on 6 separate determinations. With one exception all laboratories used CGHE method with detection by thermal conductivity. One laboratory used IPAA. The results of this laboratory are lying not too far from the mean of the laboratory mean values. Therefore nitrogen could be certified without being a method depending parameter. No serious outlier was identified by statistical tests and no set of values was removed although the lowest set of values was not overlapping with other ones. All laboratory mean values lie within the tolerance interval.

7.2.2.4 **Total Boron** (Tab. Xs1)

16 Laboratories delivered their results each based on 6 separate determinations and one laboratory delivered only five single values. Most laboratories used titrimetry. One laboratory delivered a result based on measurements by ID-ICP-MS. This set of values was identified as a clear outlier at 1% level by three statistical tests and was removed after the first run. This decision was not so easy, because isotope dilution mass spectrometry is usually assessed as an elite method. However, in this special case the overwhelming majority of all the differing other results coming from experienced laboratories was trusted. In the second run no further outlier was found. Both sets of values not coming from determination by titrimetry but by ICP OES were identified by Cochran test at 1% level as having a wide spread of single values. But the spread was in both cases corresponding to the state of the art of this method, so that also these sets of values were accepted. They lie within the narrow distribution of all mean values reaching from a mass fraction of about 78.09% to a mass fraction of about 79.6 %. All values of the distribution are overlapping and all mean values lie within the tolerance interval.

7.2.2.5 **HNO_3 soluble Boron** (Tab. Xt1; Xt2; Xt3)

9 laboratories delivered their results five of them based on 6 separate determinations, one laboratory delivered only five single values. Most laboratories used titrimetry. In the first run of evaluation the set with highest values was identified as a statistical outlier at 1% level by two statistical tests and removed. In the second run the set with the then highest values was identified as a statistical outlier at 1% level by three statistical tests and removed. In the third run carried out with the results of the remaining seven laboratories no further outlier was found. but. A positive fact was that the three results coming from ICP-OES measurements are well mixed with the four results coming from titrimetric measurements. All mean values of the distribution lie within the tolerance interval.

7.2.2.6 **Boron Oxide** (Tab. Xu1)

9 laboratories delivered their results 5 of them based on 6 separate determinations, one laboratory delivered only four values. Six laboratories used titrimetry. The other three used ICP OES. In the first run of evaluation no clear outlier was identified. However all four single results of the set with the lowest values was under long discussion because of the very wide spread of the single values. In the end this set of values was not removed. All results from ICP OES measurements are lying in the higher part of the distribution of laboratory mean values but no clear indication of method depending differences between the results of both methods was found. All laboratory mean values of the distribution lie within the tolerance interval.

7.2.2.7 Isotopic abundance (amount fraction) of ^{10}B (Tab.Xv1)

8 laboratories delivered their results 6 of them based on 6 separate determinations, two laboratories delivered only three values. In the first run of the evaluation program the set with the highest values coming from ICP-MS measurements was identified as a clear outlier at 1% level by three different statistical tests and was excluded. Four of the remaining laboratories had used ICP-MS the other three had used TIMS. The distribution of the results of both methods is well mixed. Most laboratories used different types of acid digestion of the samples, one laboratory used an alkaline oxidizing decomposition and one laboratory prepared a mixed suspension of the sample. The interval of the laboratory mean values is not wide reaching from about 19.88 % to about 19.94 %. All laboratory mean values of the distribution lie within the tolerance interval.

7.2.3 Non certified analytes (indicative values)

7.2.3.1 Magnesium (Tab. Xg1)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because it were "less than" values. The remaining 18 laboratories delivered their results, with one exception, based on 6 separate determinations, one laboratory delivered only 4 single values. Many laboratories used ICP OES. Although the distribution of the laboratory values was not symmetric and had a long tailing at the side of the higher values no outlier was identified at 1% level. The mean value of the means is not only underpinned by ICP OES measurements (two of them with fusion digestion before further digestion), but also by results from measurements with ET AAS(1x), ICP-MS(3x) and from the direct solid sampling methods ETV-ICP OES(1x) and DC arc-OES(1x). All remaining laboratory mean values lie within the tolerance interval. The distribution of the laboratory mean values is far from being ideal and very broad reaching from about 1.3 mg/kg to about 7.3 mg/kg. A very big uncertainty was the result of the later on carried out calculation. Therefore this parameter was not taken as a certified but simply as an indicative parameter

7.2.3.2 Tungsten (Tab. Xm1)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because a semi quantitative XRF method had been used, additionally the results of 4 other laboratories were excluded, because it were "less than" values. The 5 laboratories which only remained delivered their results all based on 6 separate determinations. Two laboratories used ICP OES the three others used ICP-MS, all laboratories used acid digestion of the samples. Though the first two values were not overlapping with the others, no clear outlier was identified. All laboratory mean values lie within the tolerance interval. The distribution of the low number of laboratory mean values is far from being ideal and a big uncertainty was the result of the later on carried out calculation. Therefore the mass fraction of tungsten was not taken as a certified but simply as an indicative parameter

7.2.3.3 Free Carbon (Tab. Xp1)

In the beginning of the discussion of the delivered values the results of one laboratory were excluded, because it were "less than" values. The remaining 5 Laboratories delivered their results each based on 6 separate determinations. Four laboratories used the prescribed "Method M4" of wet chemical oxidation combined with coulometric titration. Although only this method was prescribed, an exception was made by accepting the results of the fifth laboratory because the results were based on an absolute coulometric method. The results of this laboratory lie within the distribution of the results of the other laboratories. The distribution of the mass fractions of the five laboratories was rather wide (from about 0.38 % to about 0,66 %) far from being ideal and not all different values were overlapping. However, no statistical outlier was identified. A big uncertainty of this parameter was the result of the later on carried out calculation. Therefore the mass fraction of Free carbon was not taken as a certified but simply as an indicative parameter

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 and 7.2.

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

7.3.1 Metallic analytes (certified and indicative analytes including Si)

Tab. 7.1: Summary of results of statistical evaluation

Element	Al	Al	Ca	Co	Co
run of evaluation program	run 1	run 2	run 1	run 1	run 2
Number of data sets	23	22	23	10	9
Total number of replicate measurements	138	132	136	60	54
Mean of means (a)	152.120	157.217	96.597	0.554	0.393
St. Dev of means (a)	25.906	8.788	17.378	0.514	0.082
Outlying or straggling mean values					
▪ Dixon test	b, c	no	no	b, c	no
▪ Grubbs test (single and pair test)	b, c	no	c	b, c	no
▪ Nalimov t-test	b, c	c	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	out of test range	out of test range	no	no	no
St. Dev. within – laboratories (a)	6.025	6.011	7.677	0.208	0.059
St. Dev. between laboratories (a)	25.789	8.439	16.677	0.507	0.078
Half-width of the 95% confidence interval (a)	11.202	3.896	7.515	0.368	0.063

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

Element	Cr	Cr	Cr	Cu	Cu
run of evaluation program	run 1	run 2	run 3	run 1	run 2
Number of data sets	19	18	17	14	13
Total number of replicate measurements	114	108	102	84	78
Mean of means (a)	12.989	5.960	5.636	2.379	2.228
St. Dev of means (a)	30.690	1.870	1.304	0.824	0.626
Outlying or straggling mean values					
▪ Dixon test	b, c	c	no	no	no
▪ Grubbs test (single and pair test)	b, c	b, c	b, 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	no	no	no	no	no
St. Dev. within – laboratories (a)	2.380	0.847	0.854	0.298	0.274
St. Dev. between laboratories (a)	30.675	1.838	1.257	0.815	0.616
Half-width of the 95% confidence interval (a)	14.792	0.930	0.671	0.476	0.378

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

Element	Fe	Fe	Mg	Mn	Mn
run of evaluation program	run 1	run 2	run 1	run 1	run 2
Number of data sets	24	23	18	22	21
Total number of replicate measurements	144	138	106	132	126
Mean of means (a)	664.230	686.298	3.206	10.523	10.484
St. Dev of means (a)	116.456	44.265	2.010	0.985	0.992
Outlying or straggling mean values					
▪ Dixon test	b, c	no	no	no	no
▪ Grubbs test (single and pair test)	b, c	no	no	no	no
▪ Nalimov t-test	b, c	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	no	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	out of test range	out of test range
St. Dev. within – laboratories (a)	33.653	34.131	0.461	1.249	0.481
St. Dev. between laboratories (a)	115.643	42.015	2.020	0.834	0.972
Half-width of the 95% confidence interval (a)	49.175	19.142	0.999	0.437	0.452

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

Element	Na	Na	Ni
run of evaluation program	run 1	run 2	run 1
Number of data sets	11	10	15
Total number of replicate measurements	64	58	90
Mean of means (a)	6.625	6,288	8.022
St. Dev of means (a)	1.353	0.801	1.636
Outlying or straggling mean values			
▪ Dixon test	c	no	no
▪ Grubbs test (single and pair test)	b, c	no	no
▪ Nalimov t-test	b, c	no	c
Differences between labs statistically significant?			
▪ Snedecor F-test	b, c	b, c	b, c
Outlying or straggling variances			
▪ Cochran test	c	c	no
Variances homogeneous			
▪ Bartlett test	out of test range	no	no
St. Dev. within – laboratories (a)	0.692	0.727	0.763
St. Dev. between laboratories (a)	1.342	0.744	1.606
Half-width of the 95% confidence interval (a)	0.909	0.573	0.906

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

Element	Si	Si	Si	Si
run of evaluation program	run 1	run 2	run 3	run 4
Number of data sets	16	15	14	13
Total number of replicate measurements	94	88	83	77
Mean of means (a)	327.77	262.18	276.62	267.77
St. Dev of means (a)	271.60	72.64	48.10	36.31
Outlying or straggling mean values				
▪ Dixon test	b, c	c	no	no
▪ Grubbs test (single and pair test)	b, c	b, c	c	no
▪ Nalimov t-test	b, c	b, c	b, c	no
Differences between labs statistically significant?				
▪ Snedecor F-test	b, c	b, c	b, c	b, c
Outlying or straggling variances				
▪ Cochran test	b, c	b, c	b, c	b, c
Variances homogeneous				
▪ Bartlett test	out of test range	out of test range	no	no
St. Dev. within – laboratories (a)	41.20	21.68	22.30	22.99
St. Dev. between laboratories (a)	272.13	69.07	46.80	34.49
Half-width of the 95% confidence interval (a)	144.72	40.23	27.77	21.94

Abbreviations:

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

Element	Ti	Ti	W	Zr	Zr
run of evaluation program	run 1	run 2	run 1	run 1	run 2
Number of data sets	23	22	5	21	20
Total number of replicate measurements	138	132	30	126	120
Mean of means (a)	94.484	95.915	3.593	49.741	48.903
St. Dev of means (a)	8.219	4.630	2.251	5.494	4.032
Outlying or straggling mean values					
▪ Dixon test	b, c	no	no	b, c	no
▪ Grubbs test (single and pair test)	b, c	no	no	b, c	c
▪ Nalimov t-test	b, c	no	no	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)	3.815	3.606	0.511	3.210	2.631
St. Dev. between laboratories (a)	8.070	4.390	2.241	5.336	3.886
Half-width of the 95% confidence interval (a)	3.554	2.053	2.795	2.501	1.887

Abbreviations:

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

7.3.2 Non-metallic analytes (certified and indicative ones)

Tab. 7.2: Summary of results of statistical evaluation

Element	Total C	Free C	O	N
run of evaluation program	run 1	run 2	run 1	run 1
Number of data sets	22	5	12	12
Total number of replicate measurements	132	30	72	72
Mean of means (a)	21.006	0.506	0.0965	0.2091
St. Dev of means (a)	0.259	0.118	0.0174	0.0198
Outlying or straggling mean values				
▪ Dixon test	no	no	no	no
▪ Grubbs test (single and pair test)	no	no	no	no
▪ Nalimov t-test	c	no	no	c
Differences between labs statistically significant?				
▪ Snedecor F-test	b, c	b, c	b, c	b, c
Outlying or straggling variances				
▪ Cochran test	no	b, c	b, c	b, c
Variances homogeneous				
▪ Bartlett test	no	no	yes	no
St. Dev. within – laboratories (a)	0.065	0.024	0.0039	0.0078
St. Dev. between laboratories (a)	0.257	0.117	0.0174	0.0195
Half-width of the 95% confidence interval (a)	0.115	0.146	0.0111	0.0126

Abbreviations:

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

Element run of evaluation program	Total B run 1	Total B run 2	Soluble B run 1	Soluble B run 2	Soluble B run 3
Number of data sets	17	16	9	8	7
Total number of replicate measurements	101	95	52	46	40
Mean of means (a)	77.785	78.466	0.1953	0.1476	0.1163
St. Dev of means (a)	2.828	0.331	0.1655	0.0891	0.0116
Outlying or straggling mean values					
▪ Dixon test	b, c	no	no	b, c	no
▪ Grubbs test (single and pair test)	b, c	no	c	b, c	no
▪ Nalimov t-test	b, c	no	b, 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	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	0.322	0.290	0.0113	0.0114	0.0119
St. Dev. between laboratories (a)	2.838	0.309	0.1680	0.0908	0.0108
Half-width of the 95% confidence interval (a)	1.454	0.177	0.1272	0.0745	0.0108

Abbreviations:

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

Element run of evaluation program	B$_2$O$_3$ run 1	^{10}B **amount fraction** run 1	^{10}B **amount fraction** run 2
Number of data sets	9	8	7
Total number of replicate measurements	52	42	36
Mean of means (a)	0.0745	19.9271	19.9072
St. Dev of means (a)	0.0162	0.0587	0.0183
Outlying or straggling mean values			
▪ Dixon test	no	b, c	no
▪ Grubbs test (single and pair test)	no	b, c	no
▪ Nalimov t-test	c	b, c	no
Differences between labs statistically significant?			
▪ Snedecor F-test	b, c	b, c	c
Outlying or straggling variances			
▪ Cochran test	b, c	b, c	b, c
Variances homogeneous			
▪ Bartlett test	no	no	no
St. Dev. within – laboratories (a)	0.0074	0.0413	0.0227
St. Dev. between laboratories (a)	0.0157	0.0587	0.0142
Half-width of the 95% confidence interval (a)	0.0124	0.0491	0.0169

Abbreviations:

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

8 Calculation and compilation of certified and indicative values and their uncertainties

8.1 Calculation of certified mean mass fractions

The certified (or indicative) values of mass fractions of certified or indicative elements were calculated as the mean values "*M*" of all accepted means from the participating laboratories of the interlaboratory comparison (see 7.1, Tab. 6).

8.2 Calculation of uncertainties

The combined uncertainties of the certified mass fractions contain contributions from the interlaboratory comparison for certification, from (potential) inhomogeneity of the samples and from (potential) time instability of the samples (see below equations (2) and (6)).

The contributions coming from sample inhomogeneity 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 [3] and ISO Guide 35 [4]

s_M = standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 6)

n = number of accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 6)

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

whereas

$$s_{inhom} = \sqrt{\left(s_{\mathrm{b}}^2 - s_{\mathrm{HS}}^2\right) + \left(s_{\mathrm{w}}^2 - s_{\mathrm{HS}}^2\right)} \tag{22}$$

In equation (22) 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 (= assumed as the variance of the analytical procedure) was subtracted. Thus an effective contribution of the inhomogeneity (without the contribution of the analytical procedure) was calculated. The contribution of s^2_{HS} was subtracted from both variances, s^2_b and s^2_w, although their values are not independent one from the other. On the other hand, the contribution of the variance of the analytical procedure is contained in both empirically determined variances s^2_b and s^2_w. Therefore equation (22) was treated as the best approximation to calculate the standard deviation resulting from (potential) inhomogeneity of the samples.

If accidentally a standard deviation when using the homogeneous sample was measured having a greater value than one or both of the two other empirical standard deviations, i. e. if:

$s_{HS} > s_b$ and/or $s_{HS} > s_w$)
) (22´)
then the corresponding difference term(s) in (22) is (are) set to zero.)

The combined uncertainty u_c is calculated as the sum of three contributions, - on the one hand resulting from the interlaboratory comparison for certification - and on the other hand from inhomogeneity of the sample and from the potential time instability of the sample:

$$u_c = \sqrt{\frac{s_{\mathrm{M}}^2}{n} + s_{\mathrm{inhom}}^2 + u_{lts}^2} \qquad (23)$$

(whereas u_{lts} stands for the uncertainty contribution from potential long term instability of the corresponding parameter)

Equation (23) 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 [4]), which could be masked by the variance of the analytical procedure s^2_{HS}, i. e. equation (23) was used when:

$$s^2_{inhom} > u^2_{bb} \,, \qquad (24)$$

whereas

$$u_{bb} = \sqrt{\frac{s_{\mathrm{HS}}^2}{n_{\mathrm{HS}}}} \bullet \sqrt[4]{\frac{2}{v_{s_{\mathrm{HS}}^2}}} \qquad (25)$$

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 (24) was not valid , i. e. when

$$s^2_{inhom} \leq u^2_{bb} \,, \qquad (26)$$

the following equation was used instead of equation (23):

$$u_c = \sqrt{\frac{s_{\mathrm{M}}^2}{n} + u_{\mathrm{bb}}^2 + u_{lts}^2} \qquad (27)$$

In this case the combined uncertainty is consisting of the contribution of the interlaboratory comparison for certification and of the long-term instability and of a contribution representing a potential inhomogeneity which could be masked by the imprecision of the analytical procedure used in the homogeneity investigation.

In the case when no homogeneity investigation was carried out, the following equation was used instead of equations (23) or (27):

$$u_c = \sqrt{\frac{s_{\mathrm{M}}^2}{n} + u_{lts}^2} \qquad (28)$$

The contribution u_{lts} of an uncertainty caused by the possible aging of the material was discussed in chapter 5.

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

$$U = 2\, u_c \ . \qquad (29)$$

The following equations were used for the calculation of the combined uncertainties of the different analytes according to the different boundary conditions :

- for Ca, Co*, Cr, Fe, Na, Ni, Ti : Zr, C_{total}, C_{free}, N, B $_{\text{HNO3 soluble}}$	equation (23) combined with equation (22)
- for Al, Cu, Mg, O, B_{total}, B_2O_3:	equation (23) combined with equations (22) and (22´)
- for Mn and Si:	equation (27) combined with equation (25)
- for W** and $^{10}B_{\text{amount fraction}}$***:	equation (28)

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* For Co no homogeneity investigation had been carried out because of technical reasons (very low content resulting in low precision of analytical methods which could be used for homogeneity investigation). Based on the assumption of a strong correlation of the local mass content distribution of the higher concentrated nickel and of the lower concentrated cobalt, the relative standard deviations within and between the bottles as well as in the homogenized sample determined for nickel were also taken for cobalt and were converted to absolute standard deviations which were used as the basis for the calculation according to equations 1 and 2.

** For W no homogeneity investigation was carried out because its mass fraction is an indicative value only and not enough precisely to measure.

*** For ^{10}B amount fraction no homogeneity investigation was carried out because no reason could be found to assume that the isotopes of boron would be not homogenously distributed in the sample. Just as well no long time stability investigation was carried out, because no reason could be found to assume that this parameter could change in course of time. Therefore equation (7) was used for this parameter only based on the uncertainty term coming from the interlaboratory comparison for certification

In Tab. 8 the numerical basic values and the results of the calculation of the expanded uncertainties are given based on the equations (22) to (29) and the explanation given before, which equation was applied to the calculation of which parameter. The numerical values were compiled and calculated from the values in the Tables X in Appendix 7 (concerning s_M and n in Tab. 8) and from the values in the Tables in Appendix 5 (concerning s_b, s_w, s_{HS} and u_{bb}) as well as the values in the Tables 4.a – 4.f in chapter 5 (concerning u_{lts}).

Tab. 8: Numerical basic values for the calculation of the expanded uncertainty U of the certified and of the indicative parameters and final values of calculation

	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Si
s_M	8.7882	17.3778	0.0818	1.3044	0.6260	44.2650	2.0095	0.9919	0.8012	1.6364	36.3096
n	22	23	9	17	13	23	18	21	10	15	13
s_b	2.4750	1.2560	0.0312	0.4390	0.2090	5.6840	0.2050	0.0830	0.3408	0.6430	9.8700
s_w	1.7490	1.2150	0.0145	0.3170	0.1590	6.9300	0.0850	0.1270	0.2134	0.2980	15.2600
s_{HS}	2.0820	1.1170	0.0114	0.1410	0.1920	5.3890	0.1370	0.1430	0.1512	0.2350	17.0000
u_{bb}	0.265176	0.142268	0.001574	0.018676	0.024454	0.686376	0.018912	0.018213	0.032828	0.032440	3.6910
u_{lts}	0.5345	0.3284	0.001337	0.01916	0.00758	2.3334	0.01091	0.03527	0.0214	0.02727	0.91041
u_c	2.3636	3.714	0.0410	0.595	0.1921	10.603	0.4981	0.2198	0.4245	0.7555	10.764
U	4.73	7.43	0.0820	1.19	0.384	21.21	0.996	0.440	0.84910	1.51	21.53
~U	**5**	**8**	**0.09**	**1.2**	**0.4**	**22**	**1.0**	**0.5**	**0.9**	**1.6**	**22**
$^*U_{beg}$	**5**	**8**	**0.09**	**1.2**	**0.4**	**21**	**1.0**	**0.5**	**0.9**	**1.6**	**22**

	Ti	W	Zr	C-total	C-free	O	N	B-total	B-sol.	B_2O_3	B-isotope ratio
s_M	4.6300	2.2509	4.0316	0.2589	0.1178	0.0174	0.0198	0.3304	0.0116	0.0162	0.0183
n	22	5	20	22	5	12	12	16	7	9	7
s_b	2.1060		1.2140	0.0590	0.0240	0.0036	0.0064	0.2328	0.0031	0.0014	
s_w	1.8350		1.2040	0.0440	0.0225	0.0025	0.0047	0.2257	0.0040	0.0021	
s_{HSt}	1.5180		1.1120	0.0375	0.0186	0.0027	0.0023	0.1979	0.0019	0.0015	
u_{bb}	0.19334		0.141631	0.00814	0.00604	0.0005862	0.0004994	0.0285397	0.0006169	0.0002828	
u_{lts}	0.3261	0.01222	0.16627	0.11680	0.01045	0.0166	0.00928	0.06914	0.00121	0.00997	
u_c	2.068	1.0071	1.1362	0.1388	0.05721	0.01751	0.01308	0.1526	0.00626	0.01143	0.00694
U	4.14	2.01	2.27	0.278	0.114	0.0350	0.0262	0.305	0.0125	0.0229	0.0139
~U	**5**	**2.1**	**2.3**	**0.28**	**0.12**	**0.035**	**0.026**	**0.31**	**0.013**	**0.023**	**0.014**
$^*U_{beg}$	**5**	**2.1**	**2.3**	**0.15**	**0.12**	**0.011**	**0.018**	**0.28**	**0.012**	**0.011**	**0.014**

***$^*U_{beg}$* = Expanded uncertainty without the contribution of the potential long time instability**

8.3 Compilation of certified values and their uncertainties

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

Certified Values

	Certified value 1)	**Uncertainty 2)**
Parameter	**Mass fraction in mg/kg**	
Aluminium	157	± 5 (5)
Calcium	97	± 8 (8)
Cobalt	0.39	± 0.09 (0.09)
Chromium	5.6	± 1.2 (1.2)
Copper	2.2	± 0.4 (0.4)
Iron	686	± 22 (21)
Manganese	10.4	± 0.5 (0.5)
Sodium	6.3	± 0.9 (0.9)
Nickel	8.0	± 1.6 (1.6)
Silicon	268	± 22 (22)
Titanium	96	± 5 (5)
Zirconium	48.9	± 2.3 (2.3)
	Mass fraction in %	
Total Carbon	21.01	± 0.28 (0.15)
Oxygen	0.01	± 0.04 (0.011)
Nitrogen	0.209	± 0.026 (0.018)
Total Boron 3)	78.47	± 0.31 (0.28)
HNO_3 Soluble Boron 4)	0.116	± 0.013 (0.012)
Boron Oxide 5)	0.075	± 0.023 (0.011)
	Amount fraction in %	
^{10}Boron 6)	19.907	± 0.014 (0.014)

1) The certified values are the means calculated from the laboratory means of 7- 24 sets of single values (depending on the parameter) which were reported by the participating laboratories. Between 2 and 8 different analytical methods were used for the measurement of each parameter. The calibration of the methods applied for determination of element mass fractions was carried out by using pure substances of known stoichiometry or by solutions prepared from them, thus achieving traceability to the SI unit.

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. It includes contributions from sample inhomogeneity and from potential deterioration of the sample until the expiration of the validity of the certificate. Note: Values in parentheses do not include contributions from potential deterioration of the sample. These values were merely valid at the time of the measurements wich were carried out in the frame of the interlaboratory comparison for certification.

3) The recommended "Method M1" described in Appendix 1 can be used for the determination of total mass fraction of boron.

4) The recommended "Method M2" described in Appendix 2 can be used for the determination of mass fraction of in HNO_3 soluble boron.

5) The recommended "Method M3" described in Appendix 3 can be used for the determination of mass fraction of boron oxide.

6) Abundance sensitivity (amount fraction) of ^{10}Boron related to total amount of Boron.

8.4 Compilation of indicative values and their uncertainties

The following indicative values were also determined by using results of interlaboratory comparison and of calculations as described in 8.1 and 8.2.

Non certified, indicative values are given for additional analytes determined in the interlaboratory comparison by participating laboratories. They are given as indicative values, because the spread of values obtained was considerably larger than can be accepted for certified values.

	Indicative value 1)	**Uncertainty 2)**	
Parameter	**Mass fraction in mg/kg**		
Magnesium	3.2	±	1.0
Tungsten	3.6	±	2.1
	Mass fraction in %		
Free Carbon 3)	0.51	±	0.12

1) Indicative values are the means of 5-18 series of results (depending on the parameter) obtained by different laboratories. Between 1 and 4 different analytical methods have been used for the measurement of each parameter. The methods applied for the determination of mass fraction were not calibrated in all cases by pure substances of known stoichiometry or by solutions prepared from them.
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. The values are quoted for information purposes.
3) The prescribed “Method M4” described in attachment shall be used for the determination of mass fraction of free carbon.

8.5 Compilation of additional material data

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

		Particle size in µm
Particle size 1)	D_{10}	21.5
	D_{50}	33.6
	D_{90}	51.4
	D_{97}	60.4

1) The particle size distribution (volume) was determined by laser light diffraction method. Terms D_{xy} according to ISO 9276-1 [5].

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 boron carbide material are determined by a laboratory in the frame of the validation or the verification of a concerned analytical method. Additionally, 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 and a similar thermal decomposition behaviour or it can used for calibration in this context. .

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 parenthesis /mg): Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, W, Zr(250); Na, Si(10), C_{total}(25); O, N(50), C_{free}, B_{total}(100); $B_{soluble}$, B_2O_3(4000).. 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. For subsequent elemental analysis the sample has to be treated thermally at (135 ± 5) °C for 12 hours to achieve defined starting conditions. The pressure digestion procedure used before the determination of metallic analytes has to be checked to ensure that no analyte losses occur during the procedure.

9.3 Recommendations for correct storage

The sample should be stored in a dust-free and dry environment at room temperature (about 15 °C – 25 °C) avoiding contamination and moisture. No special cooling of the sample is necessary.

9.4 Expiration of certification

The date of expiry of certification is ten years after the date of interlaboratory comparison for certification, i. e. June 30, 2015. Before this date a new certificate will be prepared with a new date of expiry, if necessary.

9.5 Safety guidelines

1. First aid measures

   In the event of contact with the skin, rinse off with water and soap. After contamination of the eyes, they must be rinsed immediately with plenty of water. Seek medical advice in case of continuous irritation.
   If product is swallowed and in case of sickness seek medical advice. 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. Keep away from sources of ignition and do not smoke. Fine dust may form explosive mixture with air. Powder with particle size < 10 µm: Substance is rated to dust explosion class ST 1 according to German VDI 2263.

4. Exposure restriction and personal protection

   Do not smoke when handling. Do not breathe dust.
   Respiratory protection:
   Respirator fine mask with filter type P1 according to DIN EN 143
   Hand protection: not required
   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 the material is not contaminated and if possible. Address manufacturer. Or: May be disposed of in approved special landfills provided local regulations are observed.

10 References

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

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12 Appendices

- Appendix 1: Recommended Method 1: Determination of Total Boron (B_{total}) in Boron Carbide (B_4C) by Titrimetric Method (potentiometric titration)
- Appendix 2: Recommended Method M2: Determination of HNO_3 soluble Boron in Boron Carbide (B_4C) by Titrimetric Method
- Appendix 3: Recommended Method M3: Determination of Adherent Boron Oxide (B_2O_3) in Boron Carbide (B_4C) by Titrimetric Method
- Appendix 4: Prescribed Method M4: Determination of Free Carbon (C_{free}) in Boron Carbide (B_4C) by Wet Chemical Oxidation
- Appendix 5: Homogeneity investigations of the CRM-candidate material „Boron Carbide Powder“ (type 305F422)
- Appendix 6: Compilation of sample preparation procedures, calibrations and methods of final determination used by participating laboratories in interlaboratory comparison for certification of ERM®–ED102
- Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of ERM®–ED102

Determination of Total Boron (B_{total}) in Boron Carbide (B_4C) by Titrimetric Method (potentiometric titration)

Scope:

Determination of total boron content in technical boron carbide products such as B_4C raw material, grains, powders, and sintered and/or shaped parts by titrimetric method.

Summary of Method:

Powdered B_4C is decomposed with sodium-carbonate or a mixture of potassium-sodium-carbonate and subsequently dissolved in hydrochloric acid. The boron in the aqueous solution is titrated as boric acid with sodium hydroxide solution via mannitoboric acid after addition of mannitol.

Note 1: The final determination of total boron by means of ICP OES is possible but not object of this standard. It is to take into account, that great efforts are necessary to get sufficiently high precision and accuracy if ICP OES is used.

Note 2: Metals in higher contents may distort the inflection points of the titration and should be separated by barium carbonate precipitation.
No disturbances were found at contents of Al < 0,2 %, Fe < 2 %, Ti < 1 %.

Apparatus:

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

Potentiometric titration system, including dosing apparatus, magnetic stirrer and computer with appropriate titration software.

Burner, Bunsen-Burner.

Muffle Furnace, capable of maintaining a temperature of at least 750° C with a precision of at least ± 10°C.

Platinum crucible with close-fitting cover.

Analytical balance, capable of measuring to the nearest 0,01 mg.

Reagents:

All reagents must be of known analytical grade and it should ascertained that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination.

The used water shall be distilled water or water which has been fully demineralised by ion exchange (deionised water). Unless otherwise specified solutions are aqueous solutions.

Sodium hydroxide solution, NaOH, 0,1 n, CO_2-free, in an airtight plastic container with an airtight connection to the titration device, preferential in 10 L or 20 L container.

Sodium carbonate, $NaCO_3$, powdered or sodium carbonate / potassium carbonate, Na_2CO_3 / K_2CO_3, powdered, mixed 1:1.

Barium carbonate, $BaCO_3$, powdered.

Hydrochloric acid, 32% by volume and diluted 1:1 with water.

Sodium hydroxide, NaOH, 20 % by weight.

Sodium nitrate, $NaNO_3$, .

Mannitol, solid or as solution 10 % by weight.

Nitrogen, 99.998% v/v.

Sample preparation:

For analysis grain sizes of less than 0.15 mm are required. For samples with grain sizes greater than 0.15 mm or sintered or shaped bodies crush the sample in a suitable crushing device to pass a 0.150 mm sieve.
If the dryness of the sample is not warranted, dry the sample at 120ºC ± 5ºC for a minimum of 2 h. After cooling store the sample has to be stored in a desiccator.
If the homogeneity of the sample is not warranted, a representative quantity of sample has to be homogenized before analysis.

Procedure:

About 80 mg of the boron carbide (grain size < 0.15mm) are weighed to the nearest ± 0.01 mg and thoroughly mixed in a platinum crucible with 5 g Na_2CO_3 or 6 g K_2CO_3 / Na_2CO_3 .

Note 3: Boron contamination that can come from reagents and glassware has to be considered. Check all new lots of any reagents for boron contamination and use low boron glassware, thus boron contamination should be negligible.

Two different procedures of decomposition by fusion are described.

<u>i) Decomposition by fusion with a combination of a Bunsen burner and a second burner:</u>

Place a lid on the crucible with the mixture of digesting agent and sample powder and heat with a low flame of a Bunsen burner for 15 min. Continue heating while increasing the temperature for a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Allow the melt to cool down to room temperature.

Note 4: Most samples require about 1 to 1.5 h for complete decomposition.

Carefully add a spatula-tip of $NaNO_3$ (20 to 30 mg) to the cold molten mass and heat up again in the flame of a Bunsen burner to decompose the last residues of boron carbide. Conclude the melting process by swirling the crucible outside the flame using a crucible tongs until the liquid melt begins to solidify and covers the crucible wall. To liquefy the melt again, place back the crucible to the flame until crucible and lid are glowing. The heating of the upper part of the crucible and the lid is performed by means of a second burner.

Note 5: As second burner, hand torches with gas cartridge are very useful.

ii) Decomposition by fusion with a combination of muffle furnace and Bunsen burner

Place a close-fitting lid on the crucible with the mixture of digesting agent and sample powder and put it into the muffle furnace at ambient temperature. The crucibles should be placed into ceramic crucible supports.
At use of Na_2CO_3 heat up the furnace to 730°C ± 10 °C in 45 min (constant heating rate).
At use of K_2CO_3 / Na_2CO_3 heat up the furnace to 680°C ± 10 °C in 60 min (constant heating rate).
Keep the crucible at this temperature for at least 4 h. Allow cooling down to at least 400°C and take out the crucible.

Note 6: Advantageously perform the muffle furnace treatment over night by time programmer.

Place the crucible to the hot flame of a Bunsen burner until the sintered mixture is completely molten. Keep the temperature for about 5 to 10 min, until the whole sample has been decomposed, then allow the melt to cool down to room temperature.
Carefully add a spatula-tip of $NaNO_3$ (20 to 30 mg) to the cold molten mass and heat up again in the flame of a Bunsen burner to decompose the last residues of boron carbide. Conclude the melting by swirling the crucible outside the flame using a crucible tongs until the liquid melt begins to solidify and covers the crucible wall. To liquefy the melt again, place back the crucible to the flame until crucible and lid are glowing. The heating of the upper part of the crucible and the lid is performed by means of a second burner.

After cooling down to room temperature the melt is dissolved with 45 mL HCl 1:1 while gently heating the crucible.

Note 7: During dissolving the temperature should not exceed 40 °C to avoid losses of boric acid.

The hydrochloric - acid solution is transferred to a 250 mL volumetric flask and filled up to volume with water. An aliquot portion of 50 mL is pipetted into a 400 mL tall-form baker and neutralized with 20 % NaOH solution using universal pH-indicator paper or pH-meter.

With barium carbonate precipitation:
After admixing 1.5 mL concentrated HCl, 5 g barium carbonate is added carefully. The beaker is covered with a watch glass and the suspension heated to boiling for 5 minutes.

Note 8: A barium carbonate precipitation is not necessary when the content of hydroxide forming metal impurities is negligible, see **Note 2**.

The suspension is heated for 30 min at 60°C using a sand bath, then it is suction-filtered through an open-textured filter paper and subsequently washed 4 to 6 times with hot water. Filtrate and washing solution are collected in a 400 mL beaker.
The solution is acidified with diluted HCl to pH 2.5 - 3.0, covered with a watch glass and boiled for 3 minutes to remove CO_2.

Without barium carbonate precipitation:
The neutralized aliquot portion of 50 mL is diluted to 200 mL and acidified with diluted HCl to pH 2.5 - 3.0, covered with a watch glass and boiled for 3 minutes to remove CO_2.

Note 9: Alternatively CO_2 can also be removed by purging the solution with N_2.

Allow the solution to cool down to 20°C ± 1°C and begin to purge the sample solution with N_2 10 min before the titration starts.

Titration of Boron:

The solution is titrated to the first inflection point using the adjusted CO_2-free 0.1mol/L NaOH.
35 mL of a 10% mannitol solution (alternatively 4g of mannitol, powdered) is added and after the change of pH the titration is carried on to the second inflection point. During the whole titration the solution is purged with N_2.
The consumption of 0.1 mol/L NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron.

Note 10: For routine analysis it is highly recommended to perform the analysis in an air-conditioned room at a constant temperature of 20 °C.

Calculation:

The content of Total boron (B_{total}) shall be calculated as a percentage by mass, to the nearest 0.1%, using the following equation:

$$B_{total}\,\% = \frac{V_{NaOH} \times F \times f \times a \times 100}{m_S}$$

with:
V_{NaOH} = consumption of 0.1 mol/L NaOH, in mL
F = gravimetric factor in mg boron / ml 0.1 mol/L NaOH (theoretically 1.0811)
f = titer of NaOH (near 1,000)
a = aliquot part
m_S = mass of sample (B_4C), in mg

Note 11: In the case of automatically titration this calculation is done by the computer software.

Note 12: See Appendix for the evaluation of boron titration.

Precision:

The precision of this method is ± 0.2 % absolute at percentages by mass of 76-79%

Calibration:

The method can be calibrated by means of boric acid in using the same procedure like the sample; the certified reference material NBS SRM 951 is recommended.

Documentation:

- Sample identification,
- date of measurement,
- sample mass,
- data for calculation of result (additional),
- calculated results

Literature:

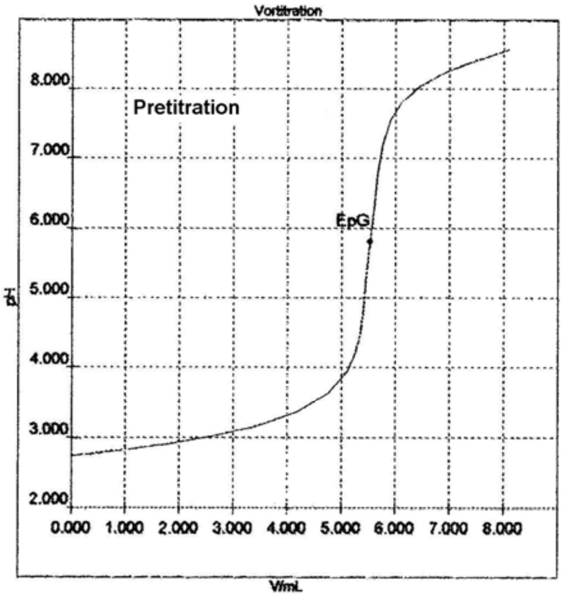
H. Blumenthal, Anal. Chem. 23 (1951) 992-994

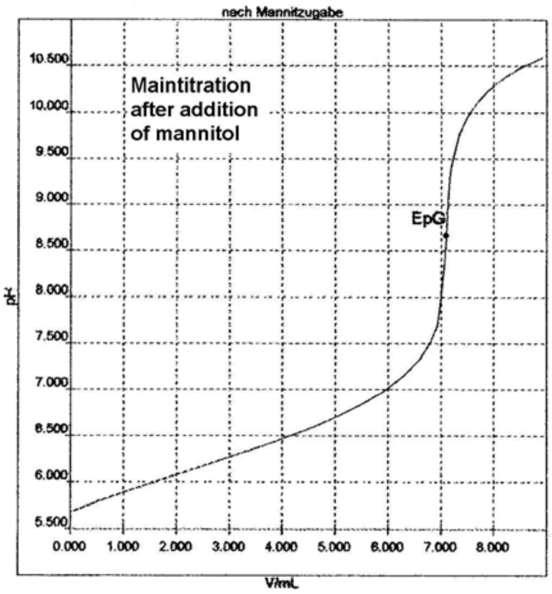
ASTM-C-791-83

Operating instruction of the titration system

Appendix:

Example of Boron titration via mannitoboric acid:





The titration curve on the left shows the pre-titration, starting at pH 2.75 and first inflection point at pH 5.76
The titration curve on the right shows the main-titration after mannitol addition, starting at pH 5.65 and second inflection point at pH 8.45.
In this example, the consumption between first inflection point and mannitol addition is 2.5741 mL and the consumption after mannitol addition and second inflection point is 7.0956 mL. This leads to a consumption of 0.1 mol/L NaOH between first and second inflection point of 9.6697 mL (2.5741 mL+7.0956 mL = 9.6697 mL).
The shown evaluation procedure is performed automatically using a state of the art, computer-aided, potentiometric titration system.

Determination of HNO_3 soluble Boron in Boron Carbide (B_4C) by Titrimetric Method

Scope:

Determination of boron soluble in HNO_3 in B_4C-grains, -powder and sintered parts by means of titrimetry.

Summary of Method:

Solid-liquid extraction of HNO_3 soluble boron in powdered B_4C with boiling 1.6 mol/L HNO_3.
The dissolved boric acid is then titrated in presence of mannitol as mannitoboric acid by potentiometric titration after separation of the metals dissolved by HNO_3-treatment as hydroxides.

NOTE 1: The final determination of boron by means of ICP OES is possible but not object of this standard.

Apparatus:

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

Potentiometric titration system, including dosing apparatus, magnetic stirrer and computer with appropriate titration software.

Reflux condenser with standard ground glass joint and heating plate.

200 ml Erlenmeyer flask with standard ground glass joint appropriate to the reflux condenser.

Analytical balance, capable of measuring to the nearest 0.1 mg.

Reagents:

All reagents must be of known analytical grade and it should ascertained that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination.
The used water shall be distilled water or water which has been fully demineralised by ion exchange (deionised water). Unless otherwise specified solutions are aqueous solutions.

Sodium hydroxide solution, NaOH, 0.1 mol/L, CO_2-free, in an airtight plastic container with an airtight connection to the titration device, preferential in 10 L or 20 L container.

Hydrochloric acid, HCl, 32% by volume, diluted 1 :1 with water.

Mannitol, solid or as solution, 10 % by weight.

Nitric acid, HNO_3 1.6 mol/L.

Sodium hydroxide solution, NaOH, 20 % by weight.

Sample preparation:

For analysis grain sizes of less than 0.15 mm are required. For samples with grain sizes greater than 0.15 mm or sintered bodies crush the sample in a suitable crushing device to pass a 0.150 mm sieve.
If the dryness of the sample is not warranted, dry the sample at 120 ºC ± 5 ºC for a minimum of 2 h. After cooling the sample has to be stored in a desiccator.
If the homogeneity of the sample is not warranted, a representative quantity of the sample has to be homogenized before analysis.

Procedure:

Weigh depending on the expected soluble B-content 1 to 5 g of sample into a 200 mL Erlenmeyer flask to the nearest 0.1 mg.

NOTE 2: For an expected HNO_3 soluble boron content of 0.1 to 0.2 % a sample amount of 3 g is recommended.

Add 100 ml of 1.6 mol/L HNO_3 to the Erlenmeyer flask. After connecting the reflux condenser, the sample is slightly boiled for 3 h on a heating plate. After cooling to room temperature filter the solution through filter paper (“Blaubandfilter”) and wash with H_2O.
Adjust the pH of the filtrate to about 11 using NaOH 20 %, then adjust back to pH 5.5 ± 0.5 using diluted HCl.
To precipitate metal hydroxides, the filtrate is heated to 60 °C (e.g. using a sand bath) for at least 1 h. The solution is filtered through filter paper to separate the hydroxides. Wash out the filter with hot water and collect both filtrate and washing solution in a 400 mL beaker.
The filtrate is acidified with diluted HCl to pH 3 ± 0.2, boiled for 5 minutes and then let cool down to room temperature.
Using the titration-system the solution is titrated with 0.1 mol/L NaOH to pH 7, then 40 mL of a 10% Mannitol-solution or 4 g of solid Mannitol is added and finally titrated to pH 8. The consumption of NaOH from pH 7 to pH 8 corresponds to the boron in the analysis solution.

NOTE 3: A titration-device with an end-point titrator can also be used.
Two titrations shall be carried out for each sample solution. The deviation of the common mean value may not exceed 5 %rel. If the deviation is more than 5 %rel., a third titration is required.

Evaluation:

The content of HNO_3 soluble boron shall be calculated as a percentage by mass, to the nearest 0.01%, using the following equation:

$$\text{soluble}B[\%] = \frac{V_{NaOH} * f * F * 100}{m_{sample}}$$

with:
V_{NaOH} = consumption of 0.1 mol/L NaOH, in mL
f = titre of NaOH (near 1.000)
m_{sample} = mass of sample, in mg
F = gravimetric factor in mg boron / ml 0.1 mol/L NaOH (theoretically 1.0811)

Precision:

The precision of this method is ± 0.02 absolute (at contents of 0.05 to 0.5% sol. boron).

Calibration:

The factor f can be determined with potassium hydrogen phthalate.
The gravimetric factor F is checked by using boric-acid.

Documentation:

- sample identification,
- date of analysis,
- sample mass,
- data for calculation of result, (additional),
- calculated results

Literature:

H. Blumenthal, Anal. Chem. 23 (1951) 992-994

ASTM-C-791-83

Operating instructions of the titration system

Determination of Adherent Boron Oxide (B_2O_3) in Boron Carbide (B_4C) by Titrimetric Method

Scope:

Determination of adherent boron oxide (B_2O_3) in B_4C-grains, B_4C-powder and sintered parts by means of titrimetry (calculated as B_2O_3)

Summary of Method:

Dissolution of the adherent boron oxide in H_2O at 60°C, the boric acid is then titrated in presence of mannitol as mannitoboric acid by potentiometric titration.

NOTE 1: Final determination of boron by means of ICP OES is possible but not object of this standard.

Apparatus:

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

Potentiometric titration system, including dosing apparatus, magnetic stirrer and computer with appropriate titration software.

Water bath with heating and temperature control to 60 ºC ± 5 ºC.

Analytical balance, capable of measuring to the nearest 0.1 mg.

Reagents:

All reagents must be of known analytical grade and it should ascertained that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination. The used water shall be distilled water or water which has been fully demineralised by ion exchange (deionised water). Unless otherwise specified solutions are aqueous solutions.

Sodium hydroxide solution, NaOH, 0.1 mol/L, CO_2-free, in an airtight plastic container with an airtight connection to the titration device, preferential in 10 L or 20 L container.

Hydrochloric acid, HCl, 32 % by volume, diluted 1:5 with water.

Mannitol, solid or as solution 10 % by weight.

Sample preparation:

For analysis grain sizes of less than 0.15 mm are required. For samples with grain sizes greater than 0.15 mm or sintered bodies crush the sample in a suitable crushing device to pass a 0.150 mm sieve.
If the dryness of the sample is not warranted, dry the sample at 120 ºC ± 5 ºC for a minimum of 2 h. After cooling the sample has to be stored in a desiccator.
If the homogeneity of the sample is not warranted, a representative quantity of the sample has to be homogenized before analysis.

Procedure:

Depending on the expected B_2O_3-content about 1-6 g of the sample are weighed into a 400 mL beaker to an accuracy of ± 0.1 mg. 200 mL of water is added, the mixture is stirred for 5 minutes with a magnetic stirrer and then placed into a water bath of 60 °C ± 5 °C for 1 h or of 100 °C ± 5 °C for 1h, in last case using a Erlenmeyer flask connected with a reflux condenser.

NOTE 2: For an expected B_2O_3 content of 0.1 to 0.2 % a sample amount of 4 g is recommended.

NOTE 3: If the sample contains a significant amount of Fe, visible through a slight yellow colour, Fe has to be removed by precipitation of iron-hydroxide at pH 6 and filtering of the solution.

The solution is cooled down to room temperature and acidified to pH 3 ± 0.2 with diluted HCl. Using the titration-system the solution is titrated with 0.1 mol/L NaOH to pH 7, then 35 ml of a 10% mannitol-solution or 4 g of solid Mannitol is added and finally titrated to pH 8. The consumption of NaOH from pH 7 to pH 8 corresponds to B_2O_3 in the analysis solution

NOTE 4: A titration-device with an end-point titrator can also be used.

Two titrations shall be carried out for each sample solution. The deviation of the common mean value may not exceed 5 %rel. If the deviation is more than 5 %rel., a third titration is required.

Evaluation:

The B_2O_3 content shall be calculated as a percentage by mass, to the nearest 0.01%, using the following equation:

$$B_2O_3[\%] = \frac{V_{NaOH} * f * F * 3.22 * 100}{m_{sample}}$$

with:
V_{NaOH} = consumption of 0.1 mol/L NaOH, in mL
f = titer of NaOH (near to 1.000)
m_{sample} = mass of sample, in mg
F = gravimetric factor in mg boron / ml 0.1 mol/L NaOH (theoretically 1.0811)
3.22 = factor $B \rightarrow B_2O_3$

Precision:

The precision of this method is ± 0.02 absolute (at contents of 0.05 to 0.50% B_2O_3).

