BAM Federal Institute for Materials Research and Testing

in Co-operation with the

**Committee of Chemists of
GDMB**
GDMB Society for Mining, Metallurgy, Resource and Environmental Technology

The Characterization of Mass Fractions of
Al, Ca, Co, Cr, Fe, Mg, Na, Si, Ti,
$C_{(total)}$, O, N, $B_{(total)}$, and B_2O_3

European Reference Material

Boron Nitride Powder

ERM®-ED103

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Certification Report

Abstract

This report describes the preparation and certification of the European Reference Material ERM®-ED103, a boron nitride powder with certified mass fractions of impurities and main components. The certification work was 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 reference material ERM®-ED103 consists of a boron nitride powder "grade A 01". The material is supplied in glass bottles containing 50 g each. The reference material was developed for the use in the calibration of analytical instruments and to validate or verify analytical methods intended to be used for the determination of impurities and main components in boron nitride materials.

Boron Nitride Powder		
Characteristic	**Value** [1]	**Uncertainty** U [2]
Parameter	**Mass fraction in mg/kg**	
Aluminium	7.0	1.4
Calcium	273	13
Chromium	4.7	1.1
Iron	15.0	2.1
Magnesium	56	4
Sodium	12.3	0.9
Silicon	17	4
Titanium	4.9	0.7
	Mass fraction in %	
Oxygen	0.68	0.19
Nitrogen	55.6	0.6
Total Boron [3]	43.5	0.5
Adherent Boron oxide	0.070	0.014

1) The certified values are the means of 5 - 13 series of results (depending on the parameter) obtained by different laboratories. Up to 6 different analytical methods were used for the measurement of each parameter. The calibration of the methods applied for determination of element mass fractions were carried out by using pure substances of definite stoichiometry or solutions prepared from them, thus, ensuring traceability to SI units.
2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor k = 2. It includes contributions from sample inhomogeneity and sample stability.
3) The recommended "Method M1" described in attachment 1 can be used for the determination of the total mass fraction of boron.

Indicative Values

	Mass Fraction	
	Indicative value [1] [3]	Uncertainty [2]
Carbon	0.018 %	0.002 %
Cobalt	< 0.1 mg/kg	
Water	< 0.1 %	

1) The indicative values are the means of 3 or 5 series of results (depending on the parameter) obtained by different laboratories. 4 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of mass fractions were not calibrated in all cases by pure substances of definite stoichiometry or by solutions prepared from them.
2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.
3) Values were not certified, but given as indicative values, when the number of accepted data sets was considered to be too low, when the spread from the round robin certification was considerably larger than the state of the art.

Additional Material Information

Particle size [1]	d_{10}	4.22 µm
	d_{50}	11.28 µm
	d_{90}	29.74 µm
Specific surface area [2]		5.02 m^2/g

1) The particle size distribution (volume) was determined by laser light diffraction method.
2) The specific surface area was determined as multi point BET according to DIN ISO 9277.

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

NOTE

European Reference Material ERM®-ED103 was certified under the responsibility of BAM Federal Institute for Materials Research and Testing in cooperation with the Committee of Chemists of the GDMB Society for Mining, Metallurgy, Resource and Environmental Technology 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).

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Validity of the Certificate: until June 30, 2021

Contents

List of abbreviations

(if not explained elsewhere)

CRM	certified reference material
ERM	European reference material
M	arithmetic mean of means
n	number of accepted data sets
SD	standard deviation of an individual data set
SD_M	standard deviation of the mean of means

Analytical Methods used for certification

CGHE-IR	Carrier gas hot extraction/combustion method with infrared detection
CGHE-TC	Carrier gas hot extraction method with thermal conductivity detection
Comb.-IR	Combustion method with infrared detection
Coulom.	Coulometric determination
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
GRAV	Gravimetry
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-SF-MS	Inductively coupled plasma sector field mass spectrometry
SS ET AAS	Solid sampling electrothermal atomic absorption spectrometry
TITR Method M1	Recommended method: determination of total Boron in Boron Nitride by titrimetric method (potentiometric method) (described in APPENDIX 1)
LiOH TITR	Determination by potentiometric titration after fusion decomposition with LiOH
Kjeldahl TITR	Titration after digestion and Kjeldahl distillation
TITR	Titrimetry
XRF	X-ray fluorescence spectrometry

1. Introduction

Boron nitride (BN) represents an important advanced ceramic material. The widespread application of BN materials in various industrial fields is based on a unique combination of special properties including low density, high-temperature stability (up to 800 °C and 2000 °C in air and inert gas, respectively), chemical inertness, no wetting by molten metals and salts, stability to thermal shock, extremely low electrical conductivity, high thermal conductivity, excellent lubrication properties and easy machining of sintered parts with conventional tools. Even very small variations in the composition of these materials, not just concerning the main but also the minor and trace elements, can have a large impact on various important properties. Therefore, the availability of powerful, rapid and reliable analytical methods for the determination of trace impurities in boron nitride is essential for process and quality control. The reference material was developed for the calibration of analytical instruments and to validate or verify analytical methods intended to be used for the determination of impurities and main components in boron nitride materials.

2. Companies/laboratories involved

Preparation of the material
The material was produced by H. C. Starck GmbH & Co. KG; Germany
The material was filled into cleaned sample bottles by BAM under clean air conditions

Homogeneity investigation
The analytical investigations for the homogeneity testing were carried out by ESK Ceramics GmbH & Co. KG, Germany and by BAM. For details of the investigations see chapter 4.

Long-term stability investigation
The investigations of the long-term stability were carried out by ESK Ceramics GmbH & Co. KG, Germany and by BAM. For details see chapter 5.

Participants in the certification interlaboratory comparison
To achieve a high international acceptance, renowned laboratories world wide were asked to participate. These laboratories were either involved in BN analysis on a regular basis or had well known ability to analyze difficult materials by adequate analytical methods and have shown their ability in round robin tests before. The participating laboratories of the interlaboratory comparison for certification are listed in alphabetic order:

Participants (in alphabetic order)

BAM Federal Institute for Materials Research and Testing, Germany
Ceram Testing & Environmental Services, U.K.
ESK Ceramics GmbH Co. KG, Germany
Forschungszentrum Jülich GmbH. Zentralabt. für chemische Analysen, Germany
H. C. Starck GmbH & Co. KG; Germany
     Werk Goslar
     Werk Laufenburg
HORIBA. Ltd. Application Center, Japan
JFE Refractories R & D Laboratory, Japan
Krosaki Harima Co. LTD. Technical Examination Center, Japan
Leibnitz-Institut für Festkörper- und Werkstoffforschung, Germany
Max-Planck-Institut für Metallforschung, Germany
Osram GmbH, Germany
Revierlabor Chemische Laboratorien für Industrie und Umwelt GmbH, Germany
Rigaku Industrial Corporation, Japan
TYK Corporation, Research & Development Center, Japan

Determination of additional material parameter
The determination of particle size distribution was carried out by H. C. Starck GmbH & Co. KG, Laufenburg, Germany.

Statistical evaluation of the data
BAM Bundesanstalt für Materialforschung und -prüfung, Berlin

3. Candidate material

The boron nitride powder material (grade A 01) was taken from the customary production line of the producer and was bottled into 320 bottles each containing 50 g of the material.
The bottles were filled with Ar, closed and sealed with a shrinking foil.

4. Homogeneity testing

For the homogeneity testing 20 bottles were representatively taken from the totality of 320 bottles by a combination of random access and systematic selection. Each bottle contained 50 g of candidate material. From each of the 20 bottles 4 sub-samples of 2 g to 3 g were filled into vials.

For comparison, a thoroughly homogenized sample was produced. For this purpose about 10 g of the material were highly homogenized in the "Mixer/Mill" (Spex. Ind., USA) for 10 min. (5 · 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.

The analytical investigations for the homogeneity testing of the mass fractions of Al, Ca, Cr, Fe, Mg, Na, Si and Ti were carried out by BAM Federal Institute for Materials Research and Testing

The analytical investigations for the homogeneity testing of mass fractions of total C, O, N, total B, and adherent B_2O_3 were carried out by ESK Ceramics GmbH & Co. KG, Germany.

4.1 Homogeneity testing of metallic analytes and Si

The homogeneity testing for most metallic traces was carried out by ICP OES. Sodium was investigated by FAAS. Co was not measured due to its very low mass fraction in the material leading to a very low precision of ICP OES. The obtained value for the Co content of the material is only considered as indicative. Si could not be determined by ICP OES with sufficient accuracy. Therefore the direct solid sampling method of ETV-ICP OES was used. For all metallic elements the measurements were carried out with aliquots of digestion solutions prepared from samples from the 20 selected bottles picked for the homogeneity testing as well as from the 20 sub-samples taken from the highly homogenized material. To minimize the influence of drifts, drift corrections were made. Additionally, the solutions of the sub-samples were measured at two different days.

A one-way analysis of variance was carried out on the 20 bottles (the square of equation 2 is equal to the within-group mean square, and the square of equation 3 is equal to the between-group mean square. 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. The contribution to the Uncertainty budget follows;

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

For comparison the contribution of the round robin is summarized as U_{RR}

$$s_w = \sqrt{\sum_1^{20} SD^2 \Big/ N} \ ; \qquad N = 20 \qquad (2)$$

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

$$s_b = \sqrt{SD^2_{means\ of\ sub-samples} \cdot M} \ ; \qquad (M = 4), \qquad (3)$$

In Table 1 the results of equation 2 and 3 and the contribution of the homogeneity and the round robin on the uncertainty budget of the certified values are summarized.

Table 1: *standard deviation and contribution of the homogeneity to the uncertainty budget of the certified values for the metallic analytes.*

Element	Standard deviation between the bottles (s_b)	Standard deviation within the bottles (s_w)	Standard deviation of the homogenous sample (s_{HS})	U_{RR} with $k=2$	U_{inhom} with $k=2$
Al	0.263	0.120	0.189	1.3	0.44
Ca	3.526	2.052	2.688	9.1	6.14
Cr	0.296	0.144	0.035	0.87	0.66
Fe	0.499	0.413	0.065	1.58	1.30
Mg	1.417	0.464	0.099	1.62	2.89
Na	0.108	0.103	0.095	0.82	0.23
Si	0.984	0.526	0.425	2.26	1.98
Ti	0.189	0.177	0.021	0.40	0.49

4.2 Homogeneity testing for total B, adherent B_2O_3, C, N and O

Different methods were applied for the homogeneity investigation of different non-metallic analytes. The results of the measurements are listed in form of tables in Appendix 2. For these analysts only 10 instead of 20 subsamples were investigated. and the number of sub-samples taken from the homogenized sample was 10 (for all analytes) instead of up to 20 as used for the investigation described in 4.1. The used analytical methods and the results are summarized in Table 2.

Table 2: *standard deviation and contribution of the homogeneity to the uncertainty budget of the certified values for the metallic analytes*

Analyt	Method	Standard deviation between the bottles (s_b)	Standard deviation within the bottles (s_w)	Standard deviation of the homogenous sample (s_{HS})	U_{RR} with $k=2$	U_{inhom} with $k=2$
total B	TITR	0.040	0.037	0.039	0.22	0.076
B_2O_3	TITR	7.149 E-04	1.072 E-03	1.776 E-03	0.003	0.001
C	Comb.-IR	1.424	3.707	3.425	0.001	0.00015
N	CGHE-TC	0.107	0.057	0.059	0.37	0.21
O	CGHE-IR	3.462 E-03	3.912 E-03	2.266 E-03	0.22	0.009

5. Long-term stability testing and corresponding uncertainty contributions

From theoretical considerations the BN material can be assumed to be stable. If at all, oxidation/hydrolyse reaction with air moisture to B_2O_3 as shown below is most likely to occur:

$$2BN(s) + 3H_2O(g) \rightarrow B_2O_3(s) + 2NH_3(g)$$
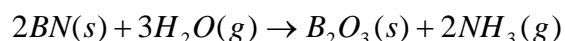
Since this type of reaction cannot be excluded completely B_2O_3, N and O could be sensitive parameters to indicate an aging of the material.
The analytical methods used for the stability studies are the same as used for the investigations of the homogeneity.

5.1 Long-term stability testing of mass fractions of total B, adherent B_2O_3, C, N and O

Long-term stability testing of mass fractions of N, B and B_2O_3 were carried out by ESK and for C and O by BAM.

The non-metallic analytes were determined in the candidate material over a period of 26 month. A t-test for the obtained results indicates no significant change of the analyte contents over time.

The long-term instability contribution from change of oxygen, nitrogen, boron and boron oxide mass fractions over a 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 20-26 months. The methods of the calculation are described below

Calculation of instability contribution for elements with

1. w_{mean} (analyte; start) < w_{mean} (analyte; end)

u_{lts} {w(analyte;120 months)} = Δw_{max}(analyte;120 months) = w_{max}(analyte;120 months) – w_{mean}(analyte;0 months)

(4a)

w_{max}(analyte; x months) $= a \cdot x + b$ (5)

b=w_{mean}(analyte; start) – SD_{mean}{w(analyte; start)} (6a)

a = (1/months) * [w_{mean}(analyte; end) + SD{w_{mean}(analyte; end)}-b] (7a)

w_{max}(analyte; 120 months) $= a \cdot x + b$ (8)

u_{lts} {analyte(120 months)-analyte(0 months) (9)

2. w_{mean} (analyte; start) > w_{mean} (analyte; end)

u_{lts} {w(analyte;120 months)} = Δw_{min}(analyte;120 months) = -w_{min}(analyte;120 months) + w_{mean}(analyte;0 months)

(4b)

w_{max}(analyte; x months) $= a \cdot x + b$ (5)

b=w_{mean}(analyte; start) + SD_{mean}{w(analyte; start)} (6b)

a = -(1/months) * [-w_{mean}(analyte; end) + SD{w_{mean}(analyte; end)}+b] (7b)

w_{min}(analyte; 120 months) $= a \cdot x + b$ (8´)

u_{lts}{ analyte(0 months) -analyte(120 months)} (9)

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 Table 3. This contribution was included into the calculation of the combined uncertainties of the certified mass fractions.

Table 3: *Long-term stability of non-metallic analytes (massfractions in %)*

Sub-sample	Carbon		Nitrogen		Oxygen		Total Boron		Adherent Boron Oxide	
	July 2008	Sep 2010	Nov 2006	Oct 2010	April 2008	Dec 2009	April 2008	Sep 2010	April 2008	Sep 2010
1	0.0137	0.0156	55.52	55.59	0.65	0.65	43.1	43.2	0.073	0.071
2	0.0143	0.0141	55.64	55.60	0.66	0.73	43.0	43.1	0.070	0.070
3	0.0134	0.0130	55.64	55.70	0.67	0.67	43.2	43.2	0.071	0.072
4	0.0142	0.0120	55.49	55.65	0.67	0.68	43.3	43.2	0.072	0.071
5	0.0143	0.0145		55.60	0.68	0.66	43.2	43.1	0.071	0.073
6	0.0140	0.0120		55.74	0.68	0.70	43.0	43.2	0.073	0.070
7	0.0125	0.0114		55.53	0.69	0.68		43.1		0.072
8	0.0126	0.0125		55.57	0.68	0.69		43.1		0.069
9	0.0129	0.0136		55.59	0.69	0.70		43.1		0.070
10	0.0126	0.0118		55.48	0.71	0.62		43.2		0.071
11	0.0135							43.2		0.069
12	0.0137							43.2		0.072
w_{mean}	0.01348	0.01306	55.573	55.605	0.678	0.678	43.133	43.138	0.0717	0.0708
Δw_{mean}	*0.000422*		*0.032*		*0.000*		*0.005*		*-0.024*	
SD	0.00067	0.00135	0.079	0.076	0.017	0.030	0.121	0.048	0.0012	0.0013
SD_{mean}	0.00019	0.00043	0.0395	0.0241	0.0053	0.0096	0.0494	0.0139	0.00049	0.00037
a	7.36E-06		0.002044		-0.0007486		0.00225		-0.0000565	
b	0.013285		55.533		0.6833		43.084		0.07219	
$W_{max;min}$	0.014202		55.778		0.5935		43.354		0.06539	
u_{lts}	0.00074		0.20577		0.06376		0.22072		0.00628	

5.2 Long-term stability of metallic analytes and Si

For the metallic analytes Al, Ca, Co, Cr, Fe, Mg, Na, Ti, as well as for Si, oxidative processes of the sample material will not lead to a change of their absolute <u>masses</u> in a definite (50 g) sample, because no volatile compounds can be formed under normal storage conditions of the material. However, due to the mass variations of other components of the material the mass fractions can change.

To study this effect, the total sample masses in five selected CRM bottles were measured at different times to assess the mass change of the samples over time. In table 4 the resulting contributions to the combined uncertainties of the mass fractions of the analytes are summarized.

The time period between both measurements in Table 4 was 36 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 50 g sample in a period of 120 months was set up to:

$$\Delta_{max} \text{ (sample mass; 120 months)} = (120/36) \cdot (\Delta_{mass1,2; mean} + 2SD_{mean})$$
$$= 3.33 \cdot 0.32 = 1.20 \text{ \% rel.}$$

$u_{lts, relative}$ ($w_{metallic\ analytes}$; 120 months) %rel = 1.20 %rel

Table 4: *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 relative uncertainty of 1.20 %$_{rel}$ in 10 years; all values in mg/kg*

Elements	Al	Ca	Cr	Fe	Mg	Na	Si	Ti	Co
mass fraction	7.0	273.2	4.75	14.97	56.3	12.26	17.0	4.91	0.036
u_{lts}	0.077	3.00	0.052	0.165	0.62	0.135	0.19	0.054	0.077

These contributions were included into the calculation of the combined uncertainty of the certified mass fractions of the metallic analytes.

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 characterization (certified and indicative values)

In Table 6 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 Table 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 above) are indicated belonging to the related line numbers (of Table. 7). Thus it is possible to identify which result in Table 7 is based on which analytical method.

Table 6: *Analytical methods used for final determination*

Element	Line No.	Analytical method used
Al	6	ET AAS
	4, 8	ETV-ICP OES
	7	ICP-SF-MS
	1, 2, 3, 5, 9, 10, (12)	ICP OES
	11	XRF
Ca	4	ETV-ICP OES
	6, 7	F AAS
	8	ICP-SF-MS
	1, 2, 3, 5, 10, (11), (12)	ICP OES
	9	XRF
Co	1	ET AAS
	3	ETV-ICP OES
	(4)	F AAS
	2	ICP-SF-MS
	(5)	ICP OES

Element	Line No.	Analytical method used
Cr	5	ET AAS
	11, 12...	ETV-ICP OES
	4	ICP-SF-MS
	1, 2, 3, 6, 7, 8, 9, 10	ICP OES
	13..	XRF
Fe	2	ET AAS
	6	ETV-ICP OES
	4, 13...	F AAS
	3	ICP-SF-MS
	1, 5, 7, 9, 10, 11, 12	ICP OES
	8	XRF
Mg	3	ETV-ICP OES
	2, 10..	F AAS
	11..	ICP-SF-MS
	4, 5, 6, 7, 8, 9, (12)...	ICP OES
	(1)	XRF
Na	8	ET AAS
	5	ETV-ICP OES
	2, 3, 9, 10..	F AAS
	6	ICP-SF-MS
	4, 7..	ICP OES
	1	XRF
Si	4	ETV-ICP OES
	3	ICP-SF-MS
	1, 2	ICP OES
	5	XRF
Ti	4	ET AAS
	13..	ETV-ICP OES
	6	ICP-SF-MS
	1, 2, 3, 5, 8, 9, 10, 11, 12	ICP OES
	7	XRF
C	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, (11), (12)......................	Comb.-IR.
N	1, 2, 3, 4, 5, 7, 8, 10, 11, 12	CGHE-TC
	6	LiOH-TITR
	9	Kjeldahl TITR
O	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	CGHE-IR
B$_{total}$	5	ICP OES
	1, 2, 3, 4, 6..	TITR (Method M1)
Adherent	1, 2, 3..	ICP OES
B$_2$O$_3$	4, 5...	TITR
H$_2$O	5	Coulom.
	1, 2, 4..	GRAV
	3	TITR

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

For the analysis of analytes with certified values a sufficient variety of different methods was used by the participating laboratories.

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 requiring chemical sample preparation. In Appendix 3 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 Table 6 as well as 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).

6.2 Analytical 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 Analytical methods used for homogeneity testing and stability investigation

The used methods are summarized in Appendix 2. For all parameters well established methods also applied for the certification round robin were used.

7. Results and discussion of the interlaboratory comparison

All submitted results of the certification analyses were summarized and checked with a statistical program of BCR for evaluation of results of interlaboratory comparisons for certification [3]. After this the data were technically discussed at the biannual meetings of the Working Group "Special Materials" of the Committee of Chemists of the GDMB, where several of the participating laboratories of the interlaboratory comparison were present. At the sessions it was decided to take the parameters Cobalt, Carbon and H_2O as indicative parameters because of their relatively high uncertainty.

For the determination of the parameter "total boron" the method described in Appendix 1 was discussed and agreed as recommended method.

In the following Table 7 all accepted laboratory mean values are summarized.

Table 7: MEANS OF ACCEPTED DATA SETS

Line no.	Al [mg/kg]	Ca [mg/kg]	Cr [mg/kg]	Fe [mg/kg]	Mg [mg/kg]	Na [mg/kg]	Si [mg/kg]	Ti [mg/kg]	N [%]	O [%]	B_{total} [%]	B_2O_3*) [%]		C [%]	Co [mg/kg]	H_2O [%]
1	3.5	250	2.6	12.1	-	10.2	13.2	4.0	54.49	0.500	43.13	0.066		*0.015*	*0.01*	*0.04*
2	3.6	262	3.2	12.2	52.6	10.9	15.8	4.0	54.94	0.569	43.27	0.068		*0.016*	*0.01*	*0.05*
3	6.2	263	3.4	12.7	52.8	11.2	17.8	4.0	55.22	0.618	43.45	0.070		*0.016*	*0.09*	*0.05*
4	6.6	265	3.5	12.7	54.7	11.9	18.6	4.5	55.26	0.635	43.47	0.072		*0.016*	-	*0.09*
5	6.9	271	3.7	13.6	54.8	12.0	19.5	4.7	55.48	0.637	43.66	0.075		*0.017*	-	*0.14*
6	7.3	274	4.2	13.6	55.8	12.8		4.7	55.59	0.680	43.88			*0.018*		
7	7.6	274	4.5	14.2	56.3	12.9		4.8	55.70	0.692				*0.019*		
8	7.7	285	4.8	14.3	57.4	13.0		5.0	55.71	0.737				*0.019*		
9	8.0	290	5.2	14.8	59.4	13.1		5.1	55.73	0.867				*0.021*		
10	9.8	297	5.3	15.8	59.4	14.6		5.4	55.92	0.869				*0.022*		
11	9.8	-	6.6	18.3	60.0			5.5	56.47					-		
12	-	-	6.8	19.4	-			5.6	56.85					-		
13			7.8	20.8				6.5								
Mean:	7.0	273	4.7	15.0	56.3	12.3	17.0	4.9	55.61	0.68	43.48	0.070		*0.018*	*0.04*	*0.07*
s_{Mean}:	2.0	14	1.6	2.8	2.7	1.3	2.5	0.7	0.63	0.12	0.27	0.004		*0.002*	*0.04*	*0.04*

The " - " indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion in GDMB meetings.
Values given in *italic type* are indicative values only.
Note: The line number should not be mistaken for the laboratory code number.

Mean: Arithmetic mean of the laboratory means

s_{Mean}: Standard deviation of the laboratory means

*) Boron oxide was determined as an adherent parameter.

The results of Table 7 are listed and described in more detail in tables compiled in Appendix 4-1.

Data and results of the statistical evaluation of the interlaboratory comparison using the BCR program [3] are summarized for metallic analytes in Table xx8.1 and for non-metallic parameters in Table yy8.2. in Appendix 4-2.

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

8.1 Calculation of mean mass fractions

The certified (or indicative) mass fractions of the resp. elements were calculated as the mean values "*Mean*" of all accepted means from the participating laboratories of the interlaboratory comparison (see chapter 7, Table 7).

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 time instability of the samples.

The basic parameter of further calculations (see below) have been calculated in the context of the homogeneity investigations as described in chapter 4. and as documented in detail in Appendix 2. These basic parameters are:

s_b = standard deviation of homogeneity investigation "between the bottles"
        (see Appendix 2) (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 2) (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 2). 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 [4] and ISO
        Guide 35 [5]
s_{Mean} = standard deviation of the accepted laboratory mean values of interlaboratory
        comparison for certification (see Table 7)

n = number of accepted laboratory mean values of interlaboratory
        comparison for certification (see Table 7)

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

whereas

$$s_{in\,hom} = \sqrt{s_b^2 + s_w^2 - s_{HS}^2}$$ (11)

In Equation (11) from each of the variances s_b^2 (between the bottles) and s_w^2 (within the bottles) the variance s_{HS}^2 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. Equation (11) was treated as the best approximation to calculate the standard deviation resulting from (potential) inhomogeneity of the material although values of $s^2{}_b$ and $s^2{}_w$ are not independent from each other and contain both contribution of the analytical procedure.

If

$$s_{HS} > s_b \quad \text{and/or} \quad s_{HS} > s_w \tag{11'}$$

then the corresponding difference term(s) in (11) is set to zero.

The combined uncertainty u_c is calculated as: the

$$u_c = \sqrt{\frac{s^2_{\text{Mean}}}{n} + s^2_{\text{inhom}} + u^2_{lts}} \tag{12}$$

u_{lts} is the uncertainty contribution from potential long term instability of the corresponding parameter)

Equation (12) was applied for all cases where

$$s^2{}_{inhom} > u^2{}_{bb}\,, \tag{13}$$

the variance $u^2{}_{bb}$, represents the blind part of the variances (see [4]), which could be masked by the variance of the analytical procedure $s^2{}_{HS}$

$$u_{bb} = \sqrt{\frac{s^2_{\text{HS}}}{n_{\text{HS}}}} \bullet \sqrt[4]{\frac{2}{v_{s^2_{\text{HS}}}}} \tag{14}$$

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 where

$$s^2{}_{inhom} \leq u^2{}_{bb}\,, \tag{15}$$

the combined uncertainty was calculated as:

$$u_c = \sqrt{\frac{s^2_{\text{M}}}{n} + u^2_{\text{bb}} + u^2_{lts}} \tag{16}$$

If no homogeneity investigation was carried out, the following equation was used:

$$u_c = \sqrt{\frac{s_M^2}{n}} \tag{17}$$

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 $k = 2$) of the certified mass fraction was calculated according to GUM as

$$U = 2\,u_c \tag{18}$$

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

- for Al, $B_{total,}$, Ca, Cr, Fe, Mg, N, O, Na, Si, Ti   Equation (12) combined with equations   (18)

- for C and B_2O_3 Equation (16) combined with Equation   (18)

- for *Co and H_2O Equation (17) combined with Equation   (18)

---

* For Co and H_2O no homogeneity investigation was carried out because its mass fraction is an indicative value only and not enough precise to measure.

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:

Boron Nitride Powder		
Characteristic	**Value [1]**	**Uncertainty U [2]**
Parameter	**Mass fraction in mg/kg**	
Aluminium	7.0	1.4
Calcium	273	13
Chromium	4.7	1.1
Iron	15.0	2.1
Magnesium	56	4
Sodium	12.3	0.9
Silicon	17	4
Titanium	4.9	0.7
	Mass fraction in %	
Oxygen	0.68	0.19
Nitrogen	55.6	0.6
Total Boron[3]	43.5	0.5
Adherent Boron oxide	0.070	0.014

1) The certified values are the means of 5 - 13 series of results (depending on the parameter) obtained by different laboratories. Up to 6 different analytical methods were used for the measurement of each parameter. The calibration of the methods applied for determination of element mass fractions were carried out by using pure substances of definite stoichiometry or solutions prepared from them, thus, ensuring traceability to SI units.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor k = 2. It includes contributions from sample inhomogeneity and sample stability.

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

Indicative Values		
	Mass Fraction	
	Indicative value [1] [3]	Uncertainty [2]
Carbon	0.018 %	0.002 %
Cobalt	< 0.1 mg/kg	
Water	< 0.1 %	

1) The indicative values are the means of 3 or 5 series of results (depending on the parameter) obtained by different laboratories. 4 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of mass fractions were not calibrated in all cases by pure substances of definite stoichiometry or by solutions prepared from them.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor k = 2.

3) Values were not certified, but given as indicative values, when the number of accepted data sets was considered to be too low, when the spread from the round robin certification was considerably larger than the state of the art.

8.5 Compilation of additional material data

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

Additional Material Information		
Particle size [1]	d_{10}	4.22 µm
	d_{50}	11.28 µm
	d_{90}	29.74 µm
Specific surface area [2]		5.02 m^2/g
1) The particle size distribution (volume) was determined by laser light diffraction method.		
2) The specific surface area was determined as multi point BET according to DIN ISO 9277.		

9. Instruction for use and safety-Information

9.1 Safety Information

The usual laboratory safety precautions apply. For detailed information to safety guidelines and handling of the material, please see the Material Safety Data Sheet distributed by the producer of the candidate material.

9.2 Intended Use

The reference material was developed for the calibration of analytical instruments and to validate or verify analytical methods intended to be used for the determination of impurities and main components in boron nitride materials.

9.3 Instructions for use

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, Cr, Fe, Mg, Na and Ti (500), Si (15), C (150), O and N (30), B_{total} (200), adherent B_2O_3 (5000). The opening time of the bottle should be kept as short as possible. The samples were closed in the bottles under Ar-stream. The lid of the bottle equipped with a special sealing gasket should be locked tightly immediately after usage. It is not required to dehydrate the sample before starting the measurements. For the determination of metallic analytes, the required pressure digestion has to be tested concerning the loss of analytes.

9.4 Storage

The sample should be stored in a dust-free and dry environment at room temperature (20°C). However, BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.5 Expiration of certification

The date of expiration of certification is ten years after the date of certification.

10. References and Literature

[1] Barth, P., Hassler, J., Kudrik, I. & Krivan, V. 2007, *Spectrochimica Acta Part B-Atomic Spectroscopy* **62**, 924-932.

[2] Gruner, W.,Hassler, J., Barth, P., Behm, J., Sunderkotter, J., 2009, *Journal of the European Ceramic Society* **29***, 2029-2035.*

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

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

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

Additional information/literature:

ISO Guide 31, Contents of certificates of reference materials, 1981

ISO Guide 34, General requirements for the competence of reference material producers, 2000

Guidelines for the production of BAM Reference Materials, 2006

Technical Guidelines for the Production and Acceptance of a European Reference Material
(www.erm-crm.org)

Karl A. Schwetz, Boron Carbide, Boron Nitride, and Metal Borides in: Ullmann's Encyclopedia of Industrial Chemistry, sixth edition Vol. 5, WILEY-VCH (1999), 497-513

Herman Blumenthal, Determination of Boron in Metal Borides, Anal. Chem. 23, No 7, (1951), 992-994
F. Thevenot and J. Cueilleron, Analytical problems in boron and refractory borides, Analusis, 5, No 3, (1977), 105-121

11. Information on and supply of the CRM

Information and sale is done by:

BAM Federal Institute for Materials Research and Testing
Division 1.6: Inorganic Reference Materials
Richard-Willstätter-Straße 11, 12489 Berlin
Phone   +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 1117
Email: sales.crm@bam.de
www.bam.de

Each bottle of ERM®-ED103 will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.

Appendix 1:

Recommended method M1:
Determination of total Boron (B_{total}) in Boron Nitride (BN) by a Titrimetric method

Scope:

Determination of total boron content in BN-grains, BN-powder and sintered parts by means of titrimetry.

Summary of method:

Powdered BN is decomposed by melt-fusion with sodium-carbonate or a mixture of potassium/sodium-carbonate and subsequently dissolved in hydrochloric acid. The boric acid in the sample solution is then determined in presence of mannitol as mannitoboric-acid by potentiometric titration with sodium hydroxide solution.

NOTE 1: In principal, the boron concentration in the sample solution can also be determined by ICP OES. However, great efforts are necessary to achieve a precision and accuracy comparable to that of the titrimetric method.

NOTE 2: Metallic impurities in high concentrations may distort the inflection points of the titration and should be precipitated from the sample solution using barium carbonate. No distortion was found for concentrations of Al < 0,2 %, Fe < 2 %, Ti < 1 %.

Apparatus:

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

- Potentiometric titration system.
- Burner, Bunsen type.
- Muffle Furnace, capable of maintaining a temperature of 680 °C ± 10 °C or 730 °C ± 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 be 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 demineralized by ion exchange (deionized water). Unless otherwise specified solutions are aqueous solutions.

- Sodium hydroxide solution, NaOH, 0.1 n, CO_2-free, preferably in an airtight plastic container with an airtight connection to the titration system.
- Sodium carbonate ($NaCO_3$), powdered or a 1:1 mixture of sodium/potassium carbonate (Na_2CO_3 / K_2CO_3), powdered.
- Hydrochloric acid, 32% by volume, diluted 1:1 with water.
- Sodium hydroxide solution, 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 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 sample has to be homogenized before analysis.

Procedure:

About 150 mg of boron nitride is 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.

Two different procedures of decomposition by melt-fusion are described.

Decomposition by melt-fusion using a Bunsen burner:
Place a lid on the platinum crucible and heat with the low flame of a Bunsen burner for 15 min. Continue heating while increasing the temperature (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: When heating with the hot flame of the Bunsen burner a clear melt is readily obtained. However, this does not necessarily indicate complete sample decomposition. During further heating and increasing the temperature the formation of gas bubbles in the melt can often be observed. In this case, keep the high temperature until gas formation has disappeared.

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 residues of boron nitride mostly located near the rim of the platinum crucible. Finally, swirl the platinum crucible outside the flame using a crucible tongs until the liquid melt begins to solidify and covers the crucible wall. Place back the platinum crucible to the flame, liquefy the melt again and heat with hot flame until

crucible and lid are glowing. Simultaneously heat the upper part of the platinum crucible and the lid by means of a second burner. After this, the decomposition procedure is finished.

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

NOTE 6: Most samples require about 1 to 1.5 h for complete decomposition.

Decomposition by melt-fusion using a combination of muffle furnace and Bunsen burner:
Place a lid on the platinum crucible and place it into the muffle furnace at ambient temperature. The platinum crucible should be placed into ceramic crucible supports. Using Na_2CO_3, heat up the muffle furnace to 730°C ± 10 °C in 45 min. Using a K_2CO_3 / Na_2CO_3 mixture, heat up the muffle furnace to 680°C ± 10 °C in 60 min. Keep the crucible at this temperature for at least 4 h. Allow cooling down and take out the crucible from the muffle furnace.

Place the platinum crucible on 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.

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 residues of boron nitride mostly located near the rim of the platinum crucible. Finally, swirl the platinum crucible outside the flame using a crucible tongs until the liquid melt begins to solidify and covers the crucible wall. Place back the platinum crucible to the flame, liquefy the melt again and heat with hot flame until crucible and lid are glowing. Simultaneously heat the upper part of the platinum crucible and the lid by means of a second burner. After this, the decomposition procedure is finished.

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

NOTE 7: The temperature should not exceed 40 °C to avoid losses of boric acid.

The solution is transferred to a 250 ml volumetric flask and filled up to volume with water. An aliquot of 50 ml is pipetted into a 400 ml tall-form beaker and neutralized with 20 % NaOH solution using pH-indicator paper or pH-meter. The aliquot is diluted to 200 ml with water and acidified with HCl 1:1 to pH 2.5 - 3.0, covered with a watch glass and boiled for 3 minutes to remove CO_2.

NOTE 8: Alternatively CO_2 can also be removed by purging the solution with N_2.

Allow the solution to cool down to room temperature and purge the solution with N_2 at least 10 min before starting the titration procedure. Continue purging with nitrogen during the whole titration procedure.

<u>Titration of Boron:</u>
Using the titration-system, the solution is titrated to the first inflection point with 0.1n NaOH. Then 35 ml of a 10% mannitol-solution or 4 g of solid mannitol is added and finally titrated to the second inflection point. The consumption of 0.1 n NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron (see also Appendix 1).

NOTE 9: For best precision and accuracy it is highly recommended to perform the analysis in an air-conditioned room at constant temperature.

Calculation:

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

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

V_{NaOH} = consumption of 0.1 n NaOH [ml]
F = titrimetic factor in mg B / ml 0.1 n NaOH (theoretically 1.0811)
f = titration correction factor of NaOH (should be near to 1.000)
a = aliquot of sample solution [ml]
m_S = sample mass [mg]

Precision:

The precision of this method is ± 0.2 % absolute at around 40 mass% of boron.

Calibration:

The titration correction factor f can be determined using potassium hydrogen phthalate. The titrimetric factor F is checked by using boric acid.

Literature:

- H. Blumenthal, Anal. Chem. 23 (1951) 992-994
- ASTM C791

Example of Boron titration via mannitoboric acid:
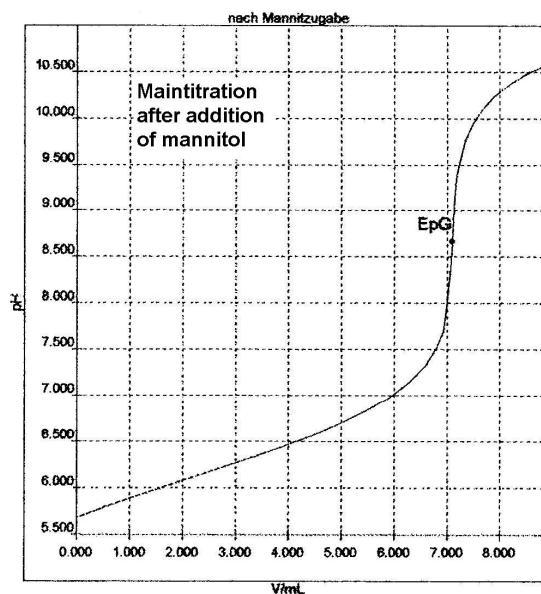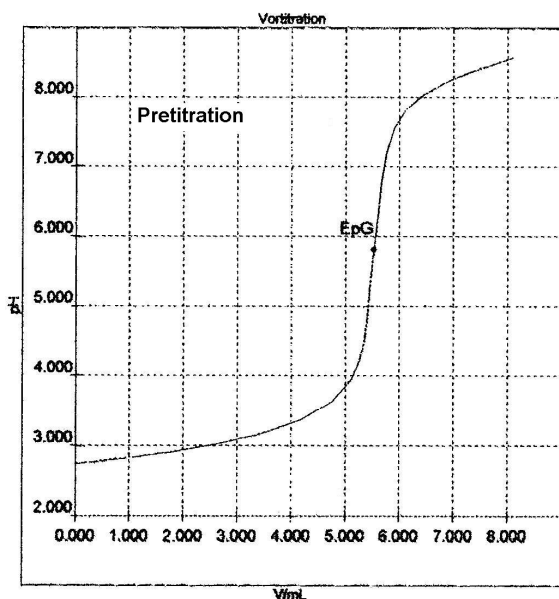
The titration curve on the left shows the pre-titration, starting at pH 2.75. The first inflection point is at pH 5.76. The titration is continued to pH 8.50. After that, mannitol is added.

After waiting until the pH has stabilized (pH 5.65) the main-titration is started. The second inflection point is at pH 8.45.

The consumption of 0.1 n NaOH 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 total consumption of 0.1 n NaOH between first and second inflection point of 9.6697 ml.

Appendix 2: Details to homogeneity investigations

Analytical Methods used for homogeneity investigations

Parameter	Sample Preparation	Final Determination
Al, Ca, Cr, Fe, Mg, Ti	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - micro wave oven (ultra clave III, MLW) - 1,5 h at 240 °C 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL flask	ICP OES
Na	**ACID DECOMPOSITION**: See above	F AAS
Si	**No SAMPLE PREPARATION** - M: 3 x 2.5 mg - ETV-program: 30 s-400 °C; 4s-1950 °C, 26 s-1950 °C. - Reaction gas Freon R12	ETV-ICP OES
C	**MEASUREMENT PARAMETER:** - M: 150 mg; combustion of sample with oxygen in aluminia crucibles (induction furnace); - accelerator: Fe/W Purge time: 15 s; Delay time: 15 s, minimum time: 40s	CGHE-IR
N	**MEASUREMENT PARAMETER:** - M: 30 mg; - sample in high temperature crucibles and Sn capsules - 10 s purge time; outgas 5500 W 20 s; analysis: low power = 4000 W, high power = 5200 W, ramp rate = 100 W/s.	CGHE-TC
O	**MEASUREMENT PARAMETER:** - M: 30 mg; - sample in high temperature crucibles and Sn capsule - Analyse parameter see N	CGHE-IR
B-total	**DIGESTION**: - M: 200 mg; - melting fusion with 5 g $NaKCO_3$ - dissolution in 1+1 HCl - titrated after addition of mannitol (recommended method M1, ASTM C971)	TITR
B_2O_3	**DIGESTION:** - M: 6 g; - Extraction with water1 h at 60 °C - Titrated with NaOH in presence of mannitol	TITR

Calculated results of the homogeneity testing

The results of the homogeneity testing are listed in form of tables arranged by parameters (elements)., The first table contains the measured mass fractions of all samples from the 20 investigated bottles (from each bottle four sub-samples). The mass fractions are indicated by the spectral line used. If more than one spectral line was 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 1 - 3 lines") were used for the subsequent calculation and evaluation. The last column contains these values expressed as relative standard deviations RSD_w. The index "w" stands for "within the bottles".