Calibration:

The factor f can be determined with potassium hydrogen phthalate.
The gravimetric factor F is checked by using boric-acid.

Documentation:

- sample identification,
- date,
- sample mass,
- data for calculation of result (additional),
- calculated results

Literature:

H. Blumenthal, Anal. Chem. 23 (1951) 992-994

ASTM-C-791-83

Operating instruction of the titration system

Determination of Free Carbon (C_{free}) in Boron Carbide (B_4C) by Wet Chemical Oxidation

Scope:

The method describes the sample decomposition and the determination of Free carbon (C_{free}) in B_4C-grains and B_4C-powders and shaped or sintered bodies of B_4C after crushing by wet chemical oxidation.
The method is applicable to Free carbon contents of 0.01 % m/m to 5 % m/m. At higher concentrations incomplete recovery is possible.
By this method organic carbon and carbonate is determined as well.

Summary of Method:

The Free carbon of the sample is oxidized to carbon dioxide by hot chromic-sulfuric-iodic acid at a temperature of 100ºC. The inert gas carries the CO_2 to the coulometric detection system. The released CO_2 is detected as a function of the oxidation time.

NOTE 1: B_4C does react under these conditions, depending on the grain size, to a more or less pronounced extent. In case of B_4C samples with a narrow grain range this systematic error can be compensated by graphical extrapolation, in case of fine powders (less than 10 µm) the result may be wrong.

NOTE 2: Conductometric or infrared absorption CO_2 detection systems can be used as well.

Apparatus:

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

Coulometric analytical device with computer to record counts versus time and calculate the contend of C_{free} via graphical evaluation (see Appendix Fig.1)

Drying oven, with heating and temperature control to 135 ºC ± 5 ºC.

Reaction vessel, with cooling device and drying trap (see Appendix Fig. 2).

Aluminium heating-block, appropriate to the reaction vessel,
with temperature control to 100 ºC ± 5 ºC .

Aluminium capsules, e.g. ∅ 6 mm, L 15 mm, prepared from aluminium foil.

Analytical balance, capable of measuring to the nearest 0.01 mg.

Reagents and equipment:

All reagents must be of known analytical grade and it should ascertained that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination. The used water shall be distilled water or water which has been fully demineralised by ion exchange (deionised water). Unless otherwise specified solutions are aqueous solutions.

Sodium dichromate, $Na_2Cr_2O_7 * 2\ H_2O$.

Potassium iodate, KIO_3.

Calcium carbonate, $CaCO_3$.

Sulfuric acid, H_2SO_4, d = 1.84 g/mL.

Argon Ar, or nitrogen N_2 99.998 % v/v.

Chromic sulfuric iodic acid solution:
Prepared by dissolving 22 g of sodium dichromate in 300 mL of H_2O, and adding 700 mL of sulfuric acid. The solution is heated for 30 min at 150 °C ± 10 °C. Then 10 g of potassium iodate are added. After cooling the solution is stored in a glass bottle.

WARNING: Chromic-sulfuric-iodic acid should be handled with care in accordance with local safety regulations.

Sample preparation:

For the wet chemical oxidation grain sizes of less than 50 µm are required. For samples with grain sizes greater than 50 µm or sintered bodies crush the sample in a suitable crushing device to pass a 50 µm sieve.
If the dryness of the sample is not warranted, dry the sample at 120ºC ± 5ºC for a minimum of 2 h. After cooling the sample has to be stored in a desiccator .
If the homogeneity of the sample is not warranted, a representative quantity of the sample has to be homogenized before analysis.

Procedure:

The operation of the coulometric device has to be carried out in line with the operating instructions. The correct operation of the analysis system should be checked with $CaCO_3$ at least within 24 hours before usage.

NOTE 3: Usually 10 mg of $CaCO_3$ are used, which corresponds to a carbon content of 12.0 %.

Adjust the argon-gas stream to 50 L/h.

Put the reaction tube into the heating block and connect it with the coulometric system. Heat up the heating block to 100 °C ± 5 °C.
Add 40 mL of chromic-iodic-sulphuric acid to the reaction vessel.
Check the blank value of the system after the acid mixture has reached the required temperature for a minimum of 10 minutes.

According to the nature of the sample and the expected Free carbon content 20 to 100 mg of B_4C are weighed to the nearest 0.01 mg into an aluminum capsule. The capsule is closed with tweezers. The capsule is put into the heated acid mixture of the reaction tube via the sample introduction port. Simultaneously the coulometric system has to be started.
The reaction time should be 90 to 120 minutes.
The detector response, which is proportional to the released CO_2, should be recorded during the whole reaction time by means of a digital recording system (computer).
The recording is necessary for the graphical extrapolation as mentioned in NOTE 1 (see Appendix Fig. 3).

Calculation, evaluation:

For calculation, a graphical extrapolation from the printed plot is principally needed. This extrapolation can be done manually or by using an appropriate software.

In the case of equipment which produces impulses as analytical information (like the commonly used Ströhlein Coulomat) the C_{free} content shall be calculated as a percentage by mass, to the nearest 0,01%, using the following equation:

$$C_{free}[\%] = \frac{I_c * f_c * 100}{m_{sample}}$$

with:

I_c = corrected impulses (see Appendix Fig. 3)

m_{sample} = mass of sample, in mg

f_c = specific factor of the coulometric analytical device for conversion impulses into carbon mass, in mg. (In case of Ströhlein Coulomat is $f_c = 0.0002$)

Computer controlled modern equipments with the appropriate extrapolation software do not need this calculation procedure. In this case the C_{free} content is directly indicated as percentage by mass after entering the mass of sample.

Calibration:

The coulometric method is an absolute (true) method, therefore a calibration is not necessary.

The coulometric analytical device is checked by using $CaCO_3$, which corresponds to a carbon content of 12.0 %.

Documentation:

Storage of the computer-plot on which the following must be recorded:
- number of analysis,
- sample description,
- date of measurement,
- sample mass,
- content of Free carbon in % (result).

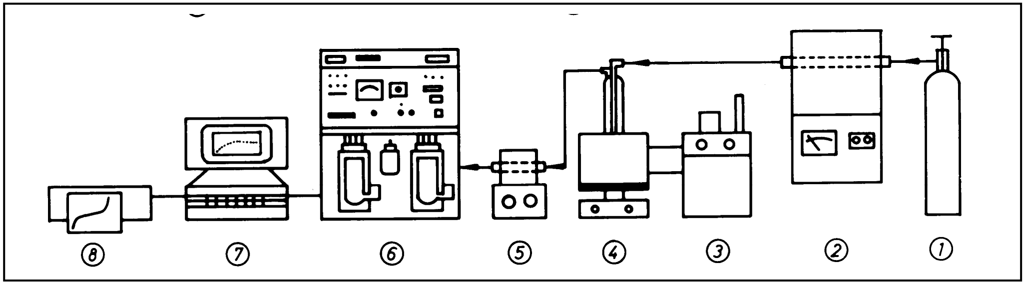
Literature:

K.A. Schwetz and J. Hassler "A wet chemical method for the determination of Free carbon in boron carbide, silicon carbide and mixtures thereof", Journal of the Less-Common Metals, 117 (1986), 7-15
Operating instructions of the coulometric system

Appendix:

Figure 1:

Coulometric detection device for Free carbon analysis of boron carbide



1 Argon- or Nitrogen-gas
2 Tube furnace
3 Thermostat
4 Reaction tube in Al-heating block
5 catalyst furnace optional
6 coulometric CO_2 detector
7 personal computer
8 printer

Coulometric method:

To determine the Free carbon content, the carbon present in the sample is oxidized to carbon dioxide by hot chromic-sulfuric-iodic acid in a reaction cell purged with argon or nitrogen. Together with the carrier- or reaction gas the combustion gases are drawn off by a pump through a tube containing percarbamide, which absorbs the oxidation products of the sulfur contained in the sample. The carbon dioxide is transferred to a titration cell filled with alkaline barium perchlorate solution, where it is absorbed with a consequent reduction in the alkalinity of the solution. Automatic back titration to the initial pH value of the solution is carried out using electrolytically generated barium hydroxide. According to Faraday's law, the amount of electricity consumed is deemed to be a measure of the absolute carbon content of the sample.

Figure 2:

Example of a reaction vessel of Free carbon determination by wet oxidation

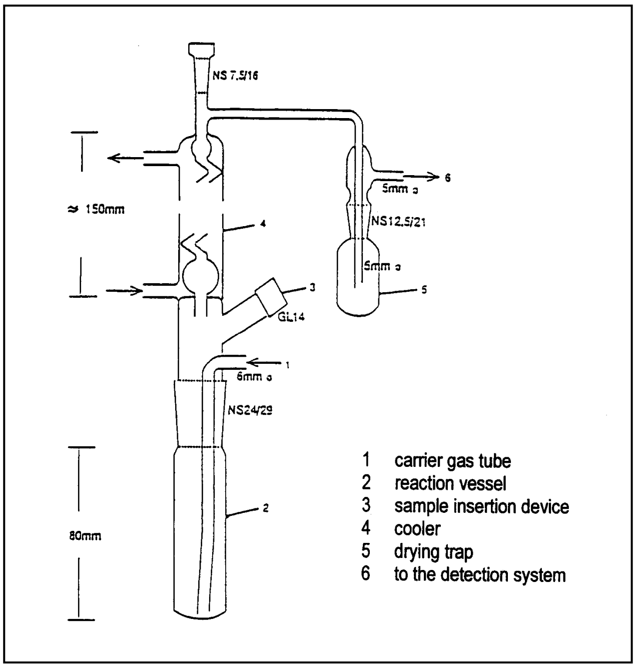
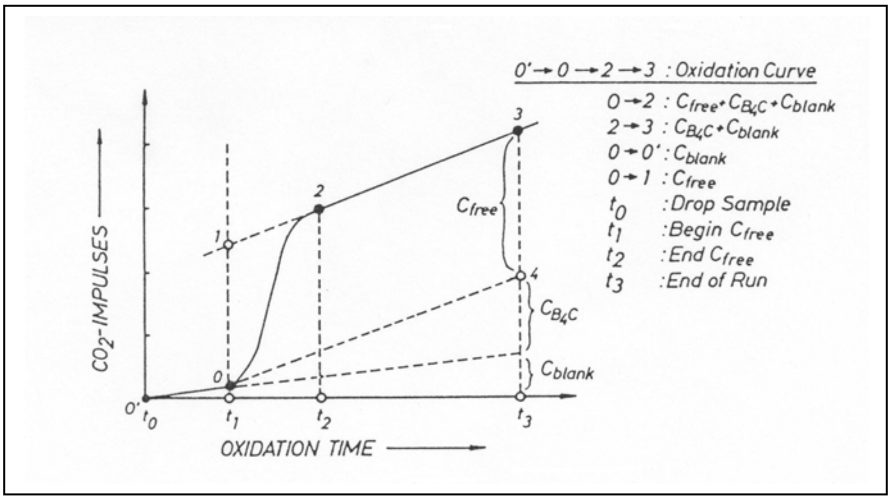


Figure 3:

A plot of CO_2 concentration (impulses) vs. time with graphical extrapolation



The calculation/evaluation of I_c is demonstrated by the graphical extrapolation.
The graphical extrapolation is executed by the following steps:

1. the starting point t_1 is determined from the first inflection (point 0) on the oxidation curve, which corresponds to the destruction of the capsule and the start of reaction.
2. an ordinate is drawn trough t_1.
3. the line between points 2 and 3 is extended to the left were it intersects the ordinate in point 1; and
4. the extrapolated impulses are converted to corrected impulses (I_c) by subtracting the blank impulses at t_1.

It is also possible to calculate the graphical extrapolation by computer with adequate software.

Appendix 5 of the Certification Report of ERM®-ED102

Homogeneity investigations of the CRM-candidate material "Boron Carbide Powder (type 305F422)"

Content

The tables are listed in the following order of investigated parameters (analytes):

Al, Ca, Cr, Cu, Mg, Mn, Na, Ni, Si, Ti, Zr, Total C, Free C, O, N, B, HNO_3 soluble B, B_2O_5

The explanation of the tables and the conclusions from the results of the investigation can be found in chapters 4.2.2 – 4.2.5 of this Certification Report

Analyte: Al

mass fraction in mg/kg

Line number	Sample number	Al 394.4	Al 396.1	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
1	4/1	146.9445	153.4555	150.2000			
	4/2	147.2839	151.9201	149.6020			
	4/3	148.3193	153.6559	150.9876			
	4/4	149.4105	155.2619	152.3362	150.781	1.182	0.78
2	27/1	148.0434	153.7063	150.8749			
	27/2	149.2688	155.1642	152.2165			
	27/3	146.6960	152.9004	149.7982			
	27/4	156.7922	163.0833	159.9378	153.207	4.595	3.00
3	48/1	147.0082	152.9410	149.9746			
	48/2	147.9828	154.5940	151.2884			
	48/3	148.8717	155.6304	152.2511			
	48/4	151.4321	159.0913	155.2617	152.194	2.248	1.48
4	58/1	147.3149	150.6339	148.9744			
	58/2	144.2845	147.9666	146.1256			
	58/3	150.8097	154.1389	152.4743			
	58/4	146.8259	153.3661	150.0960	149.418	2.636	1.76
5	79/1	146.6166	153.6897	150.1531			
	79/2	147.9936	153.8663	150.9300			
	79/3	148.3832	154.2343	151.3087			
	79/4	148.7349	155.9312	152.3331	151.181	0.906	0.60
6	91/1	147.5899	154.1364	150.8631			
	91/2	149.9291	156.3776	153.1534			
	91/3	147.5027	154.7449	151.1238			
	91/4	151.4391	158.4001	154.9196	152.515	1.902	1.25
7	104/1	148.1709	154.7010	151.4359			
	104/2	146.9399	152.8553	149.8976			
	104/3	148.3114	153.9261	151.1188			
	104/4	148.3903	154.5068	151.4485	150.975	0.734	0.49

Analyte: Al

Line number	Sample number	Al 394.4	Al 396.1	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
8	116/1	145.7032	152.2276	148.9654			
	116/2	147.7137	154.1399	150.9268			
	116/3	146.5643	152.0883	149.3263			
	116/4	147.3951	151.9599	149.6775	149.724	0.853	0.57
9	143/1	148.1247	153.6582	150.8915			
	143/2	145.9482	153.1741	149.5611			
	143/3	144.9121	152.1369	148.5245			
	143/4	144.3093	151.6844	147.9969	149.243	1.276	0.86
10	145/1	145.8408	153.4278	149.6343			
	145/2	142.8224	150.2498	146.5361			
	145/3	146.0612	153.7875	149.9244			
	145/4	146.9264	154.3301	150.6282	149.181	1.812	1.21
11	175/1	144.9094	152.6796	148.7945			
	175/2	145.9202	153.0738	149.4970			
	175/3	146.4482	154.4950	150.4716			
	175/4	145.7914	153.0512	149.4213	149.546	0.693	0.46
12	190/1	147.7128	153.1891	150.4510			
	190/2	146.2411	152.7113	149.4762			
	190/3	146.3899	153.0006	149.6953			
	190/4	147.5961	154.5154	151.0558	150.170	0.723	0.48
13	207/1	149.7545	156.8915	153.3230			
	207/2	150.0349	158.7263	154.3806			
	207/3	144.8299	151.5445	148.1872			
	207/4	144.6755	152.4982	148.5868	151.119	3.189	2.11
14	212/1	145.8099	152.3688	149.0893			
	212/2	145.6531	152.8053	149.2292			
	212/3	146.8775	153.1352	150.0064			
	212/4	145.7469	151.7639	148.7554	149.270	0.530	0.35
15	228/1	146.3371	154.2370	150.2870			
	228/2	145.9180	153.4947	149.7063			
	228/3	146.5474	153.7185	150.1329			
	228/4	144.4608	152.2259	148.3433	149.617	0.884	0.59

Analyte: Al

Line number	Sample number	Al 394.4	Al 396.1	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
16	247/1	144.5444	152.4971	148.5208			
	247/2	145.3784	153.9289	149.6537			
	247/3	146.2230	152.0181	149.1206			
	247/4	146.5622	152.9468	149.7545	149.262	0.567	0.38
17	270/1	147.2885	154.1416	150.7150			
	270/2	145.5686	153.1190	149.3438			
	270/3	146.6195	154.1141	150.3668			
	270/4	143.3583	151.9002	147.6292	149.514	1.385	0.93
18	285/1	146.6090	155.4132	151.0111			
	285/2	147.6508	156.1791	151.9150			
	285/3	149.4231	157.8266	153.6248			
	285/4	147.9822	156.0661	152.0241	152.144	1.087	0.71
19	298/1	145.9783	153.8078	149.8931			
	298/2	146.8855	154.6136	150.7496			
	298/3	147.1649	154.2225	150.6937			
	298/4	146.2682	154.5954	150.4318	150.442	0.391	0.26
20	313/1	146.5952	155.2955	150.9454			
	313/2	145.6003	153.9846	149.7925			
	313/3	145.4311	154.4078	149.9194			
	313/4	145.6598	154.9207	150.2903	150.237	0.517	0.34

M_{ss} - mean of means of the sub-samples 1-4	150.487
SD of means of the sub-samples 1-4	1.237
RSD (rel.%)	0.82

mean RSD_w (%) 0.93

Analyte: Al

HS = Homogeneous sample

Line number	Sample number	Al 394.4	Al 396.1	mean over 2 lines
1	HS1	146.4332	153.5615	149.9973
2	HS2	146.2800	152.4779	149.3790
3	HS3	145.3445	151.7401	148.5423
4	HS4	146.8344	152.4838	149.6591
5	HS5	147.4453	154.0101	150.7277
6	HS6	148.7060	154.9020	151.8040
7	HS7	145.9778	152.0780	149.0279
8	HS8	148.2859	156.3803	152.3331
9	HS9	154.5032	161.3458	157.9245
10	HS10	147.1130	152.7276	149.9203
11	HS11	147.7288	153.7799	150.7543
12	HS12	145.6358	151.6875	148.6617
13	HS13	146.6328	153.3573	149.9951
14	HS14	147.5295	154.6517	151.0906
15	HS15	146.7159	152.8566	149.7862
16	HS16	148.4822	152.5667	150.5245
17	HS17	147.8760	151.0614	149.4687
18	HS18	147.4566	150.4994	148.9780
19	HS19	147.4932	149.5909	148.5420
20	HS20	150.1083	153.5929	151.8506

M_{HS} - mean of homogeneous sample	150.4483
SD_{HS}	2.0816
RSD_{HS} (%)	1.38

Analyte: Al

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w	1.749	**M_{ss}** 150.49	**RSD %** 0.82
standard deviation between the samples s_b	2.475	**F_{value}**	1.768
test value s_b^2/s_w^2	2.001	**Characteristic no. for homogeneity between the samples**	1.132
Homogeneity between the samples: Not very strong inhomogeneity			

Homogeneity within the samples			
Analysis of variance: α = 0.05			
standard deviation of homogeneous sample SD_{HS}	2.082	**M_{HS}** 150.45	**RSD_{HS} %** 1.38
		F_{value}	1.980
test value s_w^2/s_{HS}^2	0.706	**Characteristic no. for homogeneity within the samples**	0.356
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Ca

mass fraction in mg/kg

Line number	Sample number	Ca 393,3 radial	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	90.8146			
	4/2	89.9003			
	4/3	90.8106			
	4/4	88.6824	90.052	1.009	1.12
2	27/1	91.7003			
	27/2	91.2596			
	27/3	90.7805			
	27/4	89.6478	90.847	0.883	0.97
3	48/1	90.4389			
	48/2	92.6593			
	48/3	91.7356			
	48/4	90.7296	91.391	1.012	1.11
4	58/1	91.4488			
	58/2	86.5460			
	58/3	93.1416			
	58/4	89.4314	90.142	2.837	3.15
5	79/1	91.2183			
	79/2	92.1487			
	79/3	92.5295			
	79/4	92.6020	92.125	0.636	0.69
6	91/1	91.5098			
	91/2	90.3505			
	91/3	91.9436			
	91/4	91.1009	91.226	0.678	0.74
7	104/1	91.1328			
	104/2	90.3064			
	104/3	90.8035			
	104/4	90.7270	90.742	0.340	0.37
8	116/1	88.0105			
	116/2	91.5151			
	116/3	89.1215			
	116/4	90.4529	89.775	1.531	1.70
9	143/1	91.8836			
	143/2	91.5561			
	143/3	90.1395			
	143/4	90.9575	91.134	0.766	0.84
10	145/1	89.6875			
	145/2	88.0075			
	145/3	90.0249			
	145/4	91.9059	89.906	1.599	1.78

Analyte: Ca

Line number	Sample number	Ca 393,3 radial	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
11	175/1	90.5904			
	175/2	90.0869			
	175/3	91.7129			
	175/4	89.4226	90.453	0.966	1.07
12	190/1	90.5818			
	190/2	90.2329			
	190/3	91.2767			
	190/4	91.3084	90.850	0.531	0.58
13	207/1	91.1359			
	207/2	89.9047			
	207/3	90.3305			
	207/4	90.4497	90.455	0.511	0.56
14	212/1	89.7310			
	212/2	88.3217			
	212/3	92.2650			
	212/4	90.5317	90.212	1.645	1.82
15	228/1	90.5108			
	228/2	91.2587			
	228/3	88.3500			
	228/4	92.2259	90.586	1.648	1.82
16	247/1	90.3251			
	247/2	91.4061			
	247/3	89.4579			
	247/4	91.6982	90.722	1.029	1.13
17	270/1	92.8285			
	270/2	90.8606			
	270/3	91.3113			
	270/4	91.9978	91.750	0.858	0.94
18	285/1	89.1670			
	285/2	91.8848			
	285/3	89.5543			
	285/4	90.6244	90.308	1.219	1.35
19	298/1	90.4263			
	298/2	90.6340			
	298/3	90.0565			
	298/4	92.1422	90.815	0.917	1.01
20	313/1	91.2511			
	313/2	89.3704			
	313/3	88.7454			
	313/4	90.2276	89.899	1.087	1.21

M_{ss} - mean of means of the sub-samples 1-4 90.670

SD of means of the sub-samples 1-4 0.628

RSD (rel.%) 0.69 **mean RSD$_w$ (%)** 1.20

Analyte: Ca

HS = Homogeneous sample

Line number	Sample number	Ca 393,3 radial
1	HS1	90.8198
2	HS2	90.3527
3	HS3	89.0451
4	HS4	91.3769
5	HS5	91.2689
6	HS6	92.5711
7	HS7	92.4234
8	HS8	90.7894
9	HS9	92.0365
10	HS10	92.8188
11	HS11	90.8053
12	HS12	90.9725
13	HS13	91.9692
14	HS14	94.0085
15	HS15	91.9275
16	HS16	92.0994
17	HS17	92.9489
18	HS18	90.2802
19	HS19	91.6656
20	HS20	91.3981

M_{HS} - mean of homogeneous sample	91.579
SD_{HS}	1.117
RSD_{HS} (%)	1.22

Analyte: Ca

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w	1.215	**M_{ss}** 90.67	**RSD %** 0.69
standard deviation between the samples s_b	1.256	**F_{value}**	1.768
test value s_b^2/s_w^2	1.069	**Characteristic no. for homogeneity between the samples**	0.605
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: α = 0.05			
standard deviation of homogeneous sample SD_{HS}	1.117	**M_{HS}** 91.58	**RSD_{HS} %** 1.22
		F_{value}	1.980
test value s_w^2/s_{HS}^2	1.183	**Characteristic no. for homogeneity within the samples**	0.598
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Cr

mass fraction in mg/kg

Line number	Sample number	Cr 205.5	Cr 206.1	Cr 267.7	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	4.8720	3.8249	4.9198	4.5389			
	4/2	5.0667	3.9234	4.9842	4.6581			
	4/3	5.0607	3.9966	5.0723	4.7099			
	4/4	4.9998	3.8019	5.0166	4.6061	4.628	0.073	1.58
2	27/1	4.8969	3.9706	4.9567	4.6081			
	27/2	5.0167	4.0625	5.0275	4.7023			
	27/3	4.9829	3.9293	5.0335	4.6486			
	27/4	5.0473	3.9438	4.9618	4.6510	4.652	0.039	0.83
3	48/1	5.0841	3.8961	5.1990	4.7264			
	48/2	5.0115	3.9485	4.8722	4.6107			
	48/3	4.8581	3.6491	4.7028	4.4033			
	48/4	5.1058	4.0291	4.9787	4.7045	4.611	0.147	3.20
4	58/1	4.9711	3.9316	4.8556	4.5861			
	58/2	4.7533	3.6961	4.6462	4.3652			
	58/3	5.1438	4.1007	5.0292	4.7579			
	58/4	4.8518	3.7776	4.7329	4.4541	4.541	0.171	3.76
5	79/1	5.4468	4.1502	5.4770	5.0247			
	79/2	4.7491	3.6571	4.8158	4.4073			
	79/3	5.0818	4.0666	4.9871	4.7118			
	79/4	4.9478	3.8131	4.8372	4.5327	4.669	0.268	5.74
6	91/1	5.0186	4.0422	4.9474	4.6694			
	91/2	5.1519	4.1511	5.1746	4.8259			
	91/3	5.0470	4.0082	4.8454	4.6335			
	91/4	5.0506	3.9351	4.8745	4.6201	4.687	0.095	2.02

Analyte: Cr

Line number	Sample number	Cr 205.5	Cr 206.1	Cr 267.7	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
7	104/1	5.1606	4.1314	4.9499	4.7473			
	104/2	4.9622	3.9620	4.8099	4.5781			
	104/3	4.9246	3.9221	4.7697	4.5388			
	104/4	4.8669	3.7108	4.8514	4.4764	4.585	0.116	2.53
8	116/1	4.9054	3.6619	4.7687	4.4453			
	116/2	5.0050	3.8622	4.9669	4.6114			
	116/3	5.7517	4.6764	5.6829	5.3703			
	116/4	5.1438	3.9476	5.0687	4.7200	4.787	0.405	8.46
9	143/1	4.8042	3.7790	4.8623	4.4818			
	143/2	4.9751	3.9658	4.8907	4.6105			
	143/3	5.0491	4.0843	4.8409	4.6581			
	143/4	5.2846	4.3743	5.2213	4.9601	4.678	0.202	4.33
10	145/1	5.1258	4.2588	4.8759	4.7535			
	145/2	4.7852	3.7916	4.5583	4.3784			
	145/3	5.5844	4.3685	5.1292	5.0273			
	145/4	4.9386	3.9993	4.7279	4.5552	4.679	0.278	5.95
11	175/1	5.1159	4.0968	4.7389	4.6505			
	175/2	5.3845	4.2246	5.2148	4.9413			
	175/3	5.3595	4.2301	5.1240	4.9045			
	175/4	5.3841	4.2488	4.9973	4.8767	4.843	0.131	2.71
12	190/1	5.4738	4.3550	5.1181	4.9823			
	190/2	5.6625	4.3379	5.2993	5.0999			
	190/3	5.2568	3.9140	4.8702	4.6803			
	190/4	5.7068	4.6304	5.4724	5.2699	5.008	0.248	4.96
13	207/1	5.6870	4.5717	5.2903	5.1830			
	207/2	4.9427	3.8806	4.6837	4.5023			
	207/3	6.1125	5.1725	5.8772	5.7207			
	207/4	5.4393	4.2996	5.0141	4.9176	5.081	0.510	10.04

Analyte: Cr

Line number	Sample number	Cr 205.5	Cr 206.1	Cr 267.7	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
14	212/1	5.3188	4.1149	5.0892	4.8410			
	212/2	5.3802	4.2817	5.0888	4.9169			
	212/3	5.7973	4.5527	5.6687	5.3396			
	212/4	5.8650	4.7918	5.7421	5.4663	5.141	0.308	6.00
15	228/1	5.0505	4.0154	4.8934	4.6531			
	228/2	6.1232	5.1287	5.9814	5.7444			
	228/3	5.7177	4.5728	5.5228	5.2711			
	228/4	5.1593	4.0999	4.8476	4.7023	5.093	0.517	10.15
16	247/1	5.1421	3.8579	5.1438	4.7146			
	247/2	5.2611	4.1227	5.1168	4.8336			
	247/3	6.1464	5.0342	5.9781	5.7195			
	247/4					5.089	0.549	10.79
17	270/1							
	270/2	5.4107	4.3723	5.1364	4.9731			
	270/3	5.2032	4.0042	4.9618	4.7230			
	270/4	5.8319	4.6790	5.5988	5.3699	5.022	0.326	6.50
18	285/1	6.0342	4.8694	5.5002	5.4679			
	285/2	5.3853	4.2808	4.9998	4.8886			
	285/3	5.4559	4.1151	4.8951	4.8220			
	285/4	6.3427	4.9549	5.7593	5.6856	5.216	0.427	8.18
19	298/1	5.3369	4.1433	4.7623	4.7475			
	298/2	5.4157	4.0952	5.0383	4.8497			
	298/3	6.4742	5.1765	5.9524	5.8677			
	298/4	5.5613	4.3694	4.8581	4.9296	5.099	0.518	10.16
20	313/1	5.2658	4.0494	4.7028	4.6727			
	313/2	5.3746	4.0381	4.8579	4.7569			
	313/3	5.5362	4.0559	5.1760	4.9227			
	313/4	5.5456	4.2340	5.1383	4.9727	4.831	0.140	2.90

M_{ss} - mean of means of the sub-samples 1-4 4.847

SD of means of the sub-samples 1-4 0.222

RSD (rel.%) 4.58

mean RSD_w(%) 8.55

Analyte: Cr

HS = Homogeneous sample

Line number	Sample number	Cr 205.5	Cr 206.1	Cr 267.7	mean over 3 lines
1	HS1	5.0493	4.1260	4.9569	4.7107
2	HS2	4.8497	3.6998	4.8594	4.4696
3	HS3	5.0599	3.9551	4.9484	4.6544
4	HS4	4.9735	3.7967	4.7712	4.5138
5	HS5	4.9761	3.8702	4.8789	4.5751
6	HS6	5.3386	4.1006	5.2416	4.8936
7	HS7	5.2257	4.0414	5.1359	4.8010
8	HS8				
9	HS9	5.0386	3.7748	4.8004	4.5379
10	HS10	5.3424	4.1440	5.3951	4.9605
11	HS11	4.9639	3.7010	4.7691	4.4780
12	HS12	5.3341	4.1104	5.1794	4.8746
13	HS13	4.9493	3.9479	4.9862	4.6278
14	HS14	5.0884	4.0360	5.0490	4.7245
15	HS15	4.9991	4.0316	5.0582	4.6963
16	HS16	5.0036	4.0397	4.9063	4.6498
17	HS17	4.9758	4.0183	5.0326	4.6756
18	HS18	4.9881	4.0964	5.1595	4.7480
19	HS19	4.8777	3.6591	4.9984	4.5117
20	HS20	5.0397	3.9541	4.9918	4.6619

M_{HS} - mean of homogeneous sample	4.672
SD_{HS}	0.141
RSD_{HS} (%)	3.03

Analyte: Cr

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w	0.317	**M_{ss}** 4.847	**RSD %** 4.58
standard deviation between the samples s_b	0.439	**F_{value}**	1.7946
test value s_b^2/s_w^2	1.914	**Characteristic no. for homogeneity between the samples**	1.067
Homogeneity between the samples: Not very strong inhomogeneity			

Homogeneity within the samples			
Analysis of variance: α = 0.05			
standard deviation of homogeneous sample SD_{HS}	0.141	**M_{HS}**	**RSD_{HS} %**
		4.672	3.03
		$F_{(Tab.)}$	2.024
test value s_w^2/s_{HS}^2	5.034	**Characteristic no. for homogeneity within the samples**	2.487
Homogeneity within the samples: Strong inhomogeneity			

Analyte: Cu

mass fraction in mg/kg

Line number	Sample number	Cu 327.3	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	2.9326			
	4/2	2.9910			
	4/3	3.0236			
	4/4	3.0054	2.988	0.039	1.32
2	27/1	3.1034			
	27/2	3.1125			
	27/3	2.9445			
	27/4	3.1946	3.089	0.105	3.39
3	48/1	3.1255			
	48/2	3.1011			
	48/3	3.3006			
	48/4	2.9936	3.130	0.127	4.06
4	58/1	2.9216			
	58/2	2.9469			
	58/3	2.8699			
	58/4	3.0870	2.956	0.093	3.14
5	79/1	3.0230			
	79/2	2.8187			
	79/3	2.9691			
	79/4	3.0027	2.953	0.092	3.13
6	91/1	2.9735			
	91/2	3.0217			
	91/3	3.0583			
	91/4	3.1286	3.046	0.065	2.15
7	104/1	3.0015			
	104/2	2.7829			
	104/3	2.7644			
	104/4	2.7144	2.816	0.127	4.51
8	116/1	3.0533			
	116/2	3.0808			
	116/3	2.7802			
	116/4	3.2219	3.034	0.185	6.09
9	143/1	2.8923			
	143/2	2.9117			
	143/3	2.8922			
	143/4	2.8349	2.883	0.033	1.15
10	145/1	2.8142			
	145/2	2.4640			
	145/3	3.0626			
	145/4	2.8601	2.800	0.249	8.88
11	175/1	3.0685			
	175/2	2.7769			
	175/3	2.9427			
	175/4	2.9384	2.932	0.119	4.08

Analyte: Cu

Line number	Sample number	Cu 327.3	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
12	190/1	2.7860			
	190/2	3.0356			
	190/3	2.8465			
	190/4	2.9621	2.908	0.112	3.86
13	207/1	2.7218			
	207/2	2.9475			
	207/3	3.0576			
	207/4	3.0498	2.944	0.157	5.32
14	212/1	2.9706			
	212/2	3.2076			
	212/3	3.0644			
	212/4	3.0494	3.073	0.099	3.21
15	228/1	2.7666			
	228/2	2.5846			
	228/3	2.6796			
	228/4	2.9879	2.755	0.172	6.26
16	247/1	2.9489			
	247/2	2.5466			
	247/3	3.1467			
	247/4	2.7986	2.860	0.253	8.85
17	270/1	2.9974			
	270/2	2.9613			
	270/3	2.7446			
	270/4	2.8175	2.880	0.119	4.14
18	285/1	2.8388			
	285/2	2.5166			
	285/3	2.7928			
	285/4	3.0407	2.797	0.216	7.72
19	298/1	2.8849			
	298/2	2.8217			
	298/3	2.9126			
	298/4	2.9931	2.903	0.071	2.45
20	313/1	2.7175			
	313/2	2.5061			
	313/3	2.8964			
	313/4	3.3348	2.864	0.352	12.30

M_{ss} - mean of means of the sub-samples 1-4	2.931
SD of means of the sub-samples 1-4	0.105
RSD (rel.%)	3.57

mean RSD_w (%) 4.80

Analyte: Cu

HS = Homogeneous sample

Line number	Sample number	Cu 327.3
1	HS1	3.1566
2	HS2	3.3187
3	HS3	3.1281
4	HS4	3.2410
5	HS5	2.9276
6	HS6	3.2583
7	HS7	2.8015
8	HS8	3.0332
9	HS9	3.0782
10	HS10	3.1684
11	HS11	3.1291
12	HS12	3.0895
13	HS13	2.8227
14	HS14	2.8004
15	HS15	3.1717
16	HS16	2.7611
17	HS17	2.6332
18	HS18	3.0136
19	HS19	3.0805
20	HS20	2.8058

M_{HS} - mean of homogeneous sample	3.021
SD_{HS}	0.192
RSD_{HS} (%)	6.35

Analyte: Cu

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.159	**M_{ss}** 2.93	**RSD %** 3.57
standard deviation between the samples s_b	0.209	**F_{value}**	1.768
test value s_b^2/s_w^2	1.725	**Characteristic no. for homogeneity between the samples**	0.976
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.192	**M_{HS}** 3.021	**RSD_{HS} %** 6.35
		F$_{value}$	1.980
test value s_w^2/s_{HS}^2	0.690	**Characteristic no. for homogeneity within the samples**	0.348
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Fe

mass fraction in mg/kg

Line number	Sample number	Fe 238.2	Fe 240.4	Fe 258.5	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	656.4358	651.1325	649.0652	652.2111			
	4/2	663.9898	656.9303	655.8203	658.9135			
	4/3	670.6699	665.4864	662.1205	666.0923			
	4/4	665.7079	660.3993	657.5740	661.2271	659.611	5.770	0.87
2	27/1	668.4574	664.9384	661.3600	664.9186			
	27/2	669.8752	666.5974	663.0370	666.5032			
	27/3	660.6637	655.1050	651.6897	655.8195			
	27/4	663.5373	658.3353	655.4465	659.1064	661.587	4.990	0.75
3	48/1	661.2499	655.4344	653.9452	656.8765			
	48/2	665.9525	660.8337	658.4952	661.7605			
	48/3	664.1906	656.6524	655.4971	658.7801			
	48/4	669.5797	663.2635	662.6668	665.1700	660.647	3.624	0.55
4	58/1	665.7509	659.6917	656.8911	660.7779			
	58/2	639.2783	633.8883	630.7715	634.6460			
	58/3	678.2354	672.1575	669.6940	673.3623			
	58/4	655.1046	649.9844	647.8217	650.9702	654.939	16.341	2.50
5	79/1	662.9316	657.4945	655.7697	658.7320			
	79/2	660.7511	654.2350	652.5564	655.8475			
	79/3	665.8513	659.4709	658.1386	661.1536			
	79/4	669.2609	664.1080	661.2934	664.8874	660.155	3.829	0.58
6	91/1	661.6831	656.7400	653.9390	657.4540			
	91/2	660.6595	654.9971	652.6492	656.1019			
	91/3	661.8027	655.2314	654.0289	657.0210			
	91/4	666.1221	660.3459	657.7373	661.4018	657.995	2.340	0.36
7	104/1	666.3518	660.0713	658.1766	661.5332			
	104/2	665.0280	658.1173	655.8224	659.6559			
	104/3	663.5165	658.6486	655.4103	659.1918			
	104/4	658.0491	653.5092	649.5279	653.6954	658.519	3.371	0.51

Analyte: Fe

Line number	Sample number	Fe 238.2	Fe 240.4	Fe 258.5	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
8	116/1	661.0573	654.2774	652.8830	656.0726			
	116/2	666.0089	657.8647	656.6149	660.1628			
	116/3	663.4108	658.6724	655.0525	659.0452			
	116/4	662.7826	657.2639	653.9022	657.9829	658.316	1.740	0.26
9	143/1	662.0559	657.5417	653.4572	657.6849			
	143/2	657.4280	651.7124	649.2226	652.7876			
	143/3	662.4433	657.7874	655.1270	658.4526			
	143/4	659.0371	654.4203	653.0654	655.5076	656.108	2.541	0.39
10	145/1	660.2897	656.1572	654.4129	656.9533			
	145/2	645.6995	641.8136	639.6322	642.3818			
	145/3	658.0124	652.7109	651.4537	654.0590			
	145/4	663.2385	658.2669	656.4138	659.3064	653.175	7.509	1.15
11	175/1	654.8367	650.8757	649.3085	651.6736			
	175/2	647.8738	644.5770	642.1628	644.8712			
	175/3	660.4564	655.3965	653.2238	656.3589			
	175/4	657.8195	652.3882	650.1963	653.4680	651.593	4.879	0.75
12	190/1	662.9837	658.9877	656.6105	659.5273			
	190/2	660.9537	657.1230	654.4982	657.5250			
	190/3	659.3196	654.4993	653.2906	655.7031			
	190/4	664.8754	661.0335	658.6526	661.5205	658.569	2.512	0.38
13	207/1	662.2563	657.8454	656.2469	658.7829			
	207/2	656.8205	653.1002	650.3241	653.4150			
	207/3	659.5736	655.8176	654.0083	656.4665			
	207/4	658.4364	653.3617	651.8081	654.5354	655.800	2.354	0.36
14	212/1	655.5362	650.3100	648.8098	651.5520			
	212/2	656.7272	653.4204	650.0884	653.4120			
	212/3	669.4426	663.9798	662.8983	665.4402			
	212/4	655.3924	649.9479	649.6036	651.6480	655.513	6.673	1.02

Analyte: Fe

Line	Sample number	Fe 238.2	Fe 240.4	Fe 258.5	mean over	mean of	SD of	RSD$_w$
15	228/1	663.6527	658.1550	656.7632	659.5236			
	228/2	671.5000	666.9188	666.4671	668.2953			
	228/3	664.8264	659.7965	658.2616	660.9615			
	228/4	659.0525	654.3064	654.0581	655.8057	661.147	5.238	0.79
16	247/1	656.8279	649.8066	649.6031	652.0792			
	247/2	657.3886	652.7766	651.1725	653.7792			
	247/3	657.5295	654.2511	650.9792	654.2533			
	247/4	675.5179	666.7653	664.4141	668.8991	657.253	7.820	1.19
17	270/1	685.6063	677.3445	676.4034	679.7847			
	270/2	655.5800	649.6866	646.6674	650.6446			
	270/3	651.8686	644.9415	643.4346	646.7483			
	270/4	656.6330	650.5485	650.9989	652.7268	657.476	15.077	2.29
18	285/1	673.9652	665.7407	664.9598	668.2219			
	285/2	658.8534	653.3514	652.0342	654.7463			
	285/3	652.5068	647.6088	645.2829	648.4662			
	285/4	660.6409	658.8737	655.2903	658.2683	657.426	8.261	1.26
19	298/1	657.2032	653.6779	650.8101	653.8971			
	298/2	667.0335	662.0019	661.1258	663.3871			
	298/3	659.6428	655.6931	654.8812	656.7390			
	298/4	655.7842	650.5976	648.2737	651.5518	656.394	5.122	0.78
20	313/1	665.1481	659.5550	656.9732	660.5587			
	313/2	652.3172	648.9629	647.2249	649.5017			
	313/3	651.6252	646.7050	643.9480	647.4260			
	313/4	653.5439	649.9464	647.8836	650.4580	651.986	5.854	0.90

M_{ss} - mean of means of the sub-samples 1-4 657.21

SD of means of the sub-samples 1-4 2.842

RSD (rel.%) 0.43

mean RSD$_w$ (%) 0.88

Analyte: Fe

HS = Homogeneous sample

Line number	Sample number	Fe 238.2	Fe 240.4	Fe 258.5	mean over 3 lines
1	HS1	673.5874	667.9935	667.1569	669.5793
2	HS2	664.8194	660.6722	658.4384	661.3100
3	HS3	666.7651	659.6477	659.2907	661.9011
4	HS4	670.6792	662.8434	662.4240	665.3155
5	HS5	666.2373	660.3959	658.3898	661.6743
6	HS6	667.2094	662.2610	659.6902	663.0535
7	HS7	659.9736	654.9700	652.8532	655.9323
8	HS8	685.2733	679.2383	677.8488	680.7868
9	HS9	668.0592	662.0788	660.5786	663.5722
10	HS10	675.4264	669.5000	668.1958	671.0407
11	HS11	671.8308	667.4523	664.3044	667.8625
12	HS12	675.1728	668.3926	667.1064	670.2239
13	HS13	670.3386	665.3970	662.1130	665.9495
14	HS14	674.7793	670.1950	667.8184	670.9309
15	HS15	670.5031	666.3913	663.4512	666.7819
16	HS16	666.4399	662.5400	658.2855	662.4218
17	HS17	673.8486	667.8800	665.9855	669.2380
18	HS18	663.7680	658.7472	655.9786	659.4979
19	HS19	667.8101	662.1096	659.1114	663.0104
20	HS20	670.2910	667.1344	663.2773	666.9009

M_{HS} - mean of homogeneous sample	665.85
SD_{HS}	5.389
RSD_{HS} (%)	0.81

Analyte: Fe

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	6.930	**M_{ss}** 657.21	**RSD %** 0.43
standard deviation between the samples s_b	5.684	**F_{value}**	1.768
test value s_b^2/s_w^2	0.673	**Characteristic no. for homogeneity between the samples**	0.381
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	5.389	**M_{HS}** 665.85	**RSD_{HS} %** 0.81
		F_{value}	1.980
test value s_w^2/s_{HS}^2	1.653	**Characteristic no. for homogeneity within the samples**	0.835
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Mg

mass fraction in mg/kg

Line number	Sample number	Mg 279.5	Mg 280.2	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	1.4963	1.5038	1.5001			
	4/2	1.4442	1.4512	1.4477			
	4/3	1.3836	1.3896	1.3866			
	4/4				1.445	0.057	3.93
2	27/1	1.6368	1.6552	1.6460			
	27/2	1.7821	1.7918	1.7870			
	27/3	1.5117	1.5181	1.5149			
	27/4	1.4037	1.3991	1.4014	1.587	0.166	10.49
3	48/1	1.4117	1.4103	1.4110			
	48/2	1.4729	1.4923	1.4826			
	48/3	1.4746	1.4891	1.4819			
	48/4	1.6300	1.6265	1.6282	1.501	0.091	6.08
4	58/1	1.4467	1.4515	1.4491			
	58/2	1.5427	1.5472	1.5450			
	58/3	1.4707	1.4813	1.4760			
	58/4	1.5515	1.5494	1.5504	1.505	0.050	3.35
5	79/1	1.5432	1.5547	1.5490			
	79/2	1.4018	1.4055	1.4037			
	79/3	1.4862	1.4986	1.4924			
	79/4	1.3961	1.4141	1.4051	1.463	0.071	4.85
6	91/1	1.3358	1.3521	1.3440			
	91/2	1.5390	1.5490	1.5440			
	91/3	1.5370	1.5455	1.5412			
	91/4				1.476	0.115	7.77

Analyte: Mg

Line number	Sample number	Mg 279.5	Mg 280.2	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
7	104/1	1.4569	1.4530	1.4550			
	104/2	1.4567	1.4568	1.4568			
	104/3	1.4075	1.3919	1.3997			
	104/4	1.5232	1.5291	1.5261	1.459	0.052	3.55
8	116/1	1.4450	1.4450	1.4450			
	116/2	1.4464	1.4525	1.4494			
	116/3	1.4193	1.4224	1.4209			
	116/4	1.4118	1.4218	1.4168	1.433	0.017	1.15
9	143/1	1.4109	1.4367	1.4238			
	143/2	1.2366	1.2410	1.2388			
	143/3	1.2319	1.2425	1.2372			
	143/4	1.2167	1.2116	1.2142	1.278	0.098	7.63
10	145/1	1.2903	1.2658	1.2781			
	145/2	1.2258	1.2126	1.2192			
	145/3	1.2804	1.2513	1.2659			
	145/4	1.3236	1.3193	1.3215	1.271	0.042	3.31
11	175/1	1.2506	1.2387	1.2447			
	175/2	1.2522	1.2592	1.2557			
	175/3	1.2860	1.2799	1.2830			
	175/4	1.2318	1.2339	1.2329	1.254	0.021	1.71
12	190/1	1.3422	1.3194	1.3308			
	190/2	1.2496	1.2306	1.2401			
	190/3	1.2592	1.2545	1.2569			
	190/4	1.2629	1.2593	1.2611	1.272	0.040	3.15
13	207/1	1.2657	1.2590	1.2623			
	207/2	1.3804	1.3472	1.3638			
	207/3	1.2058	1.1983	1.2020			
	207/4	1.2141	1.2156	1.2148	1.261	0.073	5.82
14	212/1	1.2682	1.2769	1.2725			
	212/2	1.3746	1.3441	1.3594			
	212/3	1.2745	1.2737	1.2741			
	212/4	1.3398	1.3389	1.3393	1.311	0.045	3.41

Analyte: Mg

Line number	Sample number	Mg 279.5	Mg 280.2	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
15	228/1	1.2301	1.2429	1.2365			
	228/2	1.2114	1.2054	1.2084			
	228/3	1.2413	1.2116	1.2264			
	228/4	1.3130	1.2963	1.3046	1.244	0.042	3.38
16	247/1	1.2561	1.2692	1.2627			
	247/2	1.3730	1.3628	1.3679			
	247/3	1.4868	1.4838	1.4853			
	247/4	1.4151	1.4049	1.4100	1.381	0.093	6.73
17	270/1	1.6255	1.6106	1.6181			
	270/2	1.3525	1.3248	1.3386			
	270/3	1.2513	1.2416	1.2464			
	270/4	1.2405	1.2241	1.2323	1.359	0.179	13.18
18	285/1	1.2884	1.2706	1.2795			
	285/2	1.4447	1.4450	1.4449			
	285/3	1.4223	1.4110	1.4166			
	285/4	1.3104	1.3051	1.3078	1.362	0.081	5.93
19	298/1	1.2534	1.2352	1.2443			
	298/2	1.2483	1.2481	1.2482			
	298/3	1.4076	1.3909	1.3992			
	298/4	1.3432	1.3385	1.3409	1.308	0.075	5.76
20	313/1	1.4090	1.4006	1.4048			
	313/2	1.2525	1.2458	1.2492			
	313/3	1.2400	1.2473	1.2437			
	313/4	1.2379	1.2180	1.2279	1.281	0.083	6.46