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 tables are listed in the following order of investigated parameters (analytes):
Al, Ca, Cr, Fe, Mg, Na, Si, Ti, B, B_2O_3, C, N, O

Analyte Al

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Al 396.152	Mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSD$_w$ (rel.%)
1	20-1	6.82			
	20-2	6.53			
	20-3	6.73			
	20-4	6.76	6.708	0.123	1.83
2	29-1	6.83			
	29-2	6.71			
	29-3	6.84			
	29-4	6.98	6.839	0.111	1.62
3	47-1	6.87			
	47-2	6.83			
	47-3	6.77			
	47-4	6.87	6.837	0.047	0.69
4	68-1	6.86			
	68-2	7.05			
	68-3	6.92			
	68-4	6.77	6.901	0.114	1.66
5	89-1	6.98			
	89-2	6.89			
	89-3	6.94			
	89-4	6.66	6.869	0.141	2.05
6	100-1	6.93			
	100-2	6.89			
	100-3	6.97			
	100-4	6.80	6.897	0.074	1.07
7	109-1	7.13			
	109-2	6.93			
	109-3	6.99			
	109-4	7.04	7.020	0.084	1.19
8	133-1	6.90			
	133-2	7.07			
	133-3	7.03			
	133-4	7.19	7.048	0.117	1.66
9	146-1	6.93			
	146-2	7.16			
	146-3	6.93			
	146-4	6.96	6.994	0.112	1.60
10	164-1	6.68			
	164-2	6.90			
	164-3	7.06			
	164-4	7.05	6.920	0.180	2.59
11	184-1				
	184-2	6.92			
	184-3	7.02			
	184-4	6.92	6.956	0.059	0.84

Analyte Al

Line number	Sample number	Mass fraction Al 396.152	Mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
12	191-1	7.03			
	191-2	6.93			
	191-3				
	191-4	6.72	6.892	0.160	2.32
13	207-1	6.98			
	207-2	6.89			
	207-3	6.80			
	207-4	6.79	6.865	0.088	1.28
14	220-1	6.93			
	220-2	6.96			
	220-3	6.85			
	220-4	6.79	6.882	0.081	1.17
15	245-1	6.821			
	245-2	6.681			
	245-3	6.806			
	245-4	6.983	6.823	0.124	1.82
16	258-1	6.734			
	258-2	7.066			
	258-3	6.915			
	258-4	6.979	6.924	0.141	2.03
17	278-1	6.741			
	278-2	6.614			
	278-3	6.747			
	278-4	6.528	6.657	0.106	1.59
18	293-1	6.738			
	293-2	6.882			
	293-3	7.046			
	293-4	6.690	6.839	0.160	2.35
19	314-1	6.718			
	314-2	6.790			
	314-3	7.100			
	314-4	6.791	6.850	0.170	2.49
20	325-1	6.506			
	325-2	6.544			
	325-3	6.295			
	325-4	6.482	6.456	0.111	1.72

M_{SS} – mean of means of the sub-samples 1-4	6.859	
SD of means of the sub-samples 1-4	0.132	
RSD (rel.%)	1.92	mean RSD_w (%) 1.68

Analyte Al

HS = sample solution for comparison

Line number	Sample number	Mass fraction Al 396.152
1	HS 1	6.759
2	HS 2	6.309
3	HS 3	6.644
4	HS 4	6.490
5	HS 5	6.614
6	HS 6	6.656
7	HS 7	6.940
8	HS 8	6.926
9	HS 9	6.636
10	HS 10	6.873
11	HS 11	6.673
12	HS 12	6.451
13	HS 13	6.493

M_{HS} – mean of homogenous sample	6.651
SD_{HS}	0.189
RSD_{HS} (%)	2.84

Analyte Ca

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Ca 393.3	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	265.44			
	20-2	260.24			
	20-3	266.13			
	20-4	266.58	264.601	2.943	1.11
2	29-1	262.65			
	29-2	265.95			
	29-3	261.76			
	29-4	264.68	263.760	1.903	0.72
3	47-1	267.04			
	47-2	264.15			
	47-3	267.98			
	47-4	265.08	266.063	1.756	0.66
4	68-1	266.30			
	68-2	264.91			
	68-3	265.48			
	68-4	266.12	265.701	0.635	0.24
5	89-1	264.26			
	89-2	262.61			
	89-3	265.47			
	89-4	262.01	263.589	1.572	0.60
6	100-1	265.38			
	100-2	264.61			
	100-3	267.33			
	100-4	265.48	265.700	1.156	0.44
7	109-1	267.31			
	109-2	266.79			
	109-3	264.24			
	109-4	267.96	266.575	1.627	0.61
8	133-1	267.26			
	133-2	266.24			
	133-3	266.99			
	133-4	265.05	266.386	0.991	0.37
9	146-1	267.05			
	146-2	265.96			
	146-3	272.34			
	146-4	272.59	269.488	3.469	1.29
10	164-1	268.47			
	164-2	266.21			
	164-3	269.54			
	164-4	269.21	268.357	1.498	0.56
11	184-1	266.27			
	184-2	265.06			
	184-3	265.09			
	184-4	263.25	264.918	1.248	0.47

Analyte Ca

Line number	Sample number	Mass fraction Ca 393.3	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
12	191-1	262.89			
	191-2	264.65			
	191-3	261.64			
	191-4	265.40	263.649	1.702	0.65
13	207-1	262.55			
	207-2	260.65			
	207-3	267.96			
	207-4	269.14	265.077	4.113	1.55
14	220-1	264.97			
	220-2	263.97			
	220-3	268.01			
	220-4	268.13	266.270	2.119	0.80
15	245-1	265.104			
	245-2	264.058			
	245-3	265.091			
	245-4	265.505	264.939	0.619	0.23
16	258-1	268.535			
	258-2	267.980			
	258-3	268.693			
	258-4	268.473	268.420	0.308	0.11
17	278-1	265.905			
	278-2	269.848			
	278-3	269.479			
	278-4	269.748	268.745	1.900	0.71
18	293-1	266.665			
	293-2	268.675			
	293-3	267.799			
	293-4	266.784	267.481	0.945	0.35
19	314-1	273.221			
	314-2	267.670			
	314-3	263.994			
	314-4	267.049	267.984	3.843	1.43
20	325-1	264.202			
	325-2	266.749			
	325-3	265.655			
	325-4	265.748	265.588	1.049	0.39

M_{SS} – mean of means of the sub-samples 1-4	266.164	
SD of means of the sub-samples 1-4	1.763	
RSD (rel.%)	0.66	mean RSDw (%) 0.66

Analyte Ca

HS = sample solution for comparison

Line number	Sample number	Mass fraction Ca 393.3
1	HS 1	264.484
2	HS 2	263.005
3	HS 3	267.050
4	HS 4	263.005
5	HS 5	266.630
6	HS 6	263.032
7	HS 7	268.043
8	HS 8	267.858
9	HS 9	270.324
10	HS 10	270.911
11	HS 11	267.974
12	HS 12	268.299
13	HS 13	268.436

M_{HS} – mean of homogenous sample	266.850
SD_{HS}	2.688
RSD_{HS} (%)	1.01

Analyte Cr

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Cr 206.1	Mass fraction Cr 267.7	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	3.6893	3.6647				
	20-2	3.1844	3.0955	3.1400			
	20-3	3.2379	3.3505	3.2942			
	20-4	3.2861	3.4122	3.3491	3.261	0.108	3.33
2	29-1	3.0230	3.2236	3.1233			
	29-2	3.2688	3.3509	3.3098			
	29-3	3.5586	3.6365	3.5976			
	29-4	3.4341	3.5684	3.5013	3.383	0.210	6.22
3	47-1	3.4049	3.3390	3.3720			
	47-2	3.5436	3.6290	3.5863			
	47-3	3.4198	3.5625	3.4912			
	47-4	3.4051	3.5369	3.4710	3.480	0.088	2.53
4	68-1	3.3309	3.4024	3.3667			
	68-2	3.2987	3.3158	3.3073			
	68-3	3.0490	3.1423	3.0957			
	68-4	3.1228	3.1818	3.1523	3.230	0.127	3.95
5	89-1	3.7287	3.6872	3.7079			
	89-2	3.6834	3.7737	3.7285			
	89-3	3.3484	3.4073	3.3779			
	89-4	3.4862	3.5219	3.5041	3.580	0.168	4.70
6	100-1	3.8132	3.9305	3.8718			
	100-2	3.2864	3.3679	3.3271			
	100-3	3.7704	3.8980	3.8342			
	100-4	3.5061	3.6169	3.5615	3.649	0.255	6.99

Analyte Cr

Line number	Sample number	Mass fraction Cr 206.1	Mass fraction Cr 267.7	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
7	109-1	3.3484	3.7810	3.5647			
	109-2	3.5435	3.8690	3.7063			
	109-3	3.4090	3.8399	3.6244			
	109-4	3.2921	3.6504	3.4713	3.592	0.099	2.76
8	133-1	3.5742	3.8741	3.7242			
	133-2	3.1828	3.4556	3.3192			
	133-3	3.1930	3.5204	3.3567			
	133-4	3.2699	3.6342	3.4520	3.463	0.183	5.28
9	146-1	3.6088	4.0188	3.8138			
	146-2	3.3051	3.6078	3.4564			
	146-3	3.5722	3.9938	3.7830			
	146-4	3.2709	3.9423	3.6066	3.665	0.166	4.54
10	164-1	3.3082	3.8047	3.5565			
	164-2	3.2161	3.5432	3.3797			
	164-3	3.4062	3.7652	3.5857			
	164-4	3.1233	3.5385	3.3309	3.463	0.127	3.66
11	184-1	2.9492	3.3466				
	184-2	3.8193	4.2208				
	184-3	3.5344	3.9499	3.7422			
	184-4	3.6740	3.9398	3.8069	3.775	0.046	1.21
12	191-1	3.5084	3.7378	3.6231			
	191-2	3.1972	3.3360	3.2666			
	191-3	3.1778	3.4193	3.2986			
	191-4	3.0808	3.3385	3.2096	3.349	0.186	5.56

Analyte Cr

Line number	Sample number	Mass fraction Cr 206.1	Mass fraction Cr 267.7	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
13	207-1	3.4173	3.7304	3.5739			
	207-2	3.1901	3.4226	3.3064			
	207-3	3.3203	3.5616	3.4410			
	207-4	3.2798	3.6785	3.4791	3.450	0.111	3.21
14	220-1	3.2014	3.6368	3.4191			
	220-2	3.4772	3.9488				
	220-3	3.3557	3.7333	3.5445			
	220-4	2.9910	3.3320		3.482	0.089	2.55
15	245-1	3.5342	4.0424	3.7883			
	245-2	3.5353	3.9730	3.7542			
	245-3	3.2767	3.6225	3.4496			
	245-4	3.5422	4.0232	3.7827	3.694	0.163	4.42
16	258-1	3.4914	3.5748	3.5331			
	258-2	3.6325	3.7084	3.6705			
	258-3	3.4878	3.6313	3.5596			
	258-4	3.4808	3.5677	3.5243	3.572	0.067	1.89
17	278-1	3.7377	3.7437	3.7407			
	278-2	3.6941	3.6561	3.6751			
	278-3	3.6922	3.5239	3.6081			
	278-4	3.5959	3.4890	3.5425	3.642	0.085	2.35
18	293-1	3.5059	3.4102	3.4581			
	293-2	3.7387	3.6994	3.7191			
	293-3	3.6795	3.6456	3.6626			
	293-4	4.3606	4.4757		3.613	0.137	3.80

Analyte Cr

Line number	Sample number	Mass fraction Cr 206.1	Mass fraction Cr 267.7	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
19	314-1	3.8837	3.9913	3.9375			
	314-2	3.6025	3.6430	3.6227			
	314-3	3.9241	3.9038	3.9139			
	314-4	3.5695	3.5396	3.5546	3.757	0.197	5.24
20	325-1	3.6938	3.7426				
	325-2	3.1987	3.2991	3.2489			
	325-3	3.3344	3.3294	3.3319			
	325-4	3.3446	3.3857	3.3651	3.315	0.060	1.81

M_{SS} – mean of means of the sub-samples 1-4	3.518	
SD of means of the sub-samples 1-4	0.163	
RSD (rel.%)	4.62	Mean RSDw (%) 3.80

Analyte Cr

HS = sample solution for comparison

Line number	Sample number	Mass fraction Cr 206.1	Mass fraction Cr 267.7	Mean over 2 lines
1	HS 1	3.154	3.188	3.171
2	HS 2	3.252	3.239	3.245
3	HS 3	3.231	3.202	3.217
4	HS 4	3.241	3.267	3.254
5	HS 5	3.129	3.201	3.165
6	HS 6	3.127	3.270	3.198
7	HS 7	3.060	3.245	3.153
8	HS 8	3.112	3.208	3.160
9	HS 9	3.059	3.259	3.159
10	HS 10	3.150	3.129	3.140
11	HS 11	3.071	3.293	3.182
12	HS 12	3.159	3.201	3.180
13	HS 13	3.171	3.203	3.187

M_{HS} – mean of homogenous sample	3.186
SD_{HS}	0.0349
RSD_{HS} (%)	1.09

Analyte Fe

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Fe 238.204	Mass fraction Fe 258.588	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	11.694	11.545	11.620			
	20-2	11.196	11.103	11.150			
	20-3	12.469	12.398	12.434			
	20-4	12.479	12.463	12.471	11.918	0.646	5.42
2	29-1	12.923	12.962	12.942			
	29-2	11.948	11.942	11.945			
	29-3	11.682	11.619	11.650			
	29-4	13.041	12.934	12.988	12.381	0.685	5.53
3	47-1	12.147	12.099	12.123			
	47-2	12.312	12.330	12.321			
	47-3	12.938	13.007	12.973			
	47-4	11.700	11.648	11.674	12.273	0.540	4.40
4	68-1	12.058	11.911	11.985			
	68-2	12.056	12.001	12.028			
	68-3	11.439	11.374	11.407			
	68-4	12.844	12.819	12.831	12.063	0.585	4.85
5	89-1	16.018	15.784				
	89-2	12.013	11.840	11.927			
	89-3	12.547	12.361	12.454			
	89-4	11.934	11.860	11.897	12.093	0.313	2.59
6	100-1	12.825	12.708	12.767			
	100-2	12.496	12.466	12.481			
	100-3	11.769	11.750	11.759			
	100-4	11.829	11.640	11.734	12.185	0.520	4.26

Analyte Fe

Line number	Sample number	Mass fraction Fe 238.204	Mass fraction Fe 258.588	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
7	109-1	12.866	12.785	12.826			
	109-2	12.051	12.034	12.043			
	109-3	12.130	12.145	12.137			
	109-4	12.145	12.239	12.192	12.299	0.356	2.90
8	133-1	12.140	12.261	12.201			
	133-2	11.650	11.648	11.649			
	133-3	12.410	12.353	12.381			
	133-4	12.005	11.990	11.998	12.057	0.314	2.60
9	146-1	11.459	11.465	11.462			
	146-2	12.523	12.553	12.538			
	146-3	11.856	11.833	11.845			
	146-4	12.116	12.086	12.101	11.986	0.452	3.77
10	164-1	11.986	12.019	12.003			
	164-2	12.141	12.157	12.149			
	164-3	11.772	11.630	11.701			
	164-4	12.426	12.354	12.390	12.061	0.288	2.39
11	184-1	11.683	11.625	11.654			
	184-2	11.335	11.286	11.310			
	184-3	11.856	11.829	11.843			
	184-4	12.179	12.230	12.204	11.753	0.373	3.17
12	191-1	11.591	11.596	11.594			
	191-2	11.447	11.344	11.396			
	191-3	11.402	11.431	11.416			
	191-4	12.341	12.452	12.397	11.701	0.473	4.04

Analyte Fe

Line number	Sample number	Mass fraction Fe 238.204	Mass fraction Fe 258.588	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
13	207-1	12.202	12.178	12.190			
	207-2	11.683	11.762	11.723			
	207-3	12.248	12.213	12.231			
	207-4	12.261	12.167	12.214	12.089	0.245	2.03
14	220-1	11.701	11.584	11.643			
	220-2	11.712	11.807	11.760			
	220-3	12.018	12.020	12.019			
	220-4	11.898	11.944	11.921	11.836	0.167	1.41
15	245-1	11.378	11.242	11.310			
	245-2	11.899	11.861	11.880			
	245-3	11.376	11.278	11.327			
	245-4	12.362	12.336	12.349	11.716	0.498	4.25
16	258-1	12.344	12.096	12.220			
	258-2	12.263	12.080	12.171			
	258-3	12.193	11.918	12.056			
	258-4	12.277	12.068	12.173	12.155	0.070	0.58
17	278-1	12.550	12.258	12.404			
	278-2	12.770	12.413	12.591			
	278-3	12.179	11.968	12.073			
	278-4	12.737	12.626	12.681	12.437	0.269	2.16
18	293-1	12.551	12.390	12.471			
	293-2	12.281	12.089	12.185			
	293-3	12.381	12.180	12.280			
	293-4	12.854	12.825	12.839	12.444	0.289	2.32

Analyte Fe

Line number	Sample number	Mass fraction Fe 238.204	Mass fraction Fe 258.588	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
19	314-1	12.152	12.085	12.118			
	314-2	11.795	11.643				
	314-3	12.491	12.468	12.479			
	314-4	13.152	13.106		12.299	0.256	2.08
20	325-1	12.432	12.455	12.444			
	325-2	12.498	12.481	12.490			
	325-3	13.060	12.972	13.016			
	325-4	12.381	12.304	12.343	12.573	0.302	2.40

M_{SS} – mean of means of the sub-samples 1-4   12.116

SD of means of the sub-samples 1-4   0.251

RSD (rel.%)   2.07   Mean RSD_w (%)   3.16

Analyte Fe

HS = sample solution for comparison

Line number	Sample number	Mass fraction Fe 238.204	Mass fraction Fe 258.588	Mean over 2 lines
1	HS 1	11.286	11.291	11.288
2	HS 2	11.266	11.200	11.233
3	HS 3	11.310	11.233	11.271
4	HS 4	11.266	11.326	11.296
5	HS 5	11.328	11.380	11.354
6	HS 6	11.335	11.222	11.278
7	HS 7	11.374	11.382	11.378
8	HS 8	11.330	11.232	11.281
9	HS 9	11.293	11.063	11.178
10	HS 10	11.273	11.052	11.162
11	HS 11	11.252	11.221	11.237
12	HS 12	11.314	11.279	11.297
13	HS 13	11.397	11.330	11.364

M_{HS} – mean of homogenous sample	11.278
SD_{HS}	0.065
RSD_{HS} (%)	0.58

Analyte Mg

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Mg 279.553	Mass fraction Mg 280.270	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	54.992	55.003	54.997			
	20-2	54.903	54.981	54.942			
	20-3	56.161	56.268	56.215			
	20-4	55.659	55.722	55.690	55.461	0.607	1.09
2	29-1	54.980	55.097	55.039			
	29-2	54.743	54.778	54.761			
	29-3	54.383	54.384	54.384			
	29-4	55.092	55.116	55.104	54.822	0.328	0.60
3	47-1	55.174	55.262	55.218			
	47-2	54.594	54.663	54.629			
	47-3	55.562	55.568	55.565			
	47-4	55.722	55.703	55.712	55.281	0.482	0.87
4	68-1	55.461	55.424	55.443			
	68-2	54.742	54.760	54.751			
	68-3	55.151	55.164	55.157			
	68-4	55.157	55.126	55.141	55.123	0.284	0.52
5	89-1	54.996	54.966	54.981			
	89-2	55.778	55.795	55.786			
	89-3	55.426	55.464	55.445			
	89-4	56.343	56.393	56.368	55.645	0.584	1.05
6	100-1	54.991	54.976	54.984			
	100-2	55.604	55.629	55.617			
	100-3	55.989	55.195	55.592			
	100-4	56.322	54.785	55.553	55.436	0.303	0.55

Analyte Mg

Line number	Sample number	Mass fraction Mg 279.553	Mass fraction Mg 280.270	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
7	109-1	58.265	55.829	57.047			
	109-2	57.867	55.345	56.606			
	109-3	58.928	56.325	57.627			
	109-4	58.206	55.736	56.971	57.063	0.422	0.74
8	133-1	57.883	55.595	56.739			
	133-2	57.637	55.315	56.476			
	133-3	57.521	55.214	56.367			
	133-4	57.638	55.256	56.447	56.508	0.161	0.29
9	146-1	58.077	55.621	56.849			
	146-2	58.642	56.150	57.396			
	146-3	58.367	56.018	57.193			
	146-4	58.264	56.090	57.177	57.154	0.227	0.40
10	164-1	57.843	55.833	56.838			
	164-2	58.511	56.533	57.522			
	164-3	58.139	56.178	57.158			
	164-4	57.479	55.578	56.528	57.012	0.426	0.75
11	184-1	57.546	55.538	56.542			
	184-2	57.471	55.319	56.395			
	184-3	57.127	54.856	55.991			
	184-4	57.061	54.690	55.875	56.201	0.318	0.57
12	191-1	57.437	54.940	56.189			
	191-2	57.655	55.111	56.383			
	191-3	57.823	55.175	56.499			
	191-4	57.935	55.289	56.612	56.421	0.181	0.32

Analyte Mg

Line number	Sample number	Mass fraction Mg 279.553	Mass fraction Mg 280.270	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
13	207-1	58.053	55.405	56.729			
	207-2	58.117	55.535	56.826			
	207-3	57.381	54.995	56.188			
	207-4	57.978	55.551	56.764	56.627	0.295	0.52
14	220-1	57.280	55.044	56.162			
	220-2	57.572	55.333	56.452			
	220-3	58.231	56.056	57.143			
	220-4	57.066	54.764	55.915	56.418	0.531	0.94
15	245-1	58.349	55.754	57.052			
	245-2	57.962	55.251	56.607			
	245-3	58.260	55.588	56.924			
	245-4	57.520	55.020	56.270	56.713	0.350	0.62
16	258-1	54.977	55.088	55.033			
	258-2	56.442	56.458	56.450			
	258-3	56.021	56.069	56.045			
	258-4	54.522	54.475	54.499	55.507	0.898	1.62
17	278-1	56.525	56.502	56.514			
	278-2	55.760	55.790	55.775			
	278-3	55.558	55.635	55.596			
	278-4	55.674	55.723	55.699	55.896	0.418	0.75
18	293-1	55.819	55.809	55.814			
	293-2	55.387	55.392	55.389			
	293-3	55.688	55.692	55.690			
	293-4	50.643	49.785		55.631	0.218	0.39

Analyte Mg

Line number	Sample number	Mass fraction Mg 279.553	Mass fraction Mg 280.270	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
19	314-1	56.814	56.791	56.803			
	314-2	55.726	55.784	55.755			
	314-3	57.795	57.796	57.796			
	314-4	56.353	56.340	56.346	56.675	0.862	1.52
20	325-1	58.181	56.009	57.095			
	325-2	57.721	55.497	56.609			
	325-3	58.353	56.123	57.238			
	325-4	57.213	55.044	56.128	56.767	0.504	0.89

M_{SS} – mean of means of the sub-samples 1-4	56.12
SD of means of the sub-samples 1-4	0.711
RSD (rel.%)	1.27

Mean RSD_w (%) 0.75

Analyte Mg

HS = sample solution for comparison

Line number	Sample number	Mass fraction Mg 279.553	Mass fraction Mg 280.270	Mean over 2 lines
1	HS 1	53.699	53.677	53.688
2	HS 2	53.580	53.530	53.555
3	HS 3	53.790	53.767	53.778
4	HS 4	53.898	53.824	53.861
5	HS 5	53.651	53.637	53.644
6	HS 6	53.723	53.778	53.750
7	HS 7	53.547	53.529	53.538
8	HS 8	53.845	53.810	53.827
9	HS 9	53.780	53.724	53.752
10	HS 10	53.778	53.797	53.788
11	HS 11	53.707	53.627	53.667
12	HS 12	53.782	53.745	53.764
13	HS 13	53.795	53.783	53.789

M_{HS} – mean of homogenous sample   53.72

SD_{HS} 0.099

RSD_{HS} (%)   0.18

Analyte Na

Line number	Sample number	Mass fraction Na 589.0	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	13.374			
	20-2	13.373			
	20-3	13.455			
	20-4	13.445	13.412	0.045	0.33
2	29-1	13.220			
	29-2	13.220			
	29-3	13.290			
	29-4	13.277	13.252	0.037	0.28
3	47-1	13.332			
	47-2	13.303			
	47-3	13.332			
	47-4	13.303	13.318	0.017	0.13
4	68-1	13.363			
	68-2	13.316			
	68-3	13.726			
	68-4	13.430	13.459	0.184	1.37
5	89-1	13.350			
	89-2	13.726			
	89-3	13.252			
	89-4	13.225	13.388	0.231	1.73
6	100-1	13.325			
	100-2	13.380			
	100-3	13.317			
	100-4	13.225	13.312	0.064	0.48
7	109-1	13.363			
	109-2	13.409			
	109-3	13.325			
	109-4	13.345	13.360	0.036	0.27
8	133-1	13.316			
	133-2	13.231			
	133-3	13.270			
	133-4	13.363	13.295	0.057	0.43
9	146-1	13.375			
	146-2	13.376			
	146-3	13.360			
	146-4	13.335	13.362	0.019	0.14
10	164-1	13.430			
	164-2	13.231			
	164-3	13.270			
	164-4	13.178	13.277	0.109	0.82
11	184-1	13.280			
	184-2	13.368			
	184-3	13.335			
	184-4	13.381	13.341	0.045	0.34

Analyte Na

Line number	Sample number	Mass fraction Na 589.0	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
12	191-1	13.335			
	191-2	13.185			
	191-3	13.405			
	191-4	13.462	13.347	0.120	0.90
13	207-1	13.385			
	207-2	13.397			
	207-3	13.172			
	207-4	13.280	13.309	0.105	0.79
14	220-1	13.312			
	220-2	13.300			
	220-3	13.188			
	220-4	13.308	13.277	0.060	0.45
15	245-1	13.310			
	245-2	13.185			
	245-3	13.324			
	245-4	13.369	13.297	0.079	0.59
16	258-1	13.293			
	258-2	13.331			
	258-3	13.397			
	258-4	13.172	13.298	0.094	0.71
17	278-1	13.399			
	278-2	13.319			
	278-3	13.191			
	278-4	13.544	13.363	0.148	1.11
18	293-1	13.438			
	293-2	13.169			
	293-3	13.308			
	293-4	13.118	13.258	0.144	1.09
19	314-1	13.180			
	314-2	13.357			
	314-3	13.215			
	314-4	13.303	13.264	0.081	0.61
20	325-1	13.443			
	325-2	13.293			
	325-3	13.315			
	325-4	13.280	13.333	0.075	0.56

M_{SS} – mean of means of the sub-samples 1-4	13.326	
SD of means of the sub-samples 1-4	0.054	
RSD (rel.%)	0.41	Mean RSD_w (%) 0.66

Analyte Na

HS = homogeneous sample

Line number	Sample number	Mass fraction Na 589.0
1	HS 1	13.431
2	HS 2	13.370
3	HS 3	13.267
4	HS 4	13.309
5	HS 5	13.136
6	HS 6	13.136
7	HS 7	13.157
8	HS 8	13.158
9	HS 9	13.305
10	HS 10	13.324
11	HS 11	13.371
12	HS 12	13.324
13	HS 13	13.365
14	HS 14	13.362
15	HS 15	13.259
16	HS 16	13.369

M_{HS} – mean of homogenous sample	13.290
SD_{HS}	0.095
RSD_{HS} (%)	0.72

Analyt Si

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Si 212.4	Mass fraction Si 221.6	Mass fraction Si 252.4	Mean over 3 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	16.622	17.085	16.604	16.770			
	20-2	15.509	16.025	15.770	15.768			
	20-3	15.207	15.990	15.488	15.562			
	20-4	14.634	15.440	15.000	15.025	15.781	0.730	4.63
2	29-1	14.653	15.108	14.665	14.808			
	29-2	13.367	13.752	13.428	13.516			
	29-3	13.956	14.336	14.071	14.121			
	29-4	14.308	14.812	14.509	14.543	14.247	0.564	3.96
3	47-1	15.579	15.808	15.473	15.620			
	47-2	15.089	15.567	15.407	15.354			
	47-3	14.889	15.559	15.137	15.195			
	47-4	14.540	15.401	14.798	14.913	15.271	0.296	1.94
4	68-1	14.349	14.665	14.276	14.430			
	68-2	14.102	14.542	14.210	14.285			
	68-3	14.665	15.166	14.934	14.922			
	68-4	14.615	15.038	14.788	14.814	14.612	0.304	2.08
5	89-1	15.459	15.809	15.402	15.556			
	89-2	15.089	15.621	15.398	15.369			
	89-3	13.826	14.485	14.068	14.126			
	89-4	13.536	14.407	13.886	13.943	14.749	0.831	5.64
6	100-1	14.594	14.922	14.485	14.667			
	100-2	13.999	14.392	14.020	14.137			
	100-3	14.528	15.083	14.732	14.781			
	100-4	13.745	14.470	14.056	14.090	14.419	0.356	2.47

Analyte Si

Line number	Sample number	Mass fraction Si 212.4	Mass fraction Si 221.6	Mass fraction Si 252.4	Mean over 3 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
7	109-1	15.046	15.417	15.102	15.188			
	109-2	14.481	15.101	14.809	14.797			
	109-3	14.350	14.979	14.545	14.625			
	109-4	13.826	14.684	14.142	14.218	14.707	0.403	2.74
8	133-1	14.950	15.213	14.884	15.016			
	133-2	13.866	14.282	13.836	13.995			
	133-3	15.659	16.347	15.945	15.984			
	133-4	14.318	14.846	14.477	14.547	14.885	0.843	5.66
9	146-1	14.995	15.364	15.152	15.170			
	146-2	14.488	15.100	14.774	14.787			
	146-3	13.977	14.531	14.147	14.218			
	146-4	14.379	15.245	14.653	14.759	14.734	0.392	2.66
10	164-1	14.398	14.677	14.360	14.478			
	164-2	14.119	14.502	14.072	14.231			
	164-3	13.035	13.513	13.304	13.284			
	164-4	14.227	14.756	14.363	14.449	14.111	0.562	3.98
11	184-1	15.643	15.988	15.783	15.805			
	184-2	14.871	15.502	15.181	15.185			
	184-3	14.055	14.665	14.356	14.359			
	184-4	15.979	16.810	16.417	16.402	15.438	0.874	5.66
12	191-1	14.175	14.344	14.110	14.210			
	191-2	13.991	14.503	14.031	14.175			
	191-3	13.522	13.909	13.744	13.725			
	191-4	14.736	15.638	15.151	15.175	14.321	0.611	4.26

Analyte Si

Line number	Sample number	Mass fraction Si 212.4	Mass fraction Si 221.6	Mass fraction Si 252.4	Mean over 3 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
13	207-1	15.299	15.738	15.439	15.492			
	207-2	14.872	15.586	15.217	15.225			
	207-3	14.440	15.087	14.701	14.743			
	207-4	14.762	15.619	15.134	15.172	15.158	0.310	2.05
14	220-1	13.650	13.978	13.702	13.777			
	220-2	13.810	14.259	13.865	13.978			
	220-3	13.772	14.211	13.959	13.981			
	220-4	14.017	14.599	14.275	14.297	14.008	0.215	1.53
15	245-1	14.434	14.923	14.664	14.674			
	245-2	14.992	15.683	15.332	15.336			
	245-3	14.153	14.919	14.430	14.501			
	245-4	15.038	15.911	15.446	15.465	14.994	0.478	3.19
16	258-1	13.868	14.269	13.927	14.021			
	258-2	13.761	14.284	13.855	13.967			
	258-3	14.661	15.101	14.962	14.908			
	258-4	14.204	14.792	14.455	14.484	14.345	0.441	3.08
17	278-1	14.636	15.123	14.851	14.870			
	278-2	14.617	15.325	14.976	14.973			
	278-3	13.981	14.769	14.300	14.350			
	278-4	14.215	14.999	14.510	14.575	14.692	0.283	1.93
18	293-1	13.415	13.841	13.441	13.566			
	293-2	13.435	13.936	13.519	13.630			
	293-3	13.900	14.382	14.115	14.132			
	293-4	14.162	14.816	14.467	14.481	13.952	0.434	3.11

Analyte Si

Line number	Sample number	Mass fraction Si 212.4	Mass fraction Si 221.6	Mass fraction Si 252.4	Mean over 3 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
19	314-1	14.368	14.822	14.578	14.590			
	314-2	15.110	15.831	15.545	15.495			
	314-3	14.146	14.939	14.492	14.526			
	314-4	14.715	15.674	15.034	15.141	14.938	0.463	3.10
20	325-1	13.479	13.927	13.574	13.660			
	325-2	14.005	14.598	14.159	14.254			
	325-3	13.928	14.354	14.120	14.134			
	325-4	14.317	14.936	14.583	14.612	14.165	0.393	2.78

M_{SS} – mean of means of the sub-samples 1-4	14.676
SD of means of the sub-samples 1-4	0.495

RSD (rel.%)	3.37

Mean RSD$_w$ (%) 3.32

Analyte Si

HS = homogeneous sample

Line number	Sample number	Mass fraction Si2124	Mass fraction Si2216	Mass fraction Si2524	Mean over 3 lines
1	HS 1	18.22	18.25	19.01	18.49
2	HS 2	19.56	19.74	20.45	19.92
3	HS 3	18.60	18.93	19.76	19.10
4	HS 4	18.76	18.70	19.68	19.05
5	HS 5	19.01	19.18	20.15	19.45
6	HS 6	18.09	18.17	18.97	18.41
7	HS 7	19.10	19.29	20.11	19.50
8	HS 8	17.98	18.12	18.95	18.35
9	HS 9	19.20	19.36	20.28	19.61
10	HS 10	17.99	18.22	19.12	18.45
11	HS 11	18.82	19.08	19.84	19.24
12	HS 12	18.52	18.81	19.64	18.99
13	HS 13	18.80	19.10	20.01	19.30
14	HS 14	18.55	18.81	19.64	19.00
15	HS 15	18.42	18.68	19.54	18.88
16	HS 16	18.65	18.91	19.67	19.08
17	HS 17	18.37	18.61	19.62	18.87
18	HS 18	18.26	18.61	19.39	18.75
19	HS 19	18.44	18.76	19.60	18.93

M_{HS} – mean of homogenous sample	19.02
SD_{HS}	0.43
RSD_{HS} (%)	2.24

Analyte Ti

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Ti 334.941	Mass fraction Ti 337.280	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
1	20-1	4.383	4.297	4.340			
	20-2	4.289	4.181	4.235			
	20-3	4.129	4.082	4.105			
	20-4	4.286	4.272	4.279	4.240	0.099	2.34
2	29-1	4.256	4.188	4.222			
	29-2	4.275	4.292	4.283			
	29-3	4.255	4.224	4.240			
	29-4	4.459	4.395	4.427	4.293	0.093	2.17
3	47-1	4.295	4.250	4.273			
	47-2	4.151	4.184	4.168			
	47-3	4.007	4.073	4.040			
	47-4	4.400	4.340	4.370	4.213	0.142	3.36
4	68-1	4.233	4.223	4.228			
	68-2	4.585	4.581	4.583			
	68-3	4.098	4.032	4.065			
	68-4	4.114	4.130	4.122	4.250	0.232	5.47
5	89-1	4.516	4.519	4.517			
	89-2	4.620	4.523	4.572			
	89-3	4.347	4.231	4.289			
	89-4	4.250	4.213	4.231	4.402	0.167	3.80
6	100-1	4.352	4.314	4.333			
	100-2	4.059	3.961	4.010			
	100-3	4.509	4.462	4.486			
	100-4	4.172	4.161	4.166	4.249	0.206	4.84

Analyte Ti

Line number	Sample number	Mass fraction Ti 334.941	Mass fraction Ti 337.280	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
7	109-1	4.849	4.835	4.842			
	109-2	4.325	4.332	4.328			
	109-3	4.191	4.156	4.173			
	109-4	4.436	4.425	4.430	4.444	0.286	6.44
8	133-1	4.374	4.310	4.342			
	133-2	4.038	3.979	4.009			
	133-3	4.533	4.464	4.499			
	133-4	4.402	4.356	4.379	4.307	0.210	4.87
9	146-1	4.448	4.471	4.460			
	146-2	4.198	4.176	4.187			
	146-3	4.457	4.384	4.421			
	146-4	4.473	4.433	4.453	4.380	0.130	2.96
10	164-1	4.398	4.308	4.353			
	164-2	4.379	4.335	4.357			
	164-3	4.789	4.771	4.780			
	164-4	4.674	4.580	4.627	4.529	0.211	4.66
11	184-1	4.343	4.329	4.336			
	184-2	4.188	4.148	4.168			
	184-3	4.073	4.045	4.059			
	184-4	4.114	4.087	4.101	4.166	0.122	2.93
12	191-1	4.185	4.107	4.146			
	191-2	4.154	4.180	4.167			
	191-3	4.250	4.203	4.226			
	191-4	4.250	4.184	4.217	4.189	0.039	0.93

Analyte Ti

Line number	Sample number	Mass fraction Ti 334.941	Mass fraction Ti 337.280	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
13	207-1	4.294	4.228	4.261			
	207-2	4.414	4.356	4.385			
	207-3	4.132	4.116	4.124			
	207-4	4.152	4.119	4.136	4.227	0.122	2.89
14	220-1	4.103	4.032	4.067			
	220-2	4.611	4.602	4.606			
	220-3	4.304	4.270	4.287			
	220-4	4.134	4.106	4.120	4.270	0.243	5.69
15	245-1	4.100	4.025	4.062			
	245-2	4.529	4.459	4.494			
	245-3	4.440	4.330	4.385			
	245-4	4.375	4.340	4.358	4.325	0.185	4.27
16	258-1	4.405	4.484	4.445			
	258-2	4.297	4.412	4.354			
	258-3	4.174	3.987	4.081			
	258-4	4.182	4.079	4.131	4.253	0.175	4.11
17	278-1	4.244	3.963	4.104			
	278-2	4.403	4.254	4.328			
	278-3	4.575	4.661	4.618			
	278-4	4.011	3.858	3.935	4.246	0.296	6.96
18	293-1	4.444	4.168	4.306			
	293-2	4.114	3.952	4.033			
	293-3	4.265	4.140	4.203			
	293-4	4.338	4.087	4.212	4.189	0.114	2.71

Analyte Ti

Line number	Sample number	Mass fraction Ti 334.941	Mass fraction Ti 337.280	Mean over 2 lines	mean of the sub-samples 1-4	SD of the sub-sample 1-4	RSDw (rel.%)
19	314-1	4.244	4.185	4.215			
	314-2	4.223	4.215	4.219			
	314-3	4.091	4.043	4.067			
	314-4	4.321	4.283	4.302	4.201	0.098	2.33
20	325-1	4.364	4.306	4.335			
	325-2	4.209	4.157	4.183			
	325-3	4.129	4.092	4.110			
	325-4	4.223	4.244	4.233	4.215	0.094	2.24

M_{SS} – mean of means of the sub-samples 1-4   4.279

SD of means of the sub-samples 1-4   0.095

RSD (rel.%)   2.21   mean RSD$_w$ (%)   3.80

Analyte Ti

HS = sample solution for comparison

Line number	Sample number	Mass fraction Ti 334.941	Mass fraction Ti 337.280	Mean over 2 lines
1	HS 1	3.794	3.744	3.769
2	HS 2	3.783	3.713	3.748
3	HS 3	3.772	3.718	3.745
4	HS 4	3.758	3.736	3.747
5	HS 5	3.775	3.697	3.736
6	HS 6	3.762	3.685	3.724
7	HS 7	3.738	3.713	3.726
8	HS 8	3.782	3.791	3.786
9	HS 9	3.740	3.740	3.740
10	HS 10	3.744	3.784	3.764
11	HS 11	3.780	3.755	3.768
12	HS 12	3.793	3.785	3.789
13	HS 13	3.809	3.709	3.759

M_{HS} – mean of homogenous sample	3.754
SD_{HS}	0.021
RSD_{HS} (%)	0.56

Analyte Total Boron

Mass fraction in %

Line number	Sample number	Mass fraction Values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel.%)
1	020/1	43.25			
	020/2	43.20			
	020/3	43.30			
	020/4	43.25	43.250	0.041	0.09
2	047/1	43.25			
	047/2	43.25			
	047/3	43.25			
	047/4	43.20	43.238	0.025	0.06
3	089/1	43.20			
	089/2	43.20			
	089/3	43.20			
	089/4	43.20	43.200	0.000	0.00
4	109/1	43.20			
	109/2	43.25			
	109/3	43.15			
	109/4	43.20	43.200	0.041	0.09
5	146/1	43.20			
	146/2	43.15			
	146/3	43.25			
	146/4	43.20	43.200	0.041	0.09
6	184/1	43.15			
	184/2	43.20			
	184/3	43.20			
	184/4	43.25	43.200	0.041	0.09
7	207/1	43.15			
	207/2	43.25			
	207/3	43.25			
	207/4	43.25	43.225	0.050	0.12
8	245/1	43.20			
	245/2	43.20			
	245/3	43.25			
	245/4	43.20	43.213	0.025	0.06
9	278/1	43.15			
	278/2	43.20			
	278/3	43.25			
	278/4	43.15	43.188	0.048	0.11
10	314/1	43.20			
	314/2	43.25			
	314/3	43.25			
	314/4	43.20	43.225	0.029	0.07

M_{SS} – mean of means of the sub-samples 1-4	43.214	
SD of means of the sub-samples 1-4	0.020	
RSD (rel.%)	0.05	mean RSD_w (%) 0.08

Analyte Total Boron

HS = homogeneous sample

Line number	Sample number	Mass fraction Values
1	HS1	43.20
2	HS2	43.25
3	HS3	43.20
4	HS4	43.15
5	HS5	43.15
6	HS6	43.25
7	HS7	43.20
8	HS8	43.20
9	HS9	43.25
10	HS10	43.25

M_{HS} **- mean of homogeneous sample**	43.210
SD_{HS}	0.039
RSD_{HS} **(%)**	0.09

Analyte Boron oxide

Mass fraction in %

Line number	Sample number	Mass fraction Values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
1	020/1	0.071			
	020/2	0.072			
	020/3	0.073			
	020/4	0.072	0.0720	0.0008	1.13
2	047/1	0.070			
	047/2	0.070			
	047/3	0.071			
	047/4	0.072	0.0708	0.0010	1.35
3	089/1	0.072			
	089/2	0.071			
	089/3	0.073			
	089/4	0.071	0.0718	0.0010	1.33
4	109/1	0.072			
	109/2	0.070			
	109/3	0.071			
	109/4	0.071	0.0710	0.0008	1.15
5	146/1	0.072			
	146/2	0.072			
	146/3	0.072			
	146/4	0.070	0.0715	0.0010	1.40
6	184/1	0.070			
	184/2	0.072			
	184/3	0.070			
	184/4	0.073	0.0713	0.0015	2.11
7	207/1	0.071			
	207/2	0.072			
	207/3	0.070			
	207/4	0.072	0.0713	0.0010	1.34
8	245/1	0.072			
	245/2	0.073			
	245/3	0.070			
	245/4	0.07	0.0713	0.0015	2.11
9	278/1	0.072			
	278/2	0.070			
	278/3	0.071			
	278/4	0.072	0.0713	0.0010	1.34
10	314/1	0.072			
	314/2	0.072			
	314/3	0.070			
	314/4	0.072	0.0715	0.0010	1.40

M$_{ss}$ - mean of means of the sub-samples 1-4	0.0714	
SD of means of the sub-samples 1-4	0.0004	
RSD (rel.%)	0.50	mean RSD$_w$ (%)　1.47

Analyte Boron oxide

HS = homogeneous sample

Line number	Sample number	Mass fraction Values
1	HS1	0.106
2	HS2	0.105
3	HS3	0.106
4	HS4	0.106
5	HS5	0.107
6	HS6	0.107
7	HS7	0.110
8	HS8	0.109
9	HS9	0.110
10	HS10	0.108