M_{ss} - mean of means of the sub-samples 1-4	1.373
SD of means of the sub-samples 1-4	0.104
RSD (rel.%)	7.55

mean RSD_w (%)	5.38

Analyte: Mg

HS = Homogeneous sample

Line number	Sample number	Mg 279.5	Mg 280.2	mean over 2 lines
1	HS1	1.5372	1.5327	1.5349
2	HS2	1.2998	1.2914	1.2956
3	HS3	1.2339	1.2474	1.2406
4	HS4	1.6421	1.6246	1.6334
5	HS5	1.6543	1.6504	1.6524
6	HS6			
7	HS7	1.7441	1.7374	1.7408
8	HS8	1.6686	1.6798	1.6742
9	HS9			
10	HS10	1.5491	1.5728	1.5610
11	HS11	1.4203	1.4124	1.4164
12	HS12	1.4052	1.4011	1.4031
13	HS13	1.5724	1.5578	1.5651
14	HS14	1.5371	1.5494	1.5432
15	HS15	1.3868	1.3758	1.3813
16	HS16	1.7033	1.7150	1.7091
17	HS17	1.5379	1.5417	1.5398
18	HS18	1.5130	1.5227	1.5179
19	HS19	1.5730	1.5815	1.5772
20	HS20	1.5383	1.5224	1.5303

M_{HS} - mean of homogeneous sample	1.5287
SD_{HS}	0.1367
RSD_{HS} (%)	8.94

Analyte: Mg

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.085	**M_{ss}** 1.373	**RSD %** 7.55
standard deviation between the samples s_b	0.205	**$F_{(Tab.)}$**	1.8124
test value s_b^2/s_w^2	5.808	**Characteristic no. for homogeneity between the samples**	3.204
Homogeneity between the samples: Strong inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.137	**M_{HS}** 1.529	**RSD_{HS} %** 8.94
		F_{value}	2.114
test value s_w^2/s_{HS}^2	0.389	**Characteristic no. for homogeneity within the samples**	0.184
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Mn

Line number	Sample number	Mn 257.6	Mn 259.3	Mn 260.5	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	9.9399	10.2520	9.9842	10.0587			
	4/2	9.9413	10.2578	9.9796	10.0596			
	4/3	10.0215	10.3312	10.0689	10.1405			
	4/4	10.0023	10.2993	9.9215	10.0744	10.083	0.039	0.39
2	27/1	10.0117	10.2968	10.0192	10.1092			
	27/2	10.0927	10.3858	10.1300	10.2028			
	27/3	9.8596	10.1473	9.8890	9.9653			
	27/4	9.9318	10.2360	9.9440	10.0373	10.079	0.102	1.01
3	48/1	9.9369	10.2069	9.8628	10.0022			
	48/2	9.9189	10.2252	9.9492	10.0311			
	48/3	9.8800	10.1957	9.9463	10.0073			
	48/4	10.1032	10.3787	10.2267	10.2362	10.069	0.112	1.11
4	58/1	9.9740	10.2770	10.1039	10.1183			
	58/2	9.6678	9.9406	9.7085	9.7723			
	58/3	10.2454	10.5310	10.2513	10.3425			
	58/4	9.7916	10.0689	9.8111	9.8905	10.031	0.253	2.52
5	79/1	10.0527	10.3120	10.0719	10.1455			
	79/2	9.9004	10.1810	9.8938	9.9917			
	79/3	10.0433	10.3245	10.0519	10.1399			
	79/4	10.0079	10.3388	10.0185	10.1217	10.100	0.073	0.72
6	91/1	9.9357	10.2366	9.9549	10.0424			
	91/2	9.9473	10.2260	9.9500	10.0411			
	91/3	9.9648	10.2520	9.9685	10.0618			
	91/4	9.9653	10.2506	9.9483	10.0547	10.050	0.010	0.10

Analyte: Mn

Line number	Sample number	Mn 257.6	Mn 259.3	Mn 260.5	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
7	104/1	9.9177	10.2163	9.9272	10.0204			
	104/2	9.9494	10.2667	9.9719	10.0627			
	104/3	9.9642	10.2715	9.9869	10.0742			
	104/4	9.8748	10.2225	9.9198	10.0057	10.041	0.033	0.33
8	116/1	9.9374	10.2299	9.9478	10.0383			
	116/2	9.9693	10.2783	9.9448	10.0641			
	116/3	9.9651	10.2671	9.9709	10.0677			
	116/4	9.9838	10.3226	10.0093	10.1052	10.069	0.028	0.27
9	143/1	9.9326	10.2526	9.9693	10.0515			
	143/2	9.8929	10.2071	9.9084	10.0028			
	143/3	9.8807	10.1704	9.9309	9.9940			
	143/4	9.8670	10.1505	9.8816	9.9663	10.004	0.035	0.35
10	145/1	9.9975	10.2793	10.0026	10.0931			
	145/2	9.7172	10.0113	9.7013	9.8099			
	145/3	9.9416	10.2601	9.9816	10.0611			
	145/4	10.0165	10.2973	10.0359	10.1166	10.020	0.142	1.42
11	175/1	9.9285	10.2247	9.9620	10.0384			
	175/2	9.8496	10.1465	9.8854	9.9605			
	175/3	9.9537	10.2570	9.9905	10.0671			
	175/4	9.9615	10.2121	9.9915	10.0550	10.030	0.048	0.48
12	190/1	9.9864	10.2755	10.0127	10.0915			
	190/2	10.1012	10.3937	10.1120	10.2023			
	190/3	9.9766	10.2789	9.9967	10.0841			
	190/4	10.0409	10.3552	10.0629	10.1530	10.133	0.056	0.55
13	207/1	10.0027	10.3075	10.0031	10.1044			
	207/2	9.9487	10.2519	9.9679	10.0562			
	207/3	9.9628	10.2750	9.9749	10.0709			
	207/4	9.9716	10.2615	9.9906	10.0746	10.077	0.020	0.20
14	212/1	9.8949	10.2232	9.9349	10.0177			
	212/2	9.9414	10.2323	9.9613	10.0450			
	212/3	10.0544	10.3917	10.0890	10.1783			
	212/4	9.8897	10.2058	9.9152	10.0036	10.061	0.080	0.80

Analyte: Mn

Line number	Sample number	Mn 257.6	Mn 259.3	Mn 260.5	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
15	228/1	9.9375	10.2687	9.9877	10.0647			
	228/2	10.1549	10.4805	10.1677	10.2677			
	228/3	9.9959	10.3008	10.0308	10.1091			
	228/4	9.9529	10.2372	9.9442	10.0448	10.122	0.101	1.00
16	247/1	9.9155	10.2247	9.9134	10.0178			
	247/2	9.8880	10.1939	9.8517	9.9779			
	247/3	10.0079	10.2546	9.9745	10.0790			
	247/4	10.2805	10.5885	10.3216	10.3969	10.118	0.191	1.88
17	270/1	10.5277	10.8248	10.5529	10.6352			
	270/2	9.9318	10.2193	9.9561	10.0357			
	270/3	9.7988	10.0878	9.7935	9.8934			
	270/4	9.8819	10.1609	9.8743	9.9724	10.134	0.339	3.35
18	285/1	10.1645	10.4718	10.1469	10.2611			
	285/2	9.9520	10.2615	9.9519	10.0551			
	285/3	9.8315	10.1482	9.8533	9.9443			
	285/4	10.0604	10.3515	10.0493	10.1537	10.104	0.135	1.34
19	298/1	9.9819	10.2655	9.9658	10.0711			
	298/2	10.0768	10.3719	10.0680	10.1722			
	298/3	10.1467	10.4446	10.1190	10.2368			
	298/4	9.9642	10.2540	9.9619	10.0600	10.135	0.085	0.83
20	313/1	10.0122	10.2891	10.0543	10.1185			
	313/2	9.8901	10.1653	9.8365	9.9640			
	313/3	9.9080	10.1725	9.8950	9.9918			
	313/4	9.9397	10.2012	9.9268	10.0226	10.024	0.067	0.67

M_{ss} - mean of means of the sub-samples 1-4 10.074

SD of means of the sub-samples 1-4 0.041

RSD (rel.%) 0.41

mean RSD_w (%) 0.97

Analyte: Mn

HS = Homogeneous sample

Line number	Sample number	Mn 257.6	Mn 259.3	Mn 260.5	mean over 3 lines
1	HS1	10.1310	10.4365	10.1467	10.2381
2	HS2	9.8557	10.1817	9.8562	9.9645
3	HS3	9.9545	10.2561	9.9625	10.0577
4	HS4	9.9303	10.2613	9.9557	10.0491
5	HS5	10.0075	10.3210	9.9456	10.0914
6	HS6	10.0389	10.3190	10.0007	10.1196
7	HS7	9.9238	10.2245	9.9871	10.0451
8	HS8	10.5345	10.8260	10.5745	10.6450
9	HS9	10.0114	10.3143	9.9963	10.1073
10	HS10	10.1458	10.4585	10.1516	10.2519
11	HS11	10.0984	10.4194	10.1246	10.2141
12	HS12	10.1548	10.4736	10.1646	10.2643
13	HS13	10.0734	10.3921	10.1114	10.1923
14	HS14	10.1169	10.4333	10.1693	10.2398
15	HS15	9.9992	10.3175	10.0301	10.1156
16	HS16	9.9502	10.2448	9.9808	10.0586
17	HS17	10.0555	10.3466	10.0952	10.1658
18	HS18	9.9552	10.2244	9.9961	10.0586
19	HS19	9.9364	10.2421	9.9954	10.0580
20	HS20	10.0365	10.3569	9.9787	10.1240

M_{HS} - mean of homogeneous sample	10.1530
SD_{HS}	0.1428
RSD_{HS} (%)	1.41

Analyte: Mn

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.127	**M_{ss}** 10.074	**RSD %** 0.41
standard deviation between the samples s_b	0.083	**F_{value}**	1.768
test value s_b^2/s_w^2	0.429	**Characteristic no. for homogeneity between the samples**	0.242
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.143	**M_{HS}** 10.153	**RSD_{HS} %** 1.41
		F_{value}	1.980
test value s_w^2/s_{HS}^2	0.786	**Characteristic no. for homogeneity within the samples**	0.397
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Na

mass fraction = F (6.288/618.9)

Line number	Sample number	values		mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	004-1	636.71	6.469	6.229	0.24	3.89
	004-2	611.59	6.214			
	004-3	580.80	5.901			
	004-4	623.26	6.332			
2	048-1	652.69	6.631	6.522	0.18	2.68
	048-2	620.73	6.307			
	048-3	635.59	6.458			
	048-4	658.83	6.694			
3	079-1	614.07	6.239	6.138	0.15	2.43
	079-2	616.21	6.261			
	079-3	584.22	5.936			
	079-4	602.10	6.117			
4	104-1	602.29	6.119	6.563	0.31	4.65
	104-2	670.33	6.811			
	104-3	658.97	6.695			
	104-4	652.20	6.626			
5	143-1	603.88	6.135	5.999	0.11	1.75
	143-2	587.65	5.970			
	143-3	591.26	6.007			
	143-4	578.97	5.882			
6	175-1	585.35	5.947	6.242	0.29	4.67
	175-2	653.38	6.638			
	175-3	604.34	6.140			
	175-4	614.56	6.244			
7	207-1	620.84	6.308	6.380	0.09	1.41
	207-2	620.19	6.301			
	207-3	632.59	6.427			
	207-4	638.04	6.483			
8	228-1	617.91	6.278	6.234	0.17	2.74
	228-2	591.99	6.015			
	228-3	632.53	6.427			
	228-4	612.09	6.219			
9	270-1	610.15	6.199	6.222	0.19	3.00
	270-2	596.30	6.058			
	270-3	638.65	6.489			
	270-4	604.53	6.142			
10	298-1	604.93	6.146	6.349	0.29	4.53
	298-2	666.26	6.769			
	298-3	619.62	6.295			
	298-4	608.69	6.184			

Analyte: Na

M_{ss} - mean of means of the sub-samples 1-4	6.288
SD of means of the sub-samples 1-4	0.170
RSD (rel.%)	2.71

mean RSD_w (%) 3.17

HS = Homogeneous sample

mass fraction = F (6.288/629.5)

Line number	Sample number	values	
1	HS1	647.58	6.469
2	HS2	643.70	6.430
3	HS3	627.28	6.266
4	HS4	624.21	6.235
5	HS5	617.69	6.170
6	HS6	656.72	6.560
7	HS7	621.58	6.209
8	HS8	622.36	6.217
9	HS9	607.13	6.065
10	HS10	626.98	6.263

M_{HS} - mean of homogeneous sample	6.288
SD_{HS}	0.151
RSD_{HS} (%)	2.40

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.2134	**M_{ss}** 6.288	**RSD %** 2.71
standard deviation between the samples s_b	0.3408	**F_{value}**	2.21
test value s_b^2/s_w^2	2.551	**Characteristic no. for homogeneity between the samples**	1.154
Homogeneity between the samples: No significant inhomogeneity			

Analyte: Na

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.1512	**M_{HS}** 6.288	**RSD_{HS} %** 2.40
		F_{value}	2.860
test value s_w^2/s_{HS}^2	1.991	**Characteristic no. for homogeneity within the samples**	0.696
Homogeneity within the samples: **No significant inhomogeneity**			

Analyte: Ni

mass fraction in mg/kg

Line number	Sample number	Ni 216.5	Ni 231.6	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	7.3753	7.4733	7.4243			
	4/2	7.9981	7.8450	7.9215			
	4/3	7.6243	7.6601	7.6422			
	4/4	8.4675	7.5594	8.0135	7.750	0.269	3.47
2	27/1	7.6617	7.5507	7.6062			
	27/2	7.4355	7.5502	7.4929			
	27/3	7.5455	7.5261	7.5358			
	27/4	7.4574	7.6148	7.5361	7.543	0.047	0.62
3	48/1	8.1413	7.5551	7.8482			
	48/2	7.2863	7.7467	7.5165			
	48/3	7.3392	7.5493	7.4442			
	48/4	7.3218	7.5715	7.4467	7.564	0.192	2.54
4	58/1	7.2850	7.6805	7.4828			
	58/2	6.9536	7.2396	7.0966			
	58/3	7.5501	7.7469	7.6485			
	58/4	7.2419	7.3218	7.2819	7.377	0.240	3.25
5	79/1	7.7523	7.7856	7.7689			
	79/2	7.2536	7.5279	7.3907			
	79/3	7.3953	7.6865	7.5409			
	79/4	7.3866	7.3127	7.3497	7.513	0.190	2.52
6	91/1	7.3161	7.4238	7.3699			
	91/2	7.6631	7.6830	7.6730			
	91/3	7.3249	7.5486	7.4368			
	91/4	7.4596	7.5754	7.5175	7.499	0.131	1.74

Analyte: Ni

Line number	Sample number	Ni 216.5	Ni 231.6	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
7	104/1	7.5006	7.5142	7.5074			
	104/2	7.5814	7.5225	7.5520			
	104/3	7.0810	7.5187	7.2998			
	104/4	7.1904	7.3881	7.2892	7.412	0.137	1.85
8	116/1	7.4715	7.3859	7.4287			
	116/2	7.3393	7.5656	7.4525			
	116/3	7.5330	7.7977	7.6654			
	116/4	7.4887	7.4120	7.4503	7.499	0.111	1.48
9	143/1	7.0727	7.4622	7.2675			
	143/2	7.1460	7.1777	7.1619			
	143/3	7.3621	7.3849	7.3735			
	143/4	7.3065	7.4260	7.3663	7.292	0.099	1.36
10	145/1	7.2563	7.5563	7.4063			
	145/2	6.8022	7.1897	6.9960			
	145/3	7.5701	7.8336	7.7018			
	145/4	7.1733	7.6629	7.4181	7.381	0.291	3.94
11	175/1	7.1742	7.7293	7.4517			
	175/2	7.0356	7.4732	7.2544			
	175/3	7.4004	7.7359	7.5681			
	175/4	7.4545	7.7350	7.5947	7.467	0.155	2.07
12	190/1	7.1179	7.6940	7.4060			
	190/2	7.5069	7.8933	7.7001			
	190/3	7.2876	7.4644	7.3760			
	190/4	7.5133	7.9191	7.7162	7.550	0.184	2.43
13	207/1	7.7894	7.6531	7.7213			
	207/2	7.3075	7.5020	7.4047			
	207/3	8.2140	8.3530	8.2835			
	207/4	7.6749	7.6218	7.6483	7.764	0.372	4.79
14	212/1	7.4420	7.4365	7.4392			
	212/2	7.7219	7.6473	7.6846			
	212/3	7.9648	7.9405	7.9527			
	212/4	7.7525	8.1400	7.9463	7.756	0.245	3.16

Analyte: Ni

Line number	Sample number	Ni 216.5	Ni 231.6	mean over 2 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
15	228/1	7.5417	7.3322	7.4370			
	228/2	7.9947	8.1033	8.0490			
	228/3	7.9674	8.1230	8.0452			
	228/4	7.0023	7.7366	7.3695	7.725	0.373	4.83
16	247/1	6.9075	7.4211	7.1643			
	247/2	7.1746	7.7855	7.4801			
	247/3	7.8798	8.4382	8.1590	7.601	0.508	6.69
	247/4						
17	270/1						
	270/2	7.7415	7.6004	7.6710			
	270/3	7.6077	7.4954	7.5516			
	270/4	8.1819	8.0336	8.1077	7.777	0.293	3.76
18	285/1	8.2970	8.1357	8.2163			
	285/2	7.6218	7.5865	7.6042			
	285/3	9.4346	7.5916	8.5131			
	285/4	9.8855	8.2066	9.0460	8.345	0.601	7.21
19	298/1	8.8653	7.1768	8.0210			
	298/2	9.1276	7.7721	8.4498			
	298/3	10.0444	8.4506	9.2475			
	298/4	8.8666	7.2783	8.0724	8.448	0.566	6.71
20	313/1	9.1746	7.4556	8.3151			
	313/2	8.6414	7.6851	8.1632			
	313/3	9.0668	7.4090	8.2379			
	313/4	8.8006	7.6654	8.2330	8.237	0.062	0.75

M_{ss} - mean of means of the sub-samples 1-4 7.675

SD of means of the sub-samples 1-4 0.322

RSD (rel.%) 4.19

mean RSD$_w$ (%)

Analyte: Ni

HS = Homogeneous sample

Line number	Sample number	Ni 216.5	Ni 231.6	mean over 2 lines
1	HS1	8.8047	7.5513	8.1780
2	HS2	8.4834	7.2659	7.8747
3	HS3	7.6264	7.4815	7.5540
4	HS4	7.9285	7.5166	7.7226
5	HS5	8.3537	7.4622	7.9080
6	HS6			
7	HS7	8.3180	8.0651	8.1916
8	HS8			
9	HS9	8.0154	7.5385	7.7770
10	HS10	8.1284	7.9163	8.0224
11	HS11	7.9468	7.5106	7.7287
12	HS12	8.3028	7.7941	8.0484
13	HS13	8.6062	8.1550	8.3806
14	HS14	7.8488	7.8537	7.8512
15	HS15	7.6533	7.6740	7.6637
16	HS16	7.8538	7.7185	7.7862
17	HS17	7.6748	7.7096	7.6922
18	HS18	7.4111	7.6475	7.5293
19	HS19	7.6633	7.5704	7.6169
20	HS20	8.3223	7.6264	7.9744

M_{HS} - mean of homogeneous sample	7.8611
SD_{HS}	0.2348
RSD_{HS} (%)	2.99

Analyte: Ni

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	0.298	**M_{ss}** 7.675	**RSD %** 4.19
standard deviation between the samples s_b	0.643	**$F_{(Tab.)}$**	1.8124
test value s_b^2/s_w^2	4.666	**Characteristic no. for homogeneity between the samples**	2.574
Homogeneity between the samples: Strong inhomogeneity			

Homogeneity within the samples			
Analysis of variance: a = 0.05			
standard deviation of homogeneous sample SD_{HS}	0.235	**M_{HS}** 7.861	**RSD_{HS} %** 2.99
		$F_{(Tab.)}$	2.064
test value s_w^2/s_{HS}^2	1.608	**Characteristic no. for homogeneity within the samples**	0.779
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Si

mass fraction

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	004-1	399.72	384.43	13.70	3.56
	004-2	366.60			
	004-3	387.67			
	004-4	383.73			
2	048-1	365.34	376.46	13.55	3.60
	048-2	371.99			
	048-3	372.29			
	048-4	396.21			
3	079-1	396.83	384.89	12.95	3.36
	079-2	388.18			
	079-3	388.10			
	079-4	366.46			
4	104-1	368.13	379.49	22.35	5.89
	104-2	354.62			
	104-3	390.76			
	104-4	404.46			
5	143-1	387.95	369.79	13.01	3.52
	143-2	357.60			
	143-3	364.37			
	143-4	369.26			
6	175-1	366.16	371.41	16.10	4.33
	175-2	380.65			
	175-3	351.29			
	175-4	387.53			
7	207-1	380.82	380.26	6.84	1.80
	207-2	371.76			
	207-3	379.99			
	207-4	388.48			
8	228-1	372.99	381.29	24.82	6.51
	228-2	381.35			
	228-3	355.87			
	228-4	414.94			
9	270-1	394.56	379.58	11.15	2.94
	270-2	379.48			
	270-3	367.81			
	270-4	376.47			
10	298-1	385.18	378.36	8.68	2.29
	298-2	379.85			
	298-3	382.65			
	298-4	365.76			

Analyte: Si

M_{ss} - mean of means of the sub-samples 1-4	378.6
SD of means of the sub-samples 1-4	4.94
RSD (rel.%)	1.30

mean RSD_w (%) 3.78

HS = Homogeneous sample

Line number	Sample number	values
1	HS1	376.00
2	HS2	386.69
3	HS3	367.83
4	HS4	385.21
5	HS5	376.11
6	HS6	366.02
7	HS7	387.67
8	HS8	401.41
9	HS9	417.16
10	HS10	362.02

M_{HS} - mean of homogeneous sample	382.61
SD_{HS}	17.00
RSD_{HS} (%)	4.44

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	15.26	**M_{ss}** 618.9	**RSD %** 2.71
standard deviation between the samples s_b	9.87	**F_{value}**	2.21
test value s_b^2/s_w^2	0.418	**Characteristic no. for homogeneity between the samples**	0.189
Homogeneity between the samples: No significant inhomogeneity			

Analyte: Si

<table>
<tr><th colspan="4">Homogeneity within the samples</th></tr>
<tr><td colspan="4"></td></tr>
<tr><td colspan="4">Analysis of variance: $\alpha = 0.05$</td></tr>
<tr><td>standard deviation of homogeneous sample SD_{HS}</td><td>17.00</td><td>M_{HS}
629.52</td><td>RSD_{HS} %
4.44</td></tr>
<tr><td></td><td></td><td>F_{value}</td><td>2.86</td></tr>
<tr><td>test value s_w^2/s_{HS}^2</td><td>0.806</td><td>Characteristic no. for homogeneity within the samples</td><td>0.283</td></tr>
<tr><td colspan="4">Homogeneity within the samples:
No significant inhomogeneity</td></tr>
</table>

Analyte: Ti

mass fraction in mg/kg

Line number	Sample number	Ti 323.4	Ti 324.1	Ti 334.9	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	89.4655	88.5385	89.8831	89.2957			
	4/2	88.2080	87.4573	88.6275	88.0976			
	4/3	90.9476	89.3831	91.3167	90.5491			
	4/4	90.8652	90.5010	91.9921	91.1195	89.765	1.348	1.50
2	27/1	91.1926	89.5831	90.9771	90.5843			
	27/2	93.8022	91.8349	93.4766	93.0379			
	27/3	90.9677	89.8492	90.9973	90.6047			
	27/4	91.0356	89.5115	90.8207	90.4559	91.171	1.247	1.37
3	48/1	90.6043	90.0580	91.4680	90.7101			
	48/2	91.4943	89.9440	91.0860	90.8414			
	48/3	89.6539	88.4567	89.5680	89.2262			
	48/4	93.8976	91.8385	92.7780	92.8380	90.904	1.483	1.63
4	58/1	92.1111	89.6218	90.9352	90.8894			
	58/2	88.2152	86.0617	87.8292	87.3687			
	58/3	93.0109	91.5506	92.9507	92.5041			
	58/4	87.3874	86.2529	87.6601	87.1001	89.466	2.662	2.97
5	79/1	87.0040	85.8151	87.3520	86.7237			
	79/2	89.2353	88.0707	89.3306	88.8789			
	79/3	89.5344	88.2938	89.4551	89.0944			
	79/4	91.4065	90.2939	91.3577	91.0194	88.929	1.757	1.98
6	91/1	89.0560	87.9304	89.3200	88.7688			
	91/2	93.0857	91.4268	93.1828	92.5651			
	91/3	90.8770	89.5598	90.6728	90.3699			
	91/4	92.7196	91.3835	92.7225	92.2752	90.995	1.775	1.95
7	104/1	90.6668	89.3806	90.5176	90.1883			
	104/2	89.3360	87.8306	89.2583	88.8083			
	104/3	89.9839	87.9375	89.3121	89.0779			
	104/4	90.1540	88.5982	89.7898	89.5140	89.397	0.602	0.67

Analyte: Ti

Line number	Sample number	Ti 323.4	Ti 324.1	Ti 334.9	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
8	116/1	89.8872	89.0278	90.0347	89.6499			
	116/2	87.3993	86.9264	87.6853	87.3370			
	116/3	90.0291	88.0963	89.7936	89.3063			
	116/4	88.6983	87.4319	88.7473	88.2925	88.646	1.046	1.18
9	143/1	93.8325	92.1319	93.7775	93.2473			
	143/2	84.0862	82.3362	83.9250	83.4491			
	143/3	90.4780	88.8487	90.6335	89.9867			
	143/4	87.3649	86.1821	87.5864	87.0445	88.432	4.178	4.72
10	145/1	88.3793	87.4107	88.5277	88.1059			
	145/2	89.4372	87.7302	89.2773	88.8149			
	145/3	90.2264	89.0412	87.8555	89.0410			
	145/4	90.1074	88.7602	90.3122	89.7266	88.922	0.668	0.75
11	175/1	87.5103	86.4166	87.5459	87.1576			
	175/2	88.9586	87.4216	89.0307	88.4703			
	175/3	89.1645	87.9382	88.8916	88.6648			
	175/4	88.2096	86.9808	88.2217	87.8040	88.024	0.685	0.78
12	190/1	90.3067	88.7081	90.1940	89.7363			
	190/2	88.9201	87.3692	88.6909	88.3268			
	190/3	86.5177	85.5591	86.3382	86.1383			
	190/4	88.3323	86.6420	88.4698	87.8147	88.004	1.486	1.69
13	207/1	90.7881	89.3351	90.4726	90.1986			
	207/2	93.2199	91.6083	92.9298	92.5860			
	207/3	86.8408	85.1834	86.6687	86.2310			
	207/4	89.7249	88.7187	89.9522	89.4653	89.620	2.623	2.93
14	212/1	88.4935	87.8634	88.5260	88.2943			
	212/2	87.8327	86.6960	87.4999	87.3429			
	212/3	89.2498	88.2075	89.2902	88.9158			
	212/4	87.9707	86.9579	88.0340	87.6542	88.052	0.699	0.79
15	228/1	91.3060	89.9466	91.0973	90.7833			
	228/2	91.0772	89.8482	90.8234	90.5829			
	228/3	89.0005	87.6548	89.0254	88.5602			
	228/4	88.1667	86.8585	88.1041	87.7098	89.409	1.514	1.69

Analyte: Ti

Line number	Sample number	Ti 323.4	Ti 324.1	Ti 334.9	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
16	247/1	87.9117	86.6976	87.7030	87.4374			
	247/2	90.8794	89.5065	90.7284	90.3714			
	247/3	86.4156	85.3686	86.6612	86.1485			
	247/4	89.8289	88.9135	90.0190	89.5871	88.386	1.940	2.19
17	270/1	87.6658	86.5035	87.7174	87.2956			
	270/2	90.3067	88.9725	90.2201	89.8331			
	270/3	90.2696	88.7753	90.3003	89.7817			
	270/4	90.5349	89.7085	90.6623	90.3019	89.303	1.359	1.52
18	285/1	93.6433	92.4512	93.6800	93.2582			
	285/2	92.0159	90.5623	91.7762	91.4515			
	285/3	90.7799	89.1714	90.8343	90.2618			
	285/4	88.1223	86.2345	87.6741	87.3437	90.579	2.484	2.74
19	298/1	91.2660	89.4181	91.0522	90.5787			
	298/2	92.4867	90.8388	92.4417	91.9224			
	298/3	90.6802	88.5937	90.5394	89.9377			
	298/4	88.3668	86.3555	88.2642	87.6622	90.025	1.779	1.98
20	313/1	89.5096	87.8481	89.5716	88.9764			
	313/2	87.1021	85.0836	87.1012	86.4290			
	313/3	87.3080	85.6147	87.3228	86.7485			
	313/4	89.5983	87.3495	89.4581	88.8019	87.739	1.336	1.52

M_{ss} - mean of means of the sub-samples 1-4 89.288

SD of means of the sub-samples 1-4 1.053

RSD (rel.%) 1.18

mean RSD_w (%) 1.83

Analyte: Ti

HS = Homogeneous sample

Line number	Sample number	Ti 323.4	Ti 324.1	Ti 334.9	mean over 3 lines
1	HS1	92.5356	91.5841	92.6644	92.2614
2	HS2	88.8864	87.4126	88.9900	88.4296
3	HS3	90.9165	90.0138	90.9139	90.6147
4	HS4	90.2166	89.2028	90.7078	90.0424
5	HS5	92.1597	91.1441	92.8890	92.0643
6	HS6	91.1668	90.3531	91.6562	91.0587
7	HS7	91.5292	89.6627	91.1058	90.7659
8	HS8	91.0344	89.4419	91.2247	90.5670
9	HS9	95.0124	93.6553	94.7842	94.4840
10	HS10	89.0346	87.8988	89.2037	88.7124
11	HS11	91.6899	90.1470	91.7308	91.1892
12	HS12	90.1439	88.9683	90.2899	89.8007
13	HS13	92.5372	91.0296	92.6457	92.0708
14	HS14	93.4065	91.6403	93.5292	92.8587
15	HS15	90.4123	88.6830	90.4587	89.8513
16	HS16	91.7662	89.9514	91.4613	91.0597
17	HS17	92.4900	90.9034	91.9152	91.7696
18	HS18	91.8959	90.0084	91.5355	91.1466
19	HS19	93.6142	91.9858	93.2391	92.9463
20	HS20	93.1220	92.8121	93.8978	93.2773

M_{HS} - mean of homogeneous sample	91.2485
SD_{HS}	1.5177
RSD_{HS} (%)	1.66

Analyte: Ti

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	1.835	**M_{ss}** 89.288	**RSD %** 1.18
standard deviation between the samples s_b	2.106	**F_{value}**	1.768
test value s_b^2/s_w^2	1.318	**Characteristic no. for homogeneity between the samples**	0.745
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	1.518	**M_{HS}** 91.249	**RSD_{HS} %** 1.66
		F_{value}	1.980
test value s_w^2/s_{HS}^2	1.461	**Characteristic no. for homogeneity within the samples**	0.738
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Zr

mass fraction in mg/kg

Line number	Sample number	Zr 256.8	Zr 327.3	Zr 339.1	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	4/1	41.6619	44.6395	43.9244	43.4086			
	4/2	45.1363	47.6050	47.0352	46.5922			
	4/3	42.8916	46.4309	45.5545	44.9590			
	4/4	46.1152	46.0442	45.0299	45.7298	45.172	1.352	2.99
2	27/1	42.7157	46.6140	45.5374	44.9557			
	27/2	43.1908	46.9561	46.0827	45.4099			
	27/3	42.7898	46.1841	45.4841	44.8193			
	27/4	42.0510	45.3529	44.4907	43.9649	44.787	0.604	1.35
3	48/1	46.0496	45.9598	45.0650	45.6914			
	48/2	40.4323	44.2122	43.2350	42.6265			
	48/3	41.9689	46.0121	45.1905	44.3905			
	48/4	40.8992	46.5528	45.4931	44.3151	44.256	1.257	2.84
4	58/1	41.1764	48.3077	47.1810	45.5550			
	58/2	37.5460	43.7722	42.8770	41.3984			
	58/3	41.2953	46.3286	45.4492	44.3577			
	58/4	40.1101	44.3503	43.5998	42.6868	43.499	1.829	4.20
5	79/1	40.4269	44.2603	43.5099	42.7324			
	79/2	42.1927	45.7309	45.1560	44.3598			
	79/3	43.1292	46.3312	45.6660	45.0422			
	79/4	43.5411	46.9587	46.2609	45.5869	44.430	1.238	2.79
6	91/1	40.8188	44.3171	43.5057	42.8806			
	91/2	41.9825	46.3419	45.2486	44.5243			
	91/3	42.2004	45.6115	44.8955	44.2358			
	91/4	43.0197	46.4957	45.7588	45.0914	44.183	0.938	2.12
7	104/1	43.2136	46.7307	46.1176	45.3540			
	104/2	41.6608	45.3185	44.6265	43.8686			
	104/3	43.4639	47.5159	46.4486	45.8095			

Analyte: Zr

Line number	Sample number	Zr 256.8	Zr 327.3	Zr 339.1	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
7	104/4	40.9004	44.8335	43.8605	43.1981	44.558	1.228	2.76
8	116/1	41.6975	44.5455	43.7915	43.3448			
	116/2	43.6023	46.2865	45.3585	45.0824			
	116/3	42.6403	46.5110	45.5336	44.8950			
	116/4	43.8887	47.5465	46.4268	45.9540	44.819	1.086	2.42
9	143/1	43.1423	46.8556	45.9818	45.3266			
	143/2	38.5013	42.4734	41.4399	40.8048			
	143/3	42.9136	47.1147	46.1621	45.3968			
	143/4	40.0384	43.8986	42.9232	42.2868	43.454	2.285	5.26
10	145/1	39.7141	43.5221	42.7326	41.9896			
	145/2	40.7378	44.6200	43.7335	43.0304			
	145/3	41.1684	44.9841	44.1952	43.4492			
	145/4	41.9670	45.8994	45.0503	44.3056	43.194	0.962	2.23
11	175/1	41.4214	45.5546	44.7516	43.9092			
	175/2	40.5099	44.6259	43.6427	42.9261			
	175/3	41.6664	45.9321	45.0953	44.2313			
	175/4	41.5658	45.6087	44.9036	44.0260	43.773	0.580	1.33
12	190/1	42.7367	46.7711	46.0454	45.1844			
	190/2	41.3560	45.9734	44.8015	44.0436			
	190/3	40.8538	44.8169	43.9851	43.2186			
	190/4	41.7608	45.6077	44.8509	44.0732	44.130	0.807	1.83
13	207/1	42.5416	46.8578	45.8959	45.0984			
	207/2	42.2921	46.5340	45.7358	44.8540			
	207/3	39.9808	43.9711	43.0681	42.3400			
	207/4	39.2368	43.5817	42.5668	41.7951	43.522	1.697	3.90
14	212/1	42.0142	45.9754	45.2528	44.4141			
	212/2	42.0711	46.6045	45.6612	44.7789			
	212/3	41.1518	45.0952	44.0969	43.4480			
	212/4	41.8673	45.7929	44.8000	44.1534	44.199	0.562	1.27

Analyte: Zr

Line number	Sample number	Zr 256.8	Zr 327.3	Zr 339.1	mean over 3 lines	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
15	228/1	43.0004	46.9127	46.0423	45.3185			
	228/2	42.2251	46.2358	45.3170	44.5926			
	228/3	42.2130	46.1151	45.4693	44.5991			
	228/4	42.5415	46.3753	45.5541	44.8236	44.833	0.341	0.76
16	247/1	40.8230	44.5322	43.7160	43.0237			
	247/2	42.6627	46.4080	45.4734	44.8481			
	247/3	40.6541	44.4267	43.5730	42.8846			
	247/4	39.6199	42.8250	42.2243	41.5564	43.078	1.353	3.14
17	270/1	42.8740	47.2124	46.1160	45.4008			
	270/2	41.9050	45.7945	45.0723	44.2573			
	270/3	40.8950	46.0741	44.7705	43.9132			
	270/4	41.9370	45.8234	44.9259	44.2288	44.450	0.653	1.47
18	285/1	42.4389	46.5925	45.7213	44.9176			
	285/2	40.4829	45.7648	44.5125	43.5867			
	285/3	51.0255	41.1047	44.4965	45.5422			
	285/4	38.7465	47.6227	46.0814	44.1502	44.549	0.858	1.93
19	298/1	42.7967	44.8787	43.5278	43.7344			
	298/2	41.9767	48.4708	47.0418	45.8298			
	298/3	40.2821	45.1092	43.4517	42.9477			
	298/4	37.3699	48.3566	47.0547	44.2604	44.193	1.217	2.75
20	313/1	48.4417	43.2326	42.1790	44.6178			
	313/2	47.1131	42.2518	39.6519	43.0056			
	313/3	43.3981	42.7674	38.6243	41.5966			
	313/4	39.0624	48.8633	44.7110	44.2122	43.358	1.359	3.14

M_{ss} - mean of means of the sub-samples 1-4 44.122

SD of means of the sub-samples 1-4 0.607

RSD (rel.%) 1.38

mean RSD_w (%) 2.52

Analyte: Zr

HS = Homogeneous sample

Line number	Sample number	Zr 256.8	Zr 327.3	Zr 339.1	mean over 3 lines
1	HS1	44.7948	46.5006	45.4171	45.5709
2	HS2	43.9537	45.8356	44.7665	44.8520
3	HS3	44.2832	46.9104	46.2788	45.8242
4	HS4	45.2892	47.8573	46.9288	46.6918
5	HS5	44.8516	46.2127	45.0682	45.3775
6	HS6	45.8001	47.4380	46.3042	46.5141
7	HS7	42.4602	46.3070	45.2841	44.6838
8	HS8	43.5545	47.3769	46.5123	45.8146
9	HS9	45.2953	48.4766	47.6640	47.1453
10	HS10	42.8035	45.6548	44.5976	44.3520
11	HS11	45.1916	48.1661	47.1351	46.8309
12	HS12	44.5505	46.5958	45.8194	45.6552
13	HS13	41.7286	45.7676	45.0813	44.1925
14	HS14	45.2865	48.5292	47.8294	47.2150
15	HS15	44.9405	48.9219	48.0004	47.2876
16	HS16	41.6939	45.1104	44.2200	43.6747
17	HS17	43.9922	47.6067	46.8102	46.1364
18	HS18	41.1115	45.7202	44.8116	43.8811
19	HS19	43.2176	47.6262	46.4102	45.7513
20	HS20	45.7034	46.7664	45.5543	46.0080

M_{HS} - mean of homogeneous sample	45.6729
SD_{HS}	1.1123
RSD_{HS} (%)	2.44

Analyte: Zr

Homogeneity between the samples			
Analysis of variance: a = 0.05			
standard deviation within the samples s_w	1.204	**M_{ss}** 44.122	**RSD %** 1.38
standard deviation between the samples s_b	1.214	**F_{value}**	1.768
test value s_b^2/s_w^2	1.016	**Characteristic no. for homogeneity between the samples**	0.575
Homogeneity between the samples: **No significant inhomogeneity**			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	1.112	**M_{HS}** 45.673	**RSD_{HS} %** 2.44
		F_{value}	1.980
test value s_w^2/s_{HS}^2	1.171	**Characteristic no. for homogeneity within the samples**	0.592
Homogeneity within the samples: **No significant inhomogeneity**			

Analyte: Total Carbon

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1	21.21	21.208	0.0450	0.21
	027-2	21.21			
	027-3	21.15			
	027-4	21.26			
2	058-1	21.19	21.193	0.0411	0.19
	058-2	21.14			
	058-3	21.24			
	058-4	21.20			
3	091-1	21.23	21.228	0.0263	0.12
	091-2	21.24			
	091-3	21.25			
	091-4	21.19			
4	116-1	21.21	21.225	0.0238	0.11
	116-2	21.20			
	116-3	21.25			
	116-4	21.24			
5	145-1	21.22	21.168	0.0427	0.20
	145-2	21.15			
	145-3	21.12			
	145-4	21.18			
6	190-1	21.19	21.253	0.0492	0.23
	190-2	21.31			
	190-3	21.26			
	190-4	21.25			
7	212-1	21.20	21.203	0.0310	0.15
	212-2	21.23			
	212-3	21.16			
	212-4	21.22			
8	247-1	21.10	21.198	0.0695	0.33
	247-2	21.23			
	247-3	21.26			
	247-4	21.20			
9	285-1	21.21	21.165	0.0332	0.16
	285-2	21.16			
	285-3	21.13			
	285-4	21.16			
10	313-1	21.20	21.165	0.0574	0.27
	313-2	21.20			
	313-3	21.08			
	313-4	21.18			

Analyte: Total Carbon

M_{ss} - mean of means of the sub-samples 1-4	21.200
SD of means of the sub-samples 1-4	0.0294
RSD (rel.%)	0.14

mean RSD_w (%) 0.20

HS = Homogeneous sample (105)

Line number	Sample number	values
1	HS 1	21.20
2	HS 2	21.21
3	HS 3	21.27
4	HS 4	21.23
5	HS 5	21.26
6	HS 6	21.24
7	HS 7	21.24
8	HS 8	21.25
9	HS 9	21.29
10	HS 10	21.16

M_{HS} - mean of homogeneous sample	21.235
SD_{HS}	0.0375
RSD_{HS} (%)	0.18

Analyte: Total Carbon

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w	0.044	**M_{ss}** 21.200	**RSD %** 0.14
standard deviation between the samples s_b	0.059	**F_{value}**	2.21
test value s_b^2/s_w^2	1.779	**Characteristic no. for homogeneity between the samples**	0.805
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: α = 0.05			
standard deviation of homogeneous sample SD_{HS}	0.0375	**M_{HS}** 21.235	**RSD_{HS} %** 0.18
		F_{value}	2.86
test value s_w^2/s_{HS}^2	1.381	**Characteristic no. for homogeneity within the samples**	0.483
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Free Carbon

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1		0.445	0.0212	4.77
	027-2	0.46			
	027-3				
	027-4	0.43			
2	058-1	0.45	0.440	0.0141	3.21
	058-2				
	058-3	0.43			
	058-4				
3	091-1	0.48	0.465	0.0212	4.56
	091-2	0.45			
	091-3				
	091-4				
4	116-1		0.430	0.0141	3.29
	116-2				
	116-3	0.42			
	116-4	0.44			
5	145-1		0.420	0.0424	10.10
	145-2	0.39			
	145-3				
	145-4	0.45			
6	190-1	0.45	0.440	0.0141	3.21
	190-2				
	190-3				
	190-4	0.43			
7	212-1	0.45	0.425	0.0354	8.32
	212-2				
	212-3				
	212-4	0.40			
8	247-1		0.445	0.0071	1.59
	247-2	0.44			
	247-3	0.45			
	247-4				
9	285-1	0.49	0.475	0.0212	4.47
	285-2	0.46			
	285-3				
	285-4				
10	313-1		0.450	0.0000	0.00
	313-2				
	313-3	0.45			
	313-4	0.45			

M_{ss} - mean of means of the sub-samples 1-4	0.444		
SD of means of the sub-samples 1-4	0.0170		
RSD (rel.%)	3.83	**mean RSD_w (%)**	4.35

Analyte: Free Carbon

HS = Homogeneous sample (105)

Line number	Sample number	values
1	HS 1	0.47
2	HS 2	0.44
3	HS 3	0.44
4	HS 4	0.42
5	HS 5	0.46
6	HS 6	0.43
7	HS 7	
8	HS 8	
9	HS 9	
10	HS 10	

M_{HS} - mean of homogeneous sample	0.443
SD_{HS}	0.0186
RSD_{HS} (%)	4.20

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.0225	**M_{ss}** 0.444	**RSD %** 3.83
standard deviation between the samples s_b	0.0240	**F_{value}**	3.33
test value s_b^2/s_w^2	1.145	**Characteristic no. for homogeneity between the samples**	0.344
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.0186	**M_{HS}** 0.443	**RSD_{HS} %** 4.20
		F_{value}	4.74
test value s_w^2/s_{HS}^2	1.457	**Characteristic no. for homogeneity within the samples**	0.307
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Oxygen

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1	0.111	0.114	0.0027	2.38
	027-2	0.115			
	027-3	0.117			
	027-4	0.113			
2	058-1	0.112	0.114	0.0014	1.19
	058-2	0.115			
	058-3	0.114			
	058-4	0.114			
3	091-1	0.114	0.117	0.0031	2.65
	091-2	0.120			
	091-3	0.119			
	091-4	0.114			
4	116-1	0.117	0.117	0.0024	2.07
	116-2	0.114			
	116-3	0.120			
	116-4	0.117			
5	145-1	0.115	0.117	0.0032	2.74
	145-2	0.119			
	145-3	0.114			
	145-4	0.121			
6	190-1	0.115	0.116	0.0010	0.83
	190-2	0.117			
	190-3	0.117			
	190-4	0.116			
7	212-1	0.117	0.117	0.0013	1.08
	212-2	0.115			
	212-3	0.118			
	212-4	0.117			
8	247-1	0.121	0.118	0.0024	2.03
	247-2	0.119			
	247-3	0.115			
	247-4	0.117			
9	285-1	0.116	0.119	0.0036	2.99
	285-2	0.124			
	285-3	0.119			
	285-4	0.117			
10	313-1	0.123	0.119	0.0030	2.50
	313-2	0.120			
	313-3	0.116			
	313-4	0.118			

M_{ss} - mean of means of the sub-samples 1-4	0.117
SD of means of the sub-samples 1-4	0.0018
RSD (rel.%)	1.53

mean RSD_w (%)	2.05

Analyte: Oxygen

HS = Homogeneous sample (105)

Line number	Sample number	values
1	HS 1	0.118
2	HS 2	0.114
3	HS 3	0.117
4	HS 4	0.120
5	HS 5	0.116
6	HS 6	0.118
7	HS 7	0.115
8	HS 8	0.113
9	HS 9	0.118
10	HS 10	0.111
M_{HS} - mean of homogeneous sample		0.116
SD_{HS}		0.0027
RSD_{HS} (%)		2.37

Homogeneity between the samples			
Analysis of variance: α = 0.05			
standard deviation within the samples s_w	0.0025	**M_{ss}** 0.117	**RSD %** 1.53
standard deviation between the samples s_b	0.0036	**F_{value}**	2.21
test value s_b^2/s_w^2	1.966	**Characteristic no. for homogeneity between the samples**	0.890
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: α = 0.05			
standard deviation of homogeneous sample SD_{HS}	0.0027	**M_{HS}** 0.116	**RSD_{HS} %** 2.37
		F_{value}	2.86
test value s_w^2/s_{HS}^2	0.858	**Characteristic no. for homogeneity within the samples**	0.300
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Nitrogen

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1	0.181	0.178	0.0099	5.56
	027-2	0.187			
	027-3	0.164			
	027-4	0.181			
2	058-1	0.177	0.179	0.0047	2.62
	058-2	0.177			
	058-3	0.176			
	058-4	0.186			
3	091-1	0.174	0.182	0.0051	2.79
	091-2	0.185			
	091-3	0.183			
	091-4	0.184			
4	116-1	0.178	0.181	0.0019	1.05
	116-2	0.181			
	116-3	0.182			
	116-4	0.182			
5	145-1	0.185	0.187	0.0016	0.87
	145-2	0.187			
	145-3	0.187			
	145-4	0.189			
6	190-1	0.191	0.187	0.0039	2.06
	190-2	0.185			
	190-3	0.190			
	190-4	0.183			
7	212-1	0.184	0.186	0.0039	2.09
	212-2	0.182			
	212-3	0.185			
	212-4	0.191			
8	247-1	0.186	0.185	0.0022	1.20
	247-2	0.182			
	247-3	0.187			
	247-4	0.186			
9	285-1	0.190	0.185	0.0038	2.05
	285-2	0.182			
	285-3	0.182			
	285-4	0.184			
10	313-1	0.183	0.183	0.0047	2.55
	313-2	0.187			
	313-3	0.184			
	313-4	0.176			

M_{ss} - mean of means of the sub-samples 1-4 0.183

SD of means of the sub-samples 1-4 0.0032

RSD (rel.%) 1.76

mean RSD_w (%) 2.28

Analyte: Nitrogen

HS = Homogeneous sample (105)

Line number	Sample number	values
1	HS 1	0.184
2	HS 2	0.188
3	HS 3	0.187
4	HS 4	0.185
5	HS 5	0.189
6	HS 6	0.185
7	HS 7	0.188
8	HS 8	0.188
9	HS 9	0.183
10	HS 10	0.183