M_{HS} **mean of homogeneous sample**	0.1074
SD_{HS}	0.0018
RSD_{HS} (%)	1.65

Analyte Carbon

Mass fraction in mg/kg

Line number	Sample number	Mass fraction Values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (rel.%)
1	020/1	149.5			
	020/2	159.0			
	020/3	155.5			
	020/4	156.0	155.0	3.979	2.57
2	047/1	155.5			
	047/2	151.5			
	047/3	161.5			
	047/4	150.5	154.8	4.992	3.23
3	089/1	149.5			
	089/2	155.0			
	089/3	155.5			
	089/4	155.0	153.8	2.843	1.85
4	109/1	148.5			
	109/2	156.5			
	109/3	157.0			
	109/4	156.0	154.5	4.021	2.60
5	146/1	156.0			
	146/2	151.0			
	146/3	157.5			
	146/4	152.5	154.3	3.014	1.95
6	184/1	161.0			
	184/2	153.0			
	184/3	157.5			
	184/4	149.5	155.3	5.041	3.25
7	207/1	158.5			
	207/2	154.0			
	207/3	151.5			
	207/4	158.0	155.5	3.342	2.15
8	245/1	154.5			
	245/2	150.5			
	245/3	157.5			
	245/4	153.0	153.9	2.926	1.90
9	278/1	150.5			
	278/2	157.5			
	278/3	158.5			
	278/4	153.5	155.0	3.697	2.39
10	314/1	158.0			
	314/2	153.5			
	314/3	155.0			
	314/4	157.5	156.0	2.121	1.36

M$_{ss}$ - mean of means of the sub-samples 1-4	154.79	
SD of means of the sub-samples 1-4	0.712	
RSD (rel.%)	0.46	mean RSD$_w$ (%) 2.32

Analyte Carbon

HS = Homogeneous sample

Line number	Sample number	Mass fraction Value
1	HS1	159.5
2	HS2	154.5
3	HS3	156.5
4	HS4	152.5
5	HS5	154.5
6	HS6	149.5
7	HS7	154.5
8	HS8	160.5
9	HS9	155.0
10	HS10	151.0

M_{HS} **mean of homogeneous sample**	154.80
SD_{HS}	3.425
RSD_{HS} (%)	2.21

Analyte Nitrogen

Mass fraction in %

Line number	Sample number	Mass fraction Values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD_w (rel. %)
1	020/1	55.49			
	020/2	55.42			
	020/3	55.40			
	020/4	55.50	55.452	0.051	0.09
2	047/1	55.45			
	047/2	55.57			
	047/3	55.43			
	047/4	55.43	55.470	0.068	0.12
3	089/1	55.36			
	089/2	55.50			
	089/3	55.41			
	089/4	55.45	55.430	0.061	0.11
4	109/1	55.41			
	109/2	55.35			
	109/3	55.35			
	109/4	55.48	55.398	0.061	0.11
5	146/1	55.50			
	146/2	55.59			
	146/3	55.52			
	146/4	55.53	55.535	0.037	0.07
6	184/1	55.48			
	184/2	55.52			
	184/3	55.46			
	184/4	55.46	55.481	0.029	0.05
7	207/1	55.38			
	207/2	55.52			
	207/3	55.36			
	207/4	55.37	55.410	0.075	0.14
8	245/1	55.55			
	245/2	55.57			
	245/3	55.52			
	245/4	55.56	55.551	0.021	0.04
9	278/1	55.38			
	278/2	55.39			
	278/3	55.35			
	278/4	55.49	55.404	0.060	0.11
10	314/1	55.39			
	314/2	55.47			
	314/3	55.55			
	314/4	55.54	55.487	0.076	0.14

M_{ss} - mean of means of the sub-samples 1-4   55.462

SD of means of the sub-samples 1-4   0.053

RSD (rel.%)   0.10   mean RSD_w (%)   0.10

Analyte Nitrogen

HS = Homogeneous sample

Line number	Sample number	Mass fraction Values
1	HS1	55.40
2	HS2	55.52
3	HS3	55.42
4	HS4	55.53
5	HS5	55.46
6	HS6	55.50
7	HS7	55.41
8	HS8	55.40
9	HS9	55.35
10	HS10	55.47

M_{HS} - mean of homogeneous sample	55.447
SD_{HS}	0.059
RSD_{HS} (%)	0.11

Analyte Oxygen

Mass fraction in %

Line number	Sample number	Mass fraction Values	mean of sub-samples 1-4	SD of sub-samples 1-4	RSD$_w$ (%)
1	020/1	0.718			
	020/2	0.716			
	020/3	0.716			
	020/4	0.709	0.715	0.004	0.51
2	047/1	0.709			
	047/2	0.718			
	047/3	0.716			
	047/4	0.715	0.714	0.004	0.56
3	089/1	0.718			
	089/2	0.719			
	089/3	0.719			
	089/4	0.718	0.719	0.001	0.08
4	109/1	0.715			
	109/2	0.714			
	109/3	0.717			
	109/4	0.710	0.714	0.003	0.38
5	146/1	0.718			
	146/2	0.709			
	146/3	0.711			
	146/4	0.709	0.712	0.004	0.60
6	184/1	0.707			
	184/2	0.719			
	184/3	0.714			
	184/4	0.722	0.716	0.007	0.91
7	207/1	0.715			
	207/2	0.718			
	207/3	0.717			
	207/4	0.714	0.716	0.002	0.28
8	245/1	0.720			
	245/2	0.714			
	245/3	0.716			
	245/4	0.713	0.716	0.003	0.40
9	278/1	0.723			
	278/2	0.715			
	278/3	0.711			
	278/4	0.709	0.714	0.006	0.86
10	314/1	0.714			
	314/2	0.718			
	314/3	0.713			
	314/4	0.714	0.715	0.002	0.34

M$_{ss}$ mean of means of the sub-samples 1-4	0.715	
SD of means of the sub-samples 1-4	0.0017	
RSD (rel.%)	0.24	mean RSD$_w$ (%) 0.49

Analyte Oxygen

HS = Homogeneous sample

Line number	Sample number	Mass fraction Values
1	HS1	0.77
2	HS2	0.77
3	HS3	0.77
4	HS4	0.77
5	HS5	0.76
6	HS6	0.76
7	HS7	0.77
8	HS8	0.76
9	HS9	0.76
10	HS10	0.76

M_{HS} - mean of homogeneous sample	0.765
SD_{HS}	0.0023
RSD_{HS} (%)	0.30

Appendix 3:

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
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250 °C - 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL PFA flask	**1000 mg/L Al** Merck, Certipur - Calibration: 0 - 75 µg/L Al; - matrix matching using H$_3$BO$_3$, HNO$_3$, HF and HCl. - Sc as internal standard	ICP OES
3	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 12 h at 250 °C - resulting solution diluted to 50 mL PFA flask	**9997.2 mg/L** Al (Alfa J.M. 5N Al in 20% v/v HCl + 1% v/v HNO$_3$ - Calibration: 6, 12, 18, 24, 30 µg/L Al - matrix matching using H$_3$BO$_3$ Merck HNO$_3$, HF	ET AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO$_3$ + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250 °C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Al** Merck, Certipur is compared with ICP IV standard. - Calibration: 0, 4, 8, 12 µg/L Al; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO$_3$ + 6 mL H$_2$SO$_4$ - Molecular breaker with high pressure - 9 h at 250 °C - Fume off to near dryness - 6 mL H$_2$SO$_4$ and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Al; - Acid of quantity same as sample solution Sc as internal standard were used	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$,8 mL HF, 1 mL H$_2$SO$_4$(1+1) - High pressure oxidation - 16h at 240 °C	**1000 mg/L** - Calibration: 0, 0.1875, 0375, 0.5625, 0.750 mg/L Al	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO$_3$ + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**2279 mg/L Al** 5N from Ventron in 8 % v/v HCl + 0.2 % v/v HNO$_3$ - addition calibrate 0, 0.03613, 0.06889 mg/L Al	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO$_3$ + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Al** Merck Certipur is compared with 1000 mg/L Al (Baker) - calibration: 0 – 200 µg/L Al	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$ + 7 mL HF - DAB-II, Berghof, 24 h at 200 °C - solution fumed off in Pt dishes with 15 mL HClO$_4$ - fumed off 2 x with 10 mL H$_2$O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Al** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1 mg/L Al - Matrix matching with 2.492 g HgBO$_3$	ICP OES
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO$_3$ + HF - DAB-II, Berghof at 200 °C - The end concentration is 5 g/L B	**1000 mg/L Al** Kraft - Calibration: 0 – 5 mg/L Al; - Matrix matching with HF/HNO$_3$/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240 °C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Al** Kraft is compared with Merck Certipur - addition calibration: 0 – 0.2 mg/L were used	ICP OES

Aluminium			
Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**NO SAMPLE PREPARATION**: - M: 7.5 mg (3x2.5 mg); - ETV-program: pretreatment: 30 s at 400 °C; heating: 4s at 1950 °C, hold 26 s 1950 °C. - Carrier gas 350 mL/min - Reaction gas Freon R12.	**999.72 mg/L Al** (Alfa J.M.) - calibration with 5 mg/L Al = 10, 20, 35, 50, 65, 90 100 ng	ETV-ICP OES
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Al** Al(NO$_3$)$_3$ Merck in 0.5 mol HNO$_3$ - calibration with 10 mg/L Al = 10, 20, 30, 40, 60, 80 ng	ETV-ICP OES

Round Robin for Certification of Boron Nitride Powder

Calcium			
Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250°C - 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL PFA flask	**994.34 mg/L Ca** from 99.999 % $CaCO_3$ Alfa J.M. specpure - Calibration: 0 -2.9841 mg/L Ca; - matrix matching using H_3BO_3, HNO_3, HF and HCl. - Sc as internal standard	ICP OES
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250°C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Ca** Merck, Certipur is compared with ICP IV standard. - Calibration: 0, 100. 200, 300 µg/L Ca; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO_3 + 6 mL H_2SO_4 - Molecular breaker with high pressure - 9 h at 250°C - Fume off to near dryness - 6 mL H_2SO_4 and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 1.0, 2.0 mg/L Ca - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
11	**ACID DECOMPOSITION**: - M: 0.25 g; 3 mL HNO_3 + 3 mL HF + 5 mL H_2SO_4 - 12 h at 160°C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Ca**	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 ,8 mL HF, 1 mL H_2SO_4(1+1) - High pressure oxidation - 16h at 240°C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Ca	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO_3 + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Ca** from $CaCO_3$ in 0.5 % v/v HNO_3 - addition calibrate 0, 1.58529, 3.02297 mg/L Ca	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO_3 + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Ca** Merck Certipur is compared with 1000 mg/L Ca (Baker) - calibration: 0 – 2 mg/L Ca	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 + 7 mL HF - DAB-II, Berghof, 24 h at 200°C - solution fumed off in Pt dishes with 15 mL $HClO_4$ - fumed off 2 x with 10 mL H_2O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Ca** Alfa Aesar - Calibration: 0, 0.5, 1, 2.5, 5, 7.5 mg/L Ca - Matrix matching with 2.492 g $HgBO_3$	F AAS
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200°C - The end concentration is 5 g/L B	**1000 mg/L Ca** Kraft - Calibration: 0 – 1 mg/L Ca; - Matrix matching with HF/HNO_3/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Ca** Kraft is compared with Merck Certipur - standard addition method: 0 – 5 mg/L Ca were used	F AAS
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Ca** $Ca(NO_3)_2$ Merck in 0.5 mol HNO_3 - calibration with 50 mg/L Ca = 50, 100, 150, 200, 300, 400 ng	ETV-ICP OES

Cobalt

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
3	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 12 h at 250 °C - resulting solution diluted to 50 mL PFA flask	**7011.8 mg/L Co;** Alfa J.M. m3N5 Co in 10% v/v HNO_3 - Calibration: 0.1, 0.2, 0.3, 0.4 µg/L Co - Addition calibration technique was used. Analyte enrichment by drying 4 times 50 µL sample	ET AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250 °C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Co** Merck, Certipur is compared with ICP IV standard. - Calibration: 0, 0.4, 0.8, 1.2 µg/L Co; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO_3 + 6 mL H_2SO_4 - Molecular breaker with high pressure - 9 h at 250 °C - Fume off to near dryness - 6 mL H_2SO_4 and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Co - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 ,8 mL HF, 1 mL H_2SO_4(1+1) - High pressure oxidation - 16h at 240 °C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Co	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO_3 + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**4002.8 mg/L Co** from J.M. in 10 % v/v HNO_3 - addition calibrate 0, 0.01904, 0.03630 mg/L Co	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO_3 + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Co** Merck Certipur is compared with 1000 mg/L Co (Baker) - calibration: 0 – 0.2 mg/L Co	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 + 7 mL HF - DAB-II, Berghof, 24 h at 200 °C - solution fumed off in Pt dishes with 15 mL $HClO_4$ - fumed off 2 x with 10 mL H_2O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Co** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1 mg/L Co - Matrix matching with 2.492 g $HgBO_3$	ICP OES
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200 °C - The end concentration is 5 g/L B	**1000 mg/L Co** Kraft - Calibration: 0 – 5 mg/L Co; - Matrix matching with HF/HNO_3/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240 °C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Co** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.5 mg/L Co were used	F AAS
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Co** $Co(NO_3)_2$ Merck in 0.5 mol HNO_3 - calibration with 0.5 mg/L Co = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng	ETV-ICP OES

Chromium

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250 °C - 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL PFA flask	**9992.64 mg/L Cr** from 99.995 % Cr Alfa J.M. flake - Calibration: 0 – 39.97 µg/L Cr; - matrix matching using H_3BO_3, HNO_3, HF and HCl. - Sc as internal standard	ICP OES
3	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 12 h at 250 °C - resulting solution diluted to 50 mL PFA flask	**9992.6 mg/L Cr** Alfa J.M. 99.995 % Cr in 28% v/v HCl + 0.4% v/v HNO_3 - Calibration: 1, 2, 3, 4, 5 µg/L Cr - Addition calibration technique was used.	ET AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250 °C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Cr** Merck, Certipur is compared with ICP IV standard. - Calibration: 2, 4, 6 µg/L Cr; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO_3 + 6 mL H_2SO_4 - Molecular breaker with high pressure - 9 h at 250 °C - Fume off to near dryness - 6 mL H_2SO_4 and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Cr - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 ,8 mL HF, 1 mL H_2SO_4(1+1) - High pressure oxidation - 16h at 240 °C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Cr	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO_3 + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**1007.5 mg/L Cr** from J.M. in 3 % v/v HCl + 1% v/v HNO_3 - addition calibrate 0, 0.019166, 0.03655 mg/L Cr	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO_3 + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Cr** Merck Certipur is compared with 1000 mg/L Cr (Baker) - calibration: 0 – 0.2 mg/L Cr	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 + 7 mL HF - DAB-II, Berghof, 24 h at 200 °C - solution fumed off in Pt dishes with 15 mL $HClO_4$ - fumed off 2 x with 10 mL H_2O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Cr** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1 mg/L Cr - Matrix matching with 2.492 g $HgBO_3$	ICP OES
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200 °C - The end concentration is 5 g/L B	**1000 mg/L Cr** Kraft - Calibration: 0 – 5 mg/L Cr; - Matrix matching with HF/HNO_3/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Cr** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.2 mg/L Cr were used	ICP OES
2	**NO SAMPLE PREPARATION**: - M: 7.5 mg (3x2.5 mg); - ETV-program: pretreatment: 30 s at 400 °C; heating: 4s at 1950 °C, hold 26 s 1950 °C. - Carrier gas 350 mL/min - Reaction gas Freon R12.	**9992.6 mg/L Cr** (Alfa J.M.) - calibration with 1.25 mg/L Cr = 2.5, 5, 9, 13, 16, 20, 25 ng	ETV-ICP OES
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Cr** $Cr(NO_3)_2$ Merck in 0.5 mol HNO_3 - calibration with 2.5 mg/L Cr = 2.5, 5.0, 7.5, 10.0, 15.0, 20.0 ng	ETV-ICP OES

Iron

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250 ℃ - 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL PFA flask	**1000 mg/L Fe**, Merck Certipur - Calibration: 0 – 150 µg/L Fe; - matrix matching using H$_3$BO$_3$, HNO$_3$, HF and HCl. - Sc as internal standard	ICP OES
3	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 12 h at 250 ℃ - resulting solution diluted to 50 mL PFA flask	**21441.7 mg/L Fe** Reacton J.M. m3N Fe in 2% v/v HCl +10% v/v HNO$_3$ - Calibration:4, 8, 12, 16, 20 µg/L Fe - Addition calibration technique was used. - matrix matching using H$_3$BO$_3$, Merck HNO$_3$, HF	ET AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO$_3$ + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250 ℃ - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Fe** Merck, Certipur is compared with ICP IV standard. - Calibration: 4, 8, 12 µg/L Fe; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO$_3$ + 6 mL H$_2$SO$_4$ - Molecular breaker with high pressure - 9 h at 250 ℃ - Fume off to near dryness - 6 mL H$_2$SO$_4$ and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Fe - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
11	**ACID DECOMPOSITION**: - M: 0.25 g; 3 mL HNO$_3$ + 3 mL HF + 5 mL H$_2$SO$_4$ - 12 h at 160 ℃ - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Fe**	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$,8 mL HF, 1 mL H$_2$SO$_4$(1+1) - High pressure oxidation - 16h at 240 ℃	**1000 mg/L** - Calibration: 0, 0.1875, 0375, 0.5625, 0.750 mg/L Fe	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO$_3$ + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 ℃; rising to 15 min at 240 ℃. - resulting solution diluted to 50 mL PFA flask	**9989.5 mg/L Fe** 5N from Aldrich in 3 % v/v HCl - addition calibrate 0, 0.12669, 0.24158 mg/L Fe	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO$_3$ + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 ℃ - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Fe** Merck Certipur is compared with 1000 mg/L Fe (Baker) - calibration: 0 – 0.2 mg/L Fe	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$ + 7 mL HF - DAB-II, Berghof, 24 h at 200 ℃ - solution fumed off in Pt dishes with 15 mL HClO$_4$ - fumed off 2 x with 10 mL H$_2$O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Fe** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1 mg/L Fe - Matrix matching with 2.492 g HgBO$_3$	ICP OES
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO$_3$ + HF - DAB-II, Berghof at 200 ℃ - The end concentration is 5 g/L B	**1000 mg/L Fe** Kraft - Calibration: 0 – 5 mg/L Fe; - Matrix matching with HF/HNO$_3$/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240℃). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Fe** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.5 mg/L Fe were used	F AAS
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Fe** Fe(NO$_3$)$_3$ Merck in 0.5 mol HNO$_3$ - calibration with 50 mg/L Fe = 50, 100, 150, 200, 300, 400 ng	ETV-ICP OES

Magnesium

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250°C - 2 mL HCl and Sc as internal standard added to resulting solution and diluted to 50 mL PFA flask	**1002.7 mg/L Mg**, from Alfa J.M. 99.98 % Mg pieces - Calibration: 0 – 601.62 µg/L Mg; - matrix matching using H_3BO_3, HNO_3, HF and HCl. - Sc as internal standard	ICP OES
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250°C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Mg** Merck, Certipur is compared with ICP IV standard. - Calibration: 20, 40, 60 µg/L Mg; - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO_3 + 6 mL H_2SO_4 - Molecular breaker with high pressure - 9 h at 250°C - Fume off to near dryness - 6 mL H_2SO_4 and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Mg - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
11	**ACID DECOMPOSITION**: - M: 0.25 g; 3 mL HNO_3 + 3 mL HF + 5 mL H_2SO_4 - 12 h at 160°C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Mg**	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 ,8 mL HF, 1 mL H_2SO_4(1+1) - High pressure oxidation - 16h at 240°C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Mg	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO_3 + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**9996.7 mg/L Mg** 3N5 from J.M. in 10 % v/v HCl - addition calibrate 0, 0.47543, 0.90659 mg/L Mg	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO_3 + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Mg** Merck Certipur is compared with 1000 mg/L Mg (Baker) - calibration: 0 – 0.4 mg/L Mg	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 + 7 mL HF - DAB-II, Berghof, 24 h at 200°C - solution fumed off in Pt dishes with 15 mL $HClO_4$ - fumed off 2 x with 10 mL H_2O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Mg** Alfa Aesar - Calibration: 0, 0.5, 1, 2.5, 5, 7.5 mg/L Mg - Matrix matching with 2.492 g $HgBO_3$	F AAS
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200°C - The end concentration is 5 g/L B	**1000 mg/L Mg** Kraft - Calibration: 0 – 1 mg/L Mg; - Matrix matching with HF/HNO_3/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Mg** Kraft is compared with Merck Certipur - standard addition method: 0 – 10 mg/L Mg were used	F AAS
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Mg,** $Mg(NO_3)_2$ Merck in 0.5 mol HNO_3 - calibration with 5 mg/L Mg = 5, 10, 15, 20, 30, 40 ng	ETV-ICP OES

Sodium

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250°C - 2 mL HCl to resulting solution and diluted to 50 mL PFA flask - 0.1% CsCl as ionisations buffer added to 10 mL sample solution	**1000 mg/L Na**, Merck Certipur - Calibration: 0, 0.05, 0.1, 0.15, 0.2 mg/L Na; - matrix matching using H$_3$BO$_3$, HNO$_3$, HF and HCl. - added 0.1% CsCl as ionisations buffer	F AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO$_3$ + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250°C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Na** Merck, Certipur is compared with ICP IV standard. - Calibration: 4, 8, 12 µg/L Na; - addition calibration and Sc as internal standard were used	ICP-MS
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$,8 mL HF, 1 mL H$_2$SO$_4$(1+1) - High pressure oxidation - 16h at 240°C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Na	ET AAS
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO$_3$ + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**1000.2 mg/L Na** from Na$_2$CO$_3$ p.a. anhydrous in 2.5 % v/v HCl - addition calibrate 0, 0.19027, 0.36283 mg/L Na	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO$_3$ + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Na** Merck Certipur is compared with 1000 mg/L Na (Baker) - calibration: 0 – 0.2 mg/L Na	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO$_3$ + 7 mL HF - DAB-II, Berghof, 24 h at 200°C - solution fumed off in Pt dishes with 15 mL HClO$_4$ - fumed off 2 x with 10 mL H$_2$O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Na** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1.0 mg/L Na - Matrix matching with 2.492 g HgBO$_3$	F AAS
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO$_3$ + HF - DAB-II, Berghof at 200°C - The end concentration is 5 g/L B	**1000 mg/L Na** Kraft - Calibration: 0 – 1 mg/L Na; - Matrix matching with HF/HNO$_3$/HCl and 5 g/L B	F AAS
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO$_3$ + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Na** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.25 mg/L Na - Addition from 0.05 % CsCl	F AAS
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Na,** NaNO$_3$ Merck in 0.5 mol HNO$_3$ - calibration with 10 mg/L Na = 10, 20, 30, 40, 60, 80 ng	ETV-ICP OES