M_{HS} - mean of homogeneous sample	0.186
SD_{HS}	0.0023
RSD_{HS} (%)	1.22

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.0047	**M_{ss}** 0.183	**RSD %** 1.76
standard deviation between the samples s_b	0.0064	**F_{value}**	2.21
test value s_b^2/s_w^2	1.864	**Characteristic no. for homogeneity between the samples**	0.843
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.0023	**M_{HS}** 0.186	**RSD_{HS} %** 1.22
		F_{value}	2.86
test value s_w^2/s_{HS}^2	4.363	**Characteristic no. for homogeneity within the samples**	1.525
Homogeneity within the samples: Not very strong inhomogeneity			

Analyte: Total Boron

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1		78.099	0.0922	0.12
	027-2	78.164			
	027-3	78.033			
	027-4				
2	058-1	78.394	78.430	0.0496	0.06
	058-2	78.465			
	058-3				
	058-4				
3	091-1		78.134	0.2553	0.33
	091-2				
	091-3	78.314			
	091-4	77.953			
4	116-1	78.465	78.134	0.4681	0.60
	116-2				
	116-3				
	116-4	77.803			
5	145-1	78.181	78.270	0.1767	0.23
	145-2	78.310			
	145-3	78.499			
	145-4	78.091			
6	190-1	78.449	78.379	0.1144	0.15
	190-2	78.499			
	190-3	78.250			
	190-4	78.320			
7	212-1	78.240	78.243	0.0812	0.10
	212-2	78.340			
	212-3	78.250			
	212-4	78.141			
8	247-1	78.181	78.037	0.2047	0.26
	247-2	78.240			
	247-3	77.823			
	247-4	77.903			
9	285-1	78.012	78.176	0.2524	0.32
	285-2	77.942			
	285-3	78.250			
	285-4	78.499			
10	313-1	78.081	78.369	0.2396	0.31
	313-2	78.379			
	313-3	78.350			
	313-4	78.667			

M_{ss} - mean of means of the sub-samples 1-4	78.227		
SD of means of the sub-samples 1-4	0.1331		
RSD (rel.%)	0.17	**mean RSD_w (%)**	0.25

Analyte: Total Boron

HS = Homogeneous sample (257)

Line number	Sample number	values
1	HS 1	78.115
2	HS 2	78.477
3	HS 3	78.090
4	HS 4	78.284
5	HS 5	78.165
6	HS 6	78.437
7	HS 7	78.125
8	HS 8	78.432
9	HS 9	78.477
10	HS 10	78.289
11	HS 11	78.482
12	HS 12	78.229
13	HS 13	77.822
14	HS 14	78.016
15	HS 15	78.130
16	HS16	78.056
17	HS 17	77.996

M_{HS} - mean of homogeneous sample	78.213
SD_{HS}	0.1979
RSD_{HS} (%)	0.25

Analyte: Total Boron

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.2257	**M_{ss}** 78.227	**RSD %** 0.17
standard deviation between the samples s_b	0.2328	**F_{value}**	2.134
test value s_b^2/s_w^2	1.064	**Characteristic no. for homogeneity between the samples**	0.499
Homogeneity between the samples: **No significant inhomogeneity**			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.1979	**M_{HS}** 78.213	**RSD_{HS} %** 0.25
		F$_{value}$	2.260
test value s_w^2/s_{HS}^2	1.301	**Characteristic no. for homogeneity within the samples**	0.576
Homogeneity within the samples: **No significant inhomogeneity**			

Analyte: HNO_3 soluble Boron

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1		0.110	0.0007	0.65
	027-2				
	027-3	0.110			
	027-4	0.109			
2	058-1	0.110	0.110	0.0000	0.00
	058-2	0.110			
	058-3				
	058-4				
3	091-1		0.113	0.0007	0.63
	091-2	0.113			
	091-3				
	091-4	0.112			
4	116-1	0.111	0.114	0.0042	3.72
	116-2				
	116-3	0.117			
	116-4				
5	145-1		0.111	0.0028	2.55
	145-2				
	145-3	0.113			
	145-4	0.109			
6	190-1	0.110	0.110	0.0007	0.65
	190-2	0.109			
	190-3				
	190-4				
7	212-1		0.115	0.0078	6.79
	212-2	0.120			
	212-3				
	212-4	0.109			
8	247-1	0.110	0.110	0.0007	0.65
	247-2	0.109			
	247-3				
	247-4				
9	285-1		0.115	0.0085	7.38
	285-2	0.121			
	285-3	0.109			
	285-4				
10	313-1	0.112	0.112	0.0007	0.63
	313-2	0.111			
	313-3				
	313-4				

M_{ss} - mean of means of the sub-samples 1-4	0.112		
SD of means of the sub-samples 1-4	0.0022		
RSD (rel.%)	1.95	**mean RSD_w (%)**	2.36

Line number	Sample number	values
1	HS 1	0.116
2	HS 2	0.115
3	HS 3	0.117
4	HS 4	0.114
5	HS 5	0.112
6	HS 6	0.117
7	HS 7	
8	HS 8	
9	HS 9	
10	HS 10	

M_{HS} - mean of homogeneous sample	0.115
SD_{HS}	0.0019
RSD_{HS} (%)	1.69

Homogeneity between the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation within the samples s_w	0.0040	**M_{ss}** 0.112	**RSD %** 1.95
standard deviation between the samples s_b	0.0031	**F_{value}**	3.33
test value s_b^2/s_w^2	0.588	**Characteristic no. for homogeneity between the samples**	0.177
Homogeneity between the samples: No significant inhomogeneity			

Homogeneity within the samples			
Analysis of variance: $\alpha = 0.05$			
standard deviation of homogeneous sample SD_{HS}	0.0019	**M_{HS}** 0.115	**RSD_{HS} %** 1.69
		F_{value}	4.740
test value s_w^2/s_{HS}^2	4.274	**Characteristic no. for homogeneity within the samples**	0.902
Homogeneity within the samples: No significant inhomogeneity			

Analyte: Boron oxide

mass fraction in %

Line number	Sample number	values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	027-1	0.076	0.077	0.0024	3.11
	027-2	0.075			
	027-3	0.080			
	027-4	0.075			
2	058-1	0.076	0.076	0.0016	2.15
	058-2	0.074			
	058-3	0.078			
	058-4	0.076			
3	091-1	0.076	0.078	0.0019	2.47
	091-2	0.076			
	091-3	0.078			
	091-4	0.080			
4	116-1	0.075	0.077	0.0023	3.00
	116-2	0.075			
	116-3	0.079			
	116-4	0.079			
5	145-1	0.074	0.077	0.0026	3.46
	145-2	0.075			
	145-3	0.077			
	145-4	0.080			
6	190-1	0.076	0.077	0.0015	1.94
	190-2	0.076			
	190-3	0.078			
	190-4	0.079			
7	212-1	0.076	0.079	0.0035	4.47
	212-2	0.075			
	212-3	0.081			
	212-4	0.082			
8	247-1	0.077	0.077	0.0008	1.06
	247-2	0.076			
	247-3	0.078			
	247-4	0.077			
9	285-1	0.077	0.077	0.0016	2.12
	285-2	0.075			
	285-3	0.079			
	285-4	0.077			
10	313-1	0.076	0.077	0.0013	1.69
	313-2	0.075			
	313-3	0.077			
	313-4	0.078			

M_{ss} - mean of means of the sub-samples 1-4	0.077
SD of means of the sub-samples 1-4	0.0007
RSD (rel.%)	0.90
mean RSD_w (%)	2.55

Line number	Sample number	values
1	HS 1	0.099
2	HS 2	0.099
3	HS 3	0.097
4	HS 4	0.096
5	HS 5	0.099
6	HS 6	0.099
7	HS 7	0.100
8	HS 8	0.098
9	HS 9	0.099
10	HS 10	0.099
11	HS 11	0.095
12	HS 12	0.098

M_{HS} - mean of homogeneous sample	0.098
SD_{HS}	0.0015
RSD_{HS} (%)	1.49

Homogeneity between the samples

Analysis of variance: α = 0.05

standard deviation within the samples s_w	0.0021	**M_{ss}** 0.077	**RSD %** 0.90
standard deviation between the samples s_b	0.0014	**F_{value}**	2.125
test value s_b^2/s_w^2	0.436	**Characteristic no. for homogeneity between the samples**	0.205

Homogeneity between the samples:
No significant inhomogeneity

Homogeneity within the samples

Analysis of variance: α = 0.05

standard deviation of homogeneous sample SD_{HS}	0.0015	**M_{HS}** 0.098	**RSD_{HS} %** 1.49
		F_{value}	2.570
test value s_w^2/s_{HS}^2	2.041	**Characteristic no. for homogeneity within the samples**	0.794

Homogeneity within the samples:
No significant inhomogeneity

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Appendix 6 of the Certification Report of ERM®-ED102

Compilation of sample preparation procedures, calibrations and methods of final determination used by participating laboratories in interlaboratory comparison for certification of ERM®–ED102

Note: Most text passages were originally taken from the delivered texts of the answer sheets. Amendments were only made if harmonisation with other texts seemed to be necessary. Therefore, BAM is not responsible for the content of this Appendix.

Content

The tables are listed in the following order of investigated parameters (analytes):

Al, Ca, Cr, Cu, Mg, Mn, Na, Ni, Si, Ti, Zr, Total C, Free C, O, N, Total B, HNO_3 soluble B, B_2O_5

Round Robin for Certification of Boron Carbide Powder F360
Compilation of sample preparation procedures, calibrations and methods for final determination used

Aluminium

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from Al in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5.596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask	5N Al (Ventron); 2.279 mg/ml Al in 4% HCl, 0.06% HNO_3 Calibration solutions: 0, 0.912, 1.823, 4.558 mg/L; matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 ml.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h at 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Al (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a MLS-ETHOS-system. Final volume for measurements → 100 mL flask.	1 g/L Al (Kraft) Calibration standards: 0, 100, 200, 300 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
11	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PMP flask).	10000 mg/L Merck standard solution $Al(NO_3)_2$ in 0.5 mol/L HNO_3 Calibration solutions: 0, 0.2, 0.5, 1.0 mg/L Matrix matching: H_3BO_3, HNO_3, HF and H_2SO_4 and 10 mg/L Y as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	9997.2 mg/L Al (Alfa J.M. 5N Al in 20% HCl) Calibration solution: 1mg/L Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	9997.2 mg/L Al (Alfa J.M. 5N Al in 20% HCl) Calibration solutions: 10, 20, 30, 40, 50 µg/L and matrix matching with H_3BO_3, HNO_3, HF and H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	1072 mg/L Al (SRM 3101a, LOT 992003 (NIST) checked with Merck, Certipur) Additions calibration: 0, 85.8, 171.6 µg/L Al and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Al standard (Baker checked with Merck, Certipur) Calibration solution: 0.8 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Al standard (Merck checked with Fluka) Calibration solutions: 0, 0.5, 1.0 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Al standard (Merck, checked with Fluka) Calibration solutions: 40, 80, 120, 160, 240, 320, 400 ng.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; protective gas: 0.8 L/min Oxygen	Synthetic standards (B_4C + Oxide) 26, 230, 730, 1200 mg/kg.	DC-ARC-OES

Aluminium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Al standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions; 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7{\cdot}10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Al Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions 0, 0.2, 0.5 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7{\cdot}10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Al prepared from Al, reagent HCl Calibration solutions 0, 0.5, 1.0 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Al (Merck) Calibration solutions: 0, 0.5, 1.0 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl, transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/ml and Sc 0.1 mg/ml) and dilute to the mark.	Al_2O_3 Calibration solutions: 0, 0.0945, 0.1889, 0.2834, 0.3779, 0.4724, 0.9447, 1.4171, 1.8894 mg / 100 ml. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	(Only final determination by laboratory 31; sample preparation by external partner) ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES
34	M: 0.125 g; Give to sample 3 mL HF, 3 mL HNO_3, 4.5 mL H_2SO_4 in a pressure vessel stood at 240°C and evaporated. Then dilute into 100 mL flask.	1 mg Al_2O_3 solution was prepared using Al metal (6N), HCl (1+1) and H_2O. It contains Co solution as buffer. Calibration solutions: 0 to 0.6 mg/L and matrix matching (H_2SO_4) were used.	ICP OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Al Multi element standard Merck VI Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm).	Semi quantitative method Results excluded	XRF
38	no information	Calibration solution: 0, 0.5, 1 mg/L	ICP OES
41	M: 0.3 g; sample weighing in a platinum dish, add 6 g Na_2CO_3 and 0.03 g $NaNO_3$. Fusing in a electric furnace with SiC-heater element. Cond. 660 to 760 °C / 1 h, 760 to 900 °C / 1 h. Dissolving the sample in 30 mL of 6 mol / L HCl and dilute to 250 mL flask.	1000 mg/L Al prepared from Al (4N), reagent HCl Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 ml.	1000 mg Al /L Merck calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Calcium			
Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from high purity $CaCO_3$ (BAM) in HNO_3. Calibration solution: 1 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 ml.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	CaCO3, pA.; 1000 mg/mL in 0.5% HNO_3 Calibration solutions: 0, 0.4, 0.8, 2.4 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 ml.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Ca (Kraft checked with Merck) Method of standard addition was used.	F AAS
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a MLS-ETHOS-system. Final volume for measurements → 100 ml.	1 g/L Ca (Kraft) Calibration standards: 0, 50, 100, 150 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
11	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PMP flask).	1000.3 mg/L Ca, Merck, reinst in 10% HCl Calibration solutions: 0, 0.2, 0.5, 1.0 mg/L; Matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 and 10 mg/L Y as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	994.3 mg/L Ca (Alfa J.M. 5N $CaCO_3$ in 10% HNO_3) Calibration solution: 400 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	994.3 mg/L Ca (Alfa J.M. 5N $CaCO_3$ in 10% HNO_3) Calibration solutions: 0.08, 0.16, 0.24, 0.32, 0.40 mg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 0.1% CsCl as ionisation buffer were used.	F AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	1306 mg/L Ca (SRM 3109a, LOT 892601 (NIST) checked with Merck, Certipur) Additions calibration: 0, 41.8, 83.6 µg/L Ca and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g; no sample digestion 2h irradiation at 30 MeV	CaO solid pure substance (m3N5 Merck)	IPAA
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Ca standard (Baker checked with Merck, Certipur) Calibration solution: 0.4 mg/L; Matrix matching: H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Ca standard (Merck checked with Fluka) Calibration solutions: 0, 0.25, 0.5mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Ca standard (Merck checked with Fluka) Calibration solutions: 0, 0.25, 0.5 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen.	Synthetic standards (B4C + Oxide) 45, 210, 560, 950 mg/kg.	DC-ARC-OES

Calcium			
Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Ca standard, (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Ca Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions:0, 0.2, 0.5 mg/L and matrix matching with 1 g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Ca prepared from CaO, reagent HNO_3 Calibration solutions: 0, 0.2, 0.5 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Ca (Merck) Calibration solutions: 0, 0.5, 1.0 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl, transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/ml and Sc 0.1 mg/ml) and dilute to the mark.	CaO Calibration solutions: 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.15, 0.20 mg / 100 ml. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	1000 mg/L Ca Multi element standard Merck VI Calibration solutions: 0, 0.1, 1, 2 mg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
38	no information	calibration solution: 0, 0.5, 1 mg/L	ICP OES
41	M: 0.3 g; Acid decomposition with mixture of 4 mL HNO_3 + 4 mL HF + 6 mL H_2SO_4 in a digestion bomb for 14 h at 240°C. Transferring to platinum dish and evaporating on a sand bath → diluting to 100 mL flask.	1000 mg/L Ca prepared from $CaCO_3$ (4N), reagent HCl Calibration solutions: 0, 2, 3 mg/L; Match acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 ml.	1000 mg/L Ca Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Cobalt

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from Co in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 ml.	ICP OES (Results excluded: "less than"-values)
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	Co-metal (Alfa J.M.); 4.0028 mg/ml in 5% HNO_3 Calibration solutions: 0, 0.2, 0.06, 0.24 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 ml.	ICP OES (Results excluded: "less than"-values)
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Co (Kraft checked with Merck) method of standard addition	ICP OES (Results excluded: "less than"-values)
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a MLS-ETHOS-system. Final volume for measurements → 100 ml.	1 g/L Co (Kraft) Calibration standards: 0, 1.0, 2.0, 3.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	7011.8 mg/L Co (Alfa J.M. m3N5 Co in 10% HNO_3) Calibration solution: 0.8, 1.6, 2.4, 3.2, 4.0 µg/L. Matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 addition calibration technique used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	6860 mg/L Co (Alfa J.M. 99.95% LOT G02G19, checked with Merck, ICP IV Additions calibration: 0, 0.25, 0.50, 0.79 µg/L Al and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g no sample digestion 2h irradiation at 30 MeV	Co solid metal foil (4N Goodfellow)	IPAA
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Co standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Co standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.1 mg/L and HNO_3 were used.	ETV-ICP OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof; 260°C / 16 h) → diluted to 100 ml	1000 mg/L Co standard (Merck ICP checked with Alfa Aesar ICP) calibration solution: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L; matrix matching: H_3BO_3 were used	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Co prepared from Co, reagent HNO_3 Calibration solutions: 0, 0.04, 0.08, 0.10 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Co (Merck) Calibration solutions: 0, 0.05, 0.1 mg/L.	ICP OES (Results excluded: "less than"-values)
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Co Multi element standard Merck VI Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 ml.	1000 mg Co / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Chromium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.5 g; Sample was fused with 4 g Na_2CO_3 and 1 g KNO_3. The cake was acidified with HCl.	1 g/L prepared from CrO_3 in HNO_3. Matrix matching with boric acid, Na_2CO_3 and KNO_3.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	4N Cr (Alfa J.M.); 1,0075 mg/ml Cr in 3% HCl + 1% HNO_3) Calibration solutions: 0, 0.06, 0.121, 0.403 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 ml.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Cr (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a MLS-ETHOS-system. Final volume for measurements → 100 ml.	1 g/L Cr (Kraft) Calibration standards: 0, 3.0, 6.0, 9.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP-MS
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	9992.6 mg/L Cr (Alfa J.M. 99.995% Cr in 28% HCl / 0.04% HNO_3) Calibration solution: 30 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	9992.6 mg/L Cr (Alfa J.M. 99.995% Cr in 28% HCl / 0,04% HNO_3) Calibration solutions: 1, 2, 3, 4, 5 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	1351 mg/L Cr (SRM 3112a, LOT 990607 (NIST) checked with Merck, ICP IV) Additions calibration: 0, 2.7, 5.4, 8.7 µg/L Cr and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Cr standard (Baker checked with Merck, Certipur) Calibration solution: 4 mg/L and matrix matching: H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Cr standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/l Cr standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.1 mg/l and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 l/min oxygen	Synthetic standards (B4C + Oxide) 4.5, 25, 63, 105 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Cr standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Chromium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Cr Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions:0, 0.2, 0.5 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7 \cdot 10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Cr prepared from Cr, reagent HCl Calibration solutions: 0, 0.04, 0.08, 0,1 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Cr (Merck) Calibration solutions: 0, 0.05, 0.1 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl, transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	Cr_2O_3 Calibration solutions: 0, 0.0102, 0.0205, 0.0307, 0.0409, 0.0512, 0.1023, 0.1535, 0.2046 mg / 100 mL. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	(Only final determination by laboratory 31; sample preparation by external partner) ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Cr Multi element standard Merck VI Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
41	M: 0.3 g; Acid decomposition with mixture of 4 mL HNO_3 + 4 mL HF + 6 mL H_2SO_4 in a digestion bomb for 14 h at 240°C. Transferring to platinum dish and evaporating on a sand bath → diluting to 100 mL flask.	1000 mg/L Cr prepared from Cr (4N), reagent HCl Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L. Match acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Cr / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Copper			
Lab. code	Sample preparation	Calibration	Final determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from Cu in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES (Results excluded: "less than"-values)
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	Cu (Alfa J.M.); 25.007 mg/mL Cu in 10% HNO_3 Calibration solutions: 0, 0.02; 0.06; 0.24 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES (Results excluded: "less than"-values)
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Cu (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Cu (Kraft) Calibration standards: 0, 1.0, 2.0, 3.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP-MS
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10044.8 mg/L Cu (Alfa J.M. 99.999% Cu in 4% HNO_3) Calibration solution: 20 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10044.8 mg/L Cu (Alfa J.M. 99.999% Cu in 4% HNO_3) Calibration solution: 2, 4, 6, 8, 10 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	11171 mg/L Cu (Alfa J.M. 6N LOT G24F31 checked with Merck, ICP IV) Additions calibration: 0, 1.1, 2.2, 3.6 µg/L Cu and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Cu standard (Baker checked with Merck, Certipur) Calibration solution: 0.1 mg/L; Matrix matching: H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Cu standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Cu standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.1 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen	Synthetic standards (B4C + Oxide) 0.02, 2.4, 5.2, 8.0 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Cu standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L; Matrix matching with H_3BO_3 were used.	ICP OES

Copper			
Lab. code	Sample preparation	Calibration	Final determination
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Cu prepared from Cu, reagent HNO_3 Calibration solutions: 0, 0.04, 0.08, 0.10 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof),	1000 mg/L Cu (Merck) Calibration solutions: 0, 0.05, 0.10 mg/L.	ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Cu Multi element standard Merck VI Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Cu / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Iron			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask	1 g/L prepared from Fe in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	4N85 Fe (Ventron); 9.9866 mg/mL Fe in 10% HNO_3. Calibration solutions: 0, 1.997, 5.992, 15.979 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Fe (Kraft checked with Merck) Method of standard addition was used,	F AAS
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Fe (Kraft) Calibration standards: 0, 300, 600, 900 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
11	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PMP flask).	1000 mg/L Fe m3N4 metal powder (Alfa J.M. 5N Al in 10% HCl Calibration solutions: 0, 0.2, 0.5, 1.0 mg/L; Matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 and 10 mg/L Y as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10115.7 mg/L Fe (High purity Fe Primary RM BAM-Y002 in 8% HNO_3/ 2% HCl). Calibration solution: 4 mg/L; Matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10115.7 mg/L Fe (High purity Fe Primary RM BAM-Y002 in 8% HNO_3/ 2% HCl). Calibration solutions: 0.2, 0.4, 0.6, 0.8, 1.0 µg/L; and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	F AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	1091 mg/L Fe (SRM 3126a, LOT 792411 (NIST) checked with Merck, Certipur) Additions calibration:0, 218, 436, µg/L Fe and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g; no sample digestion 2h irradiation at 30 MeV	Fe solid metal foil (4N Goodfellow)	IPAA
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Fe-I standard (Baker checked with Merck, Certipur) Calibration solution: 4 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Fe standard (Merck checked with Fluka) Calibration solutions: 0, 1.5, 3.0 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Fe standard (Merck checked with Fluka) Calibration solutions: 0, 1.5, 3.0 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen	Synthetic standards (B4C + Oxide) 150, 740, 1400, 1900 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Fe standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Iron			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
21	M: 0.2 g; Take sample exactly in Pt-crucible, add 3 g Na_2CO_3 and 0.1 g KNO_3, put the mixture into furnace, heat with 650°C for 2 h, 700°C for 1 h, 900°C for 30 min and take out.		Spectro-photometry (MAS)
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Fe Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions: 0, 2.0, 5.0 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7 \cdot 10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Fe prepared from Fe, reagent HNO_3 Calibration solutions: 0, 1.5, 3.0 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Fe (Merck) Calibration solutions: 0, 0.5, 1.0, 2.0 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl and transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	Fe_2O_3 Calibration solutions: 0, 0.0429, 0.0858, 0.1286, 0.1716, 0.2145, 0.4289, 0.6434, 0.8578 mg / 100 mL The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	100 mg/L Fe Multi element standard Merck VI Calibration solutions: 0, 10, 100, 200 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
38	no information	Calibration solution: 0, 1, 2 mg/L	ICP OES
41	M: 0.3 g; Sample weighing in a platinum dish, add 6 g Na_2CO_3 and 0.03 g $NaNO_3$. Fusing in a electric furnace with SiC-heater element. Cond. 660 to 760 °C / 1 h, 760 to 900 °C / 1 h. Dissolving the sample in 30 mL of 6 mol / L HCl and dilute to 250 mL flask.	1000 mg/L Fe prepared from Fe (4N), reagent HCl Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Fe / l Merck Calibration solutions: 0, 0.50, 1, 1.50, 2.00 mg/100 mL.	ICP OES

Magnesium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF(40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from MgO in HNO_3 Calibration solution: 1 mg/L; Matrix matching: 5.596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	3N5 Mg (Alfa J.M.); 1.0041 mg/mL Mg in 0,5% HNO_3. Calibration solutions: 0, 0.01, 0.03, 0.161 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Mg (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Mg (Kraft) Calibration standards: 0, 3.0, 6.0, 9.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP-MS
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	1002.7 mg/L Mg (Alfa J.M. 99.98% Mg in 5% HCl) Calibration solution: 15 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	1002.7 mg/L Mg (Alfa J.M. 99.98% Mg in 5% HCl) Calibration solutions: 0.2, 0.4, 0.6, 0.8, 1.0 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	105.26 mg/L Mg (SRM 3131a, LOT 991107 (NIST) checked with Merck, ICP IV) Additions Calibration: 0, 1.7, 3.4, 5.4 µg/L Mg and 250 µg/L Be9 as internal standard were used.	ICP-SFMS
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Mg standard (Baker checked with Merck, Certipur) Calibration solution: 0.1 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Mg standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Mg standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen.	Synthetic standards (B4C + Oxide) 9, 38, 95, 150 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Mg standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Mg prepared from MgO, reagent HNO_3 Calibration solutions: 0, 0.04, 0.08, 0.10 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Mg (Merck) Calibration solutions: 0, 0.05, 0.10 mg/L.	ICP OES

Magnesium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl and transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	MgO Calibration solutions: 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.15, 0.20 mg / 100 mL. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Mg Multi element standard Merck VI and Mg standard Ultra Scientific Calibration solutions: 0, 10, 100, 200 µg/L, external calibration.	ICP-MS
41	M: 0.3 g; Sample weighing in a platinum dish, add 6 g Na_2CO_3 and 0.03 g $NaNO_3$. Fusing in a electric furnace with SiC-heater element. cond. 660 to 760 °C / 1 h, 760 to 900 °C / 1 h. Dissolving the sample in 30 mL of 6 mol / L HCl and dilute to 250 mL flask.	1000 mg/L Mg prepared from Mg (4N), reagent HCl Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Mg / l Merck Calibration solution: 0, 0.25, 0.50, 0.75, 1.00 mg/100 mL.	ICP OES

Manganese			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from $Mn(NO_3)_2$ in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	Mn (Alfa J.M.); 1.003 mg/mL Mn in 5% HNO_3) Calibration solutions: 0, 0,04, 0,08, 0,241 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Mn (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Mn (Kraft) Calibration standards: 0, 10, 20, 30 mg/kg, and matrix simulation by H_3BO_3 suprapur.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10252.2 mg/L Mn (Alfa J.M. m4N in 8% HCl) Calibration solution: 80 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10252.2 mg/L Mn (Alfa J.M. m4N in 8% HCl) Calibration solution: 1.6, 3.2, 4.8, 6.4, 8.0 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	10048 mg/L Mn (Alfa J,M, 4N LOT L01F11 checked with Merck, ICP IV) Additions calibration: 0, 5.0, 5.4, 10.0, 16.1 µg/L Mn and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g; no sample digestion 2h irradiation at 30 MeV	Mn (4N Goodfellow)in HNO_3, adsorbed at cellulose.	IPAA
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Mn standard (Baker checked with Merck, Certipur) Calibration solution: 0.1 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Mn standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Mn standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen	Synthetic standards (B4C + Oxide) 1, 40, 120, 195 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Mn standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Manganese			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Mn Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solution: 0, 0.2, 0.5 mg/L And matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7 \cdot 10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Mn prepared from Mn, reagent HNO_3 Calibration solutions: 0, 0.04, 0.08, 0.10 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Mn (Merck) Calibration solutions: 0, 0.05, 0.10 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl and transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	MnO Calibration solutions: 0, 0.0103, 0.0207, 0.0310, 0.0413, 0.0516, 0.1033, 0.1549, 0.2066 mg / 100 mL. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
34	M: 0.125 g; Give to sample 3 mL HF, 3 mL HNO_3, 4.5 mL H_2SO_4 in a pressure vessel stood at 240°C and evaporated. Then dilute into 100 mL flask.	1 mg MnO / mL solution was prepared using Mn (4N) 0.3873 g + 10 mL HCl (1+1) in 500 mL. Calibration solutions: 0 to 0.3 mg/L and matrix matching (H_2SO_4) were used.	ICP OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	10 mg/L Mn Multi element standard Merck VI Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
38	no information	Calibration solution: 0, 0.5, 1 mg/L	ICP OES
41	M: 0.3 g; Acid decomposition with mixture of 4 mL HNO_3 + 4 mL HF + 6 mL H_2SO_4 in a digestion bomb at 240°C for 14 h. Transferring to platinum dish and evaporating on a sand bath → diluting to 100 mL flask.	1000 mg/L Mn prepared from Mn (4N), reagent HNO_3 Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Mn / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1.00 mg/100 mL.	ICP OES

Sodium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask; additional 5 mL of CsCl (aq 1%).	1 g/L prepared from $NaNO_3$ in HNO_3 Calibration solution: 1 mg/L; Matrix matching: 5.596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF (40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	Na_2CO_3, p.A., anhydrous; 1,0002 mg/mL Na in 2,5% HCl Calibration solutions: 0, 0.12, 0.32, 1.00 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Al (Kraft checked with Merck) Method of standard addition was used.	F AAS
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask)	988.9 mg/L Na (Alfa J.M. 5N NaCl in 1% HCl) Calibration solutions: 0.8, 1.6, 2.4, 3.2, 4.0 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	96.69 mg/L Na (SRM 3152a, LOT 790404 (NIST) checked with Merck, ICP IV) Additions calibration:0, 3.9, 7.7, 12.4 µg/L Na and 250 µg/L Be9 as internal standard were used.	ICP-SFMS
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Na standard (Baker checked with Merck, Certipur) Calibration solution: 0.1 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Na standard (Merck checked with Fluka) Calibration solutions: 0, 0.20 mg/L and HNO_3 were used.	F AAS
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Na standard (Merck checked with Fluka) Calibration solutions: 0, 0.20 mg/L and HNO_3 were used.	ETV-ICP OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof; for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Na standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Na prepared from NaCl, reagent water Calibration solutions: 0, 0.025, 0.05, 0.10 mg/L and matrix matching were used.	AAS
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Na / l Merck Calibration solutions: 0, 0.25, 0.75, 1 mg/100 mL.	AAS

Nickel			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from $Mn(NO_3)_2$ in HNO_3 Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES (Results excluded: "less than"-values)
2	M: 0.2 g 2 mL HF (40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	4N8 Ni (Alfa J.M.); 1,0393 mg/mL Ni in 2,5% HNO_3 Calibration solutions: 0, 0,021, 0,062, 0,249 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Ni (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Ni (Kraft) Calibration standards: 0, 5.0, 10.0, 15.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP-MS
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10015.4 mg/L Ni (Alfa J.M. 4N Ni in 20% HNO_3) Calibration solution: 80 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10015.4 mg/L Ni (Alfa J.M. 4N Ni in 20% HNO_3) Calibration solution: 4, 8, 12, 16, 20 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	9221 mg/L Ni (Alfa J.M. 4N, LOT H02F08 checked with Merck, ICP IV) Additions Calibration: 0, 4.6, 9.2, 14.8 µg/L Ni and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Ni standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Ni standard (Merck checked with Fluka) Calibration solutions: 0, 0.05, 0.10 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen	Synthetic standards (B4C + Oxide) 1, 50, 125, 200 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof. For 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Ni standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Nickel			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7{\cdot}10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Ni Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions: 0, 0.2, 0.5 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7{\cdot}10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Ni prepared from Ni, reagent HNO_3 Calibration solutions: 0, 0.04, 0.08, 0.10 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Ni (Merck) Calibration solutions: 0, 0.05, 0.10 mg/L.	ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
41	M: 0.3 g; Acid decomposition with mixture of 4 mL HNO_3 + 4 mL HF + 6 mL H_2SO_4 in a digestion bomb for 14 h at 240°C. Transferring to platinum dish and evaporating on a sand bath → diluting to 100 mL flask.	1000 mg/L Ni prepared from Ni (4N), reagent HNO_3 Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Ni / l Merck Calibration solutions: 0, 0.25, 0.75, 1 mg/100 mL.	ICP OES

Silicon

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.3 g; Fused with 5 g Na_2CO_3 and 2 g KNO_3. Final determination as silico-molydato-complex after solvent extraction with butanol.	0.2139 g SiO_2 (Optipur, calcined at 1100°C). Fused with 5 g Na_2CO_3 diluted to 500 mL.	Spectrophotometry (MAS)
5	M: 0.25 g; Reagents: 3.6 g Na_2CO_3 + 2.3 g $Na_2B_4O_7$ + 1 g KNO_3 as melting agent.	25 mg SiO_2 (99.999% from Alfa J.M.) heating by 1200°C/1h, melting with 3.6 g Na_2CO_3 + 2.3 g $Na_2B_4O_7$ + 1 g KNO_3 / 500 mL flask. Calibration solutions: 0.023, 0.047, 0.070, 0.094, 0.117 mg Si; Matrix: 3.6 g Na_2CO_3 + 2.3 g $Na_2B_4O_7$ + 1 g KNO_3 pro 100 mL flask.	Spectrophotometry (MAS)
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	1000 mg/L Si (Merck Certipur, $(NH_4)_2SiF_6$ in water) Calibration solution: 6 mg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	10241 mg/L Si (Alfa J.M. 5N Ni in 10% HNO_3 / 10% HF) Calibration solutions: 40, 80, 120, 160, 200 µg/L and matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	10241 mg/L Si (Alfa J.M. 5+N, LOT J04F02 checked with Merck, Certipur) Additions calibration: 0, 81.9, 163.9, µg/L Si and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Si standard (Merck checked with Fluka) Calibration solutions: 0, 0.75,1.5 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Si standard (Merck checked with Fluka) Calibration solutions: 0, 0.75,1.5 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 l/min oxygen.	Synthetic standards (B4C + Oxide) 100, 700, 1450, 2300 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Si standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES
21	M: 0.2 g; Take sample exactly in Pt-crucible, add 3 g Na_2CO_3 and 0.1 g KNO_3, put the mixture into furnace, heat with 650°C for 2 h, 700°C for 1 h, 900°C for 30 min and take out.	self-made	Spectrophotomety (MAS)
24	M: 0.2 g; Decomposition with 5 g Na_2CO_3 at 950°C, 50 min	1000 mg/L Si prepared from SiO_2, reagent Na_2CO_3 Calibration solutions: 0, 0.05, 0.10, 0.15, 0.20, 0.25 mg/L and matrix matching were used.	Spectrophotometry (MAS)
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Si (Merck) Calibration solutions: 0, 0.5, 1.0, 2.0 mg/L.	ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	1000 mg/L Si single element standard Ultra Scientific Calibration solutions: 0, 10, 20, 50 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
41	M: 0.3 g; Sample weighing in a platinum dish, add 6 g Na_2CO_3 and 0.03 g $NaNO_3$. Fusing in a electric furnace with SiC-heater element. Cond. 660 to 760 °C / 1 h, 760 to 900 °C / 1 h. Dissolving the sample in 30 mL of 6 mol / L HCl and dilute to 250 mL flask.	1000 mg/L Si SiO_2 fusion with Na_2CO_3, Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Si / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Titanium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from TiO_2 in HF Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	99,9% Ti (Hoch-Light); 1,0038 mg/mL Ti in 1,5% HNO_3 + 1% HF Calibration solutions: 0, 0,201, 0,602, 2,008 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Ti (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Ti (Kraft) Calibration standards: 0, 100, 200, 300 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
11	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PMP flask).	4063.2 mg/L Ti (Alfa J.M. 4N Ti in 5% HNO_3 / 4% HF) Calibration solutions: 0, 0.2, 0.5, 1.0 mg/L and matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 and 10 mg/L Y as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	4063.2 mg/L Ti (Alfa J.M. 4N Ti in 5% HNO_3 / 4% HF) Calibration solution: 400 µg/L; Matrix matching with H_3BO_3, HNO_3, HF, H_2SO_4 and 1 mg/L Sc as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	4063.2 mg/L Ti (Alfa J.M. 4N Ti in 5% HNO_3 / 4% HF) Calibration solution,: 45 and 55 µg/L; bracketing technique + matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 were used.	ET AAS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	1054 mg/L Ti (SRM 3162a, LOT 992801 (NIST) checked with Merck, Certipur) Additions calibration: 0, 42.2, 84.4 µg/L Ti and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g; no sample digestion 2h irradiation at 30 MeV	Ti solid metal foil (4N Goodfellow)	IPAA
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Ti standard (Baker checked with Merck, Certipur) Calibration solution: 0.4 mg/L; Matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Ti standard (Merck checked with Fluka) Calibration solutions: 0, 0.25, 0.50 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Ti standard (Merck checked with Fluka) Calibration solutions: 0, 0.25, 0.50 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen.	Synthetic standards (B4C + Oxide) 83, 350, 920, 1460 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Ti standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Titanium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7 \cdot 10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Ti Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions:0, 0.2, 0.5 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7 \cdot 10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Ti prepared from TiO_2, reagent HF Calibration solutions: 0, 0.2, 0.5 mg/L and matrix matching were used.	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Ti (Merck) Calibration solutions: 0, 0.5, 1.0 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl and transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	TiO_2 Calibration solutions: 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1001, 0.1501, 0.20 mg / 100 mL. The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
34	M: 0.125 g; Give to sample 3 mL HF, 3 mL HNO_3, 4.5 mL H_2SO_4 in a pressure vessel stood at 240°C and evaporated. Then dilute into 100 mL flask.	1 mg Ti/L solution was prepared using Ti (4N), 0.5000 g Ti 10 mL HF, 15 mL H_2SO_4 (1+1), 0.5 mL HNO_3 in 500 mL. Calibration solutions: 0, 0.6 mg/L and matrix matching (H_2SO_4) were used.	ICP OES
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	1000 mg/L Ti Single element standard Ultra scientific Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
38	no information	calibration solution: 0, 0.5, 1 mg/L	ICP OES
41	M: 0.3 g; Sample weighing in a platinum dish, add 6 g Na_2CO_3 and 0.03 g $NaNO_3$. Fusing in a electric furnace with SiC-heater element. Cond. 660 to 760 °C / 1 h, 760 to 900 °C / 1 h. Dissolving the sample in 30 mL of 6 mol / L HCl and dilute to calibration mark of a 250 mL flask.	1000 mg/L Ti prepared from Ti (4N), reagent HF + H_2SO_4 Calibration solutions: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Ti / L Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Tungsten

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from APT in HF Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES (Results excluded: "less than"-values)
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	W (Plansee target 181293); 1,000 mg/mL W in 25% HNO_3 + 1.2% HF Calibration solutions: 0, 0.02, 0.06, 0.24 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES (Results excluded: "less than"-values)
5	M: 0.4 g; A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L W (Kraft checked with Merck) Method of standard addition was used.	ICP OES (Results excluded: "less than"-values)
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L W (Kraft) Calibration standards: 0, 3.0, 6.0, 9.0 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP-MS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	10999 mg/L Cr (Alfa J.M. m3N8, LOT HS 38881, checked with BAM-A-primary W-1) Additions calibration: 0, 2.8, 5.5, 8.8 µg/L W and 5 µg/L Lu175 as internal standard were used.	ICP-SFMS
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L W prepared from W, reagent HF Calibration solutions: 0, 0.04, 0.08, 0.1 mg/L; and matrix matching were used.	ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	1000 mg/L W Single element standard Ultra Scientific Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm).	Semi quantitative method Results excluded	XRF
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg W / l Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Zirconium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g; 4 mL HF (40%), 4 mL HNO_3 (65%), 4 mL H_2SO_4 (96%) 16 h by 250°C DAB-II digestion system → 50 mL flask.	1 g/L prepared from $ZrOCl_2$ in HCl Calibration solution: 5 mg/L; Matrix matching: 5,596 g H_3BO_3, 20 mL HF, 20 mL HNO_3 and 20 mL H_2SO_4 were added to 250 mL.	ICP OES
2	M: 0.2 g; 2 mL HF(40%), 6 mL HNO_3 (65%), 16 h by 240°C DAB-II digestion system (Berghof 50 mL Teflon liner) → 25 mL flask.	Zr (Alfa J.M.); 1,0005 mg/mL Zr in 2% HNO_3 + 1,2% HF Calibration solutions: 0, 0.12, 0.48, 1.00 mg/L; Matrix matching: 900 mg H_3BO_3, 2 mL HF, 6 mL HNO_3 were added to 25 mL.	ICP OES
5	M: 0.4 g;A 50 mL PTFE-vessel was used; 4 mL HF (40%), 4 mL HNO_3 (65%), 6 mL H_2SO_4 (96%) 20 h by 240°C in a digestion system + 5 mL CsCl solution (10g/L) → 100 mL flask.	1 g/L Zr (Kraft checked with Merck) Method of standard addition was used.	ICP OES
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	1 g/L Zr (Kraft) Calibration standards: 0, 50, 100, 150 mg/kg and matrix simulation by H_3BO_3 suprapur.	ICP OES
11	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PMP flask).	1000 mg/L Zr, ZrOCl x 8 H_2O in HCl Calibration solutions:0, 0.2, 0.5, 1.0 mg/L; Matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 and 10 mg/L Y as internal standard were used.	ICP OES
12	M: 0.25 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 12 h at 250°C → solution diluted to 50 mL (PMP flask).	6174 mg/L Zr (Alfa J.M. m3N4 Zr-foil in 5% HNO_3 / 2% HF) Calibration solution: 400 µg/L and matrix matching: H_3BO_3, HNO_3, HF, H_2SO_4 with 1 mg/L Sc as internal standard were used.	ICP OES
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:10.	10568 mg/L Zr (Alfa J.M. m3N4, LOT J17G13 checked with Merck, Certipur) Additions calibration: 0, 21.1, 42.2 µg/L Zr and 10 µg/L Rb85 as internal standard were used.	ICP-SFMS
15	M:1.0-1.3 g; no sample digestion 2h irradiation at 30 MeV	Zr solid metal foil (4N Goodfellow)	IPAA
17	M: 0.5 g; Acid decomposition with mixture of 6 mL HNO_3 + 1.5 mL HF in 150 mL PTFE liners (DAB-II, Berghof) for 8 h at 220°C → solution diluted to 100 mL flask.	1000 mg/L Zr standard (Baker checked with Merck, Certipur) Calibration solution: 0.2 mg/L and matrix matching with H_3BO_3, HNO_3, HF were used.	ICP OES
18	M: 0.25-0.40 g; Acid decomposition with 10 mL HNO_3 in 150 mL TFM-PTFE liners (DAB-III, Berghof).	1000 mg/L Zr standard (Merck checked with Fluka) Calibration solutions: 0, 0.1, 0.2 mg/L and HNO_3 were used.	ICP OES
18	M: 3x 1.0-3.5 mg; reagents: Freon R12	1000 mg/L Zr standard (Merck checked with Fluka) Calibration solutions: 0, 0.1, 0.2 mg/L and HNO_3 were used.	ETV-ICP OES
18	M: 3x 4.9-5.1 mg; Protective gas: 0.8 L/min Oxygen	Synthetic standards (B4C + Oxide) 25, 220, 680, 1230 mg/kg.	DC-ARC-OES
20	M: 0.1 g; Acid decomposition with 10 mL HNO_3 (bomb system, Berghof, for 16 h at 260°C) → diluted to 100 mL flask.	1000 mg/L Zr standard (Merck ICP checked with Alfa Aesar ICP) Calibration solutions: 0, 0.01, 0.05, 0.1, 0.3, 1.0 mg/L and matrix matching with H_3BO_3 were used.	ICP OES

Zirconium			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
22	M: 0.1g; Mixed in a platinum crucible with 1g Na_2CO_3 and 1g $Na_2B_4O_7{\cdot}10H_2O$. Place a lid on the crucible and heat of a Bunsen burner for 30 min. Continue heating with mid-flame for 30 min. Then heat the crucible with a hot flame until the mixture is completely molten. Keep the temperature until the whole sample has been decomposed. Add 10 mL deionized water into the crucible and heat it until the molten mass is dissolved into solution. After that, the solution is transferred into a 100 mL flask. The crucible is rinsed with deionized water. The washing solution is added to the flask too. And 10 mL HCl is added into the flask. Finally volume is 100 mL.	1000 mg/L Al Single standard solution from Shanghai Institute of Measurement and Testing Technology Calibration solutions:0, 2.0, 5.0 mg/L and matrix matching with 1 g Na_2CO_3 and 1 g $Na_2B_4O_7{\cdot}10H_2O$.	ICP OES
24	M: 0.2 g; Decomposition with 0.5 mL HF, 5 mL HNO_3, 3.5 mL H_2SO_4 at high pressure (14h at 240°C) → 50 mL flask.	1000 mg/L Zr prepared from ZrO_2, reagent HF Calibration solutions: 0, 0.1, 0.2 mg/L and matrix matching were used	ICP OES
25	M: 0.3 g; Decomposition with 4 mL HF, 4 mL HNO_3, 4 mL H_2SO_4 in a digestion system (Berghof).	1000 mg/L Zr (Merck) Calibration solutions: 0, 0.10, 0.20 mg/L.	ICP OES
31	Sample preparation by TYK: M: 0.25 g; After carbonate fusion with 6g Na_2CO_3 at 1050°C solve the cake with HCl and transfer into 250 mL flask and dilute to the mark. Transfer 20 mL aliquot into 100 mL flask and add 5 mL mixed solution (Y 0.1 mg/mL and Sc 0.1 mg/mL) and dilute to the mark.	ZrO_2 Calibration solutions: 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.15, 0.20 mg / 100 mL The solutions for the calibration were prepared for multi elements with buffer solution (Y and Sc).	Final determination by Horiba: ICP OES
33	M: 0.015 g; Pressing in graphite electrode, 1:1 with C.	Spex mix in CeO	DC-ARC-OES (Results excluded: "less than"-values)
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	1000 mg/L Zr Calibration solutions: 0, 1, 10, 20 µg/L, external calibration.	ICP-MS
37	The sample is put into the sample cell covered polyethylene film (6 µm)	Semi quantitative method Results excluded	XRF
38	no information	Calibration solution: 0, 0.5, 1 mg/L	ICP OES
41	M: 0.3 g; Acid decomposition with mixture of 4 mL HNO_3 + 4 mL HF + 6 mL H_2SO_4 in a digestion bomb at 240°C for 14 h; transferring to platinum dish and evaporating on a sand bath → diluting to 100 mL flask.	1000 mg/L Zr prepared from ZrO_2 (3N), in HF + H_2SO_4 Calibration solution: 0, 0.2, 0.5, 1, 2, 3 mg/L; Match flux and acid concentration, use calibration graph method with computer.	ICP OES
42	M: 0.25 g; Decomposition with 4 mL HF, 4 mL HNO_3, 6 mL H_2SO_4 in a pressure vessel stood at 240°C for 16 h. The solution was diluted to 50 mL.	1000 mg Zr /L Merck Calibration solutions: 0, 0.25, 0.50, 0.75, 1 mg/100 mL.	ICP OES