Silicon

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250°C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**10241 mg/L Si,** Si cubes 5N+ Alfa J.M. is compared with Si solution from Alfa Aesar - Calibration: 10, 20, 30 µg/L Si; - addition calibration and Sc as internal standard were used	ICP-MS
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200°C - The end concentration is 5 g/L B	**1000 mg/L Si** Kraft - Calibration: 0 – 5 mg/L Si; - Matrix matching with $HF/HNO_3/HCl$ and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Si** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.2 mg/L Si	ICP OES
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Si,** $(NO_4)_2SiF_6$ Merck in H_2O - calibration with 50 mg/L Si = 50, 100, 150, 200, 300, 400 ng	ETV-ICP OES

Titanium

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250°C - 2 mL HCl to resulting solution and diluted to 50 mL PFA flask	**1000 mg/L Ti**, Merck Certipur - Calibration: 0 – 40 µg/L Ti; - matrix matching using H_3BO_3, HNO_3, HF and HCl.	ICP OES
3	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 10 h at 250°C - to resulting solution diluted to 50 mL PFA flask - atom. 2550°C, 0/6 s, 50 mL/min gas mixture of 1% $CHClF_2$ / 2% H_2/Ar	**1000 mg/L Ti**, Merck Certipur - Calibration: 10, 20, 30, 40, 50 µg/L Ti - Additions calibration technique was used	ET AAS
4	**ACID DECOMPOSITION**: - M: 0.5 g; 5 mL HNO_3 + 10 mL HF - DAB-III, Berghof (150 mL TFM-liners) - 9 h at 250°C - resulting solution diluted to 50 mL PFA flask - sample dilution 1:10 and Sc as internal standard	**1000 mg/L Ti** Alfa Aesar is compared with Ti solution (Alfa Aesar from another charge) - Calibration: 2, 4, 6 µg/L Ti - addition calibration and Sc as internal standard were used	ICP-MS
9	**ACID DECOMPOSITION**: - M: 0.5 g; 4 mL HF, 4 mL HNO_3 + 6 mL H_2SO_4 - Molecular breaker with high pressure - 9 h at 250°C - Fume off to near dryness - 6 mL H_2SO_4 and 5 mL (1+1) HCl and - Sc as internal standard were added - resulting solution diluted to 100 mL flask	**1000 mg/L** - Calibration: 0, 0.5, 1.0 mg/L Ti - Acid of quantity same as sample solution - Sc as internal standard were used	ICP OES
11	**ACID DECOMPOSITION**: - M: 0.25 g; 3 mL HNO_3 + 3 mL HF + 5 mL H_2SO_4 - 12 h at 160°C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L MTi**	ICP OES
15	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 ,8 mL HF, 1 mL H_2SO_4(1+1) - High pressure oxidation - 16h at 240°C	**1000 mg/L** - Calibration: 0, 0.125, 0250, 0.375, 0.500 mg/L Ti	ICP OES
16	**ACID DECOMPOSITION**: - M: 0.5 g; 6.5 mL HNO_3 + 6.5 mL HF - micro wave oven (MLS Ethos 1600); MR-10 TFM vessel - 120 min at 230 °C; rising to 15 min at 240 °C. - resulting solution diluted to 50 mL PFA flask	**3491.6 mg/L Ti** 5N from in 2 % v/v HF + 1.5 % v/v HNO_3 10 % v/v HCl - addition calibrate 0, 0.03321, 0.06333 mg/L Ti	ICP OES
20	**ACID DECOMPOSITION**: - M: 0.25 g; 1.5 mL HNO_3 + 2.5 mL HF - DAB-II (150 mL TFM-liners) - 20 h at 200 °C - resulting solution diluted to 50 mL PFA flask	**1000 mg/L Ti** Merck Certipur is compared with 1000 mg/L Ti (Baker) - calibration: 0 – 0.2 mg/L Ti	ICP OES
24	**ACID DECOMPOSITION**: - M: 1.0 g; 3 mL HNO_3 + 7 mL HF - DAB-II, Berghof, 24 h at 200°C - solution fumed off in Pt dishes with 15 mL $HClO_4$ - fumed off 2 x with 10 mL H_2O - residue in 10 mL HCl (37 %) dissolved and diluted to 100 mL in TPX-flask	**1000 mg/L Ti** Alfa Aesar - Calibration: 0, 0.05, 0.1, 0.2, 0.5, 1.0 mg/L Ti - Matrix matching with 2.492 g $HgBO_3$	ICP OES
25	**ACID DECOMPOSITION**: - M: 1.148 g; HNO_3 + HF - DAB-II, Berghof at 200°C - The end concentration is 5 g/L B	**1000 mg/L Ti** Kraft - Calibration: 0 – 5 mg/L Ti; - Matrix matching with HF/HNO_3/HCl and 5 g/L B	ICP OES
26	**ACID DECOMPOSITION**: - M: 0.5 g; 3 mL HNO_3 + 5 mL HF - Multiwave, Anton Paar (PTFE-liners) - 10 min at 400 W + 30 min 800 W (T=240°C). - resulting solution diluted to 100 mL PMP flask - Addition from 0.05 % CsCl	**1000 mg/L Ti** Kraft is compared with Merck Certipur - standard addition method: 0 – 0.2 mg/L Ti	ICP OES
17	**NO SAMPLE PREPARATION**: - The sample was pressed at the pressure 150 KN. - Semi-quantitative analysis was carried out.	No calibration used	XRF
21	**NO SAMPLE PREPARATION**: - M: 5 mg	**1000 mg/L Ti,** $(NO_4)_2TiF_6$ Merck in H_2O - calibration with 100 mg/L Ti = 100, 200, 300, 400, 600, 800 ng	ETV-ICP OES

Total Boron			
Lab code	**Sample Preparation (M = mass of sub-samples)**	**Calibration**	**Final Determination**
5	**DIGESTION**: - M: 150 mg (recommended method M1, ASTM C971)	**H_3BO_3 s.p.**	Titr.
6	**DIGESTION**: - M: 100 mg - sample fused with Na_2CO_3 - dissolved in 60 mL of 1+1 HCl - yttrium as an internal standard	**1000 mg/L B** solution from VWR Calibration: - 50 mg/L B in 0.5% Na_2CO_3 and HCl - yttrium as an internal standard	ICP OES
15	**DIGESTION**: - M: 100 mg; - added 0.5 mg C_2H_5OH + 0.5 mL 20% NaOH → drying - melting fusion with 3 g Na_2CO_3 - dissolution in 1+1 HCl and neutralize to pH 6.4 - titrated after addition of 25 g mannitol with 0.1 M NaOH. (recommended method M1, ASTM C971)	**0.1 M NaOH**	Titr.
21	**DIGESTION**: - M: 200 mg; - melting fusion with 5 g $NaKCO_3$ in a Pt cricible - dissolution in 1+1 HCl - titrated after addition of mannitol (recommended method M1, ASTM C971)	**NaOH** - Potentiometric titration with in presence of mannitol. Determination of titrimetric factor using H_3BO_3 and corr. factor of 0.1 N NaOH solution using potassium hydrogen-phthalate.	Titr.
25	**DIGESTION**: - M: 500 mg; - addition 15 g Na_2CO_3 / K_2CO_3 in a muffle type furnace at 750°C - final digestion addition of $NaNO_3$ with a Bunsen Burner, leaching with H_2O, addition of HCl - boiling off removal of CO_2	**0.2 N NaOH** - with addition from mannitol - Determination of titer strength with potassium hydrogen-phthalate.	Titr.
26	**DIGESTION**: - M: 150 mg; - melting fusion in 10 g $NaKCO_3$ + 1 g KNO_3 - solved in water and titrated titrated after addition of mannitol (recommended method M1, ASTM C971)	**NaOH** - Standard solution of Merck controlled by solution of H_2SO_4 controlled with Na_2CO_3 primary substance	Titr.

Adherent Boron oxide

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	**DIGESTION:** - M: 1 g; added 150 mL water - Extraction on a heating and stirring plate 1 h at 60 °C - Added 0.1 mL HCl to solution and Sc as internal standard and filtrated - diluted to 250 mL quartz flask	**1000 mg/L B**, Merck Certipur - Calibration: 0, 0.25, 0.5, 0.75, 1.0 mg/L B in milli-Q-water	ICP OES
5	**DIGESTION:** - M: 6 g (recommended method M1, ASTM C971)	**H_3BO_3** s.p.	Titr.
20	**DIGESTION:** - M: 0.5 g; added 150 mL water - 1 h at 60 °C heated in a water bath - Added 0.2 mL HCl to solution and diluted to 250 mL quartz flask. The clear over-laying solution was measured	**1000 mg/L B**, Merck Certipur is compared with 1000 mg/L from Baker - Calibration: 0 - 2 mg/L B	ICP OES
21	**DIGESTION:** - M: 6 g; - Extraction with water 1 h at 60 °C - (recommended method M2, ASTM C971)	Potentiometric titration with NaOH in presence of mannitol. Determination of titrimetric factor using H_3BO_3 and corr. factor of 0.1 N NaOH solution using potassium hydrogen-phthalate.	Titr.
25	**DIGESTION:** - M: 1 g; added 150 mL water - 1 h at 60 °C heated in a water bath - Filtration and measured with ICP OES	**1000 mg/L B**, Kraft - Calibration: 0 - 5 mg/L B	ICP OES

Carbon

Lab-code	Sample preparation (M = mass of sub-samples)	Calibration	Final determination
6	**MEASUREMENT PARAMETER:** - M: 100 mg; - Pre-Analyse Purge time: 1 s; Pre-Analyse Delay time: 8 s; Minimum time out: 40 s; Comperator level : 1 % Power level maximum	UK Ring Standard C = 0.182 % from Elemental Mikro Analysis, UK; Euro CRM no. 085-1; UK ECISS CRM 783-1; ECISS 778-1; Euro ZRM 284-1 all from BAS. **All standard materials were verified.**	Comb.-IR
9	**MEASUREMENT PARAMETER:** - M: 100 mg; Addition from 3.0 g W + 0.3 g Sn - crucibles were pre-burned. - step 1 = 5 sec; step 2 = 35 sec 175 mA; purge time 10 sec. Blank was analyzed and subtracted	- M: 1.0 g JSS 670-3 = 0.0080 mass % C - **JSS 670-3 is a certified reference material. By a round robin test the standard is verified.**	Comb.-IR
10	**MEASUREMENT PARAMETER:** - M: 100 mg; Addition from 3.0 g W + 0.3 g Sn - crucibles were pre-burned. - step 1 = 5 sec; step 2 = 35 sec 175 mA; purge time 10 sec. Blank was analyzed and subtracted	- M: 1.0 g JSS 670-3 = 0.0080 mass % C - **JSS 670-3 is a certified reference material. By a round robin test the standard is verified.**	Comb.-IR
15	**MEASUREMENT PARAMETER:** - M: 250 mg; - Measurement temperature: 1350 °C Analyze time 90 s.	M: 100 mg **$CaCO_3$** 4N grade from RARE METALLIC Co. Ltd.	Comb.-IR
16	**MEASUREMENT PARAMETER:** - M: 150 - 170 mg; - 1 g Cu crucibles were pre-burned - sample on CuO as flux and with Al foil masked - over there 1 g Cu, that was tempered in Ar at 800 °C. Blank was analyzed and subtracted.	- WC; NIST 2768 6.10 ± 0.04 % C - **WC is a standard reference material from NIST. By a round robin test the standard is verified.**	Comb.-IR
18	**MEASUREMENT PARAMETER:** - M: 50 - 60 mg; - addition from 1.5 g W and 0.2 g Fe as flux	**$CaCO_3$**	Comb.-IR
20	**MEASUREMENT PARAMETER:** - M: 50 mg; - addition from 1.5 g Lecocel PL and 1.0 g Fe chips Alpha 673 as flux.	**Na_2CO_3** Dried 6h at 105 °C	Comb.-IR
21	**MEASUREMENT PARAMETER:** - M: 150 mg; - combustion of sample with oxygen in aluminia crucibles (induction furnace); - accelerator: Fe/W Purge time: 15 s; Delay time: 15 s, minimum time: 40s	**$CaCO_3$**	CGHE-IR
22	**MEASUREMENT PARAMETER:** - M: 30 - 40 mg; - powder in Sn caps - accelerator: Fe/W HF furnace	**Gas dosing with CO_2**	Comb.-IR
24	M: 50 – 60 mg; .		
24	**MEASUREMENT PARAMETER:** - M: 50 - 60 mg; - addition from Leco II and 2 x Fe as flux	Leco Stahl AKP No. 501-502 / R1192-6 (C 0.050 % ± 0.002 %) **Calibration is compared with Na_2CO_3 suprapur (Merck).**	Comb.-IR
25	**MEASUREMENT PARAMETER:** - M: 300 mg; - Sample in Sn capsule with CuO wire (Merck, annealed 2 h at 900 °C) as flux. RC 412 + silicon Carbide rod furnace were used for measurements. Furnace temperature 1200 °C.	**$Ba(CO_3)_2$**, 3 mg; Merck dried 2 h at 120 °C	Comb.-IR
26	**MEASUREMENT PARAMETER:** - M: 75 mg; - addition of W/Sn and Fe from LECO as flux	**$Ba(CO_3)_2$**, Na_2CO_3 Merck	Comb.-IR

Nitrogen

Lab-code	Sample preparation (M = mass of sub-samples)	Calibration	Final determination
1	**MEASUREMENT PARAMETER:** - M: 0.8 – 0.96 mg; - Outgas power 5900 W; analyze power 3000/5700 W; ramp 225/s; integrations time: 70 s. - Crucibles Leco HT 782-720; Ni capsules (0.04 mL).	**KNO_3** (Merck, > 99%) - External Calibration	CGHE-TC
9	**MEASUREMENT PARAMETER:** - M: 25 mg; - 0.3 g Ni capsule + 0.5 g Sn pellets as flux were used - Wait time: 5 s, Integration time 130 s, Comparator level 0.1 %, Comp. wait time. 100 s. Blank was analyzed and subtracted	Si_3N_4 JCRM R003; M: 35 mg 39.00 mass% N ***JCRM R003 is a certified reference material. By a round robin test the standard is verified.***	CGHE-TC
15	**MEASUREMENT PARAMETER:** - M: 5 mg; - 30 s outgas time; 50 s analyze delay; 20 s cool time; 6000 W outgas power, 5500 W analyze power	**KNO_3** 4N5 grade RARE METALLIC Co. Ltd. (18 mg) - KNO_3 is compared with Si_3N_4 JCRM R003; M: 35 mg 39.00 mass% N	CGHE-TC
16	**MEASUREMENT PARAMETER:** - M: 1 – 1.5 mg; - sample mass in Sn capsule and 90 mg Ni as flux. Analyze power 4500 W.	**Gas calibration with N_2;** 484 µl Vol. Checked with ERM®-ED101 (value: 38.26 %; s=0.078; n=3)	CGHE-TC
18	**MEASUREMENT PARAMETER:** - M: 10 mg; - sample mass in Sn capsule and high temperature crucible; Analyze power 4000 W.	**KNO_3** in solution	CGHE-TC
20	**MEASUREMENT PARAMETER:** - M: 50 mg; - sample mass in Sn capsule and 1 g Ni caps - high temperature crucible; - Analyze time 50 s; ramp: 720 A → 920 A with 20 A/s	**Gas calibration with N_2**	CGHE-TC
21	**MEASUREMENT PARAMETER:** - M: 30 mg; - sample in inert-gas atmosphere in graphite crucibles - Sn capsule for weighing of samples - 10 s purge time; outgas 5500 W 20 s; analysis: low power = 4000 W, high power = 5200 W, ramp rate = 100 W/s.	**KNO_3**	CGHE-TC
22	**MEASUREMENT PARAMETER:** - M: 30 - 40 mg; - powder in Sn caps, compacted in Ni caps	**Gas dosing with N_2**	CGHE-TC
24	**MEASUREMENT PARAMETER:** - M: 10 mg; - sample mass in Sn capsules and 1 g Ni caps and high temperature crucible were used.	Si_3N_4 ***Calibration was checked against KNO_3 suprapur (Merck).***	CGHE-TC
26	**MEASUREMENT PARAMETER:** - M: 15 mg; - Sn/Ni addition and high temperature crucible; ramp 3000 – 5000 W	**KNO_3** Merck	CGHE-TC
21	**DIGESTION:** - M: 40 mg - fusion decomposition with LiOH, determination of ammonia by potentiometric titration with diluted HCl. (according to recommended method M3)	***Calibration is not required*** Determination of titration corr. Factor of 0.1 n HCl solution using Na_2CO_3	TITR.
25	**DIGESTION:** - M: 250 mg; - digestion in HF/H_2O_2 at 200 C (Berghof DAB II), - addition of 4.7 g H_3BO_3 → Kjeldahl distillation and titration	***Calibration is not required*** 0.05 M H_2SO_4 Determination of titer strength with tris(hydroxymethyl)-aminomethane	TITR.

Oxygen			
Lab-code	Sample preparation (M = mass of sub-samples)	Calibration	Final determination
1	**MEASUREMENT PARAMETER:** - M: 20.5 – 23.3 mg; - Outgas power 5900 W; analyze power 3000/5700 W; ramp 225/s; integrations time: 70 s. - Crucibles Leco HT 782-720; Ni capsules (0.14 mL, 250 mg).	**Fe_2O_3**, Sidmar, > 99%) - External Calibration	CGHE-IR
9	**MEASUREMENT PARAMETER:** - M: 25 mg; - 0.3 g Ni capsule + 0.5 g Sn pellets as flux were used - Wait time: 5 s, Integration time 130 s, Comparator level 0.1 %, Comp. wait time. 90 s. Blank was analyzed and subtracted	Si_3N_4 JCRM R003; M: 35 mg 1.27 mass% O *JCRM R003 is a certified reference material. By a round robin test the standard is verified.*	CGHE-IR
15	**MEASUREMENT PARAMETER:** - M: 5 mg; - 30 s outgas time; 50 s analyze delay; 20 s cool time; 6000 W outgas power, 5500 W analyze power	**Y_2O_3** N5 grade; RARE METALLIC Co. Ltd. (5 mg)	CGHE-IR
16	**MEASUREMENT PARAMETER:** - M: 4 - 7 mg; - weighted sample in Ni capsule (260 mg) and 100 mg Sn as flux. Analyze power 4500 W.	**Gas calibration with CO_2**; 484 µl Vol. Checked with ZrO_2 4N, tempered at 1000 °C (value: 25.84 %; s=0.19; n=6)	CGHE-IR
18	**MEASUREMENT PARAMETER:** - M: 10 mg; - sample mass in Sn capsule and high temperature crucible used; Analyze power 4000 W.	**KNO_3** in solution	CGHE-IR
20	**MEASUREMENT PARAMETER:** - M: 50 mg; - sample mass in Sn capsule and 1 g Ni caps - high temperature crucible were used; - Analyze time 50 s; ramp: 720 A → 920 A with 20 A/s	**Gas calibration with N_2**	CGHE-IR
21	**MEASUREMENT PARAMETER:** - M: 30 mg; - sample in inert-gas atmosphere in graphite crucibles - Sn capsule for weighing of samples - 10 s purge time; outgas 5500 W 20 s; analysis: low power = 4000 W, high power = 5200 W, ramp rate = 100 W/s.	**$CaCO_3$**	CGHE-IR
22	**MEASUREMENT PARAMETER:** - M: 30 - 40 mg; - powder in Sn caps, compacted in Ni caps	**Gas dosing with CO_2**	Comb.-IR
24	**MEASUREMENT PARAMETER:** - M: 10 mg; - sample mass in Sn capsules (170 mg) and 1 g Ni caps and high temperature crucible were used.	**Ag_2O**	Comb.-IR
26	**MEASUREMENT PARAMETER:** - M: 1.5 mg; - Sn/Ni addition and high temperature crucible; ramp 3000 – 5000 W	**KNO_3** Merck	CGHE-IR

Water			
Lab-code	Sample preparation	Calibration	Final determination
16	**MEASUREMENT PARAMETER:** - M: 1 – 1.5 g: - Drying for 1 h at 130 ℃ in a drying oven		GRAV
21	**MEASUREMENT PARAMETER:** - M: 1 g; - Vaporization of moisture in an oven (nitrogen carrier gas stream) - absorption of H_2O in a P_2O_5 coated electrolytic cell (formation of H_3PO_4), coulometric regeneration of P_2O_5. - temperature = 150 ℃, vapr. time = 30 s, N_2 carrier gas flow rate = 70 mL/min.	**$Na_2WO_4 * 2H_2O$**	EL: CHEM
24	**MEASUREMENT PARAMETER:** - M: 2 g; - Drying for 24 h at 130 ℃ in a drying oven		GRAV
25	**MEASUREMENT PARAMETER:** - ´M: g; - Karl-Fischer-titration Furnace temperature 400 ℃	**Hydranal**, 5.00 mg/mL H_2O (Riedel de Haen)	TITR
26	**MEASUREMENT PARAMETER:** - M: - Drying for 1 h at 130 ℃ in a drying oven		Grav.

Methods, which were used for long term stability testing

Parameter	Sample Preparation	Final Determination
Metallic Parameter and Si: Al, Ca, Co, Cr, Fe, Mg, Na, Si, Ti	By weighing	

C	**MEASUREMENT PARAMETER:**
	- M: 100 mg;
	  combustion of sample in ceramic crucibles with Sn capsule + 2g W
	  analyse time: 65 s
		CGHE-IR

N	**DIGESTION**: - M: 40 mg - fusion decomposition with LiOH, determination of ammonia by potentiometric titration with diluted HCl. (according to recommended method M3)	TITR
O	**MEASUREMENT PARAMETER:** - M: 20.5 – 23.3 mg; - Crucibles Leco HT 782-720; Ni capsules - Outgas power 5900 W; analyze power 3000/5700 W; ramp 225/s; integrations time: 70 s.	CGHE-IR
B-total	**DIGESTION**: - M: 200 mg; - melting fusion with 5 g $NaKCO_3$ - dissolution in 1+1 HCl - titrated after addition of mannitol (recommended method M1, ASTM C971)	TITR
B_2O_3	**DIGESTION:** - M: 6 g; - Extraction with water1 h at 60°C - Titrated with NaOH in presence of mannitol (recommended method M2, ASTM C971)	TITR

Appendix 4: Statistical evaluation

Data and results of the statistical evaluation of the interlaboratory comparison using the BCR program [3] are summarized for metallic analytes in Table 1 and for non-metallic parameters in Table 2.

Table 1: *Summary of results of statistical evaluation for metallic analytes including Si*

Element run of evaluation program	Al run 1	Al run 2	Ca run 1	Ca run 2	Ca run 3
Number of data sets	12	11	12	11	10
Total number of replicate measurements	72	66	72	66	60
Mean of means (a)	7.904	7.014	293.05	280.22	273.18
St. Dev of means (a)	3.656	2.058	51.37	27.03	14.32
Outlying or straggling mean values					
▪ Dixon test	c	no	b, c	b, c	no
▪ Grubbs test (single and pair test)	b, c	no	b, c	b, c	no
▪ Nalimov t-test	b, c	no	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	no	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	0.638	0.597	9.96	8.42	6.87
St. Dev. between laboratories (a)	3.647	2.044	51.21	26.81	14.04
Half-width of the 95% confidence interval (a)	2.323	1.383	32.64	18.16	10.24

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

Element run of evaluation program	Co run 1	Co run 2	Co run 3	Cr run 1	Fe run 1
Number of data sets	5	4	3	13	13
Total number of replicate measurements	30	24	18	77	78
Mean of means (a)	0.308	0.102	0.036	4.75	14.96
St. Dev of means (a)	0.475	0.137	0.044	1.56	2.83
Outlying or straggling mean values					
▪ Dixon test	c	no	c	no	no
▪ Grubbs test (single and pair test)	c	no	c	no	no
▪ Nalimov t-test	b, c	c	b, c	c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	no	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	0.079	0.064	0.007	0.50	1.70
St. Dev. between laboratories (a)	0.474	0.134	0.044	1.54	2.74
Half-width of the 95% confidence interval (a)	0.590	0.218	0.109	0.94	1.71

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

Element run of evaluation program	Mg run 1	Mg run 2	Mg run 3	Na run 1	Si run 1	Ti run 1
Number of data sets	12	11	10	10	5	13
Total number of replicate measurements	72	66	60	59	30	77
Mean of means (a)	57.12	54.82	56.30	12.26	17.0	4.91
St. Dev of means (a)	9.55	5.54	2.69	1.30	2.5	0.72
Outlying or straggling mean values						
▪ Dixon test	b, c	c	no	no	no	no
▪ Grubbs test (single and pair test)	b, c	b, c	no	no	no	no
▪ Nalimov t-test	b, c	b, c	no	c	no	c
Differences between labs statistically significant?						
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances						
▪ Cochran test	b, c	no	no	b, c	no	no
Variances homogeneous						
▪ Bartlett test	no	no	no	no	no	out of test range
St. Dev. within – laboratories (a)	2.39	1.78	1.82	1.01	2.6	0.34
St. Dev. between laboratories (a)	9.50	5.49	2.58	1.20	2.3	0.71
Half-width of the 95% confidence interval (a)	6.07	3.72	1.92	0.93	3.1	0.44

Abbreviations:

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

Table 2: *Summary of results of statistical evaluation for non-metallic analytes*

Element run of evaluation program	Total C run 1	Total C run 2	Total C run 3	N run 1	O run 1
Number of data sets	12	11	10	12	10
Total number of replicate measurements	72	66	60	72	60
Mean of means (a)	0.02661	0.01887	0.01779	55.613	0.6803
St. Dev of means (a)	0.02708	0.00417	0.00225	0.632	0.1185
Outlying or straggling mean values					
▪ Dixon test	b, c	c	no	no	no
▪ Grubbs test (single and pair test)	b, c	b, c	no	no	no
▪ Nalimov t-test	b, c	b, c	no	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	no	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	0.00443	0.00300	0.00114	0.280	0.0168
St. Dev. between laboratories (a)	0.02702	0.00398	0.00220	0.621	0.1183
Half-width of the 95% confidence interval (a)	0.01721	0.00280	0.00161	0.401	0.0848

Abbreviations:

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

Element run of evaluation program	Total B run 1	B$_2$O$_3$ run 1	H$_2$O run 1
Number of data sets	6	5	5
Total number of replicate measurements	36	30	26
Mean of means (a)	43.477	0.0702	0.0716
St. Dev of means (a)	0.267	0.0035	0.0443
Outlying or straggling mean values			
▪ Dixon test	no	no	no
▪ Grubbs test (single and pair test)	no	no	no
▪ Nalimov t-test	no	no	c
Differences between labs statistically significant?			
▪ Snedecor F-test	b, c	b, c	b, c
Outlying or straggling variances			
▪ Cochran test	b, c	no	b, c
Variances homogeneous			
▪ Bartlett test	no	no	no
St. Dev. within – laboratories (a)	0.158	0.0023	0.0116
St. Dev. between laboratories (a)	0.259	0.0034	0.0445
Half-width of the 95% confidence interval (a)	0.28	0.0044	0.0550

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

A more detailed description of the statistical evaluation is given below.
It is arranged alphabetically by the element symbols. Each table consists of the following three parts:

- First 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 BN ("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 (C.I.) of the laboratory mean values, respectively
  #subsequent 6 columns: all single values from different sub-samples
- Second 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. This was the case for all analytes in this investigation. Furthermore there are explanations to the abbreviations of statistical tests applied and indicated in the following diagram of the lower part.
- A diagram showing the mean of all means of data sets (vertical line), the corresponding 95 % confidence interval 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).

Table 4a1: Aluminium evaluation in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 ICP OES 3	3.500	0.501	0.525	4.300	3.540	3.840	3.020	3.250	3.050
L 2	16 ICP OES 3	3.625	0.177	0.186	3.420	3.430	3.700	3.800	3.820	3.580
L 3	25 ICP OES 3	6.183	0.970	1.018	5.200	5.300	5.800	6.500	6.500	7.800
L 4	21 ETV-ICP OES 3	6.600	0.310	0.325	6.600	7.100	6.800	6.300	6.500	6.300
L 5	2 ICP OES 2	6.928	0.175	0.183	7.200	6.960	7.020	6.770	6.720	6.900
L 6	3 ET AAS 3	7.257	0.075	0.079	7.290	7.260	7.250	7.380	7.190	7.170
L 7	4 ICP-SF-MS 3	7.600	0.123	0.129	7.590	7.620	7.390	7.590	7.640	7.770
L 8	2 ETV-ICP OES 2	7.705	0.760	0.797	8.300	8.450	6.880	6.690	7.690	8.220
L 9	15 ICP OES 2	8.167	0.408	0.428	8.000	8.000	8.000	8.000	8.000	9.000
L 10	24 ICP OES 3	9.752	1.113	1.168	10.250	8.390	10.880	9.590	10.880	8.520
L 11	17 XRF 2	9.833	0.753	0.790	10.000	10.000	9.000	10.000	9.000	11.000
L 12	9 ICP OES 2	17.700	0.982	1.030	18.100	16.500	17.400	19.100	18.300	16.800

Range [min..max]	[3.020 .. 19.100]
	Case of No Pooling
Mean of means	7.904
95% H.W. Confidence Interval	2.323
95% H.W. Tolerance Interval	11.561

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**

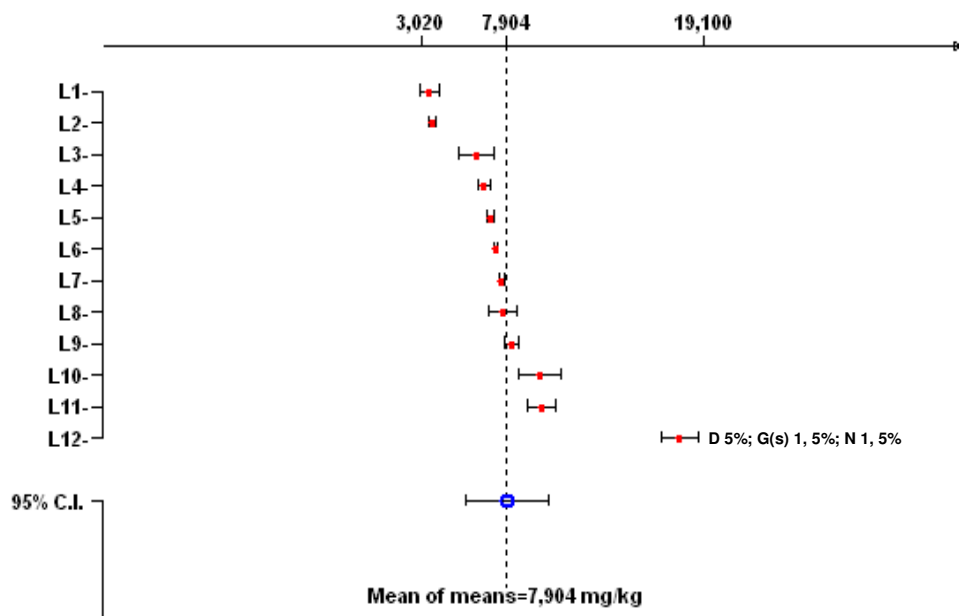**Diagram of means and 95% confidence intervals (to Tab. 4a1)**

Table 4a2: Aluminium accepted results in run 2 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 ICP OES 3	3.500	0.501	0.525	4.300	3.540	3.840	3.020	3.250	3.050
L 2	16 ICP OES 3	3.625	0.177	0.186	3.420	3.430	3.700	3.800	3.820	3.580
L 3	25 ICP OES 3	6.183	0.970	1.018	5.200	5.300	5.800	6.500	6.500	7.800
L 4	21 ETV-ICP OES 3	6.600	0.310	0.325	6.600	7.100	6.800	6.300	6.500	6.300
L 5	2 ICP OES 2	6.928	0.175	0.183	7.200	6.960	7.020	6.770	6.720	6.900
L 6	3 ET AAS 3	7.257	0.075	0.079	7.290	7.260	7.250	7.380	7.190	7.170
L 7	4 ICP-SF-MS 3	7.600	0.123	0.129	7.590	7.620	7.390	7.590	7.640	7.770
L 8	2 ETV-ICP OES 2	7.705	0.760	0.797	8.300	8.450	6.880	6.690	7.690	8.220
L 9	15 ICP OES 2	8.167	0.408	0.428	8.000	8.000	8.000	8.000	8.000	9.000
L 10	24 ICP OES 3	9.752	1.113	1.168	10.250	8.390	10.880	9.590	10.880	8.520
L 11	17 XRF 2	9.833	0.753	0.790	10.000	10.000	9.000	10.000	9.000	11.000

Range [min..max]	[3.020 .. 11.000]
	Case of No Pooling
Mean of means	7.014
95% H.W. Confidence Interval	1.383
95% H.W. Tolerance Interval	6.707

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
                         N   = Nalimov t - test   POSSIBILITY TO POOL THE DATA

Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

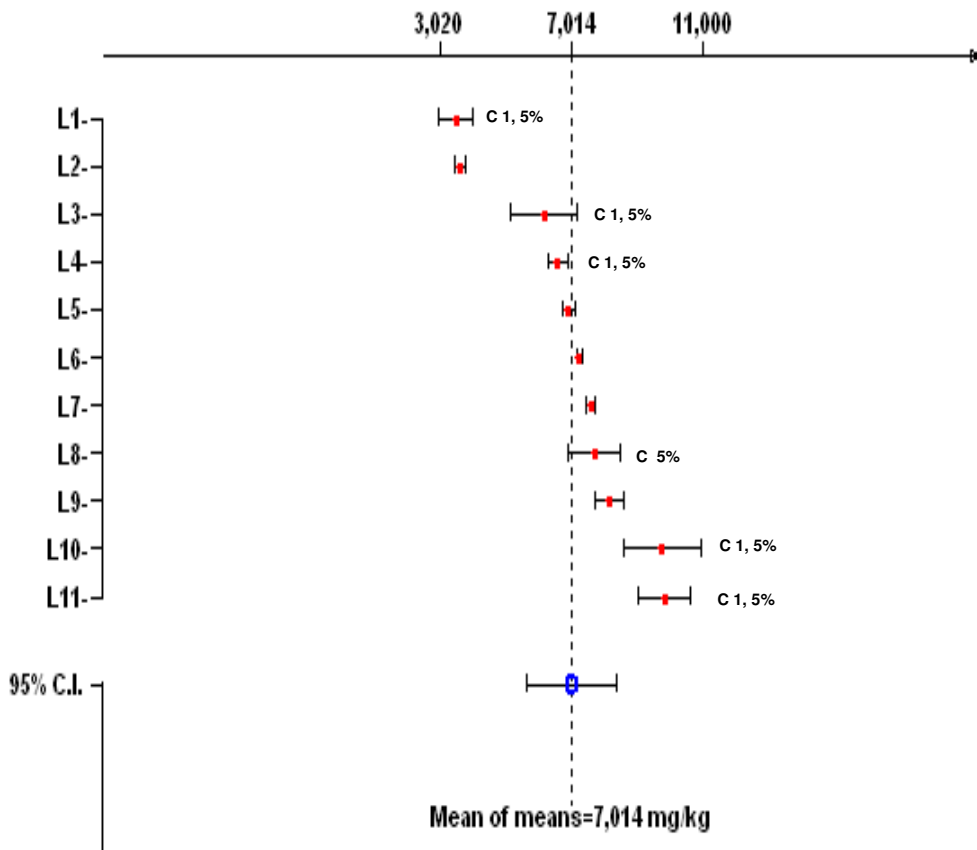**Diagram of means and 95% confidence intervals (to Tab. 4a2)**

Table 4b1: Calcium evaluation in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	15 ICP OES 2	249.67	4.89	5.13	248.00	241.00	253.00	251.00	255.00	250.00
L 2	25 ICP OES 3	262.17	15.69	16.47	239.00	249.00	280.00	264.00	265.00	276.00
L 3	2 ICP OES 2	263.33	2.25	2.36	265.00	262.00	262.00	263.00	267.00	261.00
L 4	21 ETV-ICP OES 3	265.17	7.73	8.11	255.00	266.00	260.00	275.00	262.00	273.00
L 5	20 ICP OES 1	271.33	6.50	6.82	280.00	270.00	269.00	272.00	276.00	261.00
L 6	24 F AAS 3	273.67	2.79	2.93	272.02	272.94	273.58	270.59	278.76	274.14
L 7	26 F AAS (3)	274.17	7.96	8.35	281.00	270.00	271.00	287.00	267.00	269.00
L 8	4 ICP-SF-MS 3	285.17	1.15	1.21	283.60	284.70	285.50	284.50	285.80	286.90
L 9	17 XRF 2	289.67	1.63	1.71	292.00	289.00	288.00	288.00	290.00	291.00
L 10	16 ICP OES 3	297.47	4.46	4.68	289.70	301.00	300.60	300.30	294.70	298.50
L 11	11 ICP OES 1	350.67	17.56	18.43	343.00	328.00	339.00	366.00	353.00	375.00
L 12	9 ICP OES 2	434.17	20.27	21.27	443.00	456.00	456.00	412.00	413.00	425.00

Range [min..max]	[239.00 .. 456.00]
	Case of No Pooling
Mean of means	293.05
95% H.W. Confidence Interval	32.64
95% H.W. Tolerance Interval	162.43

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

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

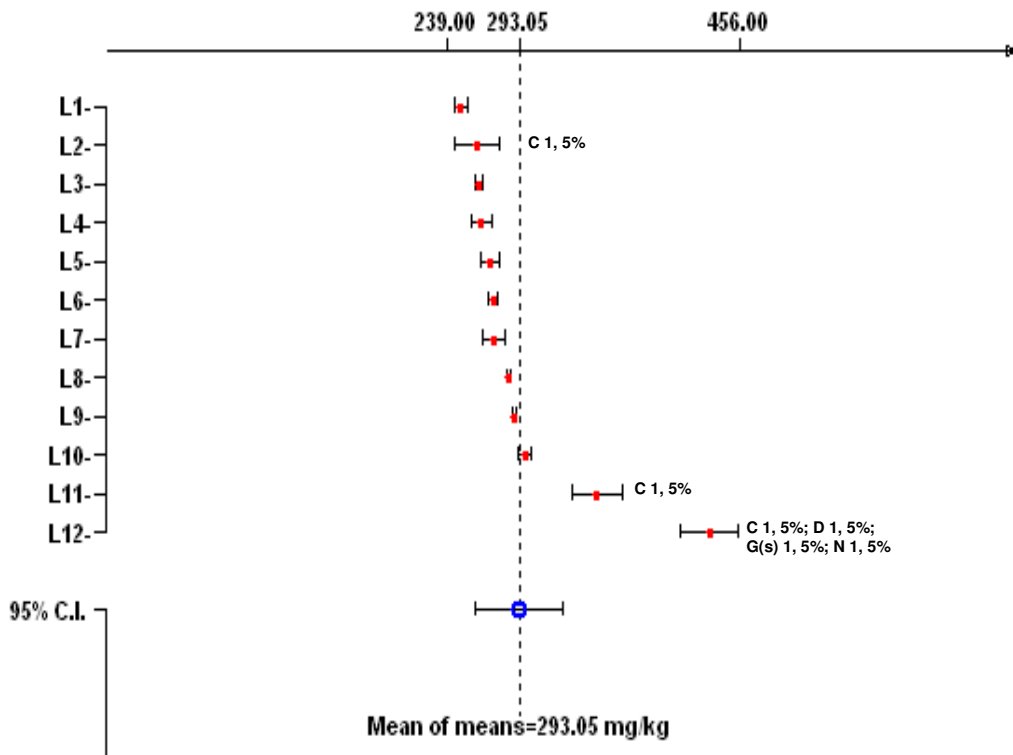**Diagram of means and 95% confidence intervals (to Tab. 4b1)**

Table 4b2: Calcium evaluation in run 2 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	15 ICP OES 2	249.67	4.89	5.13	248.00	241.00	253.00	251.00	255.00	250.00
L 2	25 ICP OES 3	262.17	15.69	16.47	239.00	249.00	280.00	264.00	265.00	276.00
L 3	2 ICP OES 2	263.33	2.25	2.36	265.00	262.00	262.00	263.00	267.00	261.00
L 4	21 ETV-ICP OES 3	265.17	7.73	8.11	255.00	266.00	260.00	275.00	262.00	273.00
L 5	20 ICP OES 1	271.33	6.50	6.82	280.00	270.00	269.00	272.00	276.00	261.00
L 6	24 F AAS 3	273.67	2.79	2.93	272.02	272.94	273.58	270.59	278.76	274.14
L 7	26 F AAS (3)	274.17	7.96	8.35	281.00	270.00	271.00	287.00	267.00	269.00
L 8	4 ICP-SF-MS 3	285.17	1.15	1.21	283.60	284.70	285.50	284.50	285.80	286.90
L 9	17 XRF 2	289.67	1.63	1.71	292.00	289.00	288.00	288.00	290.00	291.00
L 10	16 ICP OES 3	297.47	4.46	4.68	289.70	301.00	300.60	300.30	294.70	298.50
L 11	11 ICP OES 1	350.67	17.56	18.43	343.00	328.00	339.00	366.00	353.00	375.00

Range [min..max]	[239.00 .. 375.00]
	Case of No Pooling
Mean of means	280.22
95% H.W. Confidence Interval	18.16
95% H.W. Tolerance Interval	88.07