Total Carbon

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 88 mg; Embedded in Al-foil Flux: 1,5 g tungsten grid / 3 g copper chips.	High purity $CaCO_3$ (BAM)	Comb.-IR
1	M: 30 mg; + 3 g CuO / Cu_2O as a flux; furnace temperature 1200°C	High purity $CaCO_3$ (BAM)	Comb.-Coul.
2	M: 22 mg; Samples weighted in Ni-bushes. 0,5 g Fe and 1 g W as a flux; furnace temperature 1200°C.	spectral pure C from Ringsdorf M: 5 mg	Comb.-IR
3	M: 100 mg; 1,5 g Sn coated Cu + 1,2 g W as a flux.	$CaCO_3$ 99.995+% (Aldrich); dried at 120°C for 2 h. M: 0,185 g	Comb.-IR
4	M: 60 mg; 60 s pre-analyze purge, 45 s burn	22,95% B_4C; (no direct traceability, results excluded)	Comb.-IR
5	M: 75-80 mg; purge time: 30 s, burn time 70 s, post burn delay 25 s, acquire time 25 s. Addition: Cu-metal accelerator HRT 550-055.	High purity $CaCO_3$ (BAM); one point calibration used.	Comb.-IR
7	M: 50 mg; Sn-capsule, W-Fe accelerator.	High purity $CaCO_3$ (BAM)	Comb.-IR
8	M: 30 mg; coulometric determination with 10% gas split.	High purity $CaCO_3$ (BAM)	Comb.-Coul.
10	M: 10 mg; Sn capsule (89 mg) was given in Sn capsule (256 mg) with a cap to 1st combustion with 800 mg Fe + 1 g W. In a 2nd step 1.5 g W as given in the capsule once more to combustion.	$BaCO_3$ C = 33 mg, external calibration	Comb.-IR
17	M: 30 mg; 1 g Lecocel II + 1 g Fe chips as a flux; burn time 50 s	Na_2CO_3 M: 30 mg; 1 g Lecocel II + 1 g Fe chips as a flux; burn time 50 s	Comb.-IR
18	M: 25-30 mg sample flux: 2 g W + 2 g Fe; furnace temperature: 1800°C	CaCO3; dried at 280°C	Comb.-IR
20	M: 0.1 g; measurement time: 40s	$CaCO_3$ Certipur (100.10% ± 0.05%)	Comb.-IR
21	M: 30 mg; Burn the sample with combustion – supporting in the furnace via adding the oxygen $C+O_2 \rightarrow CO_2$absorb the CO_2 with KOH solution, the volume margin is the content of CO_2. Calculate the content of C according to the temperature and air pressure.		Comb.-Vol.
24	M: 150 mg; T: 1350°C, Rate(O_2): 400 mL/min, absoption time: 15 min. Flux 1 g Cu-powder	This method is an absolute method, therefore a calibration is not necessary. The determination system is checked by using $CaCO_3$ (content 12.0%)	Comb.-Grav.
25	M: 40 mg; combustion in oxygen stream with lead borate as flux; T: 1050°C	$CaCO_3$, dried at 280°C	Comb.-Coul.
28	M: 10-13 mg; standard program; 1.5g W and 0.2 g Fe as a flux	$CaCO_3$, similar carbon mass compared to sample	Comb.-IR
30	M: 150 mg; combustion with 2 g Sn at 1350°C – 100 s	Ultra Carbon – Ultra “F” PURITY (0.0378)	Comb.-IR
31	M: 100 mg; Accelerator: 2 g Sn Furnace temperature 1350°C	Pure Carbon Powder, 30 mg	Comb.-IR
33	M: 0.1 g;	Silicon Carbide Standard; (no direct traceability, results excluded)	Comb.
34	M: 0.15 g; Accelerator: 2 g Sn sample was sandwiched by Sn-powder 1 g and 1 g.	Pure Carbon Powder	Comb.-IR
36	M: 0.1 g; additional charge: Lecol and Fe	BCS-CRM Tungsten Carbide WC 6 116% C ± 0.006; (no direct traceability, results excluded)	Comb.-IR
38	M: 0.1 g;	no information about the (pure) calibration materiasl; calibration with 0 and 100 mg added	Comb.
41	M: 0.1 g; Accelerator: Sn 2 g	High purity graphite powder, 30 mg	Comb. - IR
42	M: 0.1 g; Accelerator: Sn 2 g, Furnace temperature: 1350°C	Pure carbon powder, 30 mg	Comb. - IR
44	M: 0.1 g; Accelerator: Sn powder 2.0000 g; Furnace temperature: 1350°C	Pure carbon powder, 30 mg	Comb. - IR

Free Carbon			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 70-100 mg; According to prescribed Method 4 "Wet chemical oxidation – coulometric titration" (oil-bath 100°C, reaction time 90 min, 120 min.)	High purity $CaCO_3$ (BAM)	wet chem.oxidation /coul. titation
18	M: 0.40-80 mg; According to prescribed Method 4 "Wet chemical oxidation – coulometric titration" (reaction temperature 95°C)	$CaCO_3$, dried at 280°C	wet chem.oxidation /coul. titation
21	M: 100-200 mg; The sample is in H_2SO_4 and $K_2Cr_2O_7$ solution, adding oxygen, oxidate C_{free} to CO_2, getting the content of C by (CO_2 x 0.2729).		wet chem.oxidation /coul. titation
24	M: 100 mg; T: 650°C, Rate(O_2): 180 mL/min, absoption time: 4 h. Coulometric analyteical device with computer to record counts versus time and calculate the content of Cfree via graphical evaluation.	This method is an absolute method, therefore a calibration is not necessary. The determination system is checked by using $CaCO_3$ (content 12.0%)	Coul.
25	M: 0.40-80 mg; According to prescribed Method 4 "Wet chemical oxidation – coulometric titration" (reaction temperature 95°C)	$CaCO_3$, dried at 280°C	wet chem.oxidation /coul. titation
33	M: 4000 mg;	Weight Differential of Carbon Dioxide Absorption Unit	wet chem.oxidation /coul. titation (Results excluded: "less than"-values)

Oxygen			
Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 80 mg; graphite crucible, Ni, Sn as flux (flux technique) reductive fusion	LECO 501-645; O: 0.0215 ± 0.0006% (no direct traceability, results excluded)	CGHE-IR
2	M: 70 – 120 mg; in pickled Ni-bushes; 10 mg Sn as a flux	99,99% ZrO_2, calcined at 1000°C	CGHE-IR
3	M: 50 mg	99,999% KNO_3; Aldrich	CGHE-IR
4	M: 60 mg; 30 s purge, 60 s analysis	LECO Nitrogen and Oxygen in **steel CRM**; 0,0424% O; (NIST SRM 885) (**no direct traceability**, results excluded)	CGHE-IR
5	M: 25 mg; Outgas power 5800 W, Analyze power 5000 W, Minimum time 60 s, Comparator level 1%. Crucible combination inner and outer crucible; sample in tin capsule, addition Ni-pellet	KNO3, suprapur Merck; Measurements and additions like sample determination; one point calibration used.	CGHE-IR
7	M: 50 mg; Ni-Sn capsule	CO_2 4.8 gas dosing	CGHE-IR
10	M: 85 mg; Ni capsule, analyze time 60-70 s.	Fe_2O_3 O = 400 µg Fe_2O_3 external calibration	CGHE-IR
15	M: 35-40 mg; Ni capsules	Fe_2O_3 solid pure substance (5N Aldrich) external calibration	CGHE-IR
17	M: 50 mg; sample in Sn capsule and Ni-basket; 50 s 650 A → 850 A ramp 8, outgas 950 A 20 s.	CO_2 - Gas calibration after instruction from producer	CGHE-IR
18	M: 50 mg; C-crucible and Sn-capsule were used (reaction temperature 2500°C)	$CaCO_3$; dried at 280°C	CGHE-IR
24	M: 50 mg; heat power: electric 750 A, voltage 5.5 V, Rate(Ar): 150 mL/min, heat time: 20 s, flux: Ni-Sn, determination time: 100 s.	This method is an absolute method, therefore a calibration is not necessary. The determination system is checked by using Nb powder (0.273±0.01% internal standard)	CGHE-Coul.
25	M: no information ; C-crucible and Sn-capsule were used (reaction temperature 2500°C)	$CaCO_3$; dried at 280°C	CGHE-IR
28	M: 60-70 mg; in high temp. crucibles and Sn capsules → 5300 W	KNO_3 in solution	CGHE-IR
31	M: 50 mg; sample with Ni capsule 0.3 g, adding 0.5 g Sn and 0.5 g Ni. Analyzing wattage: 5.5 KW	JCRM R021: Oxygen 1.08 mass%, **steel CRM; 50 mg,** (**no direct traceability**, results excluded)	CGHE-IR
33	M: 30 mg	steel standard AR-660 (no direct traceability, results excluded)	CGHE-IR
36	M: 100 mg; high temperature crucible, Sn capsules and Ni basket were used.	Leco steel AKP: 0.0106%±0.0004%O_2, Leco steel AKP: 0.0195%±0.0012%O_2 (no direct traceability, results excluded)	CGHE-IR
41	M: 50 mg; sample with Ni-capsule 300 mg; Analyze wattage: 5.5 kW	High purity Y_2O_3 (O = 21.25 mass%), 2 mg	CGHE-IR
42	M: 8 mg; Purge time 15 s; Analysis delay 50 s; Analyse power 5500 W, Minimum time O = 80 s. Tin capsule 5 mm was used as a high temperature crucible.	Leco steel 501-645 (O=0.0089%, N=0.0083%) (no direct traceability, results excluded)	CGHE-IR

Nitrogen			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 80 mg; graphite crucible, Ni, Sn as a flux (flux technique) reductive fusion	LECO 501-645; N : 0.0288 ± 0.0017% (no direct traceability, results excluded)	CGHE-TC
2	M: (not noted) mg in pickled Ni-capsules; 10 mg Sn as a flux	Calibration with Si_3N_4 M: 0.5 mg (no direct traceability, results excluded)	CGHE-TC
3	M: 50 mg	99,999% KNO_3; Aldrich	CGHE-TC
4	M: 60 mg; 30 s purge, 60 s analysis	LECO Nitrogen and Oxygen in **steel CRM**; 0.0021%, (NIST SRM 885) (**no direct traceability**, results excluded)	CGHE-TC
5	M: 25 mg; Outgas power 5800 W, Analyze power 5000 W, Minimum time 60 s, Comparator level 1%. Crucible combination inner and outer crucible; sample in tin capsule, addition Ni-pellet	KNO_3, suprapur Merck; measurements and additions like sample determination; one point calibration used.	CGHE-TC
7	M: 50 mg; Ni-Sn capsule	N_2 5.0 gas dosing	CGHE-TC
10	M: 85 mg; Ni capsule, analyze time 60-70 s.	KNO_3 N = 1.4 mg; external calibration	CGHE-TC
15	M: 1200 mg; no sample digestion 20 min irradiation	BN solid pure substance external calibration	IPAA
15	M: 35-40 mg; Ni capsules	KNO_3 solid pure substance external calibration	CGHE-TC
17	M: 50 mg; sample in Sn capsule and Ni-basket; 50 s 650 A → 850 A ramp 8, outgas 950 A 20 s.	N_2 - Gas calibration after instruction from producer	CGHE-TC
18	M: 50 mg; C-crucible and Sn-capsule were used (reaction temperature 2500°C)	$NaNO_3$; dried at 120°C	CGHE-TC
20	M: 3-5 mg; High Temp. crucible, Ni-basket, Sn-capsule; degassing at 7500 W, analysis ramp 5000-6000 W at 50 W/s, 2 min hold time	KNO_3 (13.85% N)	CGHE-TC
24	M: 500 mg; heat power: 5.0 KW / 70 s., integral time: 45 s, flux: Ni	The detector is calibrated by using primary KNO_3	CGHE-TC
25	M: no information ; C-crucible and Sn-capsule were used; (reaction temperature 2500°C)	$NaNO_3$; dried at 120°C	CGHE-TC
28	M: 60-70 mg; in high temp. crucibles and Sn capsules → 5300 W	KNO_3	CGHE-TC
31	M: 50 mg; sample with Ni capsule 0.3 g, adding 0.5 g Sn and 0.5 g Ni. Analyzing wattage: 5.5 KW	JSS 603-8 Nitrogen 0.025 mass% **(steel CRM); 1g,** (**no direct traceability**, results excluded)	CGHE-TC
33	M: 30 mg	steel standard AR-660 (no direct traceability, results excluded)	CGHE-TC
36	M: 0.1 g; high temperature crucible, Sn capsules and Ni basket were used.	Leco steel AKP: 0.0499%±0.0011%N_2, Leco steel AKP: 0.0266%±0.0006%N_2 (no direct traceability, results excluded)	CGHE-TC
41	M: 50 mg; sample with Ni-capsule 300 mg; Add 500 mg Sn; Analyze wattage: 5.5 kW	JCRM R003, Si3N4 powder (N = 39.00 mass%), 1 mg (no direct traceability, results excluded)	CGHE-TC
42	M: 8 mg; Purge time 15 s; Analysis delay 50 s; Analyse power 5500 W, Minimum time N = 70 s. Tin capsule 5 mm was used as a high temperature crucible.	Leco steel 501-645 (O=0.0089%, N=0.0083%) Carrier gas: He (no direct traceability, results excluded)	CGHE-TC

Total Boron			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.3 g; Sample mixed with 5 g $NaKCO_3$. Fusion in a Zr-crucible. 10 g Na_2O_2 was declared in portions. After that the sample was fused for 5 minutes.	Titration with 0.2 N NaOH; Adjusted by potassium hydrogen phthalate, which was dried for 2 h at 120°C.	TITR
4	M: 0.2 g; Standardized 0.1N NaOH (J.T. Baker) as titrant; mannitol powder A.C.S. grade used; Potentiometric titration used.	H_3BO_3 (NIST 951)	TITR
5	M: 0.1 – 0.12 g; Potentiometric titration with 10 g mannitol powdered and 1 N NaOH used.	1.000 g B +/- 0.2% (Merck comparable with Kraft)	TITR
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF + 0.1 g Mannitol in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Final volume for measurements → 100 mL.	H_3BO_3 (suprapur, Merck) in HNO_3/HF with 0.1 g mannitol Calibration standards: 45, 60, 75, 90 wt%	ICP-MS
8	M: 0.08 g; Potentiometric titration with mannitol. (according to recommended Method 1).	not information	TITR
18	M: 0.08 g; Potentiometric titration with mannitol after alkaline fusion 0.1 N NaOH (according to recommended Method 1)	H_3BO_3 solution	TITR
20	M: 0.1 g; Potentiometric titration (according to recommended Method 1).	1000 mg/L standard solution Merck, Certipur checked with Alfa Aesar)	TITR
21	M: 0.4 g; Weigh the sample, dissolve, acidification, vent CO_2, neutralization,	self-made; 0.1-0.15 N NaOH	TITR
22	M: 0.1 g;		TITR
23	M: 0.8 g; (according to recommended Method 1)	1000 mg/L B_2O_3 standard (commercially available) Calibration standards: 20, 100 mg/L	ICP OES
24	M: 0.1 g;	Potentiometric titration with pure NaOH and M(KHC8H4O4)=204.22, no further information	TITR
25	M: 0.08g; Alkaline decomposition and following potentiometric titration in addition of mannit. (according to recommended method 1)	H_3BO_3 solution	TITR
32	M: 0.08 g; Potentiometric titration; (according to recommended Method 1).	oxalic acid dehydrate Tl NaOH	TITR
33	M: 1 g; sample is weighed, fused and titrated	NIST 951, Boric Acid (17.48%B) titrated analog with samples	TITR
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask. From this solution were spiked 25 µL with 100 µL IRMM-610 (exactly weighed) and filled to 50 mL.Determination of density with pyknometer at 20°C.	100 mg/L B, natural isotope standard NBS 951 isotope dilution analysis with spike material IRMM-610 (95% of ^{10}B) determination of mass bias with natural isotope standard NBS 951 (c_{Bor}~1000µg/L)	ID-ICP-MS
41	M: 0.3 g; not automatic titration; 0.05 mol/L NaOH; initial adjustment pH 7.0 / end point pH 8.0	H_3BO_3 Merck, suprapur dry for more than 24 h in desiccator with H_2SO_4, weigh 1.776 g dissolve with water and transfer into 1000 mL flask. – transfer 25 mL of standard solution in a 300 mL beaker.	TITR
42	M: 0.1 g; After fusion with 2 g Na_2CO_3 add 10 mL HCl (1+1) to solve the cake and then transfer into 200 mL flask and dilute to the mark. Transfer 50 mL into Erlenmeyer flask and add NaOH solution up to pH 9.0. After heating and filtration adjust and add mannitol and titrate with M/10 NaOH.	B_2O_3 (4N) from Rare Metallic Co. Ltd.	TITR

HNO_3 soluble Boron

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
14	M: 5 g; (according to recommended Method 2)	H_3BO_3 suprapur Merck	TITR
18	M: 0.08 g; Potentiometric titration with mannite after handling on reflux with diluted HNO_3; consumption was measured by 0.1 N NaOH (according to recommended Method 2)	H_3BO_3 solution	TITR
20	M: 4 g; potentiometric titration (according to recommended Method 2)	1000 mg/L standard solution Merck, Certipur checked with Alfa Aesar)	TITR
21	M: 1 g; $B_{free} + H_2O_2 + HNO_3 \rightarrow B_2O_3$ and acidification to Borate, via mannitol to chromate, and titration with normal NaOH solution, then calculate the content of B.		CGHE-TC
23	M: 2.5 g; (according to recommended Method 2)	1000 mg/L B_2O_3 standard (commercially available); Calibration standards: 20, 100 mg/L	ICP OES
25	M: 4-5 g;	H_3BO_3 solution	ICP OES
33	M: 1.0 g; Sample is weighed, refluxed for 4 h in 10% HNO_3, diluted to volume and given to ICP OES.	Synthetic Standard 6 µg/mL B in solution to match detected levels. Calibrated against pre-programmed linear regression curves.	ICP OES
41	M: 1 g; Not automatic titration; 0.05 mol/L NaOH; initial adjustment pH 7.0 / end point pH 8.0. Potentiometric titration according to recommended Method 2.	H_3BO_3 Merck, suprapur dry for more than 24 h in desiccator with H_2SO_4, weigh 1.776 g dissolve with water and transfer into 1000 mL flask. – transfer 25 mL of standard solution in a 300 mL beaker.	TITR
42	M: 1 g; After 3 h reflex heating with 100 mL HNO3 60% (1+8) in a Erlenmeyer flask, filtration, adding NaOH solution up to weak alkaline, filtration and adjusting pH again, adding mannitol and titrate with M/10 NaOH.	B_2O_3 (4N) from Rare Metallic Co. Ltd.	TITR

Boron oxide

Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
14	M: 6 g; (according to recommended Method 3)	H_3BO_3 suprapur, Merck	TITR
18	M: 0.08 g; potentiometric titration with mannitol after dissolving at 60°C in H_2O; solution was measured by 0.1 N NaOH (according to recommended Method 3)	H_3BO_3 solution	TITR
20	M: 0.1 g; Potentiometric titration (according to recommended Method 3)	1000 mg/L standard solution Merck, Certipur checked with Alfa Aesar)	TITR
21	M: 1 g; B_4C does not dissolve with boiling water, but B_2O_3 does. The boron in the aqueous solution is titrated as boric acid with NaOH solution via mannitol boric acid.	H_3BO_3 solution	TITR
23	M: 3g; (according to recommended Method 3)	1000 mg/L B_2O_3 standard (commercially available); Calibration standards: 20, 100 mg/L	ICP OES
25	M: 0.08 g; Dissolving at 60°C in H_2O; following filtration.	H_3BO_3 solution	ICP OES
33	M: 2.0 g; sample is weighed, refluxed for 4 h in 0.1N HCl, diluted to volume and given to ICP OES	Synthetic Standard 2 µg/mL B in solution to match detected levels. Calibrated against pre-programmed linear regression curves.	ICP OES
41	M: 4 g; not automatically titration; 0.05 mol/L NaOH; initial adjustment pH 7.0 / end point pH 8.0. Potentiometric titration according to recommended method 3.	H_3BO_3 Merck, suprapur dry for more than 24 h in desiccator with H_2SO_4, weigh 1.776 g dissolve with water and transfer into 1000 mL flask. – transfer 25 mL of standard solution in a 300 mL beaker.	TITR
42	M: 1 g; Weigh sample into 200 mL Erlenmeyer flask and add 100 mL H_2O and stand for 1 h under ultrasonic wave. After heating and adjusting pH, adding mannitol and titrate with M/20 NaOH.	B_2O_3 (4N) from Rare Metallic Co. Ltd.	TITR

Abundance sensitivity (amount fraction) of ^{10}boron			
Lab. code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	M: 0,1 g; 2 mL type 1 DI H_2O, 5 mL HNO_3 (J.T. Baker, Ultrex II), microwave digestion system (CEM MARS 5). Sample diluted to 50 mL using 0.2% HF	H_3BO_3 (NIST 951), 0.2% HF diluent	ICP-MS
6	M: 0.1 g; Decomposition with 10 mL of an 1:1 mixture HNO_3/HF in a Teflon coated digestion bomb over 24 h by microwave heating in a mLS-ETHOS-system. Preparing a 1:1000 dilution from the 100 mL final volume after decomposition.	H_3BO_3 (suprapur, Merck) in HNO_3 with Concentrations between 500 and 1000 mg/kg; assuming an natural isotope-ratio of the H_3BO_3.	ICP-MS
9	M: 0.05 g; addition from $NaCO_3$/KCO_3 + KNO_3; alkaline oxidizing decomposition with muffle furnace and Bunsen burner.	10 mg/L B^{10}, B^{11} (Claritas ISOT)	ICP-MS
13	M: 0.225 g; Acid decomposition with mixture of 3 mL HNO_3 + 3 mL HF + 6 mL H_2SO_4 in 150 mL TFM-PTFE liners (DAB-III, Berghof) for 13 h at 250°C → solution diluted to 50 mL (PFA flask) → sample dilution 1:50000; = 70 µg/L B.	H_3BO_3 - certified isotope reference material (IRMM-011) M: 100 mg decomposed with 0.3 mL HNO_3+0.3 mL HF+ 0.6 mL H_2SO_4 → solution diluted to 50 mL (PFA flask) → sample dilution 1:5000 + 0.5% HF; = 70 µg/L B.	ICP-SFMS
16	M: ; Acid decomposition with HNO_3 in a “High Pressure Asher” at 290°C and 100 bar. → separation as methyl boron acid ester.	correction of mass fraction with certified isotope reference material (IRMM-014)	TIMS
19	M: 0.08-0.1 g; Acid decomposition with 10 mL HNO_3 in a “High Pressure Asher” at 20°C at 180 °C.	Calibration substance: NIST SRM 951 (Boric acid), K-factor: 0.9938	TIMS
35	M: 0.1-0.2 g; Decomposition with 0.25 mL HF, 3 mL HNO_3, 5 mL H_2SO_4 in a micro wave system (MLS GmbH) → 100 mL flask.	100 mg/L B, natural isotope standard NBS 951checked with ECRM 287-1 calibration solution: natural isotope standard NBS 951 (1000µg/L B)	ICP-MS
39	M: 5 mg; Sample was combined with 1.25 mL 0.14 mol Na_2CO_3 solution (sp). For each measurement 2 µL of this suspension was loaded onto a Ta V-groove shaped filament. The filaments have been pre-baked at 5A for 20 min. The suspension was dried onto the filament at a current of 1.0 A. Finally heated to a red dull colour and introduced at the same day into the mass spectrometer. - using ASTM C791 combined with total evaporation. (Romleowski & Koch, 1987)	indirectly measured against IRMM 011 (boric acid)	TIMS

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Appendix 7 of the Certification Report of ERM®-ED102

Statistical evaluation of all results of interlaboratory comparison for certification of ERM®–ED102

Content

The tables are listed in the following order of investigated parameters (analytes):

Al, Ca, Cr, Cu, Mg, Mn, Na, Ni, Si, Ti, Zr, Total C, Free C, O, N, Total B, HNO_3 soluble B, B_2O_5

For explanation see chapter 7 of this report

The results of table 6 of this report (see above, chapter 7.1) are listed in detail in the following tables. These tables are based on the statistical evaluation of the interlaboratory comparison using the BCR program [2] , they are arranged alphabetically by the element symbols. The results delivered in the frame of the interlaboratory comparison for one element were taken as the basis of the calculation carried out by the BCR program (1st run). If no serious outlier was found the results after the first run were taken as the final ones. If additional serious outliers were found, these outliers were removed after discussion and the program was run through once more (2nd run). This procedure was repeated until now serious outlier was found. For further explanation see chapter 7.2.

Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of ERM®-ED102; p.1

Tab. Xa1: 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
L1	33 DC-ARC-OES 2	40.000	6.325	6.637	30.000	40.000	50.000	40.000	40.000	40.000
L2	11 ICP OES 1	140.600	2.232	2.342	141.800	142.600	141.700	140.000	141.100	136.400
L3	18 ETV-ICP OES (3)	143.050	5.100	5.352	146.100	149.500	146.000	140.200	141.100	135.400
L4	35 ICP-MS 2	144.667	5.354	5.619	146.000	140.000	147.000	153.000	138.000	144.000
L5	5 ICP OES 2	151.667	7.992	8.387	162.000	157.000	144.000	151.000	155.000	141.000
L6	12 ICP OES 2	151.800	0.888	0.932	152.000	152.300	150.100	151.600	152.400	152.400
L7	12 ET AAS 2	153.000	2.394	2.513	153.600	153.200	150.100	155.500	150.200	155.400
L8	17 ICP OES 1	153.000	1.316	1.381	154.600	153.000	151.200	154.400	152.700	152.100
L9	18 DC-ARC-OES 3	154.130	5.205	5.462	159.310	156.230	150.170	153.720	159.160	146.190
L10	20 ICP OES 1	155.000	0.000	0.000	155.000	155.000	155.000	155.000	155.000	155.000
L11	25 ICP OES 1	155.147	4.613	4.841	151.840	150.290	155.720	151.790	160.190	161.050
L12	22 ICP OES 2	156.497	3.360	3.526	155.900	157.450	151.660	154.220	158.500	161.250
L13	18 ICP OES 3	157.800	4.473	4.695	156.600	156.200	164.600	160.300	157.900	151.200
L14	41 ICP OES 2	157.833	11.990	12.583	175.000	163.000	140.000	150.000	157.000	162.000
L15	38 ICP OES 2	158.506	6.577	6.902	162.000	164.279	165.753	156.506	149.141	153.357
L16	42 ICP OES 2	158.667	1.366	1.434	158.000	159.000	158.000	157.000	161.000	159.000
L17	1 ICP OES 3	160.167	5.345	5.609	167.000	163.000	158.000	156.000	153.000	164.000
L18	13 ICP-MS 3	162.500	4.680	4.911	155.000	168.000	162.000	167.000	162.000	161.000
L19	24 ICP OES 1	163.350	5.931	6.224	160.400	158.700	156.100	164.800	169.300	170.800
L20	34 ICP OES 2	163.650	2.615	2.744	167.600	165.000	162.400	164.400	162.500	160.000
L21	6 ICP OES 3	167.906	5.870	6.160	175.796	163.326	172.057	161.089	164.039	171.127
L22	31 ICP OES 1	172.500	16.208	17.009	161.000	181.000	154.000	180.000	197.000	162.000
L23	2 ICP OES 3	177.333	2.251	2.362	175.000	176.000	176.000	177.000	179.000	181.000

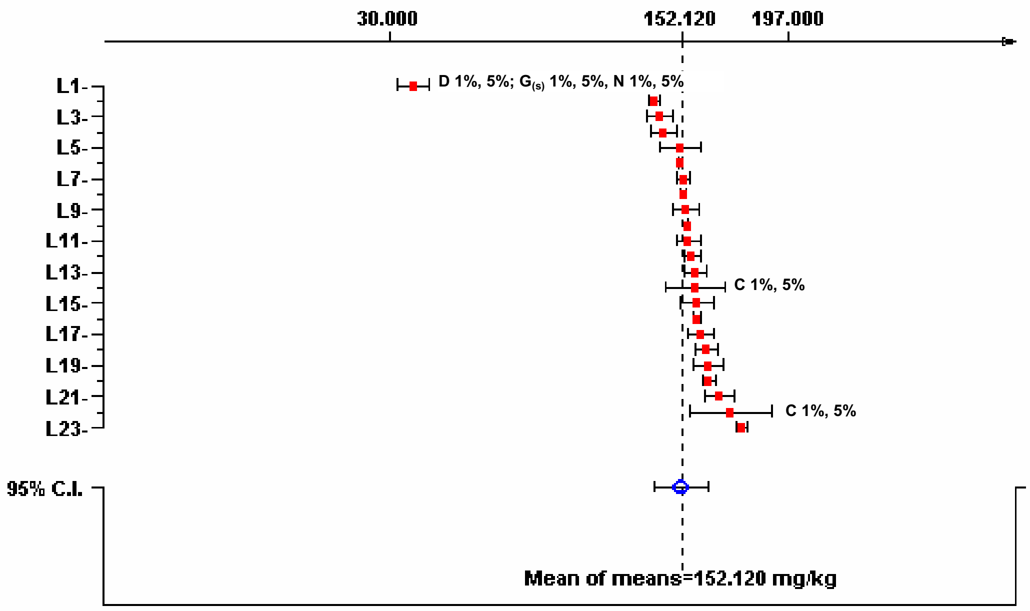
Range [min..max]	[30.000 .. 197.000]
	Case of No Pooling
Mean of means	152.120
95% H.W. Confidence Interval	11.202
95% H.W. Tolerance Interval	69.246
	Case of Pooling
Mean of All	152.120
95% H.W. Confidence Interval	4.380
95% H.W. Tolerance Interval	56.882

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. Xa1)



Tab. Xa2: 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
L1	11 ICP OES 1	140.600	2.232	2.342	141.800	142.600	141.700	140.000	141.100	136.400
L2	18 ETV-ICP OES (3)	143.050	5.100	5.352	146.100	149.500	146.000	140.200	141.100	135.400
L3	35 ICP-MS 2	144.667	5.354	5.619	146.000	140.000	147.000	153.000	138.000	144.000
L4	5 ICP OES 2	151.667	7.992	8.387	162.000	157.000	144.000	151.000	155.000	141.000
L5	12 ICP OES 2	151.800	0.888	0.932	152.000	152.300	150.100	151.600	152.400	152.400
L6	12 ET AAS 2	153.000	2.394	2.513	153.600	153.200	150.100	155.500	150.200	155.400
L7	17 ICP OES 1	153.000	1.316	1.381	154.600	153.000	151.200	154.400	152.700	152.100
L8	18 DC-ARC-OES 3	154.130	5.205	5.462	159.310	156.230	150.170	153.720	159.160	146.190
L9	20 ICP OES 1	155.000	0.000	0.000	155.000	155.000	155.000	155.000	155.000	155.000
L10	25 ICP OES 1	155.147	4.613	4.841	151.840	150.290	155.720	151.790	160.190	161.050
L11	22 ICP OES 2	156.497	3.360	3.526	155.900	157.450	151.660	154.220	158.500	161.250
L12	18 ICP OES 3	157.800	4.473	4.695	156.600	156.200	164.600	160.300	157.900	151.200
L13	41 ICP OES 2	157.833	11.990	12.583	175.000	163.000	140.000	150.000	157.000	162.000
L14	38 ICP OES 2	158.506	6.577	6.902	162.000	164.279	165.753	156.506	149.141	153.357
L15	42 ICP OES 2	158.667	1.366	1.434	158.000	159.000	158.000	157.000	161.000	159.000
L16	1 ICP OES 3	160.167	5.345	5.609	167.000	163.000	158.000	156.000	153.000	164.000
L17	13 ICP-MS 3	162.500	4.680	4.911	155.000	168.000	162.000	167.000	162.000	161.000
L18	24 ICP OES 1	163.350	5.931	6.224	160.400	158.700	156.100	164.800	169.300	170.800
L19	34 ICP OES 2	163.650	2.615	2.744	167.600	165.000	162.400	164.400	162.500	160.000
L20	6 ICP OES 3	167.906	5.870	6.160	175.796	163.326	172.057	161.089	164.039	171.127
L21	31 ICP OES 1	172.500	16.208	17.009	161.000	181.000	154.000	180.000	197.000	162.000
L22	2 ICP OES 3	177.333	2.251	2.362	175.000	176.000	176.000	177.000	179.000	181.000

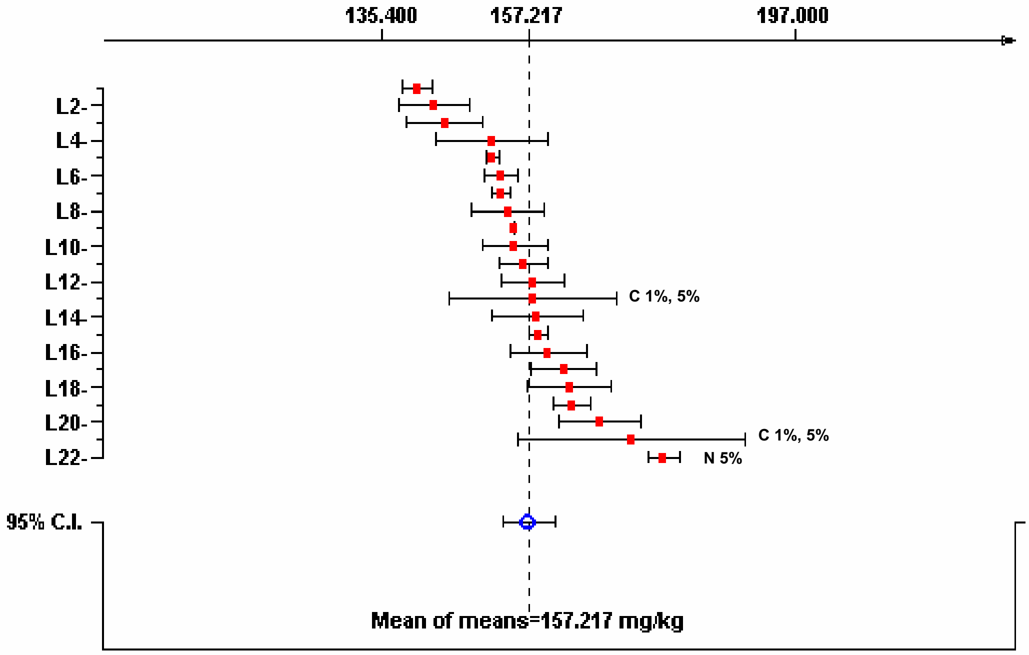
Range [min..max]	[135.400 .. 197.000]
	Case of No Pooling
Mean of means	157.217
95% H.W. Confidence Interval	3.896
95% H.W. Tolerance Interval	23.702
	Case of Pooling
Mean of All	157.217
95% H.W. Confidence Interval	1.761
95% H.W. Tolerance Interval	22.422

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. Xa2)



Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of ERM®-ED102; p.3

Tab. Xb1: Calcium 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
L1	31 ICP OES 1	61.250	2.363	3.760	63.000	63.000		58.000	61.000	
L2	33 DC-ARC-OES 2	61.667	7.528	7.900	60.000	60.000	70.000	50.000	70.000	60.000
L3	17 ICP OES 1	82.650	1.616	1.696	84.200	82.100	80.500	84.300	83.600	81.200
L4	1 ICP OES 3	87.067	1.319	1.384	86.500	84.700	87.400	87.900	87.500	88.400
L5	18 ICP OES 3	88.967	0.792	0.831	90.100	88.200	88.200	88.600	89.000	89.700
L6	25 ICP OES 2	89.568	3.725	3.909	84.090	89.470	89.250	89.820	88.980	95.800
L7	15 IPAA 2	90.750	4.192	4.399	94.400	93.500	87.000	91.600	93.800	84.200
L8	12 ICP OES 2	91.350	0.689	0.723	91.400	92.300	90.500	92.000	91.000	90.900
L9	42 ICP OES 2	91.667	1.633	1.714	90.000	94.000	92.000	91.000	93.000	90.000
L10	5 F AAS 2	92.517	2.210	2.320	91.000	95.300	95.000	90.500	92.800	90.500
L11	12 F AAS 2	93.417	1.814	1.903	95.200	94.200	92.400	90.800	92.500	95.400
L12	24 ICP OES 1	93.800	4.184	4.391	88.200	99.500	97.200	90.700	94.700	92.500
L13	13 ICP-MS 3	96.383	1.976	2.074	94.600	95.200	97.200	100.000	95.900	95.400
L14	22 ICP OES 2	96.422	1.876	1.969	97.360	95.820	94.240	97.820	98.830	94.460
L15	18 DC-ARC-OES 3	96.733	6.623	6.950	104.220	95.010	91.400	100.310	87.280	102.180
L16	2 ICP OES 3	98.550	4.177	4.384	94.500	94.400	101.000	99.900	96.500	105.000
L17	18 ETV-ICP OES (3)	102.597	4.175	4.381	99.830	97.750	103.180	103.680	101.280	109.860
L18	20 ICP OES 1	105.000	7.746	8.129	95.000	95.000	110.000	110.000	110.000	110.000
L19	38 ICP OES 2	107.223	9.417	9.882	112.128	123.128	100.288	96.685	106.455	104.655
L20	41 ICP OES 2	109.667	8.165	8.569	120.000	113.000	100.000	115.000	110.000	100.000
L21	11 ICP OES 1	114.550	16.313	17.119	115.600	133.500	111.700	132.200	101.900	92.400
L22	35 ICP-MS 2	134.833	16.364	17.172	153.000	115.000	136.000	152.000	117.000	136.000
L23	6 ICP OES 3	135.094	15.015	15.758	123.905	160.087	133.130	132.465	117.756	143.223

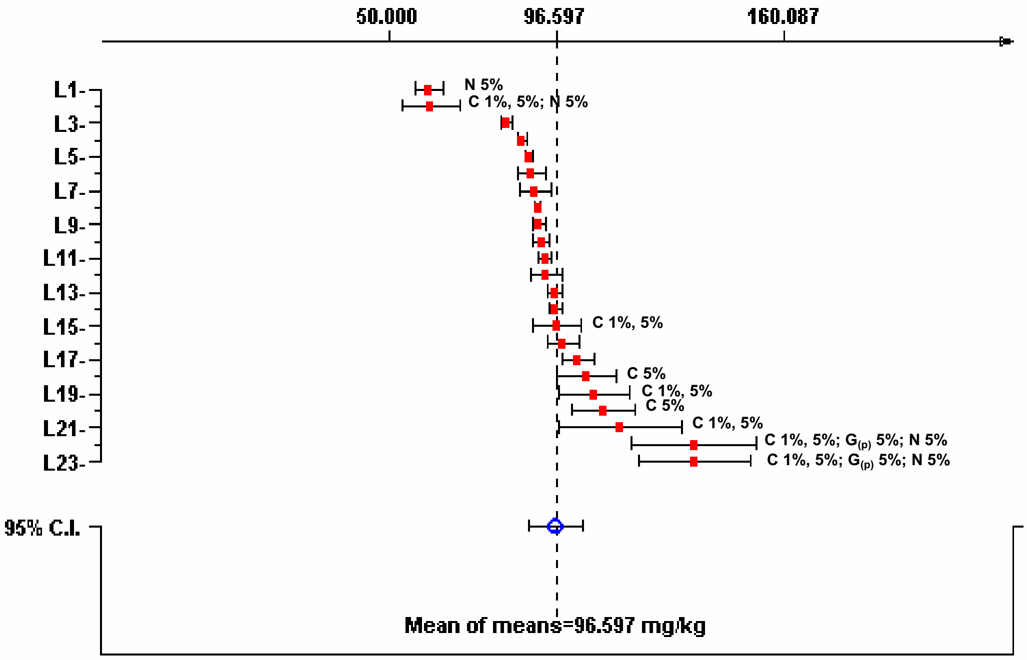
Range [min..max]	[50.000 .. 160.087]
	Case of No Pooling
Mean of means	96.597
95% H.W. Confidence Interval	7.515
95% H.W. Tolerance Interval	46.451
	Case of Pooling
Mean of All	97.116
95% H.W. Confidence Interval	3.036
95% H.W. Tolerance Interval	39.166

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. Xb1)



Tab. Xc1: Cobalt 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
L1	35 ICP-MS 2	0.280	0.023	0.024	0.289	0.311	0.248	0.276	0.261	0.296
L2	18 ETV-ICP OES (3)	0.301	0.026	0.027	0.290	0.281	0.299	0.345	0.276	0.315
L3	15 IPAA (3)	0.313	0.020	0.021	0.290	0.330	0.300	0.340	0.320	0.300
L4	12 ET AAS 2	0.388	0.008	0.009	0.379	0.383	0.402	0.394	0.384	0.388
L5	13 ICP-MS 3	0.405	0.005	0.006	0.396	0.407	0.403	0.404	0.410	0.411
L6	18 ICP OES 3	0.419	0.121	0.127	0.447	0.380	0.291	0.296	0.499	0.602
L7	42 ICP OES 1	0.450	0.055	0.057	0.400	0.500	0.400	0.500	0.500	0.400
L8	6 ICP-MS 3	0.453	0.060	0.063	0.551	0.474	0.473	0.427	0.411	0.380
L9	24 ICP OES 1	0.528	0.088	0.092	0.650	0.420	0.580	0.440	0.513	0.567
L10	20 ICP OES (1)	2.000	0.632	0.664	2.000	3.000	2.000	1.000	2.000	2.000

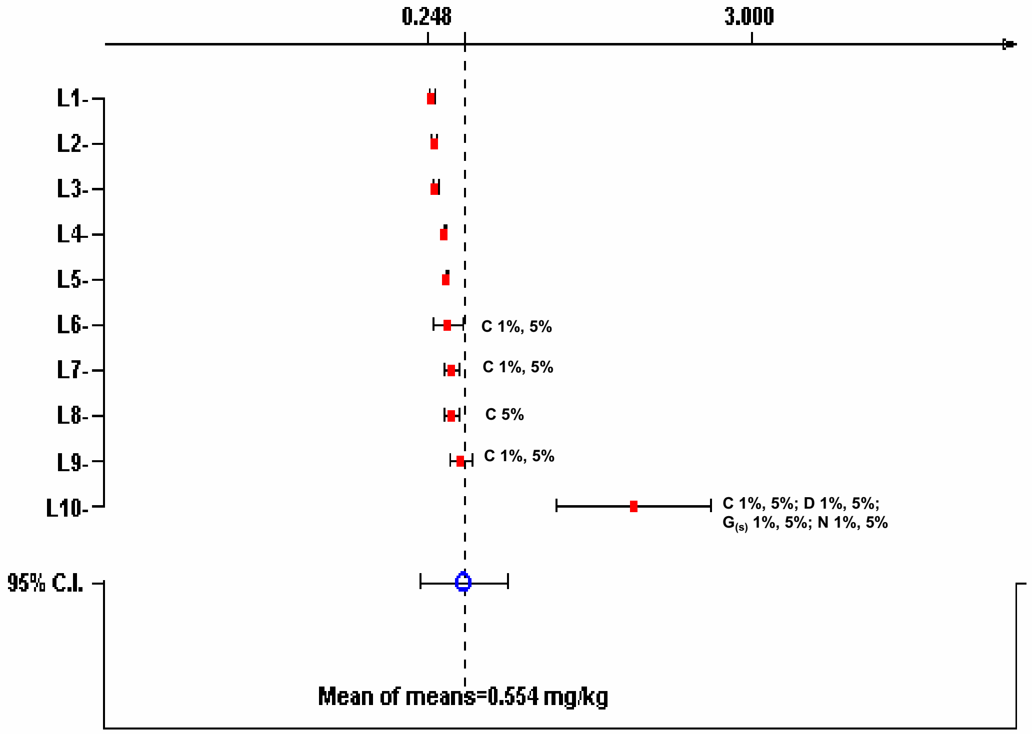
Range [min..max]	[0.248 .. 3.000]
	Case of No Pooling
Mean of means	0.554
95% H.W. Confidence Interval	0.368
95% H.W. Tolerance Interval	1.737
	Case of Pooling
Mean of All	0.554
95% H.W. Confidence Interval	0.136
95% H.W. Tolerance Interval	1,230.697

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. Xc1)



Tab. Xc2: Cobalt 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
L1	35 ICP-MS 2	0.280	0.023	0.024	0.289	0.311	0.248	0.276	0.261	0.296
L2	18 ETV-ICP OES (3)	0.301	0.026	0.027	0.290	0.281	0.299	0.345	0.276	0.315
L3	15 IPAA (3)	0.313	0.020	0.021	0.290	0.330	0.300	0.340	0.320	0.300
L4	12 ET AAS 2	0.388	0.008	0.009	0.379	0.383	0.402	0.394	0.384	0.388
L5	13 ICP-MS 3	0.405	0.005	0.006	0.396	0.407	0.403	0.404	0.410	0.411
L6	18 ICP OES 3	0.419	0.121	0.127	0.447	0.380	0.291	0.296	0.499	0.602
L7	42 ICP OES 1	0.450	0.055	0.057	0.400	0.500	0.400	0.500	0.500	0.400
L8	6 ICP-MS 3	0.453	0.060	0.063	0.551	0.474	0.473	0.427	0.411	0.380
L9	24 ICP OES 1	0.528	0.088	0.092	0.650	0.420	0.580	0.440	0.513	0.567

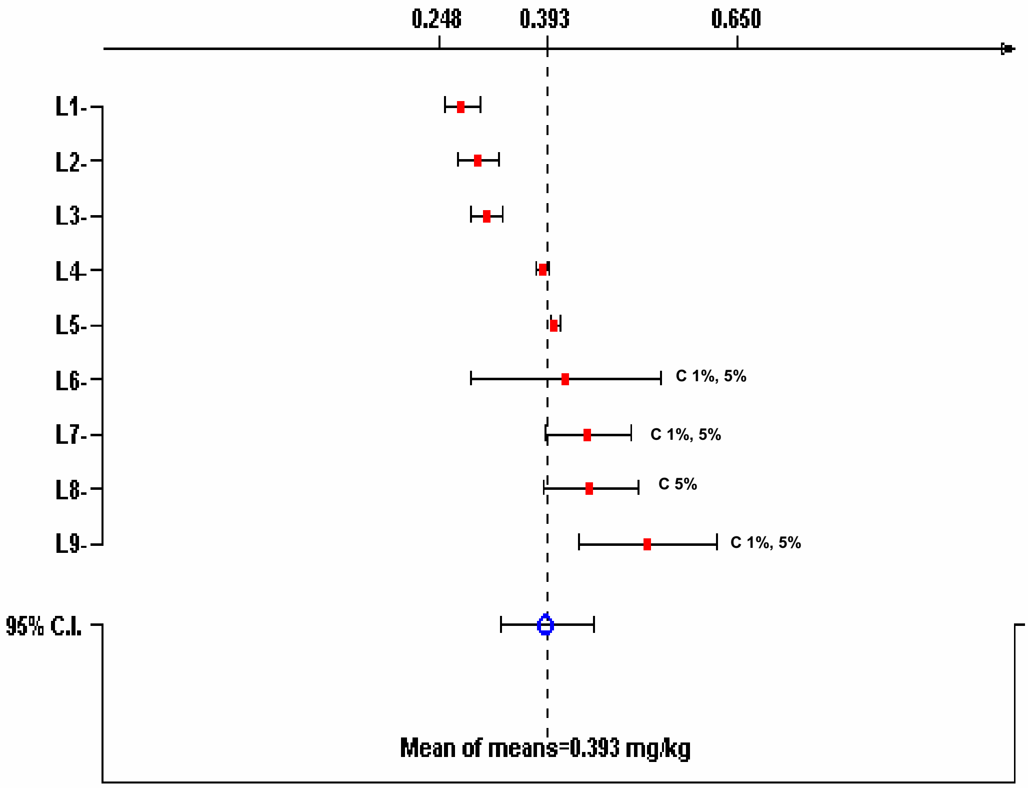
Range [min..max]	[0.248 .. 0.650]
	Case of No Pooling
Mean of means	0.393
95% H.W. Confidence Interval	0.063
95% H.W. Tolerance Interval	0.289
	Case of Pooling
Mean of All	0.393
95% H.W. Confidence Interval	0.026
95% H.W. Tolerance Interval	0.223

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. Xc2)



Tab. Xd1: 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
L1	13 ICP-MS 3	4.040	0.426	0.447	3.880	3.790	3.860	3.570	4.520	4.620
L2	12 ET AAS 2	4.453	0.097	0.101	4.420	4.290	4.500	4.480	4.580	4.450
L3	20 ICP OES (1)	4.667	0.516	0.542	5.000	5.000	4.000	5.000	5.000	4.000
L4	18 ETV-ICP OES (3)	4.675	0.570	0.598	4.950	3.700	5.040	4.270	4.930	5.160
L5	6 ICP-MS (3)	4.717	0.693	0.728	5.904	4.791	4.901	4.622	4.177	3.908
L6	24 ICP OES 1	5.165	0.323	0.339	5.430	5.320	4.780	4.850	5.040	5.570
L7	2 ICP OES 3	5.197	0.537	0.564	5.350	5.330	4.510	4.880	5.020	6.090
L8	25 ICP OES2	5.372	0.267	0.280	5.180	5.040	5.600	5.350	5.760	5.300
L9	12 ICP OES 2	5.378	0.326	0.342	5.350	6.020	5.150	5.270	5.330	5.150
L10	35 ICP-MS 2	5.428	0.282	0.296	5.500	5.450	5.820	5.070	5.590	5.140
L11	42 ICP OES 2	5.533	0.197	0.206	5.400	5.600	5.900	5.400	5.500	5.400
L12	18 ICP OES 3	5.695	0.471	0.494	6.280	5.650	5.440	5.110	5.450	6.240
L13	22 ICP OES 2	5.720	0.400	0.420	5.320	5.870	5.860	6.370	5.570	5.330
L14	17 ICP OES 1	5.732	0.288	0.302	5.620	5.530	5.820	6.220	5.400	5.800
L15	1 ICP OES 3	6.917	1.608	1.687	4.800	6.200	9.400	6.000	7.300	7.800
L16	41 ICP OES (1)	7.783	2.284	2.397	4.400	6.800	10.600	6.900	8.000	10.000
L17	5 ICP OES 2	9.337	1.478	1.551	11.400	8.000	7.900	9.790	8.330	10.600
L18	18 DC-ARC-OES 3	11.477	0.712	0.748	10.730	10.940	11.310	11.200	12.560	12.120
L19	31 ICP OES 1	139.500	9.731	10.212	124.000	147.000	146.000	131.000	142.000	147.000

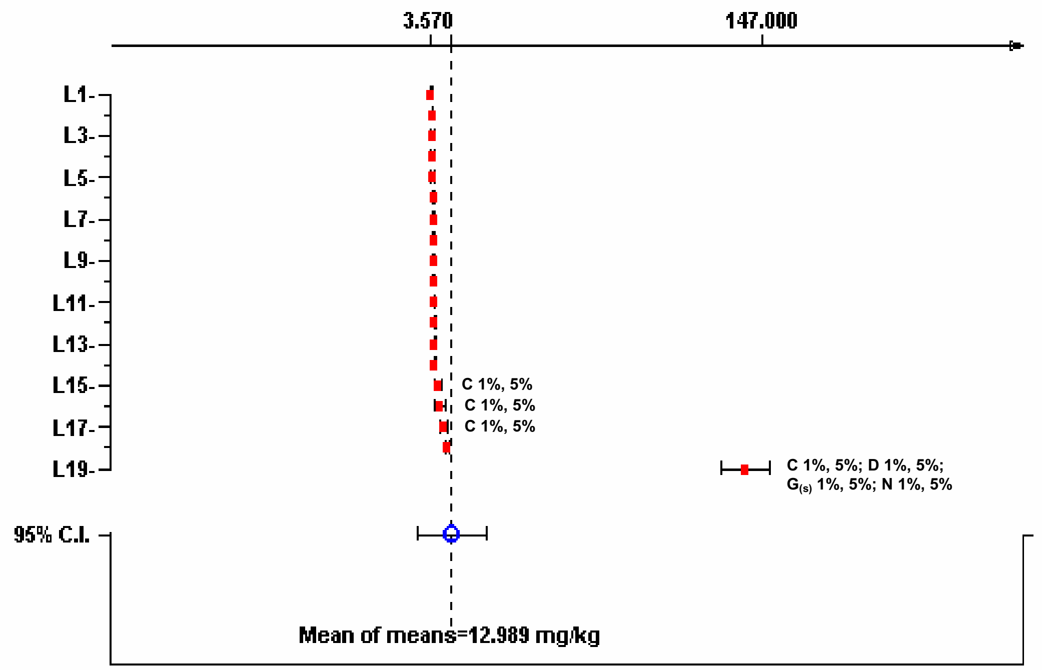
Range [min..max]	[3.570 .. 147.000]
	Case of No Pooling
Mean of means	12.989
95% H.W. Confidence Interval	14.792
95% H.W. Tolerance Interval	85.441
	Case of Pooling
Mean of All	12.989
95% H.W. Confidence Interval	5.582
95% H.W. Tolerance Interval	66.567

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. Xd1)



Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of ERM®-ED102; p.7

Tab.Xd2: Chromium 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
L1	13 ICP-MS 3	4.040	0.426	0.447	3.880	3.790	3.860	3.570	4.520	4.620
L2	12 ET AAS 2	4.453	0.097	0.101	4.420	4.290	4.500	4.480	4.580	4.450
L3	20 ICP OES (1)	4.667	0.516	0.542	5.000	5.000	4.000	5.000	5.000	4.000
L4	18 ETV-ICP OES (3)	4.675	0.570	0.598	4.950	3.700	5.040	4.270	4.930	5.160
L5	6 ICP-MS (3)	4.717	0.693	0.728	5.904	4.791	4.901	4.622	4.177	3.908
L6	24 ICP OES 1	5.165	0.323	0.339	5.430	5.320	4.780	4.850	5.040	5.570
L7	2 ICP OES 3	5.197	0.537	0.564	5.350	5.330	4.510	4.880	5.020	6.090
L8	25 ICP OES2	5.372	0.267	0.280	5.180	5.040	5.600	5.350	5.760	5.300
L9	12 ICP OES 2	5.378	0.326	0.342	5.350	6.020	5.150	5.270	5.330	5.150
L10	35 ICP-MS 2	5.428	0.282	0.296	5.500	5.450	5.820	5.070	5.590	5.140
L11	42 ICP OES 2	5.533	0.197	0.206	5.400	5.600	5.900	5.400	5.500	5.400
L12	18 ICP OES 3	5.695	0.471	0.494	6.280	5.650	5.440	5.110	5.450	6.240
L13	22 ICP OES 2	5.720	0.400	0.420	5.320	5.870	5.860	6.370	5.570	5.330
L14	17 ICP OES 1	5.732	0.288	0.302	5.620	5.530	5.820	6.220	5.400	5.800
L15	1 ICP OES 3	6.917	1.608	1.687	4.800	6.200	9.400	6.000	7.300	7.800
L16	41 ICP OES (1)	7.783	2.284	2.397	4.400	6.800	10.600	6.900	8.000	10.000
L17	5 ICP OES 2	9.337	1.478	1.551	11.400	8.000	7.900	9.790	8.330	10.600
L18	18 DC-ARC-OES 3	11.477	0.712	0.748	10.730	10.940	11.310	11.200	12.560	12.120

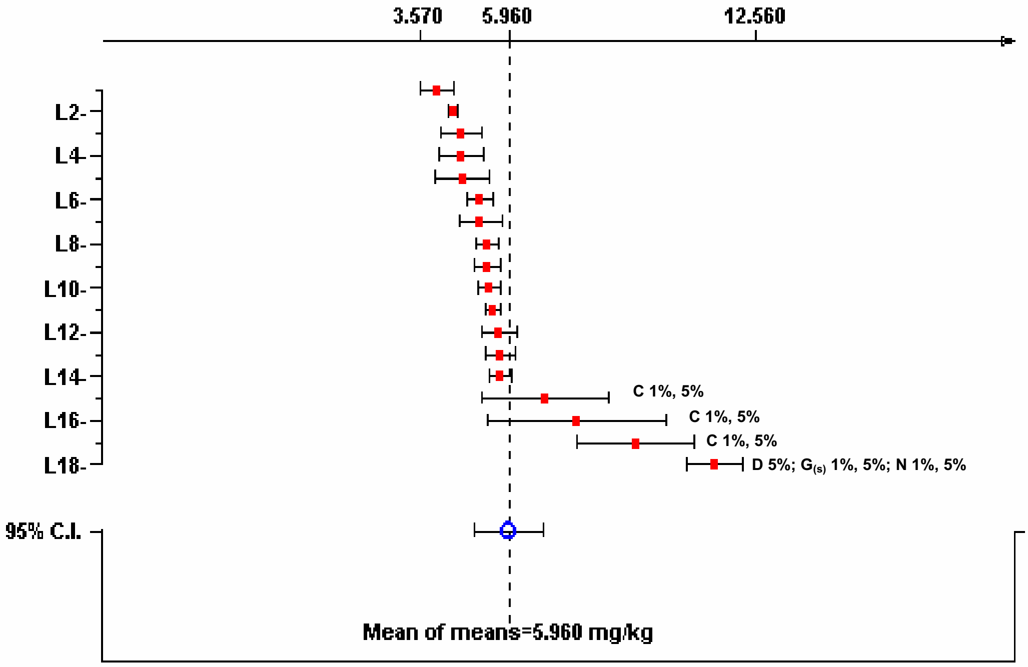
Range [min..max]	[3.570 .. 12.560]
	Case of No Pooling
Mean of means	5.960
95% H.W. Confidence Interval	0.930
95% H.W. Tolerance Interval	5.271
	Case of Pooling
Mean of All	5.960
95% H.W. Confidence Interval	0.378
95% H.W. Tolerance Interval	4.407

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. Xd2)



Appendix 7: Statistical evaluation of all results of interlaboratory comparison for certification of ERM$^{®}$-ED102; p.8

Tab. Xd3: Chromium 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
L1	13 ICP-MS 3	4.040	0.426	0.447	3.880	3.790	3.860	3.570	4.520	4.620
L2	12 ET AAS 2	4.453	0.097	0.101	4.420	4.290	4.500	4.480	4.580	4.450
L3	20 ICP OES (1)	4.667	0.516	0.542	5.000	5.000	4.000	5.000	5.000	4.000
L4	18 ETV-ICP OES (3)	4.675	0.570	0.598	4.950	3.700	5.040	4.270	4.930	5.160
L5	6 ICP-MS (3)	4.717	0.693	0.728	5.904	4.791	4.901	4.622	4.177	3.908
L6	24 ICP OES 1	5.165	0.323	0.339	5.430	5.320	4.780	4.850	5.040	5.570
L7	2 ICP OES 3	5.197	0.537	0.564	5.350	5.330	4.510	4.880	5.020	6.090
L8	25 ICP OES2	5.372	0.267	0.280	5.180	5.040	5.600	5.350	5.760	5.300
L9	12 ICP OES 2	5.378	0.326	0.342	5.350	6.020	5.150	5.270	5.330	5.150
L10	35 ICP-MS 2	5.428	0.282	0.296	5.500	5.450	5.820	5.070	5.590	5.140
L11	42 ICP OES 2	5.533	0.197	0.206	5.400	5.600	5.900	5.400	5.500	5.400
L12	18 ICP OES 3	5.695	0.471	0.494	6.280	5.650	5.440	5.110	5.450	6.240
L13	22 ICP OES 2	5.720	0.400	0.420	5.320	5.870	5.860	6.370	5.570	5.330
L14	17 ICP OES 1	5.732	0.288	0.302	5.620	5.530	5.820	6.220	5.400	5.800
L15	1 ICP OES 3	6.917	1.608	1.687	4.800	6.200	9.400	6.000	7.300	7.800
L16	41 ICP OES (1)	7.783	2.284	2.397	4.400	6.800	10.600	6.900	8.000	10.000
L17	5 ICP OES 2	9.337	1.478	1.551	11.400	8.000	7.900	9.790	8.330	10.600

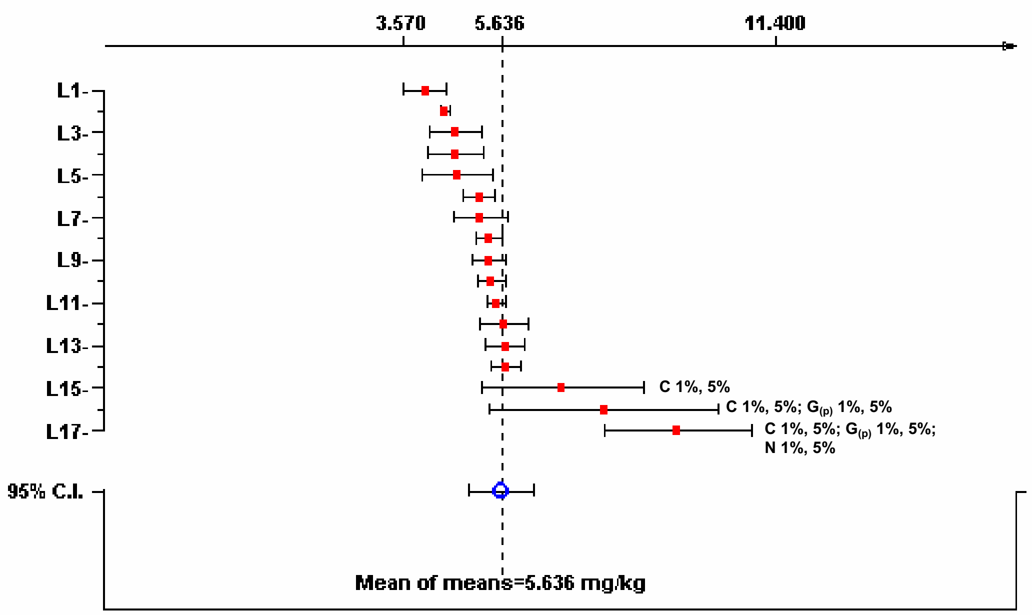
Range [min..max]	[3.570 .. 11.400]
	Case of No Pooling
Mean of means	5.636
95% H.W. Confidence Interval	0.671
95% H.W. Tolerance Interval	3.728
	Case of Pooling
Mean of All	5.636
95% H.W. Confidence Interval	0.293
95% H.W. Tolerance Interval	3.331

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. Xd3)



Tab. Xe1: 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
L1	35 ICP-MS 2	1.370	0.243	0.255	1.760	1.580	1.220	1.290	1.160	1.210
L2	18 ETV-ICP OES (3)	1.523	0.101	0.106	1.590	1.570	1.670	1.440	1.450	1.420
L3	18 DC-ARC-OES 3	1.592	0.259	0.272	1.541	1.302	1.961	1.853	1.407	1.486
L4	13 ICP-MS 3	1.668	0.061	0.064	1.620	1.600	1.720	1.650	1.760	1.660
L5	12 ET AAS 2	1.723	0.039	0.041	1.720	1.760	1.770	1.690	1.730	1.670
L6	18 ICP OES 3	2.023	0.119	0.125	1.880	2.060	1.950	2.120	1.940	2.190
L7	25 ICP OES2	2.295	0.245	0.257	2.260	2.290	2.490	1.880	2.590	2.260
L8	42 ICP OES 1	2.300	0.210	0.220	2.200	2.600	2.100	2.500	2.100	2.300
L9	6 ICP-MS 3	2.656	0.626	0.657	3.259	3.160	2.039	3.249	2.005	2.222
L10	12 ICP OES 2	2.772	0.171	0.179	2.550	2.900	2.760	2.970	2.860	2.590
L11	24 ICP OES 1	2.773	0.357	0.375	3.330	2.290	2.530	2.870	2.700	2.920
L12	5 ICP OES 1	3.025	0.396	0.416	3.610	3.290	2.500	2.810	3.120	2.820
L13	17 ICP OES 1	3.245	0.104	0.109	3.200	3.350	3.150	3.170	3.200	3.400
L14	20 ICP OES (1)	4.333	0.516	0.542	4.000	4.000	5.000	4.000	4.000	5.000

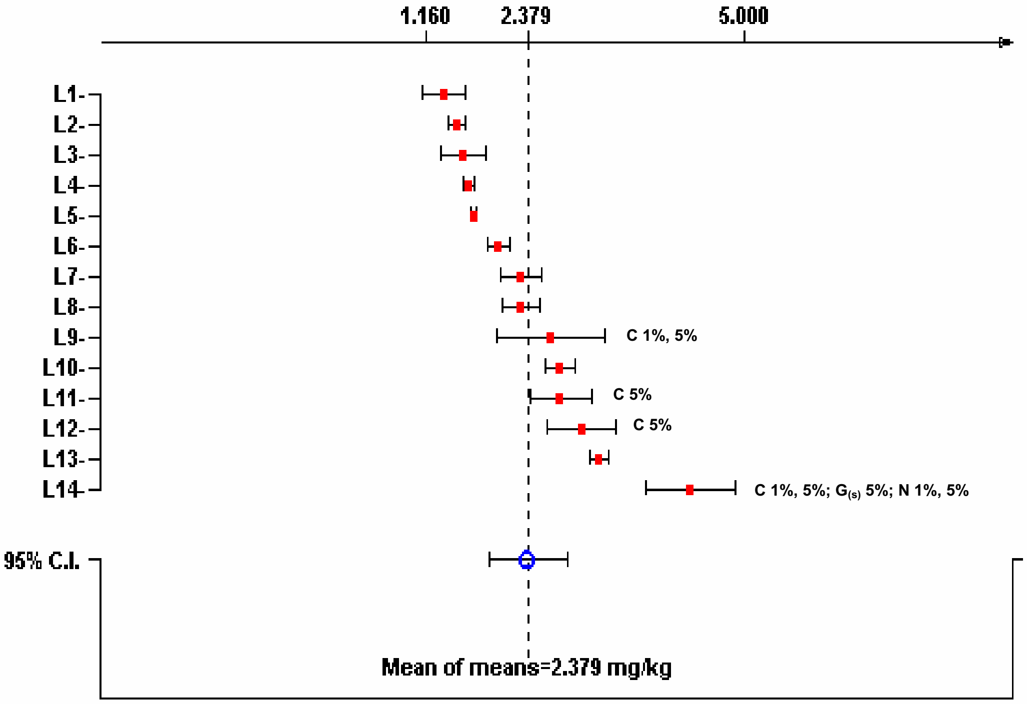
Range [min..max]	[1.160 .. 5.000]
	Case of No Pooling
Mean of means	2.379
95% H.W. Confidence Interval	0.476
95% H.W. Tolerance Interval	2.481
	Case of Pooling
Mean of All	2.379
95% H.W. Confidence Interval	0.183
95% H.W. Tolerance Interval	1.910

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. Xe1)



Tab. Xe2: 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
L1	35 ICP-MS 2	1.370	0.243	0.255	1.760	1.580	1.220	1.290	1.160	1.210
L2	18 ETV-ICP OES (3)	1.523	0.101	0.106	1.590	1.570	1.670	1.440	1.450	1.420
L3	18 DC-ARC-OES 3	1.592	0.259	0.272	1.541	1.302	1.961	1.853	1.407	1.486
L4	13 ICP-MS 3	1.668	0.061	0.064	1.620	1.600	1.720	1.650	1.760	1.660
L5	12 ET AAS 2	1.723	0.039	0.041	1.720	1.760	1.770	1.690	1.730	1.670
L6	18 ICP OES 3	2.023	0.119	0.125	1.880	2.060	1.950	2.120	1.940	2.190
L7	25 ICP OES2	2.295	0.245	0.257	2.260	2.290	2.490	1.880	2.590	2.260
L8	42 ICP OES 1	2.300	0.210	0.220	2.200	2.600	2.100	2.500	2.100	2.300
L9	6 ICP-MS 3	2.656	0.626	0.657	3.259	3.160	2.039	3.249	2.005	2.222
L10	12 ICP OES 2	2.772	0.171	0.179	2.550	2.900	2.760	2.970	2.860	2.590
L11	24 ICP OES 1	2.773	0.357	0.375	3.330	2.290	2.530	2.870	2.700	2.920
L12	5 ICP OES 1	3.025	0.396	0.416	3.610	3.290	2.500	2.810	3.120	2.820
L13	17 ICP OES 1	3.245	0.104	0.109	3.200	3.350	3.150	3.170	3.200	3.400

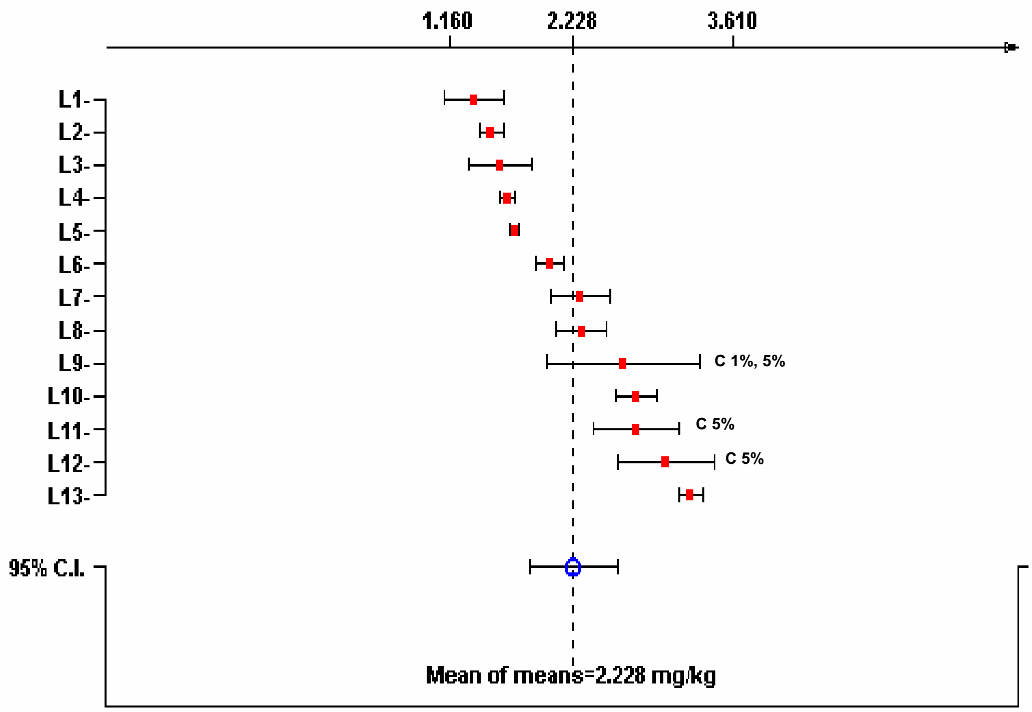
Range [min..max]	[1.160 .. 3.610]
	Case of No Pooling
Mean of means	2.228
95% H.W. Confidence Interval	0.378
95% H.W. Tolerance Interval	1.929
	Case of Pooling
Mean of All	2.228
95% H.W. Confidence Interval	0.148
95% H.W. Tolerance Interval	1.493

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. Xe2)



Tab. Xf1: 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
L1	33 DC-ARC-OES 2	156.667	19.664	20.636	170.000	170.000	180.000	130.000	150.000	140.000
L2	41 ICP OES 2	599.000	77.828	81.675	527.000	616.000	627.000	565.000	732.000	527.000
L3	22 ICP OES 2	629.678	5.508	5.780	629.150	628.220	637.620	628.240	633.500	621.340
L4	31 ICP OES 1	646.333	78.025	81.882	552.000	579.000	614.000	667.000	717.000	749.000
L5	18 ETV-ICP OES (3)	646.433	23.424	24.582	676.900	663.500	629.200	629.800	618.900	660.300
L6	21 MAS 3	650.000	44.721	46.932	700.000	650.000	600.000	650.000	600.000	700.000
L7	42 ICP OES 2	665.333	9.438	9.904	661.000	681.000	658.000	659.000	660.000	673.000
L8	6 ICP OES 3	665.852	9.425	9.891	669.447	678.070	674.345	660.063	655.032	658.157
L9	17 ICP OES 1	668.500	8.408	8.824	667.000	667.000	678.000	656.000	678.000	665.000
L10	35 ICP-MS 2	668.667	26.726	28.047	674.000	654.000	720.000	650.000	663.000	651.000
L11	13 ICP-MS 3	672.667	9.791	10.275	656.000	668.000	676.000	675.000	676.000	685.000
L12	18 ICP OES 3	679.050	11.608	12.182	660.600	669.300	690.900	686.800	682.700	684.000
L13	12 ICP OES 2	687.383	4.202	4.409	689.900	688.700	681.800	693.600	684.700	685.600
L14	12 F AAS 2	688.667	6.903	7.244	690.200	692.200	689.200	675.500	695.700	689.200
L15	15 IPAA (3)	689.000	22.874	24.004	719.000	698.000	686.000	705.000	666.000	660.000
L16	24 ICP OES 1	691.583	12.430	13.045	679.400	676.500	687.100	700.300	698.900	707.300
L17	38 ICP OES 2	691.815	16.020	16.812	702.459	687.214	683.757	680.198	677.944	719.319
L18	25 ICP OES 2	694.880	13.130	13.779	685.390	674.360	695.050	699.520	705.050	709.910
L19	18 DC-ARC-OES 3	695.583	19.117	20.062	730.300	683.300	677.600	703.800	689.400	689.100
L20	5 F AAS 2	708.667	14.841	15.575	683.000	704.000	719.000	706.000	725.000	715.000
L21	20 ICP OES (1)	720.000	9.487	9.956	735.000	725.000	720.000	710.000	720.000	710.000
L22	2 ICP OES 3	762.833	13.045	13.690	757.000	755.000	748.000	761.000	772.000	784.000
L23	1 ICP OES 3	771.167	39.575	41.531	720.000	755.000	833.000	800.000	756.000	763.000
L24	11 ICP OES 1	791.767	85.392	89.613	633.300	784.000	834.700	785.200	834.700	878.700

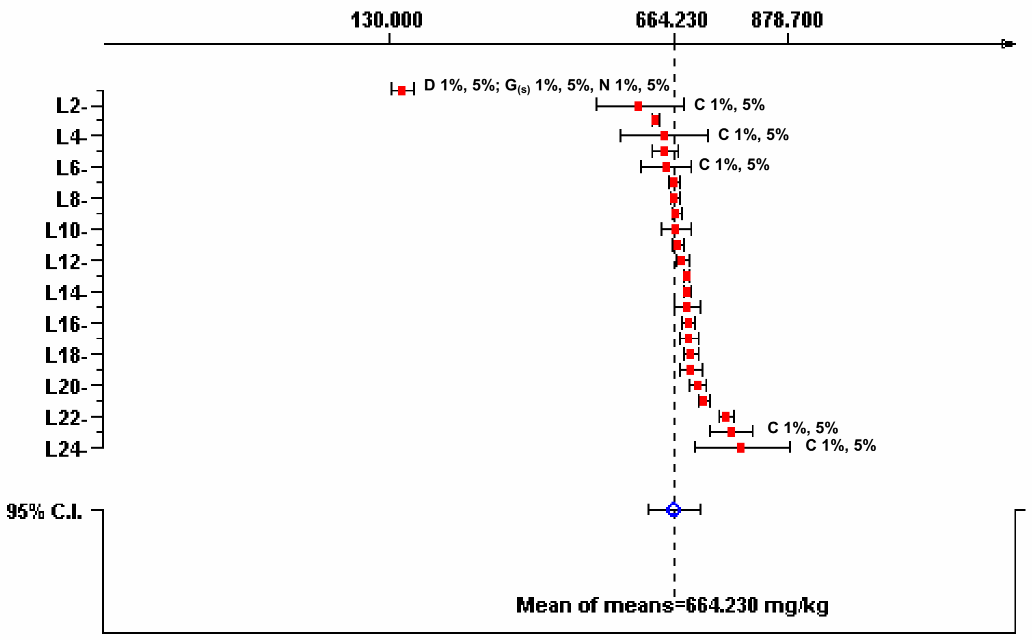
Range [min..max]	[130.000 .. 878.700]
	Case of No Pooling
Mean of means	664.230
95% H.W. Confidence Interval	49.175
95% H.W. Tolerance Interval	308.726
	Case of Pooling
Mean of All	664.230
95% H.W. Confidence Interval	19.517
95% H.W. Tolerance Interval	258.341

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. Xf1)



Tab. Xf2 : Iron 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
L1	41 ICP OES 2	599.000	77.828	81.675	527.000	616.000	627.000	565.000	732.000	527.000
L2	22 ICP OES 2	629.678	5.508	5.780	629.150	628.220	637.620	628.240	633.500	621.340
L3	31 ICP OES 1	646.333	78.025	81.882	552.000	579.000	614.000	667.000	717.000	749.000
L4	18 ETV-ICP OES (3)	646.433	23.424	24.582	676.900	663.500	629.200	629.800	618.900	660.300
L5	21 MAS 3	650.000	44.721	46.932	700.000	650.000	600.000	650.000	600.000	700.000
L6	42 ICP OES 2	665.333	9.438	9.904	661.000	681.000	658.000	659.000	660.000	673.000
L7	6 ICP OES 3	665.852	9.425	9.891	669.447	678.070	674.345	660.063	655.032	658.157
L8	17 ICP OES 1	668.500	8.408	8.824	667.000	667.000	678.000	656.000	678.000	665.000
L9	35 ICP-MS 2	668.667	26.726	28.047	674.000	654.000	720.000	650.000	663.000	651.000
L10	13 ICP-MS 3	672.667	9.791	10.275	656.000	668.000	676.000	675.000	676.000	685.000
L11	18 ICP OES 3	679.050	11.608	12.182	660.600	669.300	690.900	686.800	682.700	684.000
L12	12 ICP OES 2	687.383	4.202	4.409	689.900	688.700	681.800	693.600	684.700	685.600
L13	12 F AAS 2	688.667	6.903	7.244	690.200	692.200	689.200	675.500	695.700	689.200
L14	15 IPAA (3)	689.000	22.874	24.004	719.000	698.000	686.000	705.000	666.000	660.000
L15	24 ICP OES 1	691.583	12.430	13.045	679.400	676.500	687.100	700.300	698.900	707.300
L16	38 ICP OES 2	691.815	16.020	16.812	702.459	687.214	683.757	680.198	677.944	719.319
L17	25 ICP OES 2	694.880	13.130	13.779	685.390	674.360	695.050	699.520	705.050	709.910
L18	18 DC-ARC-OES 3	695.583	19.117	20.062	730.300	683.300	677.600	703.800	689.400	689.100
L19	5 F AAS 2	708.667	14.841	15.575	683.000	704.000	719.000	706.000	725.000	715.000
L20	20 ICP OES (1)	720.000	9.487	9.956	735.000	725.000	720.000	710.000	720.000	710.000
L21	2 ICP OES 3	762.833	13.045	13.690	757.000	755.000	748.000	761.000	772.000	784.000
L22	1 ICP OES 3	771.167	39.575	41.531	720.000	755.000	833.000	800.000	756.000	763.000
L23	11 ICP OES 1	791.767	85.392	89.613	633.300	784.000	834.700	785.200	834.700	878.700

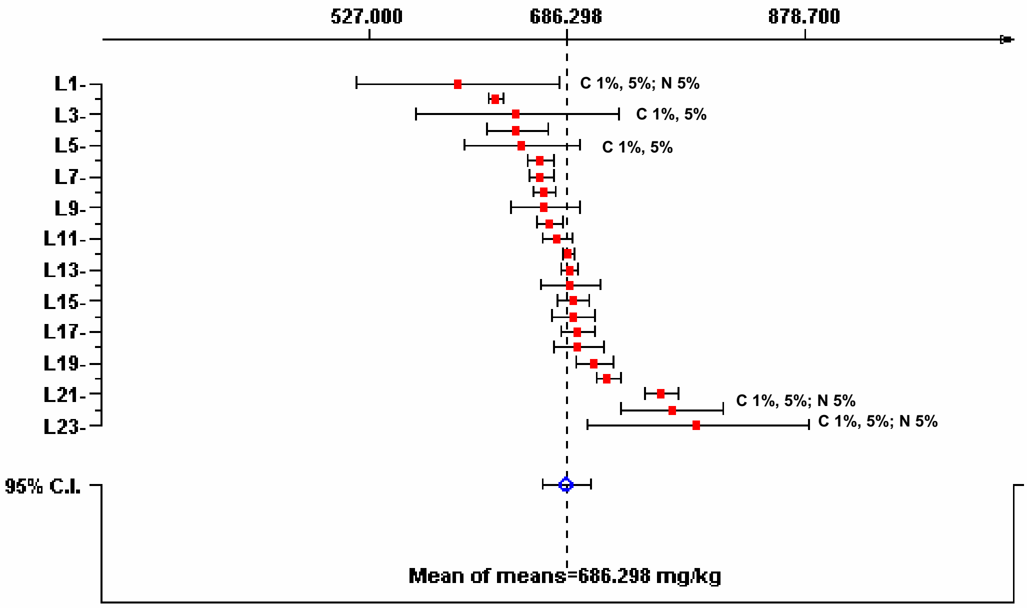
Range [min..max]	[527.000 .. 878.700]
	Case of No Pooling
Mean of means	686.298
95% H.W. Confidence Interval	19.142
95% H.W. Tolerance Interval	118.320
	Case of Pooling
Mean of All	686.298
95% H.W. Confidence Interval	9.011
95% H.W. Tolerance Interval	117.022

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. Xf2)



Tab. Xg1: Magnesium accepted results in run 1 (values in mg/kg) (indicative parameter only)

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
L1	12 ICP OES 2	1.310	0.065	0.069	1.410	1.330	1.280	1.250	1.240	1.350
L2	12 ET AAS 2	1.438	0.032	0.033	1.480	1.460	1.450	1.420	1.430	1.390
L3	18 ICP OES 3	1.447	0.144	0.151	1.520	1.330	1.590	1.280	1.350	1.610
L4	25 ICP OES 2	1.650	0.196	0.206	1.550	1.810	1.840	1.400	1.820	1.480
L5	18 ETV-ICP OES (3)	1.663	0.154	0.161	1.480	1.760	1.490	1.630	1.830	1.790
L6	13 ICP-MS 3	1.732	0.093	0.097	1.600	1.670	1.730	1.720	1.820	1.850
L7	5 ICP OES 2	1.743	0.130	0.137	1.780	1.690	1.690	1.750	1.970	1.580
L8	42 ICP OES 2	2.150	0.084	0.088	2.200	2.200	2.200	2.000	2.100	2.200
L9	2 ICP OES 3	2.253	0.843	0.885	1.160	2.090	2.920	3.530	2.020	1.800
L10	17 ICP OES 1	2.562	0.249	0.261	2.730	2.540	2.830	2.250	2.740	2.280
L11	6 ICP-MS 3	2.843	0.110	0.116	2.823	2.803	2.751	2.756	2.874	3.048
L12	24 ICP OES 1	2.853	0.301	0.316	2.610	2.500	3.210	2.970	3.160	2.670
L13	1 ICP OES 3	3.450	0.420	0.669	3.500	3.000	3.300			4.000
L14	41 ICP OES 2	4.683	0.830	0.872	5.500	5.500	3.400	4.300	4.300	5.100
L15	35 ICP-MS 2	5.583	0.798	0.837	6.050	6.290	6.320	4.270	5.380	5.190
L16	20 ICP OES (1)	6.333	0.516	0.542	6.000	7.000	6.000	6.000	7.000	6.000
L17	18 DC-ARC-OES 3	6.715	0.611	0.641	6.850	7.780	6.130	6.110	6.760	6.660
L18	31 ICP OES 1	7.333	0.816	0.857	8.000	8.000	8.000	7.000	6.000	7.000

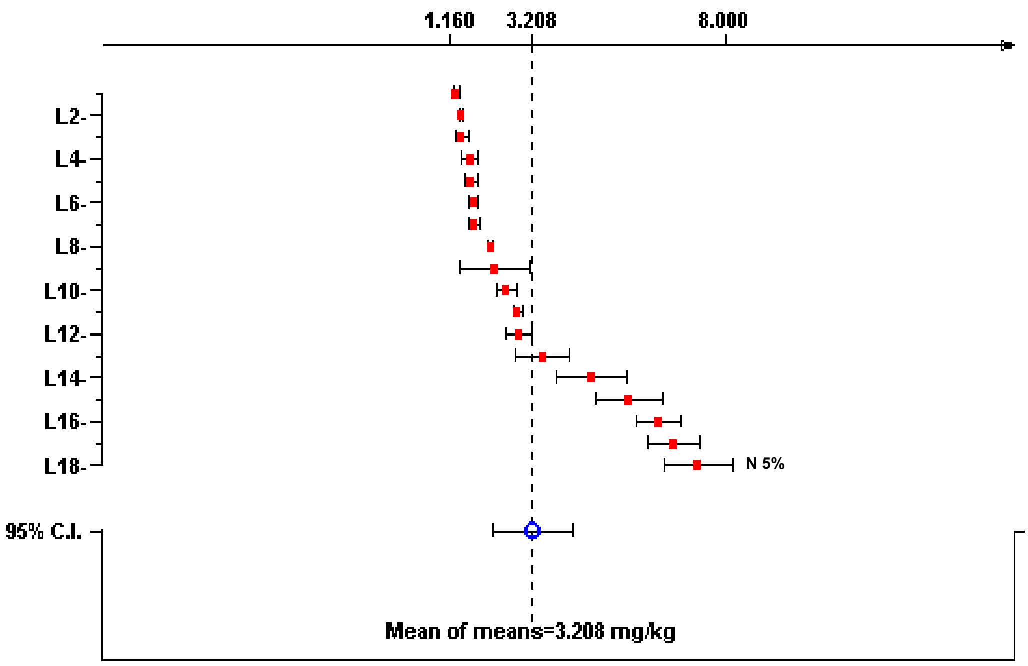
Range [min..max]	[1.160 .. 8.000]
	Case of No Pooling
Mean of means	3.208
95% H.W. Confidence Interval	0.999
95% H.W. Tolerance Interval	5.665
	Case of Pooling
Mean of All	3.203
95% H.W. Confidence Interval	0.390
95% H.W. Tolerance Interval	4.503

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. Xg1)



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
L1	18 DC-ARC-OES 3	8.088	0.392	0.411	8.210	7.420	8.180	8.600	7.930	8.190
L2	18 ETV-ICP OES (3)	9.420	0.375	0.394	10.050	9.230	9.170	9.710	9.110	9.250
L3	42 ICP OES 2	9.633	0.103	0.108	9.500	9.700	9.600	9.800	9.600	9.600
L4	34 ICP OES (2)	9.683	1.093	1.147	11.100	11.000	9.300	9.300	8.700	8.700
L5	35 ICP-MS 2	9.718	0.189	0.198	9.810	9.580	9.600	9.500	10.000	9.820
L6	12 ET AAS 2	9.910	0.169	0.178	10.190	9.990	9.840	9.720	9.940	9.780
L7	20 ICP OES 1	10.000	0.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000
L8	13 ICP-MS 3	10.112	0.183	0.192	9.770	10.200	10.100	10.300	10.100	10.200
L9	41 ICP OES 2	10.217	0.588	0.617	10.000	10.100	10.200	10.400	11.200	9.400
L10	38 ICP OES 2	10.338	0.109	0.115	10.399	10.231	10.304	10.256	10.309	10.527
L11	12 ICP OES 2	10.357	0.050	0.052	10.440	10.370	10.290	10.360	10.350	10.330
L12	22 ICP OES 2	10.568	0.609	0.639	10.340	11.060	10.990	9.960	9.820	11.240
L13	25 ICP OES 2	10.765	0.130	0.137	10.800	10.580	10.880	10.930	10.720	10.680
L14	17 ICP OES 1	10.783	0.075	0.079	10.700	10.800	10.700	10.800	10.900	10.800
L15	15 IPAA (3)	10.867	1.120	1.175	10.100	9.700	10.800	11.800	12.600	10.200
L16	1 ICP OES 3	10.983	0.546	0.573	11.900	11.000	11.000	10.800	11.000	10.200
L17	18 ICP OES 3	11.022	0.171	0.180	11.170	10.840	10.970	10.930	10.930	11.290
L18	31 ICP OES 1	11.333	5.428	5.697	12.000	13.000	20.000	5.000	6.000	12.000
L19	2 ICP OES 2	11.417	0.223	0.234	11.400	11.200	11.800	11.200	11.400	11.500
L20	24 ICP OES 1	11.683	0.581	0.610	11.100	11.700	11.900	12.100	12.400	10.900
L21	5 ICP OES 1	11.933	0.677	0.711	13.000	12.300	11.600	11.100	12.100	11.500
L22	6 ICP OES 3	12.669	0.269	0.282	12.607	12.307	13.123	12.558	12.666	12.755

Range [min..max]	[5.000 .. 20.000]
	Case of No Pooling
Mean of means	10.523
95% H.W. Confidence Interval	0.437
95% H.W. Tolerance Interval	2.656
	Case of Pooling
Mean of All	10.523
95% H.W. Confidence Interval	0.258
95% H.W. Tolerance Interval	3.283

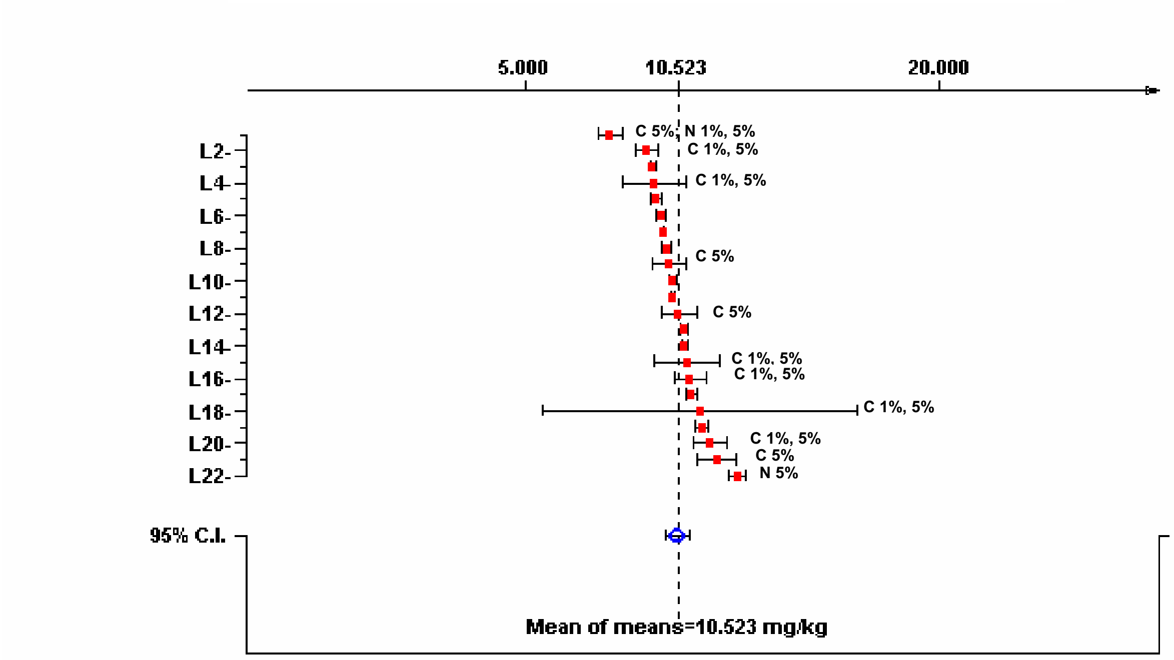
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

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. Xh1)



Tab. Xh2: 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
L1	18 DC-ARC-OES 3	8.088	0.392	0.411	8.210	7.420	8.180	8.600	7.930	8.190
L2	18 ETV-ICP OES (3)	9.420	0.375	0.394	10.050	9.230	9.170	9.710	9.110	9.250
L3	42 ICP OES 2	9.633	0.103	0.108	9.500	9.700	9.600	9.800	9.600	9.600
L4	34 ICP OES (2)	9.683	1.093	1.147	11.100	11.000	9.300	9.300	8.700	8.700
L5	35 ICP-MS 2	9.718	0.189	0.198	9.810	9.580	9.600	9.500	10.000	9.820
L6	12 ET AAS 2	9.910	0.169	0.178	10.190	9.990	9.840	9.720	9.940	9.780
L7	20 ICP OES 1	10.000	0.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000
L8	13 ICP-MS 3	10.112	0.183	0.192	9.770	10.200	10.100	10.300	10.100	10.200
L9	41 ICP OES 2	10.217	0.588	0.617	10.000	10.100	10.200	10.400	11.200	9.400
L10	38 ICP OES 2	10.338	0.109	0.115	10.399	10.231	10.304	10.256	10.309	10.527
L11	12 ICP OES 2	10.357	0.050	0.052	10.440	10.370	10.290	10.360	10.350	10.330
L12	22 ICP OES 2	10.568	0.609	0.639	10.340	11.060	10.990	9.960	9.820	11.240
L13	25 ICP OES 2	10.765	0.130	0.137	10.800	10.580	10.880	10.930	10.720	10.680
L14	17 ICP OES 1	10.783	0.075	0.079	10.700	10.800	10.700	10.800	10.900	10.800
L15	15 IPAA (3)	10.867	1.120	1.175	10.100	9.700	10.800	11.800	12.600	10.200
L16	1 ICP OES 3	10.983	0.546	0.573	11.900	11.000	11.000	10.800	11.000	10.200
L17	18 ICP OES 3	11.022	0.171	0.180	11.170	10.840	10.970	10.930	10.930	11.290
L18	2 ICP OES 2	11.417	0.223	0.234	11.400	11.200	11.800	11.200	11.400	11.500
L19	24 ICP OES 1	11.683	0.581	0.610	11.100	11.700	11.900	12.100	12.400	10.900
L20	5 ICP OES 1	11.933	0.677	0.711	13.000	12.300	11.600	11.100	12.100	11.500
L21	6 ICP OES 3	12.669	0.269	0.282	12.607	12.307	13.123	12.558	12.666	12.755

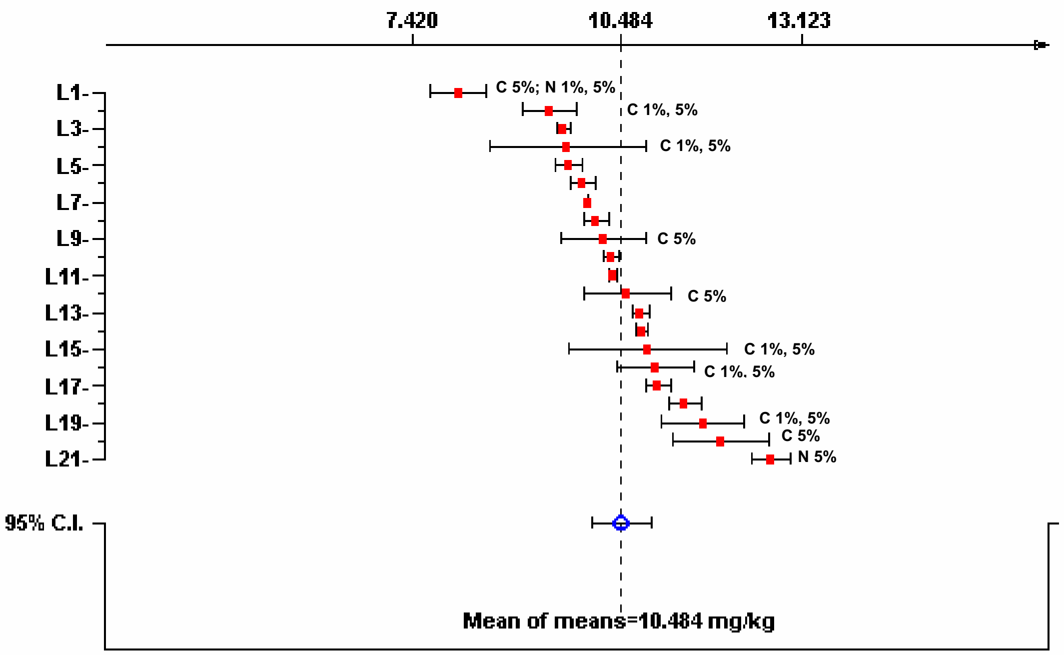
Range [min..max]	[7.420 .. 13.123]
	Case of No Pooling
Mean of means	10.484
95% H.W. Confidence Interval	0.452
95% H.W. Tolerance Interval	2.701
	Case of Pooling
Mean of All	10.484
95% H.W. Confidence Interval	0.188
95% H.W. Tolerance Interval	2.346

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. Xh2)



Tab. Xi1: 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
L1	5 F AAS 2	5.333	0.996	1.045	6.000	4.000	4.250	6.500	5.500	5.750
L2	12 ET AAS 2	5.445	0.188	0.198	5.570	5.770	5.350	5.280	5.380	5.320
L3	18 F AAS 3	5.587	0.453	0.475	5.390	5.350	6.180	5.040	5.460	6.100
L4	13 ICP-MS 3	5.742	0.133	0.140	5.750	5.710	5.980	5.730	5.710	5.570
L5	18 ETV-ICP OES (3)	5.873	0.738	0.774	5.980	6.640	6.810	5.120	5.590	5.100
L6	42 AAS 2	6.350	0.327	0.343	6.000	6.500	6.200	6.900	6.400	6.100
L7	24 AAS 1	6.843	0.821	0.861	7.690	6.390	5.980	8.000	6.750	6.250
L8	17 ICP OES 1	7.010	0.961	1.530		7.520	5.710	6.900	7.910	
L9	2 ICP OES 2	7.113	0.473	0.496	6.710	6.460	7.740	7.410	7.320	7.040
L10	1 F AAS (3)	7.583	1.314	1.379	7.300	6.400	6.500	7.900	10.000	7.400
L11	20 ICP OES 1	10.000	0.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000

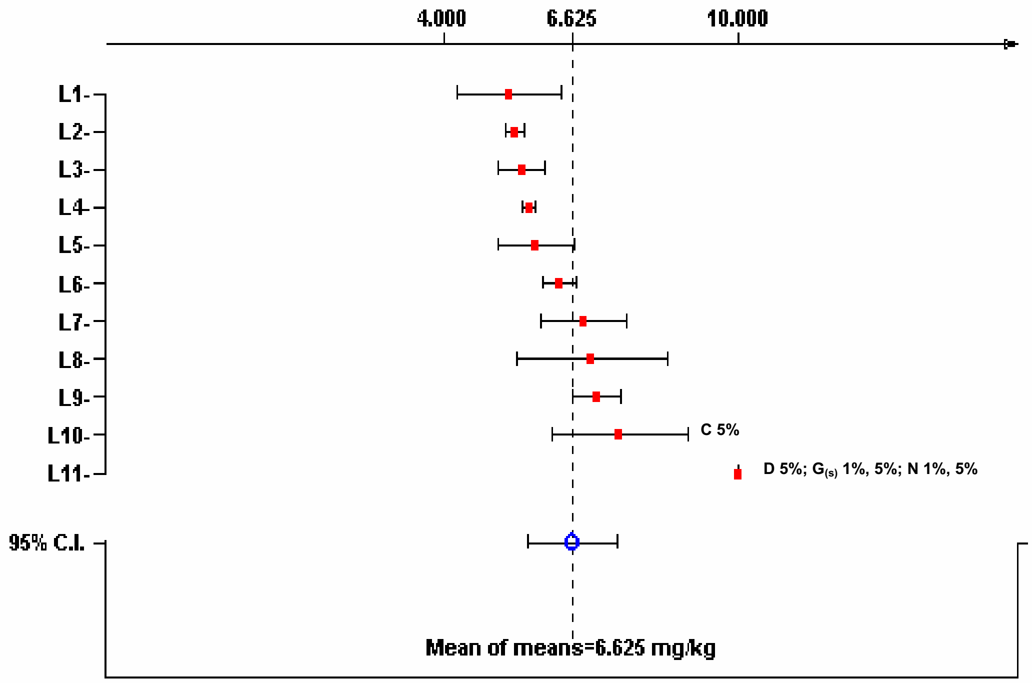
Range [min..max]	[4.000 .. 10.000]
	Case of No Pooling
Mean of means	6.625
95% H.W. Confidence Interval	0.909
95% H.W. Tolerance Interval	4.409
	Case of Pooling
Mean of All	6.613
95% H.W. Confidence Interval	0.366
95% H.W. Tolerance Interval	685.505

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. Xi1)



Tab. Xi2: Sodium 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
L1	5 F AAS 2	5.333	0.996	1.045	6.000	4.000	4.250	6.500	5.500	5.750
L2	12 ET AAS 2	5.445	0.188	0.198	5.570	5.770	5.350	5.280	5.380	5.320
L3	18 F AAS 3	5.587	0.453	0.475	5.390	5.350	6.180	5.040	5.460	6.100
L4	13 ICP-MS 3	5.742	0.133	0.140	5.750	5.710	5.980	5.730	5.710	5.570
L5	18 ETV-ICP OES (3)	5.873	0.738	0.774	5.980	6.640	6.810	5.120	5.590	5.100
L6	42 AAS 2	6.350	0.327	0.343	6.000	6.500	6.200	6.900	6.400	6.100
L7	24 AAS 1	6.843	0.821	0.861	7.690	6.390	5.980	8.000	6.750	6.250
L8	17 ICP OES 1	7.010	0.961	1.530		7.520	5.710	6.900	7.910	
L9	2 ICP OES 2	7.113	0.473	0.496	6.710	6.460	7.740	7.410	7.320	7.040
L10	1 F AAS (3)	7.583	1.314	1.379	7.300	6.400	6.500	7.900	10.000	7.400

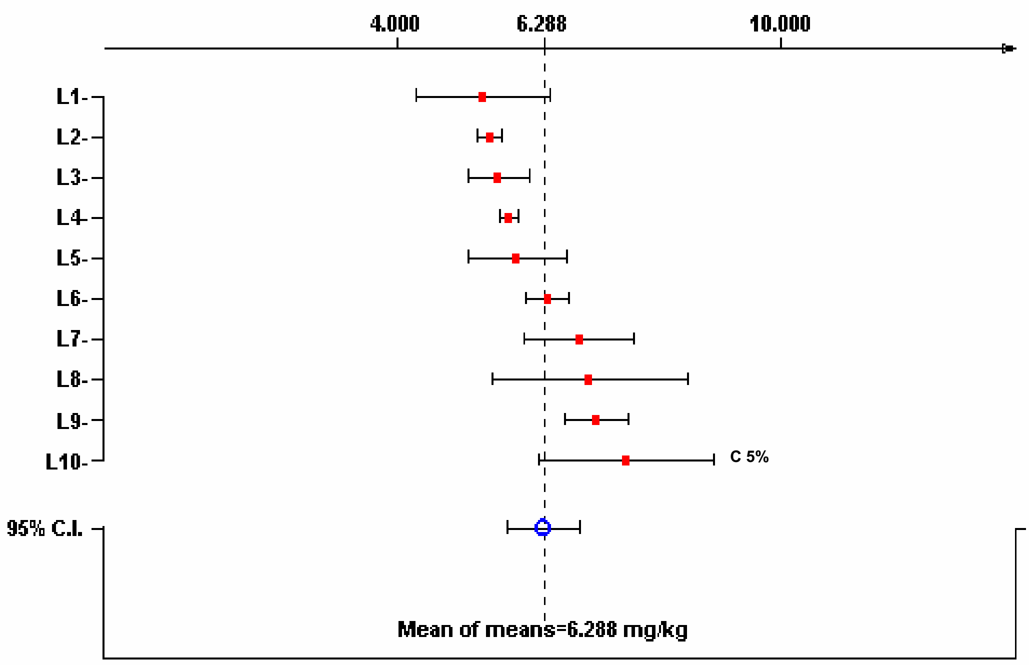
Range [min..max]	[4.000 .. 10.000]
	Case of No Pooling
Mean of means	6.288
95% H.W. Confidence Interval	0.573
95% H.W. Tolerance Interval	2.707
	Case of Pooling
Mean of All	6.263
95% H.W. Confidence Interval	0.267
95% H.W. Tolerance Interval	1.424.800

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. Xi2)



Tab. Xj1: 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
L1	6 ICP-MS (3)	6.205	1.007	1.056	7.867	6.819	6.211	5.761	5.436	5.138
L2	18 ETV-ICP OES (3)	6.208	0.214	0.225	5.850	6.070	6.380	6.370	6.210	6.370
L3	13 ICP-MS 3	6.402	0.290	0.304	6.180	6.760	6.290	6.010	6.520	6.650
L4	42 ICP OES 1	6.617	0.264	0.277	6.800	6.100	6.700	6.600	6.800	6.700
L5	2 ICP OES 3	7.145	0.826	0.867	8.350	7.810	6.040	6.860	7.130	6.680
L6	20 ICP OES 1	7.167	0.408	0.428	7.000	8.000	7.000	7.000	7.000	7.000
L7	18 ICP OES 3	7.372	0.595	0.624	8.400	7.160	6.930	6.720	7.570	7.450
L8	12 ET AAS 2	7.530	0.109	0.114	7.740	7.490	7.510	7.450	7.540	7.450
L9	25 ICP OES 1	7.790	0.298	0.313	8.080	7.680	8.000	7.690	8.000	7.290
L10	12 ICP OES 2	7.843	0.168	0.177	7.780	8.180	7.790	7.830	7.740	7.740
L11	5 ICP OES 1	8.328	0.542	0.569	8.200	7.330	8.580	8.840	8.330	8.690
L12	22 ICP OES 2	9.965	0.691	0.725	9.270	10.420	10.650	10.310	10.200	8.940
L13	24 ICP OES 1	10.085	0.335	0.351	9.640	10.300	10.100	10.600	9.990	9.880
L14	41 ICP OES 1	10.617	2.192	2.301	10.600	7.000	13.400	10.300	10.100	12.300
L15	18 DC-ARC-OES 3	11.053	0.708	0.743	12.000	11.260	11.530	10.030	10.980	10.520

Range [min..max]	[5.138 .. 13.400]
	Case of No Pooling
Mean of means	8.022
95% H.W. Confidence Interval	0.906
95% H.W. Tolerance Interval	4.834
	Case of Pooling
Mean of All	8.022
95% H.W. Confidence Interval	0.364
95% H.W. Tolerance Interval	3.910

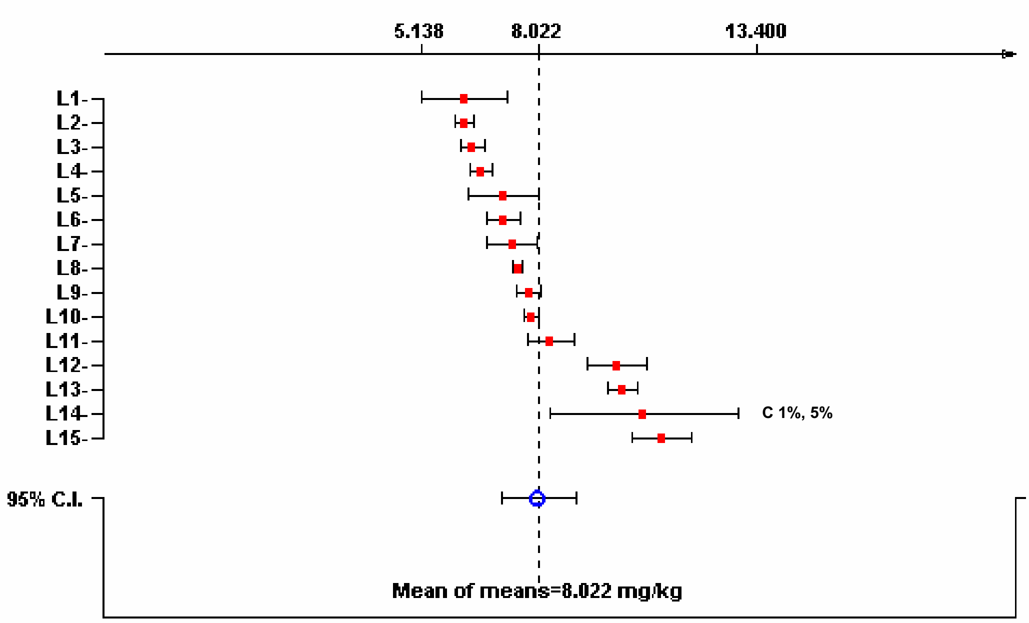
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

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. Xj1)



Tab. Xk1 : Silicon 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
L1	33 DC-ARC-OES 2	60.0	0.00	0.00		60.00	60.00	60.00	60.00	60.00
L2	12 ICP OES 2	204.74	7.44	9.24		202.00	201.10	204.50	198.60	217.50
L3	12 ET AAS 2	216.47	8.52	8.94	205.0	211.30	212.50	221.20	219.90	228.90
L4	13 ICP-MS (3)	227.17	5.42	5.69	218.00	225.00	229.00	234.00	227.00	230.00
L5	20 ICP OES 1	238.33	7.53	7.90	250.00	240.00	230.00	240.00	230.00	240.00
L6	41 ICP OES 2	264.00	66.23	69.51	300.00	373.00	274.00	213.00	230.00	194.00
L7	5 MAS 2	265.00	10.49	11.01	250.00	260.00	280.00	260.00	270.00	270.00
L8	1 MAS 3	274.83	3.87	4.06	275.00	278.00	275.00	280.00	270.00	271.00
L9	25 ICP OES 2	281.18	26.04	27.33	314.96	272.12	269.71	255.12	262.34	312.84
L10	18 ICP OES 3	292.17	25.03	26.27	289.30	320.80	279.10	320.50	287.30	256.00
L11	42 ICP OES 2	294.83	9.20	9.65	292.00	293.00	289.00	312.00	286.00	297.00
L12	24 MAS 1	295.43	8.57	8.99	299.90	302.20	306.00	292.20	288.00	284.30
L13	18 DC-ARC-OES 3	303.65	17.38	18.24	295.00	279.30	330.30	314.60	302.30	300.40
L14	18 ETV-ICP OES (3)	323.17	16.86	17.69	347.20	329.00	299.50	320.20	332.40	310.70
L15	21 MAS 3	391.67	9.83	10.32	380.00	400.00	400.00	380.00	390.00	400.00
L16	35 ICP-MS 2	1,311.67	140.06	146.98	1,230.00	1,190.00	1,470.00	1,220.00	1,250.00	1,510.00

Range [min..max]	[60.000 .. 1,510.000]
	Case of No Pooling
Mean of means	327.769
95% H.W. Confidence Interval	144.723
95% H.W. Tolerance Interval	788.442
	Case of Pooling
Mean of All	331.926
95% H.W. Confidence Interval	54.904
95% H.W. Tolerance Interval	601.262

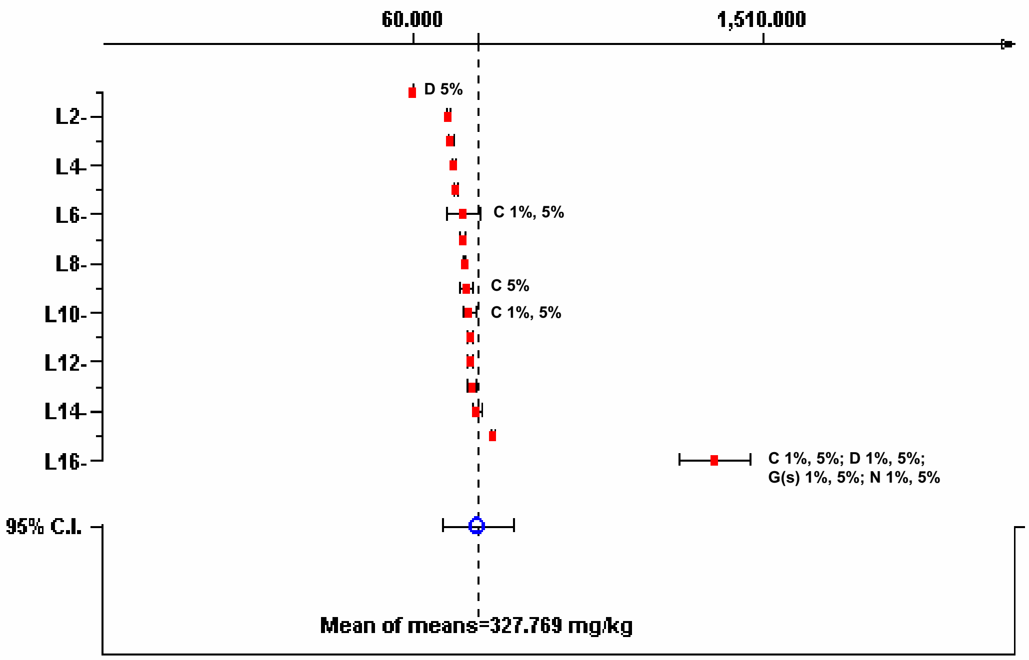
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

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. Xk1)



Tab. Xk2 : Silicon 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
L1	33 DC-ARC-OES 2	60.00	0.00	0.00		60.00	60.00	60.00	60.00	60.00
L2	12 ICP OES 2	204.74	7.44	9.24		202.00	201.10	204.50	198.60	217.50
L3	12 ET AAS 2	216.47	8.52	8.94	205.00	211.30	212.50	221.20	219.90	228.90
L4	13 ICP-MS (3)	227.17	5.42	5.69	218.00	225.00	229.00	234.00	227.00	230.00
L5	20 ICP OES 1	238.33	7.53	7.90	250.00	240.00	230.00	240.00	230.00	240.00
L6	41 ICP OES 2	264.00	66.23	69.51	300.00	373.00	274.00	213.00	230.00	194.00
L7	5 MAS 2	265.00	10.49	11.01	250.00	260.00	280.00	260.00	270.00	270.00
L8	1 MAS 3	274.83	3.87	4.06	275.00	278.00	275.00	280.00	270.00	271.00
L9	25 ICP OES 2	281.18	26.04	27.33	314.96	272.12	269.71	255.12	262.34	312.84
L10	18 ICP OES 3	292.17	25.03	26.27	289.30	320.80	279.10	320.50	287.30	256.00
L11	42 ICP OES 2	294.83	9.20	9.65	292.00	293.00	289.00	312.00	286.00	297.00
L12	24 MAS 1	295.43	8.57	8.99	299.90	302.20	306.00	292.20	288.00	284.30
L13	18 DC-ARC-OES 3	303.65	17.38	18.24	295.00	279.30	330.30	314.60	302.30	300.40
L14	18 ETV-ICP OES (3)	323.17	16.86	17.69	347.20	329.00	299.50	320.20	332.40	310.70
L15	21 MAS 3	391.67	9.83	10.32	380.00	400.00	400.00	380.00	390.00	400.00

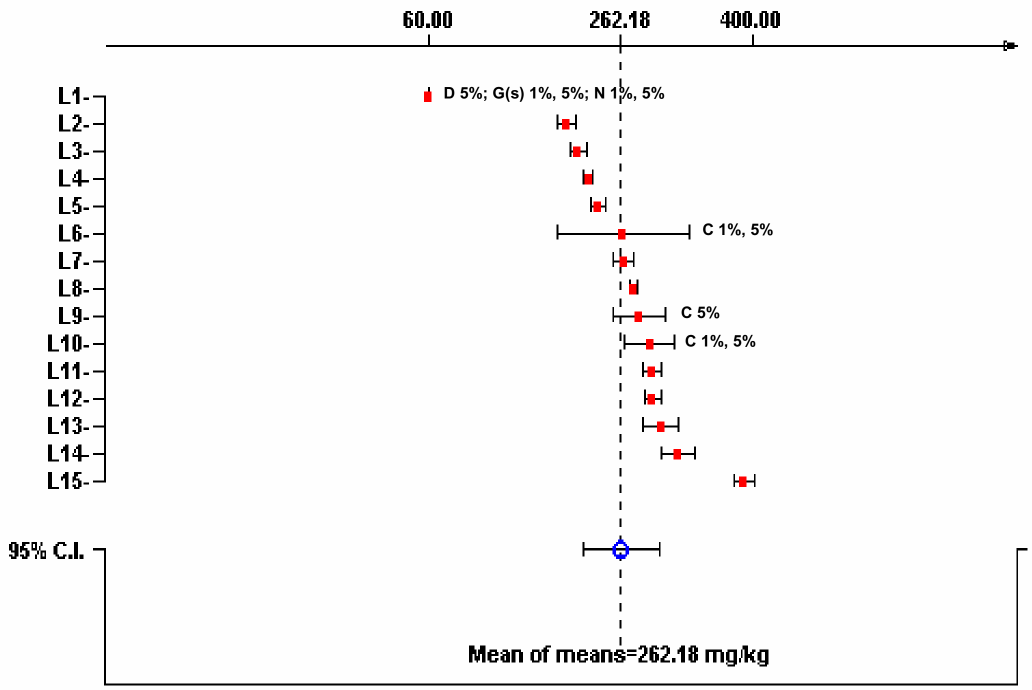
Range [min..max]	[60.00 .. 400.00]
	Case of No Pooling
Mean of means	262.18
95% H.W. Confidence Interval	40.23
95% H.W. Tolerance Interval	214.58
	Case of Pooling
Mean of All	265.13
95% H.W. Confidence Interval	14.94
95% H.W. Tolerance Interval	159.01

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. Xk2)



Tab. Xk3 : Silicon evaluation 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
L1	12 ICP OES 2	204.74	7.44	9.24		202.00	201.10	204.50	198.60	217.50
L2	12 ET AAS 2	216.47	8.52	8.94	205.00	211.30	212.50	221.20	219.90	228.90
L3	13 ICP-MS (3)	227.17	5.42	5.69	218.00	225.00	229.00	234.00	227.00	230.00
L4	20 ICP OES 1	238.33	7.53	7.90	250.00	240.00	230.00	240.00	230.00	240.00
L5	41 ICP OES 2	264.00	66.23	69.51	300.00	373.00	274.00	213.00	230.00	194.00
L6	5 MAS 2	265.00	10.49	11.01	250.00	260.00	280.00	260.00	270.00	270.00
L7	1 MAS 3	274.83	3.87	4.06	275.00	278.00	275.00	280.00	270.00	271.00
L8	25 ICP OES 2	281.18	26.04	27.33	314.96	272.12	269.71	255.12	262.34	312.84
L9	18 ICP OES 3	292.17	25.03	26.27	289.30	320.80	279.10	320.50	287.30	256.00
L10	42 ICP OES 2	294.83	9.20	9.65	292.00	293.00	289.00	312.00	286.00	297.00
L11	24 MAS 1	295.43	8.57	8.99	299.90	302.20	306.00	292.20	288.00	284.30
L12	18 DC-ARC-OES 3	303.65	17.38	18.24	295.00	279.30	330.30	314.60	302.30	300.40
L13	18 ETV-ICP OES (3)	323.17	16.86	17.69	347.20	329.00	299.50	320.20	332.40	310.70
L14	21 MAS 3	391.67	9.83	10.32	380.00	400.00	400.00	380.00	390.00	400.00

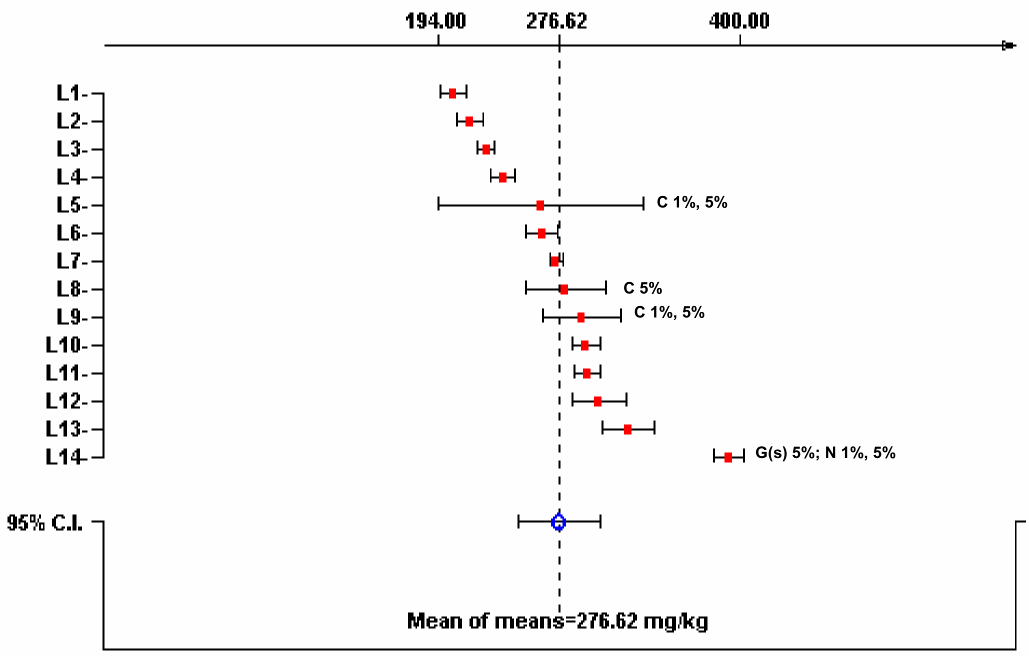
Range [min..max]	[194.00 .. 400.00]
	Case of No Pooling
Mean of means	276.62
95% H.W. Confidence Interval	27.77
95% H.W. Tolerance Interval	144.87
	Case of Pooling
Mean of All	277.48
95% H.W. Confidence Interval	11.04
95% H.W. Tolerance Interval	114.51

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. Xk3)



Tab. Xk4 : Silicon accepted results in run 4 (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
L1	12 ICP OES 2	204.74	7.44	9.24		202.00	201.10	204.50	198.60	217.50
L2	12 ET AAS 2	216.47	8.52	8.94	205.00	211.30	212.50	221.20	219.90	228.90
L3	13 ICP-MS (3)	227.17	5.42	5.69	218.00	225.00	229.00	234.00	227.00	230.00
L4	20 ICP OES 1	238.33	7.53	7.90	250.00	240.00	230.00	240.00	230.00	240.00
L5	41 ICP OES 2	264.00	66.23	69.51	300.00	373.00	274.00	213.00	230.00	194.00
L6	5 MAS 2	265.00	10.49	11.01	250.00	260.00	280.00	260.00	270.00	270.00
L7	1 MAS 3	274.83	3.87	4.06	275.00	278.00	275.00	280.00	270.00	271.00
L8	25 ICP OES 2	281.18	26.04	27.33	314.96	272.12	269.71	255.12	262.34	312.84
L9	18 ICP OES 3	292.17	25.03	26.27	289.30	320.80	279.10	320.50	287.30	256.00
L10	42 ICP OES 2	294.83	9.20	9.65	292.00	293.00	289.00	312.00	286.00	297.00
L11	24 MAS 1	295.43	8.57	8.99	299.90	302.20	306.00	292.20	288.00	284.30
L12	18 DC-ARC-OES 3	303.65	17.38	18.24	295.00	279.30	330.30	314.60	302.30	300.40
L13	18 ETV-ICP OES (3)	323.17	16.86	17.69	347.20	329.00	299.50	320.20	332.40	310.70

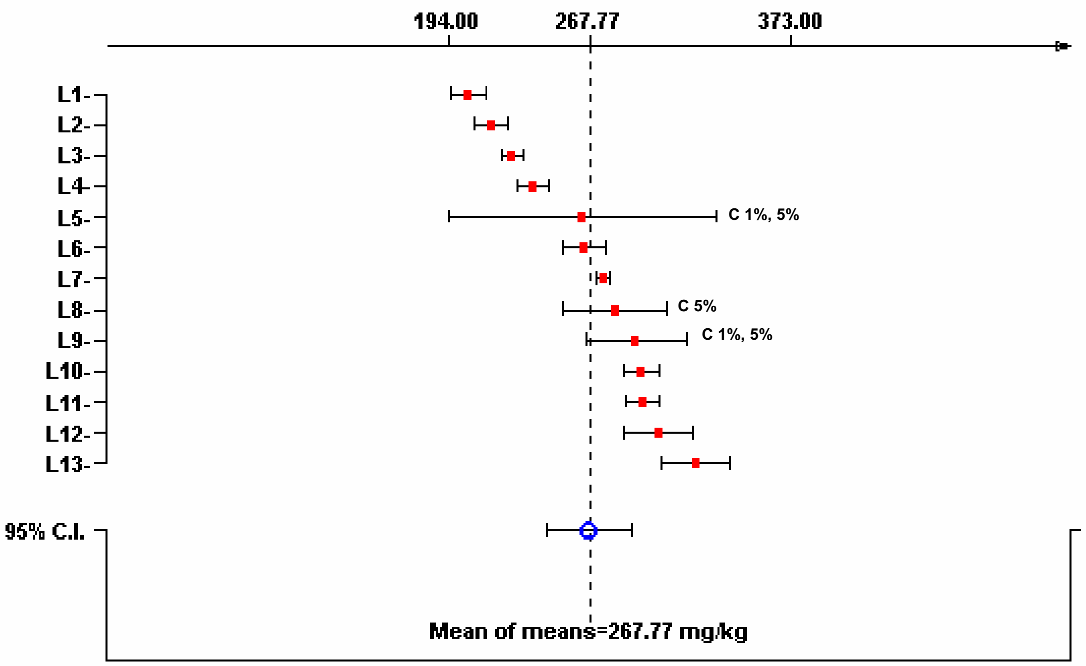
Range [min..max]	[194.00 .. 373.00]
	Case of No Pooling
Mean of means	267.77
95% H.W. Confidence Interval	21.94
95% H.W. Tolerance Interval	111.87
	Case of Pooling
Mean of All	268.59
95% H.W. Confidence Interval	9.19
95% H.W. Tolerance Interval	92.35

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. Xk4)



Tab. XI1 : 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
L1	18 ETV-ICP OES (3)	63.005	6.977	7.322	70.780	68.070	66.360	51.770	58.590	62.460
L2	12 ICP OES 2	90.133	0.958	1.006	89.100	89.500	89.400	91.600	90.600	90.600
L3	31 ICP OES 1	90.167	9.239	9.696	99.000	99.000	97.000	84.000	84.000	78.000
L4	20 ICP OES 1	90.333	0.816	0.857	90.000	92.000	90.000	90.000	90.000	90.000
L5	17 ICP OES 1	91.317	0.770	0.809	90.200	90.500	91.900	91.500	91.900	91.900
L6	5 ICP OES 1	91.650	4.473	4.695	93.700	90.600	91.600	84.800	98.500	90.700
L7	41 ICP OES 2	91.833	3.061	3.212	94.000	94.000	87.000	89.000	94.000	93.000
L8	38 ICP OES 2	92.585	2.427	2.547	93.408	93.534	93.740	95.525	90.241	89.062
L9	13 ICP-MS (3)	92.617	2.678	2.811	90.800	89.200	95.900	93.400	95.300	91.100
L10	34 ICP OES 2	94.367	4.270	4.481	94.100	99.700	94.300	98.700	89.300	90.100
L11	42 ICP OES 2	94.667	3.266	3.427	90.000	97.000	95.000	99.000	92.000	95.000
L12	15 IPAA 3	94.700	0.772	0.810	94.400	94.200	95.100	93.700	94.900	95.900
L13	11 ICP OES 1	95.750	1.115	1.170	95.700	94.200	94.800	97.300	96.300	96.200
L14	25 ICP OES 2	96.175	3.247	3.408	93.520	95.860	92.820	101.420	98.480	94.950
L15	1 ICP OES 3	96.617	3.191	3.349	97.800	97.600	97.600	100.400	91.000	95.300
L16	24 ICP OES 1	97.400	1.792	1.881	96.600	96.700	95.600	100.400	98.700	96.400
L17	18 ICP OES 3	97.478	3.228	3.388	94.890	95.400	102.040	101.010	96.750	94.780
L18	12 ET AAS 2	97.500	1.936	2.032	97.800	98.700	100.500	95.100	96.800	96.100
L19	22 ICP OES 2	100.543	1.651	1.732	99.870	101.000	102.850	97.840	101.120	100.580
L20	35 ICP-MS 2	101.667	5.759	6.044	94.500	105.000	101.000	109.000	95.500	105.000
L21	18 DC-ARC-OES 3	103.633	5.081	5.332	97.520	105.160	103.370	108.890	108.980	97.880
L22	6 ICP OES 3	104.496	4.432	4.651	110.927	109.324	101.475	102.673	100.779	101.796
L23	2 ICP OES 3	104.500	2.429	2.549	103.000	102.000	107.000	103.000	104.000	108.000

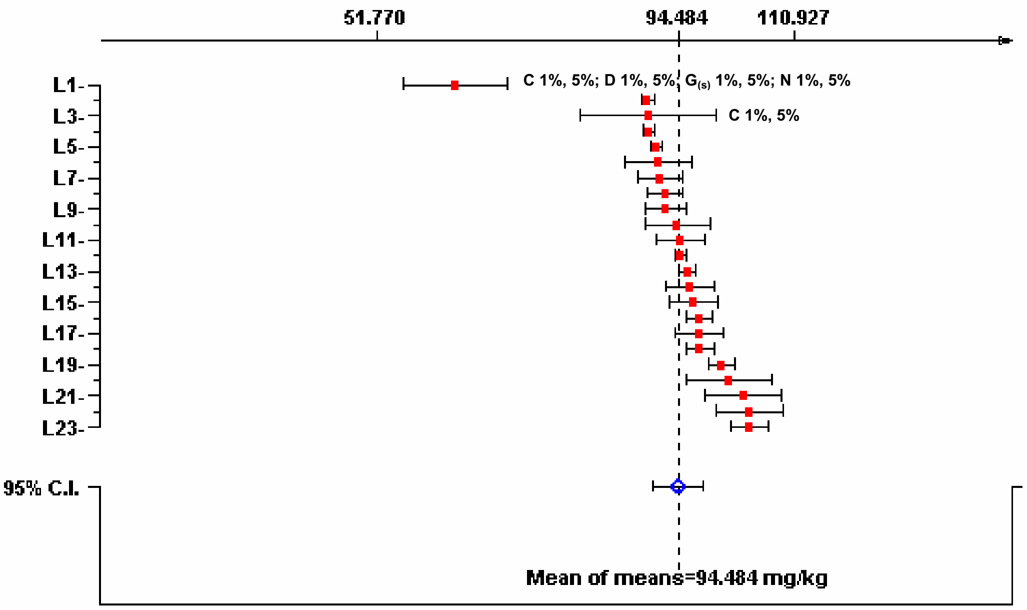
Range [min..max]	[51.770 .. 110.927]
	Case of No Pooling
Mean of means	94.484
95% H.W. Confidence Interval	3.554
95% H.W. Tolerance Interval	21.969
	Case of Pooling
Mean of All	94.484
95% H.W. Confidence Interval	1.480
95% H.W. Tolerance Interval	19.220

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. XI1)



Tab. XI2 : 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
L1	12 ICP OES 2	90.133	0.958	1.006	89.100	89.500	89.400	91.600	90.600	90.600
L2	31 ICP OES 1	90.167	9.239	9.696	99.000	99.000	97.000	84.000	84.000	78.000
L3	20 ICP OES 1	90.333	0.816	0.857	90.000	92.000	90.000	90.000	90.000	90.000
L4	17 ICP OES 1	91.317	0.770	0.809	90.200	90.500	91.900	91.500	91.900	91.900
L5	5 ICP OES 1	91.650	4.473	4.695	93.700	90.600	91.600	84.800	98.500	90.700
L6	41 ICP OES 2	91.833	3.061	3.212	94.000	94.000	87.000	89.000	94.000	93.000
L7	38 ICP OES 2	92.585	2.427	2.547	93.408	93.534	93.740	95.525	90.241	89.062
L8	13 ICP-MS (3)	92.617	2.678	2.811	90.800	89.200	95.900	93.400	95.300	91.100
L9	34 ICP OES 2	94.367	4.270	4.481	94.100	99.700	94.300	98.700	89.300	90.100
L10	42 ICP OES 2	94.667	3.266	3.427	90.000	97.000	95.000	99.000	92.000	95.000
L11	15 IPAA 3	94.700	0.772	0.810	94.400	94.200	95.100	93.700	94.900	95.900
L12	11 ICP OES 1	95.750	1.115	1.170	95.700	94.200	94.800	97.300	96.300	96.200
L13	25 ICP OES 2	96.175	3.247	3.408	93.520	95.860	92.820	101.420	98.480	94.950
L14	1 ICP OES 3	96.617	3.191	3.349	97.800	97.600	97.600	100.400	91.000	95.300
L15	24 ICP OES 1	97.400	1.792	1.881	96.600	96.700	95.600	100.400	98.700	96.400
L16	18 ICP OES 3	97.478	3.228	3.388	94.890	95.400	102.040	101.010	96.750	94.780
L17	12 ET AAS 2	97.500	1.936	2.032	97.800	98.700	100.500	95.100	96.800	96.100
L18	22 ICP OES 2	100.543	1.651	1.732	99.870	101.000	102.850	97.840	101.120	100.580
L19	35 ICP-MS 2	101.667	5.759	6.044	94.500	105.000	101.000	109.000	95.500	105.000
L20	18 DC-ARC-OES 3	103.633	5.081	5.332	97.520	105.160	103.370	108.890	108.980	97.880
L21	6 ICP OES 3	104.496	4.432	4.651	110.927	109.324	101.475	102.673	100.779	101.796
L22	2 ICP OES 3	104.500	2.429	2.549	103.000	102.000	107.000	103.000	104.000	108.000

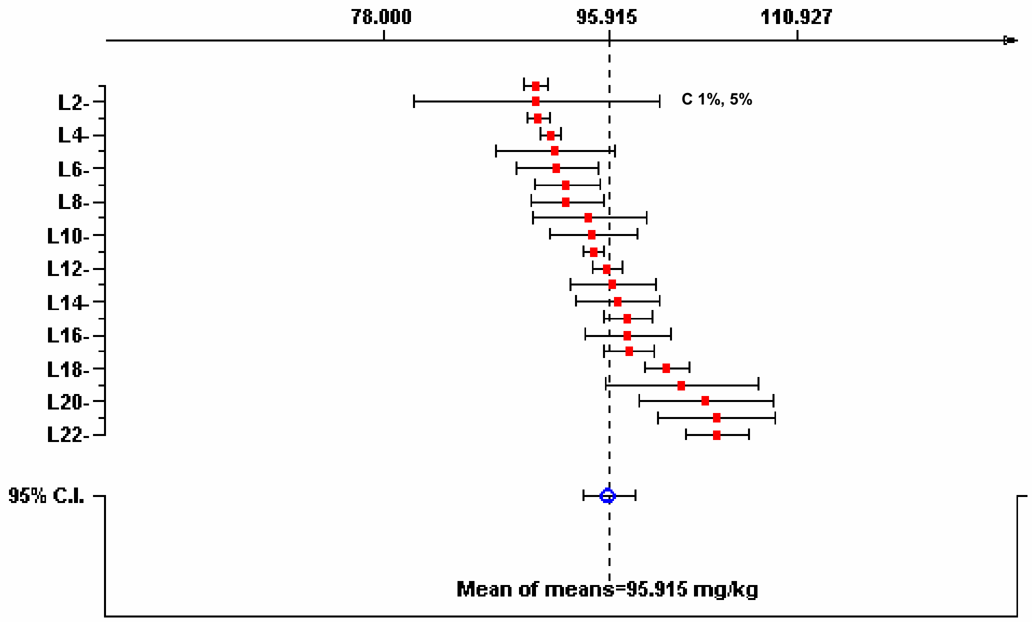
Range [min..max]	[78.000 .. 110.927]
	Case of No Pooling
Mean of means	95.915
95% H.W. Confidence Interval	2.053
95% H.W. Tolerance Interval	12.487
	Case of Pooling
Mean of All	95.915
95% H.W. Confidence Interval	0.967
95% H.W. Tolerance Interval	12.310

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. XI2)



Tab. Xm1: Tungsten accepted results in run 1 (values in mg/kg); (indicative parameter only)

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
L1	13 ICP-MS 3	1.093	0.027	0.029	1.140	1.110	1.090	1.080	1.070	1.070
L2	35 ICP-MS 2	1.185	0.058	0.060	1.180	1.240	1.220	1.230	1.090	1.150
L3	42 ICPOES 1	5.000	0.167	0.176	4.800	5.100	5.100	5.000	4.800	5.200
L4	24 ICPOES 1	5.113	0.391	0.410	5.400	4.910	5.000	5.770	4.820	4.780
L5	6 ICP-MS (2)	5.575	1.059	1.111	7.422	6.265	4.671	4.946	5.073	5.073

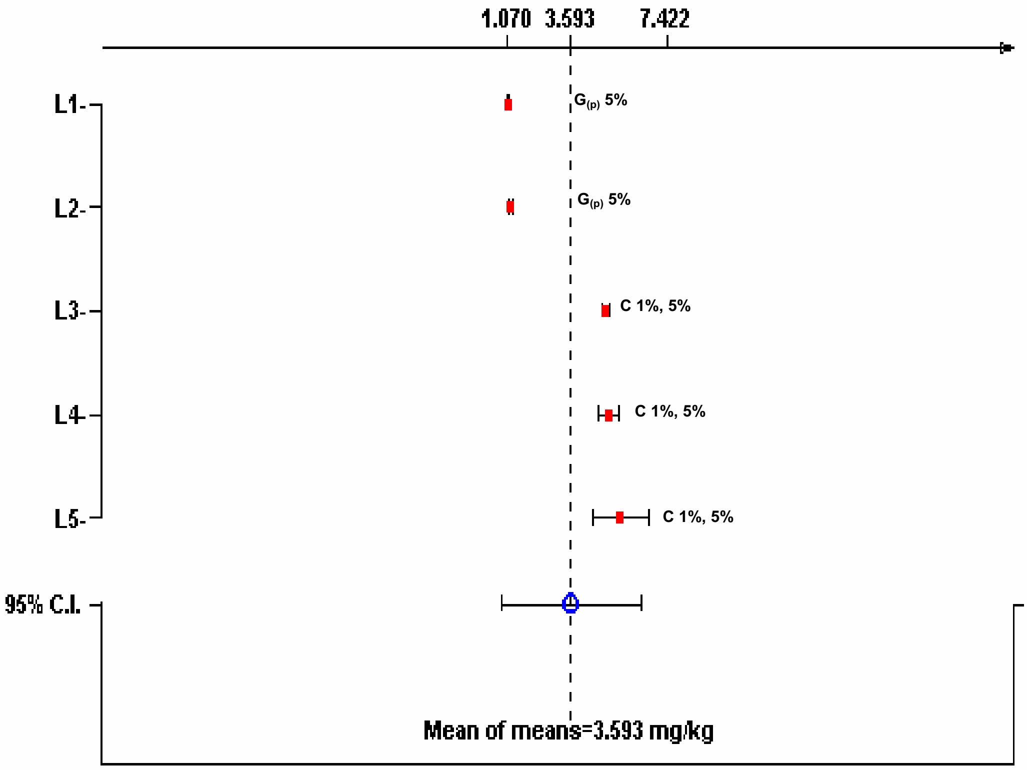
Range [min..max]	[1.070 .. 7.422]
	Case of No Pooling
Mean of means	3.593
95% H.W. Confidence Interval	2.795
95% H.W. Tolerance Interval	11.432
	Case of Pooling
Mean of All	3.593
95% H.W. Confidence Interval	0.785
95% H.W. Tolerance Interval	5.358

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. Xm1)



Tab. Xn1: 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
L1	18 ETV-ICP OES (3)	37.338	2.298	2.411	35.540	37.230	41.660	35.840	37.830	35.930
L2	20 ICP OES 1	44.667	0.816	0.857	45.000	45.000	45.000	43.000	45.000	45.000
L3	31 ICP OES 1	44.833	6.911	7.253	51.000	43.000	36.000	54.000	46.000	39.000
L4	12 ICP OES 2	45.450	0.983	1.032	44.800	44.600	46.200	47.000	45.500	44.600
L5	13 ICP-MS (3)	47.150	1.176	1.234	47.800	45.400	47.800	48.700	46.600	46.600
L6	42 ICP OES 2	47.500	1.049	1.101	49.000	47.000	47.000	46.000	48.000	48.000
L7	35 ICP-MS 2	47.733	1.840	1.931	47.900	47.500	45.800	50.400	45.700	49.100
L8	5 ICP OES 2	47.967	1.657	1.739	50.300	48.100	46.600	46.600	49.600	46.600
L9	6 ICP OES 3	48.728	1.254	1.316	48.585	49.532	49.321	50.323	47.654	46.953
L10	25 ICP OES 2	49.187	1.371	1.439	49.220	49.280	50.640	50.480	46.890	48.610
L11	22 ICP OES 2	49.512	1.545	1.621	51.370	51.360	47.550	49.050	48.570	49.170
L12	17 ICP OES 1	49.983	1.234	1.295	50.800	50.700	50.800	49.200	50.600	47.800
L13	18 ICP OES 3	50.272	1.597	1.676	52.950	48.100	50.840	50.100	50.040	49.600
L14	15 IPAA 3	50.400	1.020	1.070	49.100	51.900	51.100	50.100	50.600	49.600
L15	24 ICP OES 1	50.667	1.157	1.214	52.200	51.700	49.600	49.900	51.100	49.500
L16	1 ICP OES 3	51.267	5.903	6.195	61.600	47.100	50.800	48.900	45.200	54.000
L17	38 ICP OES 2	51.398	1.570	1.648	50.531	52.084	50.023	54.195	51.334	50.221
L18	2 ICP OES 3	54.083	1.199	1.258	54.400	51.900	55.500	54.600	53.900	54.200
L19	18 DC-ARC-OES 3	54.508	4.075	4.277	51.380	58.880	52.720	58.790	56.220	49.060
L20	11 ICP OES1	55.417	2.743	2.879	57.800	57.900	56.000	52.800	56.700	51.300
L21	41 ICP OES 2	66.500	8.826	9.262	77.000	70.000	63.000	70.000	68.000	51.000

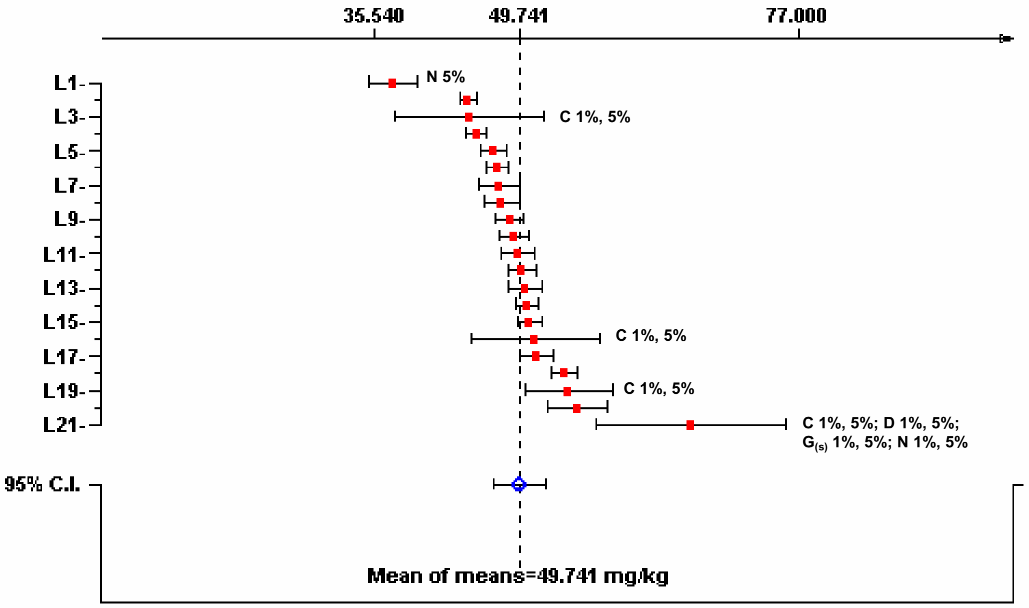
Range [min..max]	[35.540 .. 77.000]
	Case of No Pooling
Mean of means	49.741
95% H.W. Confidence Interval	2.501
95% H.W. Tolerance Interval	14.961
	Case of Pooling
Mean of All	49.741
95% H.W. Confidence Interval	1.082
95% H.W. Tolerance Interval	13.486

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. Xn1)



Tab. Xn2: 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
L1	18 ETV-ICP OES (3)	37.338	2.298	2.411	35.540	37.230	41.660	35.840	37.830	35.930
L2	20 ICP OES 1	44.667	0.816	0.857	45.000	45.000	45.000	43.000	45.000	45.000
L3	31 ICP OES 1	44.833	6.911	7.253	51.000	43.000	36.000	54.000	46.000	39.000
L4	12 ICP OES 2	45.450	0.983	1.032	44.800	44.600	46.200	47.000	45.500	44.600
L5	13 ICP-MS (3)	47.150	1.176	1.234	47.800	45.400	47.800	48.700	46.600	46.600
L6	42 ICP OES 2	47.500	1.049	1.101	49.000	47.000	47.000	46.000	48.000	48.000
L7	35 ICP-MS 2	47.733	1.840	1.931	47.900	47.500	45.800	50.400	45.700	49.100
L8	5 ICP OES 2	47.967	1.657	1.739	50.300	48.100	46.600	46.600	49.600	46.600
L9	6 ICP OES 3	48.728	1.254	1.316	48.585	49.532	49.321	50.323	47.654	46.953
L10	25 ICP OES 2	49.187	1.371	1.439	49.220	49.280	50.640	50.480	46.890	48.610
L11	22 ICP OES 2	49.512	1.545	1.621	51.370	51.360	47.550	49.050	48.570	49.170
L12	17 ICP OES 1	49.983	1.234	1.295	50.800	50.700	50.800	49.200	50.600	47.800
L13	18 ICP OES 3	50.272	1.597	1.676	52.950	48.100	50.840	50.100	50.040	49.600
L14	15 IPAA 3	50.400	1.020	1.070	49.100	51.900	51.100	50.100	50.600	49.600
L15	24 ICP OES 1	50.667	1.157	1.214	52.200	51.700	49.600	49.900	51.100	49.500
L16	1 ICP OES 3	51.267	5.903	6.195	61.600	47.100	50.800	48.900	45.200	54.000
L17	38 ICP OES 2	51.398	1.570	1.648	50.531	52.084	50.023	54.195	51.334	50.221
L18	2 ICP OES 3	54.083	1.199	1.258	54.400	51.900	55.500	54.600	53.900	54.200
L19	18 DC-ARC-OES 3	54.508	4.075	4.277	51.380	58.880	52.720	58.790	56.220	49.060
L20	11 ICP OES1	55.417	2.743	2.879	57.800	57.900	56.000	52.800	56.700	51.300

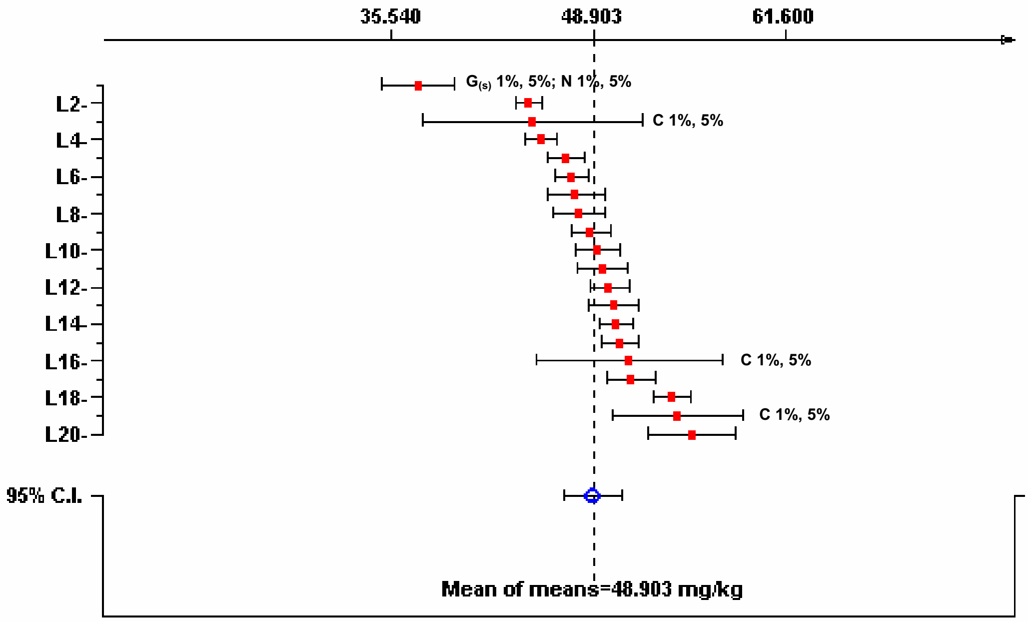
Range [min..max]	[35.540 .. 61.600]
	Case of No Pooling
Mean of means	48.903
95% H.W. Confidence Interval	1.887
95% H.W. Tolerance Interval	11.095
	Case of Pooling
Mean of All	48.903
95% H.W. Confidence Interval	0.836
95% H.W. Tolerance Interval	10.198

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. Xn2)



Tab. Xo1 : Total Carbon accepted results 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
L1	21 Comb.-Vol. 3	20.457	0.072	0.076	20.580	20.400	20.450	20.390	20.420	20.500
L2	44 Comb.-IR 3	20.648	0.034	0.036	20.640	20.660	20.680	20.610	20.610	20.690
L3	25 Comb.-Coul. (3)	20.823	0.044	0.046	20.870	20.820	20.870	20.830	20.760	20.790
L4	38 Comb.-IR 2	20.847	0.108	0.113	20.760	20.700	20.812	20.907	20.985	20.920
L5	34 Comb.-IR 2	20.882	0.053	0.056	20.920	20.930	20.800	20.930	20.860	20.850
L6	8 Comb.-Coul. (3)	20.883	0.109	0.114	20.750	20.960	20.920	20.950	20.980	20.740
L7	42 Comb.-IR 3	20.890	0.035	0.036	20.840	20.940	20.880	20.910	20.870	20.900
L8	30 Comb.-IR 3	20.910	0.072	0.076	21.010	20.920	20.930	20.860	20.800	20.940
L9	31 Comb.-IR 2	20.923	0.037	0.039	20.874	20.902	20.911	20.976	20.920	20.957
L10	1 Comb.-IR 3	20.926	0.024	0.026	20.893	20.925	20.931	20.955	20.948	20.903
L11	5 Comb.-IR3	20.950	0.051	0.054	20.870	20.980	20.960	20.950	20.920	21.020
L12	1 Comb.-IR (3)	20.956	0.010	0.010	20.947	20.944	20.950	20.962	20.965	20.965
L13	41 Comb.-IR 3	20.957	0.024	0.025	20.940	20.940	20.940	21.000	20.950	20.970
L14	24 Comb.-Grav. 1	20.997	0.022	0.023	21.005	20.995	20.967	20.986	21.034	20.996
L15	20 Comb.-IR 2	21.012	0.062	0.066	21.090	21.000	21.060	20.910	20.990	21.020
L16	7 Comb.-IR 3	21.032	0.057	0.060	21.045	21.022	20.968	21.129	20.983	21.046
L17	10 Comb.-IR 2	21.145	0.075	0.078	21.290	21.140	21.080	21.140	21.120	21.100
L18	3 Comb.-IR 3	21.232	0.019	0.020	21.210	21.230	21.250	21.220	21.220	21.260
L19	18 Comb.-IR 3	21.232	0.049	0.052	21.280	21.160	21.290	21.200	21.240	21.220
L20	17 Comb.-IR 1	21.317	0.075	0.079	21.300	21.400	21.300	21.400	21.200	21.300
L21	2 Comb.-IR 3	21.500	0.110	0.115	21.500	21.600	21.600	21.500	21.300	21.500
L22	28 Comb.-IR 2	21.624	0.114	0.120	21.556	21.537	21.797	21.505	21.717	21.632

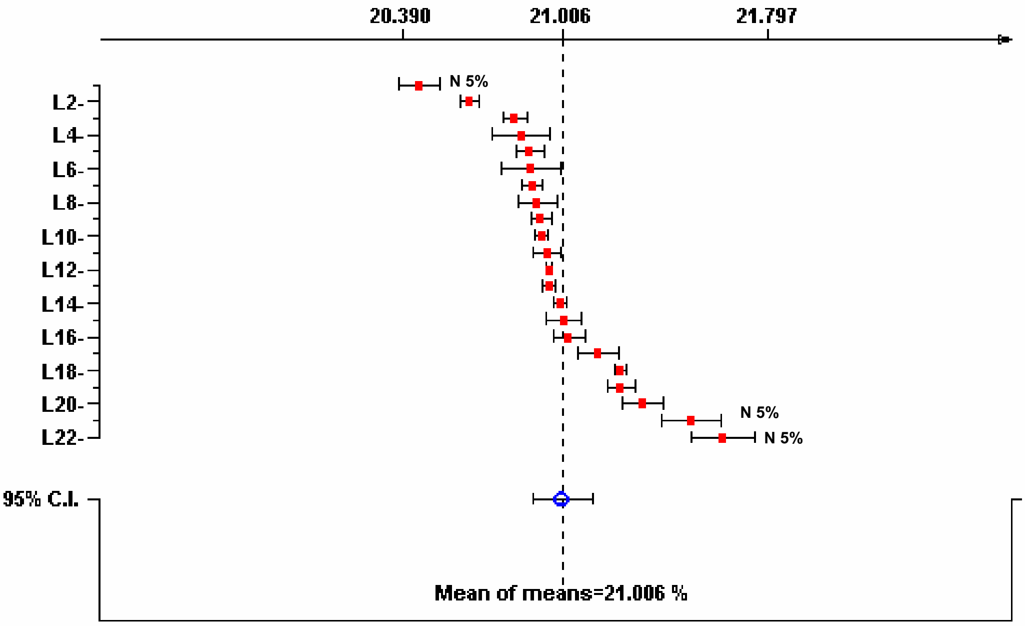
Range [min..max]	[20.390 .. 21.797]
	Case of No Pooling
Mean of means	21.006
95% H.W. Confidence Interval	0.115
95% H.W. Tolerance Interval	0.698
	Case of Pooling
Mean of All	21.006
95% H.W. Confidence Interval	0.045
95% H.W. Tolerance Interval	0.572

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. Xo1)



Tab. Xp1: Free Carbon accepted results in run 1 (values in %); (indicative parameter only)

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

Current Lab. number	Lab Abbreviation	Mean (%)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L1	21 wetchem. Oxidation / Coul. (3) *)	0.385	0.015	0.016	0.400	0.380	0.360	0.390	0.380	0.400
L2	25 wetchem. Oxidation / Coul. 3 *)	0.437	0.018	0.019	0.460	0.425	0.427	0.461	0.422	0.429
L3	18 wetchem. Oxidation / Coul. 3 *)	0.447	0.017	0.018	0.465	0.464	0.428	0.427	0.452	0.446
L4	24 Coul. 1 **)	0.604	0.041	0.043	0.570	0.613	0.584	0.644	0.555	0.656
L5	1 wetchem. Oxidation / Coul. 2 *)	0.658	0.018	0.019	0.669	0.651	0.660	0.646	0.636	0.686

*) by method M4 **) not by method M4

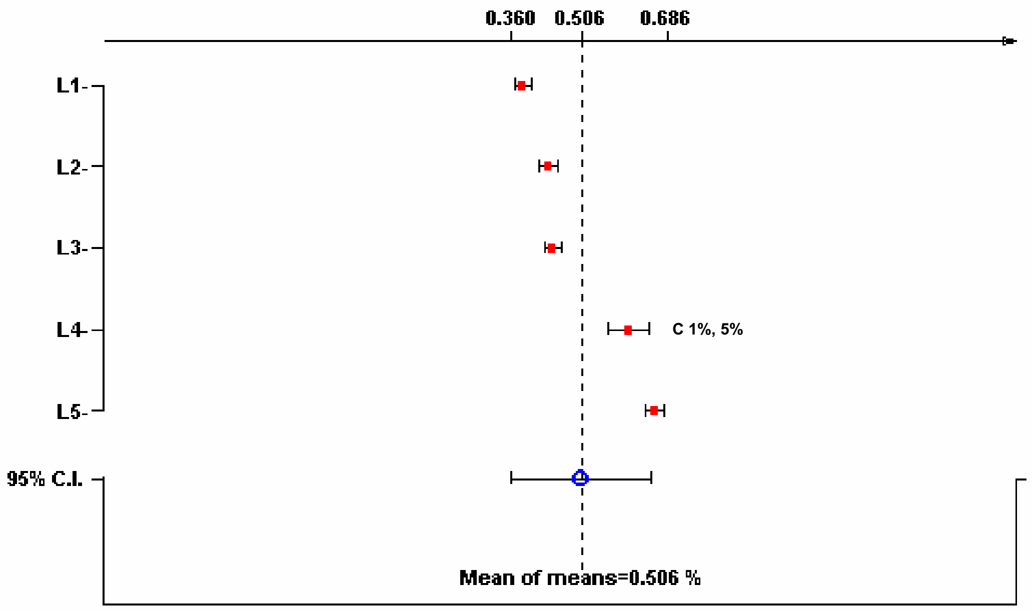
Range [min..max]	[0.360 .. 0.686]
	Case of No Pooling
Mean of means	0.506
95% H.W. Confidence Interval	0.146
95% H.W. Tolerance Interval	0.598
	Case of Pooling
Mean of All	0.506
95% H.W. Confidence Interval	0.041
95% H.W. Tolerance Interval	0.279

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. Xp1)



Tab. Xq1: Oxygen accepted results 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
L1	3 CGHE-IR 3	0.0667	0.0017	0.0018	0.0664	0.0645	0.0687	0.0662	0.0654	0.0688
L2	2 CGHE-IR 2	0.0798	0.0033	0.0035	0.0760	0.0830	0.0780	0.0810	0.0770	0.0840
L3	25 CGHE-IR 2	0.0810	0.0033	0.0035	0.0820	0.0780	0.0800	0.0830	0.0860	0.0770
L4	7 CGHE-IR 3	0.0825	0.0036	0.0038	0.0815	0.0788	0.0784	0.0876	0.0839	0.0847
L5	24 CGHE-Coul. 1	0.0885	0.0038	0.0040	0.0927	0.0883	0.0927	0.0830	0.0883	0.0861
L6	18 CGHE-IR 3	0.0913	0.0023	0.0024	0.0930	0.0950	0.0900	0.0890	0.0910	0.0900
L7	5 CGHE-IR 3	0.0998	0.0040	0.0042	0.0950	0.1040	0.1020	0.0960	0.1040	0.0980
L8	15 CGHE-IR 2	0.1064	0.0052	0.0055	0.1041	0.1030	0.1060	0.1125	0.0998	0.1127
L9	28 CGHE-IR 3	0.1087	0.0042	0.0044	0.1020	0.1090	0.1070	0.1120	0.1140	0.1080
L10	17 CGHE-IR 1	0.1140	0.0018	0.0019	0.1160	0.1120	0.1160	0.1120	0.1140	0.1140
L11	10 CGHE-IR 2	0.1176	0.0076	0.0080	0.1204	0.1275	0.1114	0.1153	0.1236	0.1074
L12	41 CGHE-IR 2	0.1218	0.0021	0.0022	0.1240	0.1190	0.1200	0.1210	0.1230	0.1240

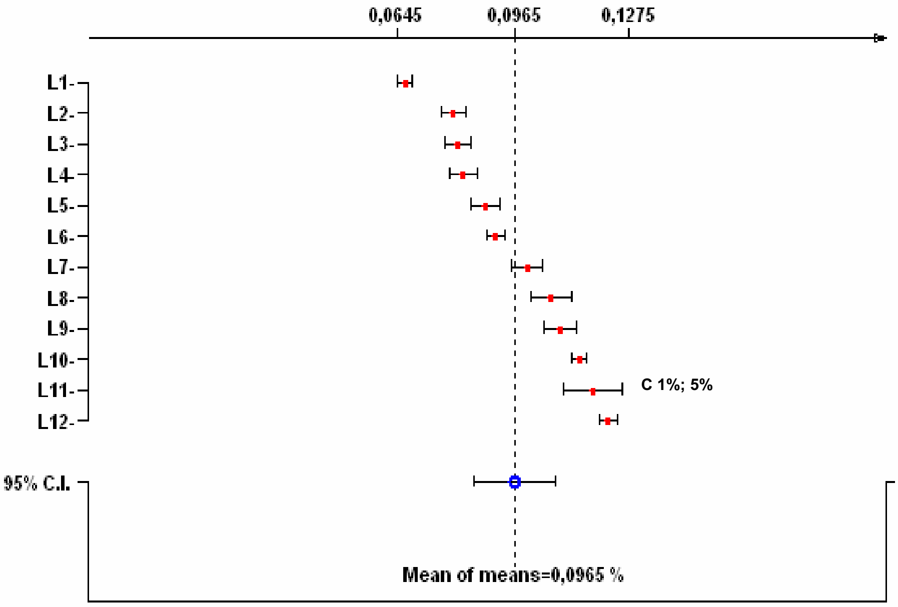
Range [min..max]	[0.0645 .. 0.1275]
	Case of No Pooling
Mean of means	0.0965
95% H.W. Confidence Interval	0.0111
95% H.W. Tolerance Interval	0.0551
	Case of Pooling
Mean of All	0.0965
95% H.W. Confidence Interval	0.0040
95% H.W. Tolerance Interval	0.0394

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. Xq1)



Tab. Xr1: Nitrogen accepted results 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
L1	28 CGHE-TC 3	0.1715	0.0015	0.0016	0.1730	0.1710	0.1710	0.1690	0.1720	0.1730
L2	18 CGHE-TC 3	0.1863	0.0041	0.0043	0.1930	0.1880	0.1870	0.1810	0.1850	0.1840
L3	25 CGHE-TC 2	0.1873	0.0060	0.0062	0.1990	0.1860	0.1850	0.1820	0.1870	0.1850
L4	5 CGHE-TC 3	0.1995	0.0088	0.0092	0.2020	0.2070	0.2120	0.1920	0.1920	0.1920
L5	7 CGHE-TC 3	0.2044	0.0056	0.0059	0.2039	0.1948	0.2030	0.2085	0.2050	0.2111
L6	24 CGHE-TC 1	0.2062	0.0078	0.0082	0.2109	0.2155	0.1931	0.2063	0.2022	0.2092
L7	20 CGHE-TC 2	0.2192	0.0187	0.0196	0.2540	0.2220	0.2100	0.2110	0.2000	0.2180
L8	3 CGHE-TC 3	0.2210	0.0019	0.0020	0.2240	0.2210	0.2220	0.2190	0.2190	0.2210
L9	17 CGHE-TC 1	0.2243	0.0038	0.0040	0.2200	0.2270	0.2280	0.2230	0.2200	0.2280
L10	15 IPAA 2	0.2257	0.0099	0.0104	0.2270	0.2200	0.2440	0.2150	0.2250	0.2230
L11	15 CGHE-TC 2	0.2303	0.0064	0.0067	0.2294	0.2386	0.2293	0.2209	0.2272	0.2364
L12	10 CGHE-TC 2	0.2331	0.0026	0.0027	0.2299	0.2337	0.2346	0.2307	0.2328	0.2369

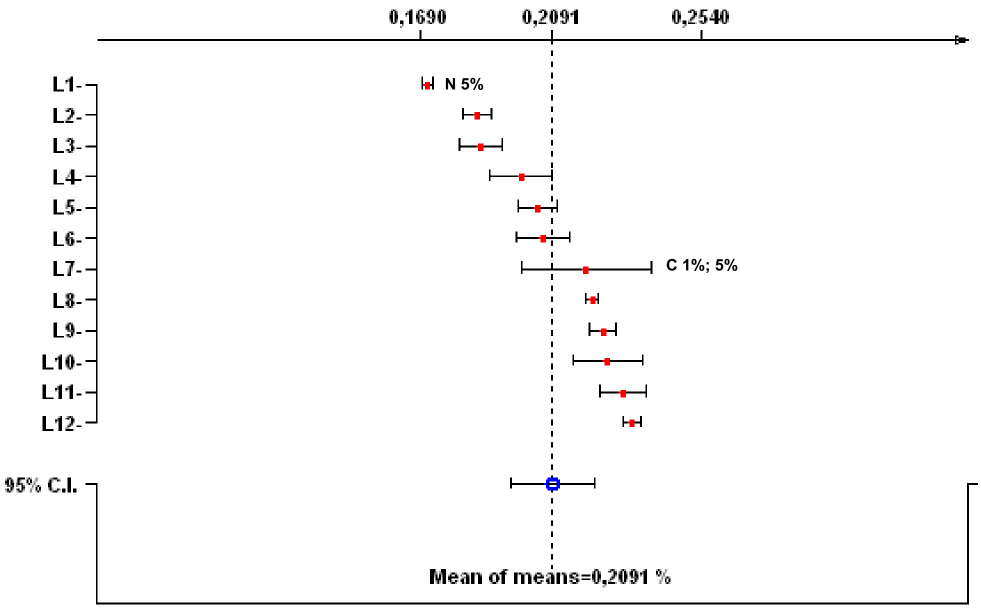
Range [min..max]	[0.1690 .. 0.2540]
	Case of No Pooling
Mean of means	0.2091
95% H.W. Confidence Interval	0.0126
95% H.W. Tolerance Interval	0.0625
	Case of Pooling
Mean of All	0.2091
95% H.W. Confidence Interval	0.0048
95% H.W. Tolerance Interval	0.0468

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. Xr1)



Tab. Xs1: Total Boron 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
L1	35 ID-ICP-MS 2	66.883	0.643	0.675	67.500	66.200	67.400	66.400	66.300	67.500
L2	33 Titr. 3	78.093	0.213	0.223	78.000	78.160	77.870	78.300	78.360	77.870
L3	21 Titr. 3	78.105	0.103	0.108	77.950	78.220	78.050	78.160	78.190	78.060
L4	8 Titr. (3)	78.160	0.220	0.273		78.320	78.350	78.290	77.920	77.920
L5	41 Titr. 3	78.167	0.163	0.171	78.300	78.000	78.000	78.100	78.400	78.200
L6	22 Titr. 2	78.232	0.049	0.051	78.210	78.150	78.260	78.220	78.280	78.270
L7	18 Titr.3	78.250	0.185	0.195	78.420	78.440	78.310	78.050	78.000	78.280
L8	20 Titr. 2	78.250	0.055	0.057	78.200	78.300	78.200	78.200	78.300	78.300
L9	1 Titr. 3	78.253	0.106	0.111	78.186	78.224	78.115	78.245	78.405	78.345
L10	25 Titr. 2	78.378	0.140	0.147	78.480	78.380	78.360	78.130	78.380	78.540
L11	5 Titr. 3	78.460	0.092	0.096	78.310	78.410	78.440	78.550	78.520	78.530
L12	23 ICP OES	78.683	0.479	0.503	77.800	78.800	79.000	78.900	79.100	78.500
L13	24 Titr. 11	78.758	0.029	0.031	78.796	78.750	78.733	78.740	78.794	78.734
L14	42 Titr. 3	78.800	0.081	0.085	78.680	78.810	78.790	78.930	78.820	78.770
L15	4 Titr. 3	78.808	0.035	0.037	78.810	78.741	78.818	78.845	78.811	78.821
L16	6 ICP OES 2	78.988	0.930	0.976	80.574	79.080	78.984	78.466	79.068	77.755
L17	32 Titr. 2	79.058	0.158	0.166	79.230	79.100	78.890	79.030	78.870	79.230

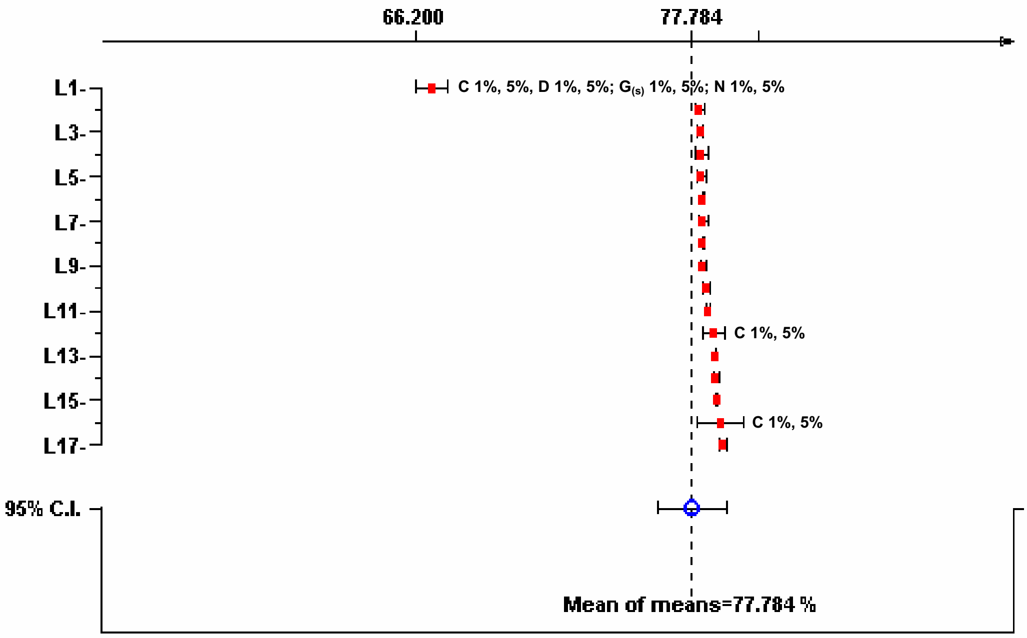
Range [min..max]	[66.200 .. 80.574]
	Case of No Pooling
Mean of means	77.784
95% H.W. Confidence Interval	1.454
95% H.W. Tolerance Interval	8.080
	Case of Pooling
Mean of All	77.780
95% H.W. Confidence Interval	0.550
95% H.W. Tolerance Interval	6.216

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. Xs1)



Tab. Xs2: Total Boron 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
L1	33 Titr. 3	78.093	0.213	0.223	78.000	78.160	77.870	78.300	78.360	77.870
L2	21 Titr. 3	78.105	0.103	0.108	77.950	78.220	78.050	78.160	78.190	78.060
L3	8 Titr. (3)	78.160	0.220	0.273		78.320	78.350	78.290	77.920	77.920
L4	41 Titr. 3	78.167	0.163	0.171	78.300	78.000	78.000	78.100	78.400	78.200
L5	22 Titr. 2	78.232	0.049	0.051	78.210	78.150	78.260	78.220	78.280	78.270
L6	18 Titr. 3	78.250	0.185	0.195	78.420	78.440	78.310	78.050	78.000	78.280
L7	20 Titr. 2	78.250	0.055	0.057	78.200	78.300	78.200	78.200	78.300	78.300
L8	1 Titr. 3	78.253	0.106	0.111	78.186	78.224	78.115	78.245	78.405	78.345
L9	25 Titr. 2	78.378	0.140	0.147	78.480	78.380	78.360	78.130	78.380	78.540
L10	5 Titr. 3	78.460	0.092	0.096	78.310	78.410	78.440	78.550	78.520	78.530
L11	23 ICP OES	78.683	0.479	0.503	77.800	78.800	79.000	78.900	79.100	78.500
L12	24 Titr. 11	78.758	0.029	0.031	78.796	78.750	78.733	78.740	78.794	78.734
L13	42 Titr. 3	78.800	0.081	0.085	78.680	78.810	78.790	78.930	78.820	78.770
L14	4 Titr. 3	78.808	0.035	0.037	78.810	78.741	78.818	78.845	78.811	78.821
L15	6 ICP OES 2	78.988	0.930	0.976	80.574	79.080	78.984	78.466	79.068	77.755
L16	32 Pot. 2	79.058	0.158	0.166	79.230	79.100	78.890	79.030	78.870	79.230

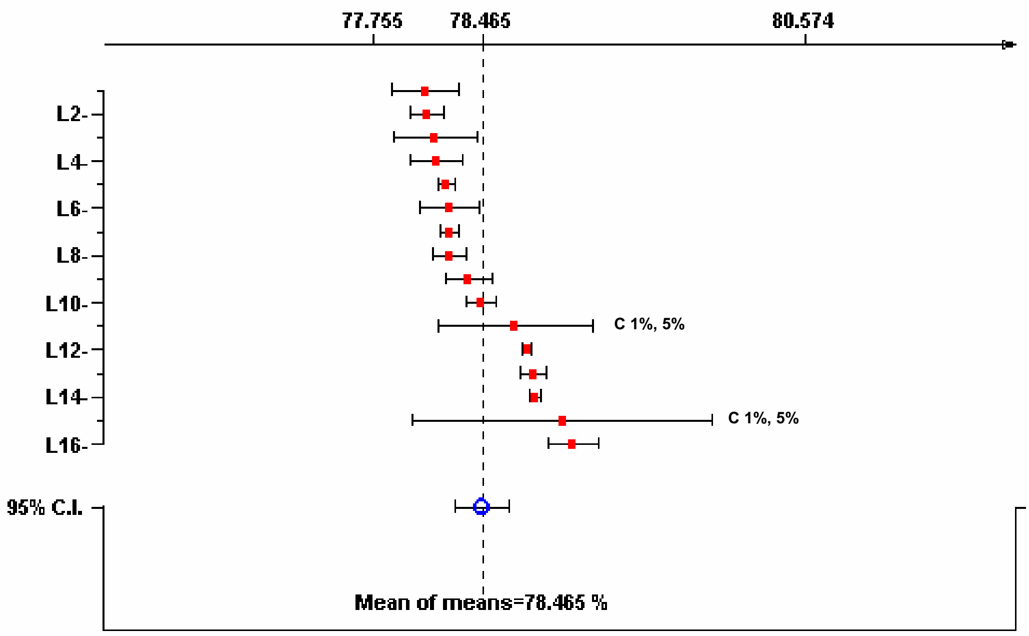
Range [min..max]	[77.755 .. 80.574]
	Case of No Pooling
Mean of means	78.465
95% H.W. Confidence Interval	0.176
95% H.W. Tolerance Interval	0.959
	Case of Pooling
Mean of All	78.468
95% H.W. Confidence Interval	0.085
95% H.W. Tolerance Interval	0.935

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. Xs2)



Tab. Xt1: HNO$_3$ soluble Boron 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
L1	20 Titr. 2	0.0979	0.0013	0.0013	0.0963	0.0968	0.0980	0.0981	0.0979	0.1000
L2	25 ICP OES 2	0.1118	0.0026	0.0028	0.1160	0.1130	0.1090	0.1100	0.1130	0.1100
L3	18 Titr. 3	0.1125	0.0016	0.0017	0.1120	0.1130	0.1120	0.1100	0.1150	0.1130
L4	23 ICP OES 2	0.1167	0.0018	0.0018	0.1170	0.1160	0.1200	0.1160	0.1160	0.1150
L5	21 Titr. 3	0.1183	0.0117	0.0123	0.1300	0.1000	0.1200	0.1100	0.1300	0.1200
L6	14 Titr 1	0.1205	0.0081	0.0128	0.1116	0.1208	0.1186	0.1311		
L7	33 ICP OES 3	0.1367	0.0273	0.0287	0.1500	0.1200	0.1000	0.1300	0.1800	0.1400
L8	41 Titr. (1)	0.3665	0.0067	0.0070	0.3700	0.3620	0.3770	0.3690	0.3590	0.3620
L9	42 Titr. (3)	0.5767	0.0103	0.0108	0.5900	0.5800	0.5800	0.5700	0.5600	0.5800

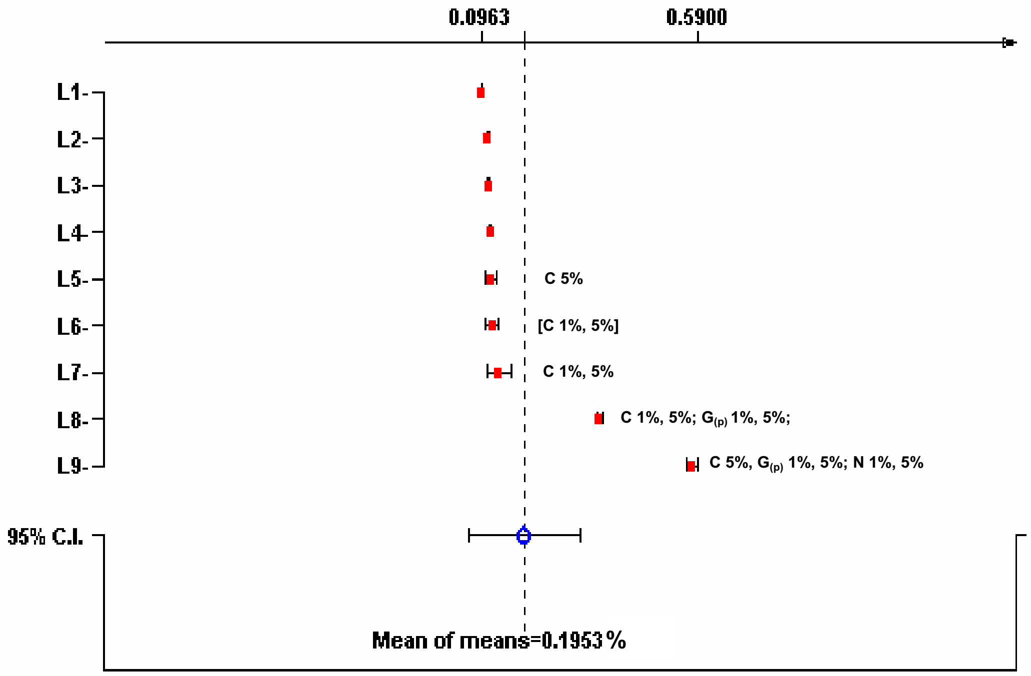
Range [min..max]	[0.0963 .. 0.5900]
	Case of No Pooling
Mean of means	0.1953
95% H.W. Confidence Interval	0.1272
95% H.W. Tolerance Interval	0.5847
	Case of Pooling
Mean of All	0.1982
95% H.W. Confidence Interval	0.0446
95% H.W. Tolerance Interval	0.3795

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. Xt1)



Tab. Xt2: HNO_3 soluble Boron evaluation 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
L1	20 Titr. 2	0.0979	0.0013	0.0013	0.0963	0.0968	0.0980	0.0981	0.0979	0.1000
L2	25 ICP OES 2	0.1118	0.0026	0.0028	0.1160	0.1130	0.1090	0.1100	0.1130	0.1100
L3	18 Titr. 3	0.1125	0.0016	0.0017	0.1120	0.1130	0.1120	0.1100	0.1150	0.1130
L4	23 ICP OES 2	0.1167	0.0018	0.0018	0.1170	0.1160	0.1200	0.1160	0.1160	0.1150
L5	21 Titr. 3	0.1183	0.0117	0.0123	0.1300	0.1000	0.1200	0.1100	0.1300	0.1200
L6	14 Titr 1	0.1205	0.0081	0.0128	0.1116	0.1208	0.1186	0.1311		
L7	33 ICP OES 3	0.1367	0.0273	0.0287	0.1500	0.1200	0.1000	0.1300	0.1800	0.1400
L8	41 Titr. (1)	0.3665	0.0067	0.0070	0.3700	0.3620	0.3770	0.3690	0.3590	0.3620

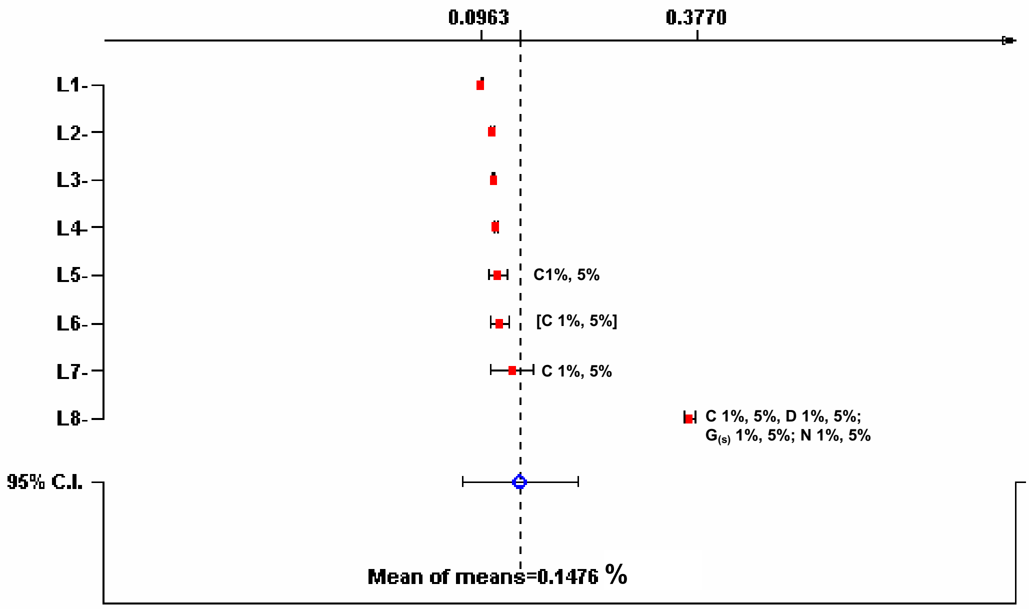
Range [min..max]	[0.0963 .. 0.3770]
	Case of No Pooling
Mean of means	0.1476
95% H.W. Confidence Interval	0.0745
95% H.W. Tolerance Interval	0.3325
	Case of Pooling
Mean of All	0.1488
95% H.W. Confidence Interval	0.0257
95% H.W. Tolerance Interval	0.2078

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. Xt2)



Tab. Xt3: HNO_3 Soluble Boron accepted results in run 3 (values in %)

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
L1	20 Titr. 2	0.0979	0.0013	0.0013	0.0963	0.0968	0.0980	0.0981	0.0979	0.1000
L2	25 ICP OES 2	0.1118	0.0026	0.0028	0.1160	0.1130	0.1090	0.1100	0.1130	0.1100
L3	18 Titr. 3	0.1125	0.0016	0.0017	0.1120	0.1130	0.1120	0.1100	0.1150	0.1130
L4	23 ICP OES 2	0.1167	0.0018	0.0018	0.1170	0.1160	0.1200	0.1160	0.1160	0.1150
L5	21 Titr. 3	0.1183	0.0117	0.0123	0.1300	0.1000	0.1200	0.1100	0.1300	0.1200
L6	14 Titr 1	0.1205	0.0081	0.0128	0.1116	0.1208	0.1186	0.1311		
L7	33 ICP OES 3	0.1367	0.0273	0.0287	0.1500	0.1200	0.1000	0.1300	0.1800	0.1400

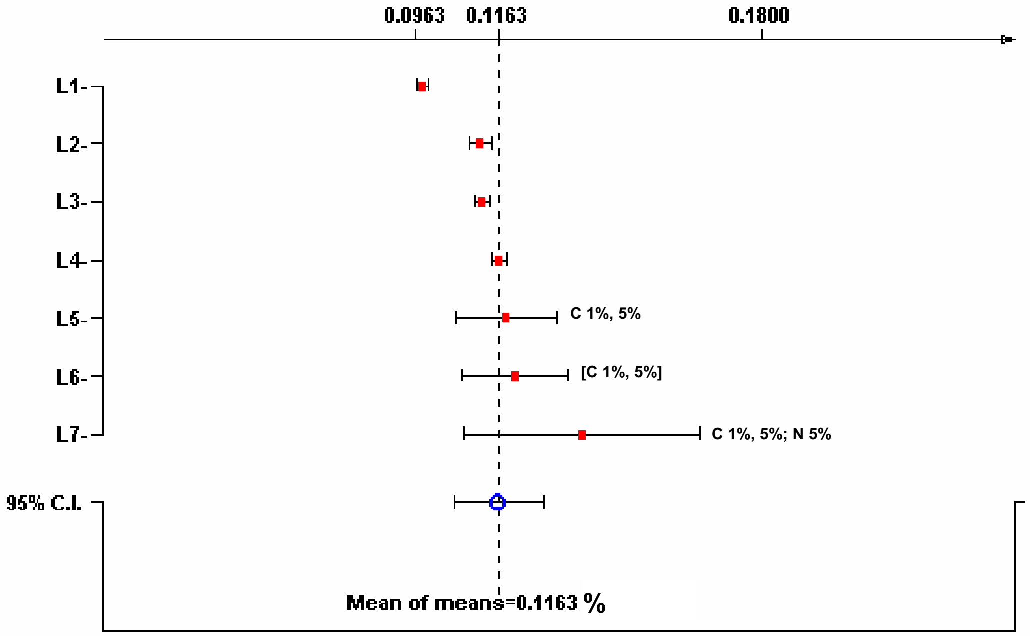
Range [min..max]	[0.0963 .. 0.1800]
	Case of No Pooling
Mean of means	0.1163
95% H.W. Confidence Interval	0.0108
95% H.W. Tolerance Interval	0.0466
	Case of Pooling
Mean of All	0.1161
95% H.W. Confidence Interval	0.0050
95% H.W. Tolerance Interval	0.0382

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. Xt3)



Tab. Xu1: Boron oxide accepted results 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
L1	14 Titr. 1	0.0557	0.0172	0.0274	0.0797	0.0523	0.0521	0.0387		
L2	42 Titr. (2)	0.0567	0.0052	0.0054	0.0500	0.0600	0.0600	0.0600	0.0500	0.0600
L3	20 Titr. 2	0.0658	0.0117	0.0123	0.0820	0.0760	0.0510	0.0560	0.0650	0.0650
L4	41 Titr. (2)	0.0674	0.0010	0.0011	0.0674	0.0657	0.0685	0.0684	0.0674	0.0670
L5	18 Titr. 3	0.0734	0.0007	0.0007	0.0735	0.0743	0.0735	0.0736	0.0727	0.0725
L6	25 ICP OES 2	0.0777	0.0054	0.0057	0.0780	0.0730	0.0740	0.0730	0.0860	0.0820
L7	33 ICP OES 3	0.0815	0.0014	0.0014	0.0820	0.0810	0.0790	0.0820	0.0830	0.0820
L8	23 ICP OES (2)	0.0840	0.0062	0.0065	0.0780	0.0780	0.0840	0.0920	0.0910	0.0810
L9	21 Titr. 3	0.1083	0.0075	0.0079	0.1100	0.1000	0.1100	0.1200	0.1100	0.1000

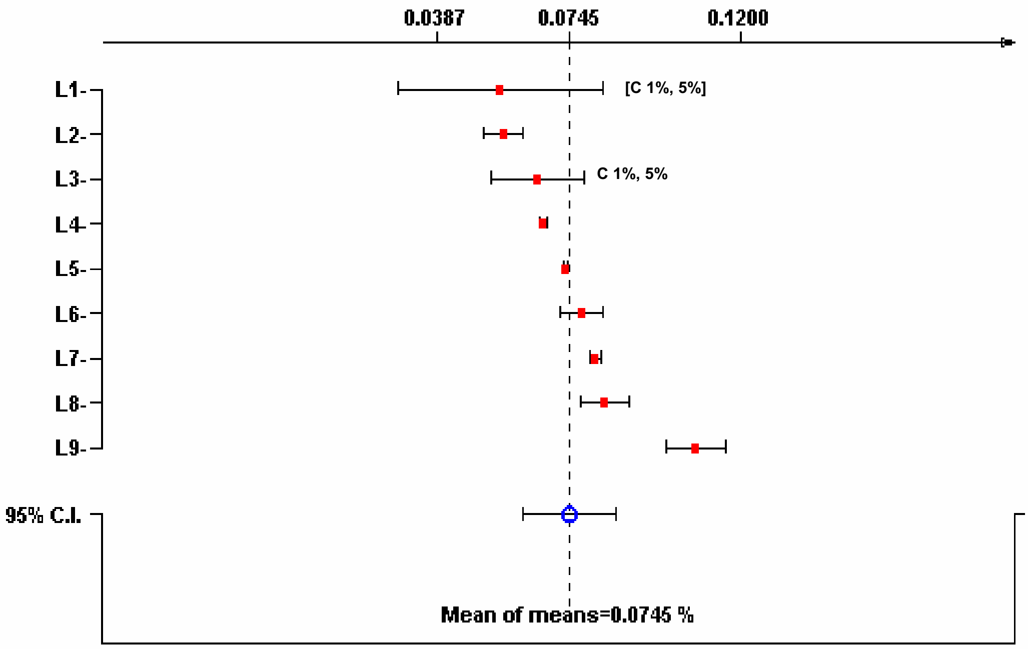
Range [min..max]	[0.0387 .. 0.1200]
	Case of No Pooling
Mean of means	0.0745
95% H.W. Confidence Interval	0.0124
95% H.W. Tolerance Interval	0.0571
	Case of Pooling
Mean of All	0.0752
95% H.W. Confidence Interval	0.0046
95% H.W. Tolerance Interval	0.0395

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. Xu1)



Tab. Xv1: ^{10}Boron related to total amount of Boron 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
L1	16 TIMS 3	19.8802	0.0070	0.0174	19.8812	19.8728	19.8867			
L2	13 ICP-MS 3	19.8973	0.0081	0.0085	19.8860	19.8970	19.9090	19.8910	19.9010	19.9000
L3	35 ICP-MS 3	19.9007	0.0056	0.0059	19.8990	19.9050	19.8960	19.8940	19.9090	19.9010
L4	9 ICP-MS 3	19.9048	0.0012	0.0012	19.9040	19.9030	19.9060	19.9050	19.9050	19.9060
L5	39 TIMS 2	19.9083	0.0084	0.0088	19.9170	19.8930	19.9070	19.9110	19.9080	19.9140
L6	19 TIMS 2	19.9217	0.0015	0.0038	19.9230	19.9220	19.9200			
L7	6 ICP-MS 3	19.9377	0.0530	0.0557	19.9690	19.8950	20.0260	19.9080	19.9410	19.8870
L8	4 ICP-MS 3	20.0663	0.0928	0.0973	20.1290	19.9570	19.9910	20.2020	20.0210	20.0980

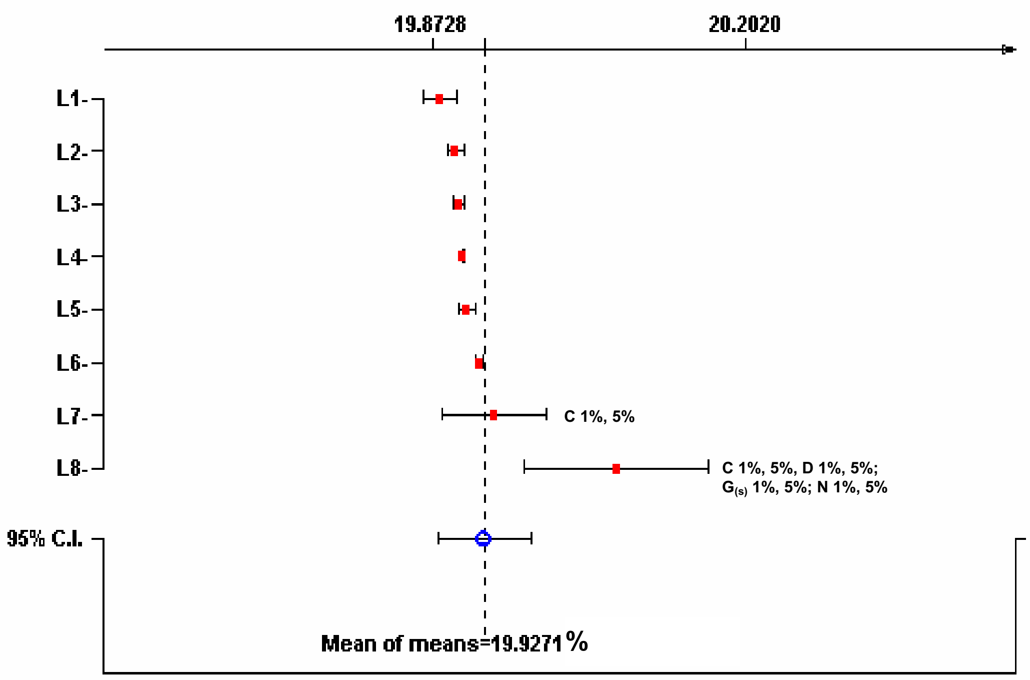
Range [min..max]	[19.8728 .. 20.2020]
	Case of No Pooling
Mean of means	19.9271
95% H.W. Confidence Interval	0.0491
95% H.W. Tolerance Interval	0.2192
	Case of Pooling
Mean of All	19.9309
95% H.W. Confidence Interval	0.0215
95% H.W. Tolerance Interval	0.1679

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. Xv1)



Tab. Xv2: ^{10}Boron related to total amount of Boron 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
L1	16 TIMS 3	19.8802	0.0070	0.0174	19.8812	19.8728	19.8867			
L2	13 ICP-MS 3	19.8973	0.0081	0.0085	19.8860	19.8970	19.9090	19.8910	19.9010	19.9000
L3	35 ICP-MS 3	19.9007	0.0056	0.0059	19.8990	19.9050	19.8960	19.8940	19.9090	19.9010
L4	9 ICP-MS 3	19.9048	0.0012	0.0012	19.9040	19.9030	19.9060	19.9050	19.9050	19.9060
L5	39 TIMS 2	19.9083	0.0084	0.0088	19.9170	19.8930	19.9070	19.9110	19.9080	19.9140
L6	19 TIMS 2	19.9217	0.0015	0.0038	19.9230	19.9220	19.9200			
L7	6 ICP-MS 3	19.9377	0.0530	0.0557	19.9690	19.8950	20.0260	19.9080	19.9410	19.8870

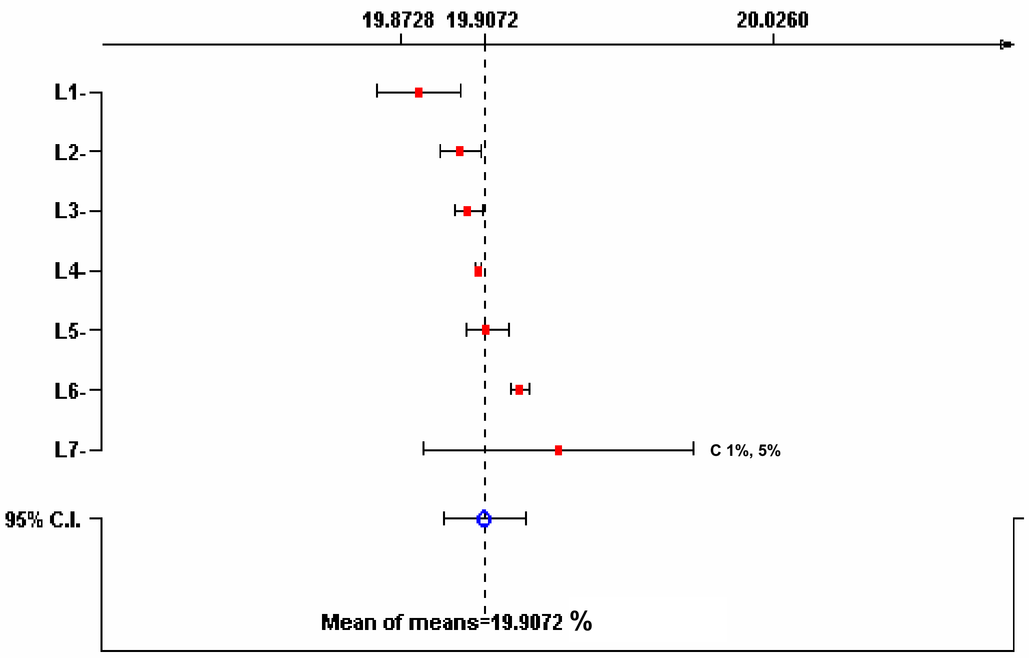
Range [min..max]	[19.8728 .. 20.0260]
	Case of No Pooling
Mean of means	19.9072
95% H.W. Confidence Interval	0.0169
95% H.W. Tolerance Interval	0.0734
	Case of Pooling
Mean of All	19.9083
95% H.W. Confidence Interval	0.0089
95% H.W. Tolerance Interval	0.0653

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. Xv2)



End of the Certification Report of ERM® -ED102 Boron Carbide Powder

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