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**

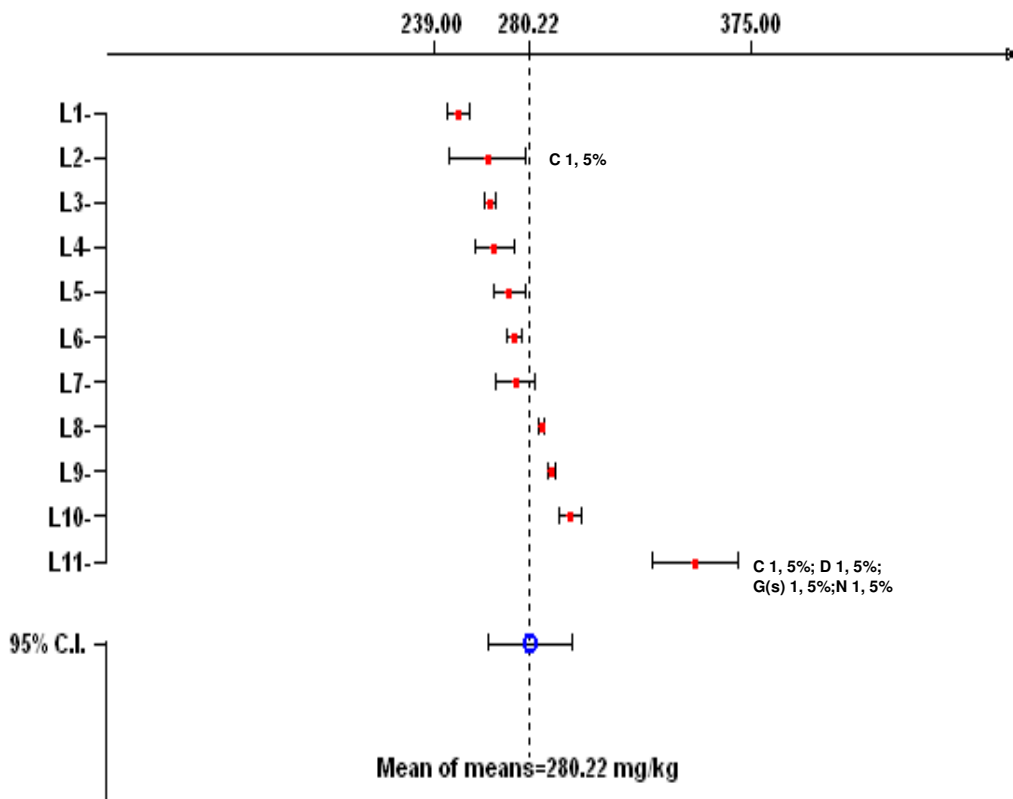**Diagram of means and 95% confidence intervals (to Tab. 4b2)**

Table 4b3: Calcium accepted results in run 3 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	15 ICP OES 2	249.67	4.89	5.13	248.00	241.00	253.00	251.00	255.00	250.00
L 2	25 ICP OES 3	262.17	15.69	16.47	239.00	249.00	280.00	264.00	265.00	276.00
L 3	2 ICP OES 2	263.33	2.25	2.36	265.00	262.00	262.00	263.00	267.00	261.00
L 4	21 ETV-ICP OES 3	265.17	7.73	8.11	255.00	266.00	260.00	275.00	262.00	273.00
L 5	20 ICP OES 1	271.33	6.50	6.82	280.00	270.00	269.00	272.00	276.00	261.00
L 6	24 F AAS 3	273.67	2.79	2.93	272.02	272.94	273.58	270.59	278.76	274.14
L 7	26 F AAS (3)	274.17	7.96	8.35	281.00	270.00	271.00	287.00	267.00	269.00
L 8	4 ICP-SF-MS 3	285.17	1.15	1.21	283.60	284.70	285.50	284.50	285.80	286.90
L 9	17 XRF 2	289.67	1.63	1.71	292.00	289.00	288.00	288.00	290.00	291.00
L 10	16 ICP OES 3	297.47	4.46	4.68	289.70	301.00	300.60	300.30	294.70	298.50

Range [min..max]	[239.00 .. 301.00]
	Case of No Pooling
Mean of means	273.18
95% H.W. Confidence Interval	10.24
95% H.W. Tolerance Interval	48.38

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**

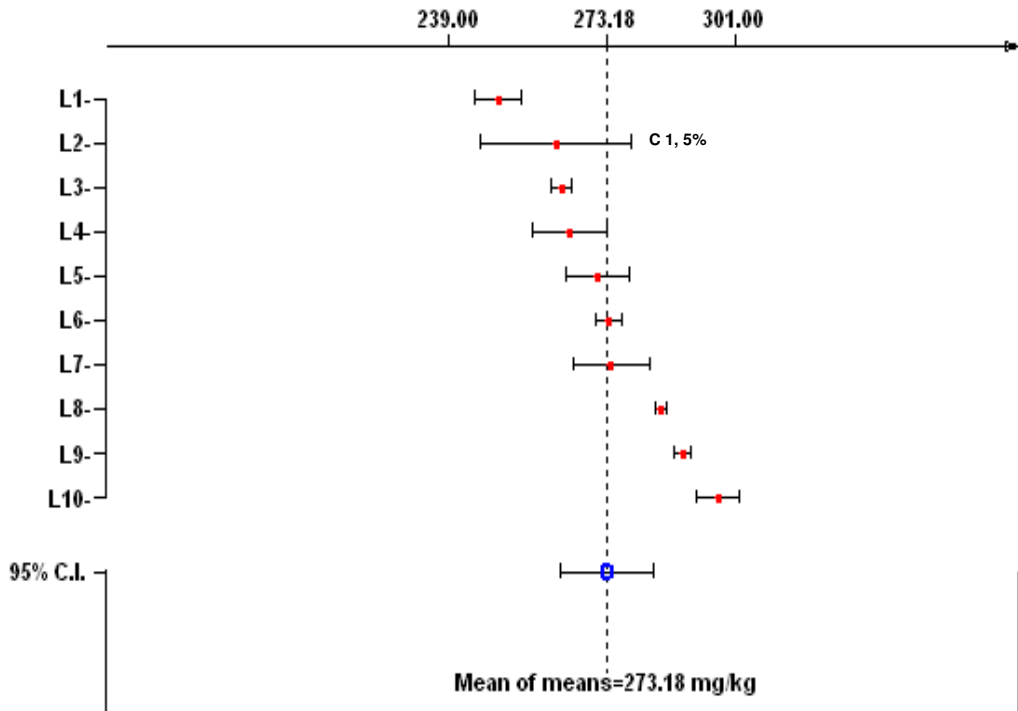**Diagram of means and 95% confidence intervals (to Tab. 4b3)**

Table 4c1: Cobalt evaluation in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	3 ET AAS 3	0.010	0.001	0.001	0.011	0.010	0.012	0.010	0.010	0.009
L 2	4 ICP-SF-MS 3	0.011	0.003	0.003	0.012	0.009	0.007	0.014	0.009	0.014
L 3	21 ETV-ICP OES 3	0.087	0.012	0.013	0.090	0.100	0.070	0.100	0.080	0.080
L 4	26 F AAS (3)	0.300	0.126	0.133	0.200	0.300	0.500	0.400	0.200	0.200
L 5	24 ICP OES (3)	1.132	0.123	0.129	0.980	1.190	1.090	1.300	1.020	1.210

Range [min..max]	[0.007 .. 1.300]
	Case of No Pooling
Mean of means	0.308
95% H.W. Confidence Interval	0.590
95% H.W. Tolerance Interval	2.415

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**

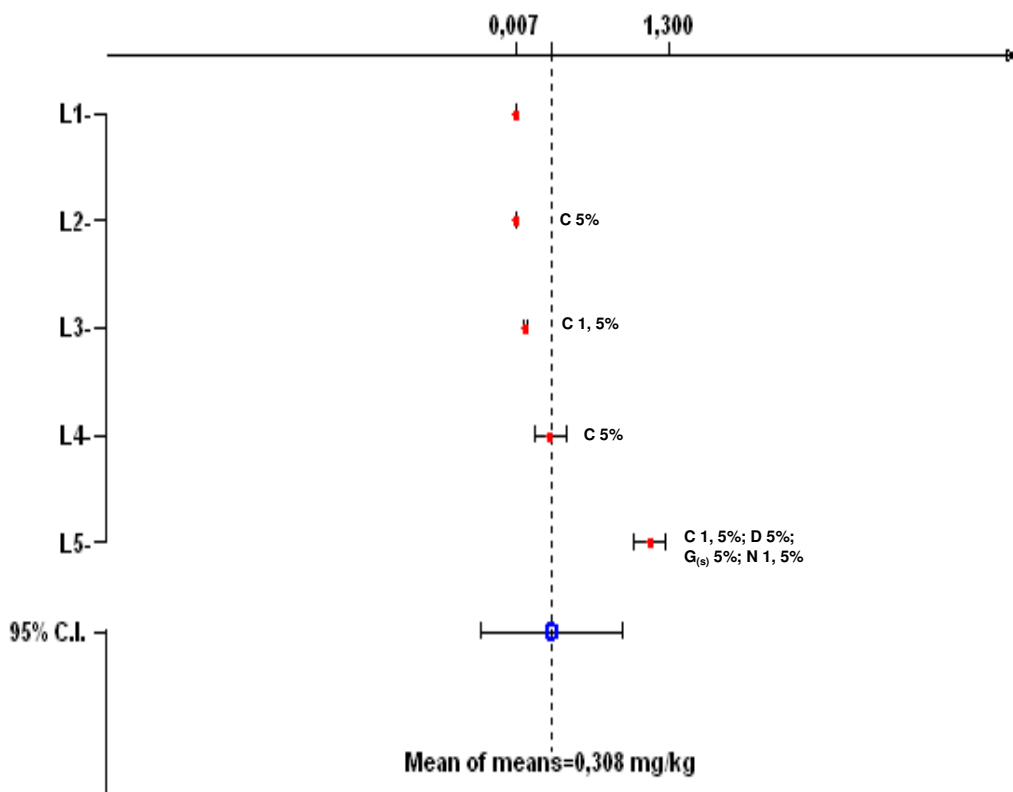**Diagram of means and 95% confidence intervals (to Tab. 4c1**

Table 4c2: Cobalt evaluation in run 2 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	3 ET AAS 3	0.010	0.001	0.001	0.011	0.010	0.012	0.010	0.010	0.009
L 2	4 ICP-SF-MS 3	0.011	0.003	0.003	0.012	0.009	0.007	0.014	0.009	0.014
L 3	21 ETV-ICP OES 3	0.087	0.012	0.013	0.090	0.100	0.070	0.100	0.080	0.080
L 4	26 F AAS (3)	0.300	0.126	0.133	0.200	0.300	0.500	0.400	0.200	0.200

Range [min..max]	[0.007 .. 0.500]
	Case of No Pooling
Mean of means	0.102
95% H.W. Confidence Interval	0.218
95% H.W. Tolerance Interval	0.871

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**

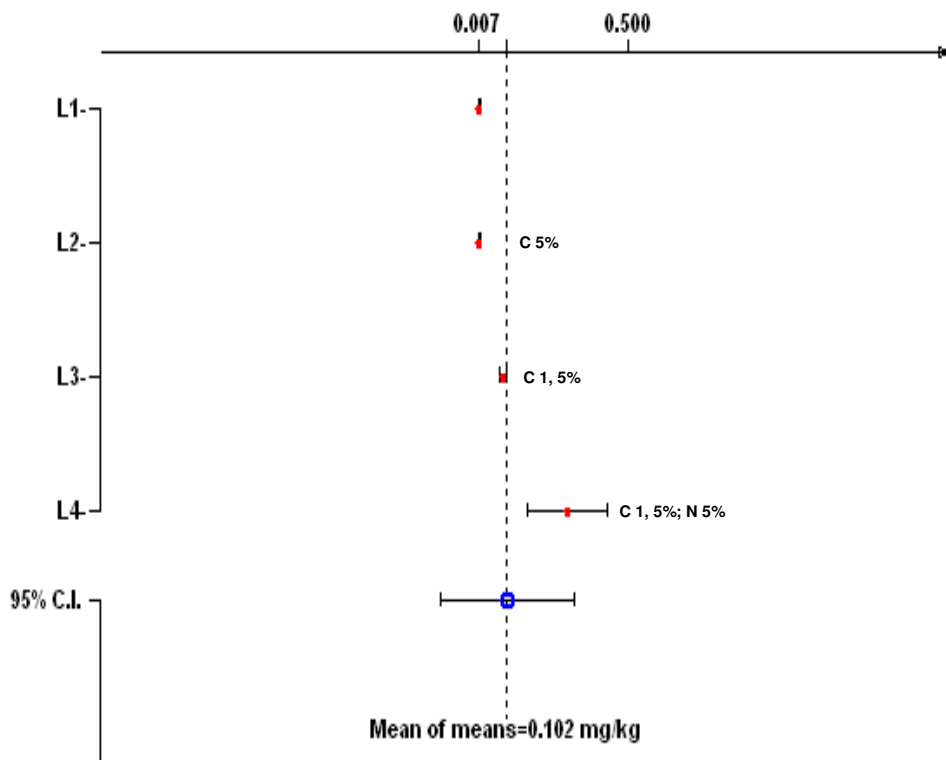**Diagram of means and 95% confidence intervals (to Tab. 4c2**

Table 4c3: Cobalt accepted results in run 3 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	3 ET AAS 3	0.010	0.001	0.001	0.011	0.010	0.012	0.010	0.010	0.009
L 2	4 ICP-SF-MS 3	0.011	0.003	0.003	0.012	0.009	0.007	0.014	0.009	0.014
L 3	21 ETV-ICP OES 3	0.087	0.012	0.013	0.090	0.100	0.070	0.100	0.080	0.080

Range [min..max]	[0.007 .. 0.100]
	Case of No Pooling
Mean of means	0.036
95% H.W. Confidence Interval	0.109
95% H.W. Tolerance Interval	0.436

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**

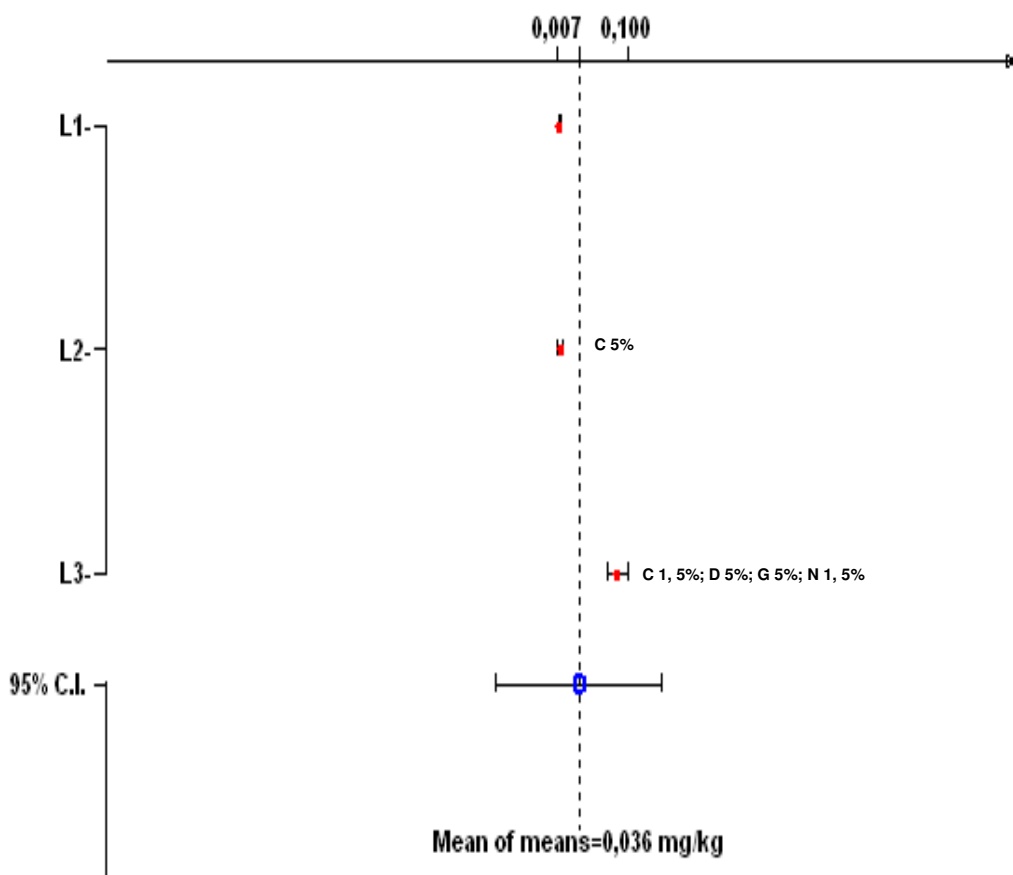**Diagram of means and 95% confidence intervals (to Tab. 4c3**

Table 4d1: Chromium accepted results in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	16 ICP OES 3	2.60	0.16	0.17	2.39	2.59	2.49	2.69	2.60	2.86
L 2	2 ICP OES 2	3.24	0.10	0.11	3.17	3.29	3.19	3.16	3.22	3.43
L 3	25 ICP OES 3	3.43	0.78	0.82	3.50	3.30	4.80	3.10	3.50	2.40
L 4	4 ICP-SF-MS 3	3.49	0.13	0.14	3.47	3.39	3.53	3.42	3.40	3.74
L 5	3 ET AAS 3	3.71	0.16	0.17	3.78	3.81	3.51	3.54	3.69	3.92
L 6	9 ICP OES 2	4.25	0.59	0.62	5.20	3.95	4.04	3.81	3.74	4.73
L 7	20 ICP OES 1	4.48	0.30	0.31	4.40	4.60	4.60	4.00	4.90	4.40
L 8	26 ICP OES 3	4.80	0.58	0.61	4.18	4.70	4.08	5.38	5.42	5.04
L 9	24 ICP OES 3	5.23	0.59	0.62	5.52	5.78	4.38	5.43	4.59	5.66
L 10	15 ICP OES 2	5.33	0.52	0.54	5.00	5.00	6.00	6.00	5.00	5.00
L 11	2 ETV-ICP OES 2	6.56	0.71	0.88		5.96	6.61	7.75	6.12	6.37
L 12	21 ETV-ICP OES 3	6.77	0.30	0.32	6.50	7.10	7.00	6.40	6.60	7.00
L 13	17 XRF 2	7.83	0.75	0.79	7.00	7.00	8.00	9.00	8.00	8.00

Range [min..max]	[2.39 .. 9.00]
	Case of No Pooling
Mean of means	4.75
95% H.W. Confidence Interval	0.94
95% H.W. Tolerance Interval	4.79

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**

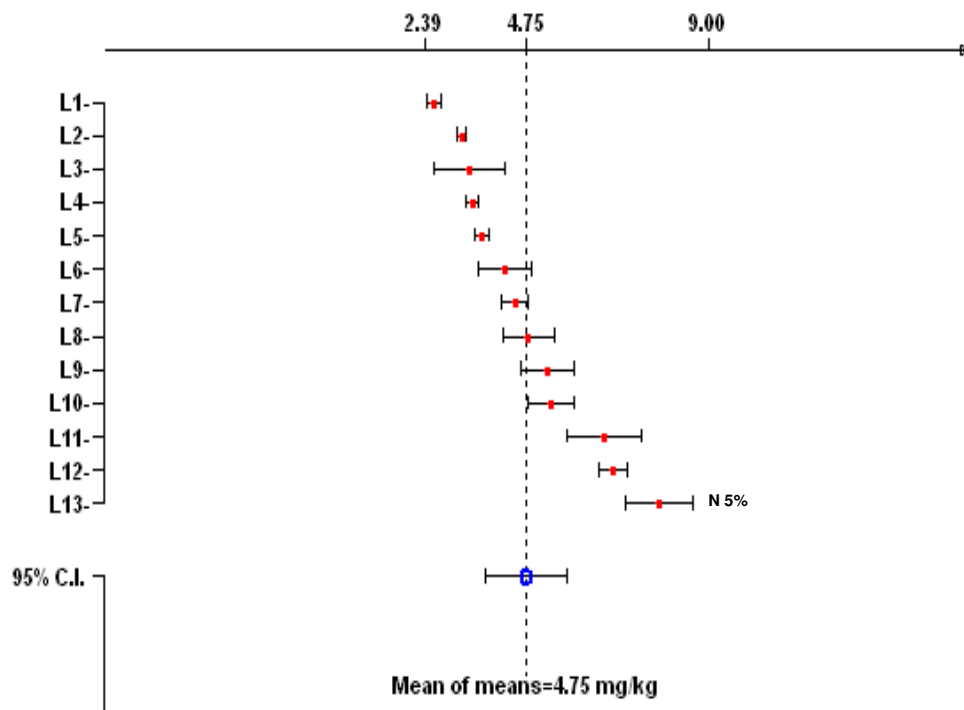**Diagram of means and 95% confidence intervals (to Tab. 4d1**

Table 4e1: Iron accepted results in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	2 ICP OES 2	12.07	0.41	0.43	11.60	12.80	11.80	12.00	12.10	12.10
L 2	3 ET AAS 3	12.17	0.10	0.11	11.99	12.17	12.19	12.16	12.22	12.30
L 3	4 ICP-SF-MS 3	12.73	0.68	0.71	11.80	13.40	12.10	12.80	12.80	13.50
L 4	26 F AAS 3	12.73	0.41	0.43	13.00	12.80	12.40	12.40	13.40	12.40
L 5	16 ICP OES 3	13.58	0.81	0.85	13.59	14.61	14.48	12.76	13.25	12.81
L 6	21 ETV-ICP OES 3	13.62	0.42	0.44	13.00	14.00	13.70	13.60	13.30	14.10
L 7	20 ICP OES 1	14.15	1.03	1.08	14.30	13.60	13.90	12.60	15.00	15.50
L 8	17 XRF 2	14.33	0.82	0.86	14.00	14.00	16.00	14.00	14.00	14.00
L 9	15 ICP OES 2	14.83	0.75	0.79	16.00	14.00	15.00	15.00	14.00	15.00
L 10	25 ICP OES 3	15.83	4.07	4.27	19.00	14.00	22.00	13.00	16.00	11.00
L 11	11 ICP OES (-)	18.25	2.81	2.95	15.40	23.40	18.80	16.40	17.20	18.30
L 12	9 ICP OES 2	19.42	2.61	2.74	22.00	21.20	21.90	18.40	16.70	16.30
L 13	24 F AAS 3	20.76	1.54	1.62	21.03	20.75	21.52	22.22	21.26	17.78

Range [min..max]	[11.00 .. 23.40]
	Case of No Pooling
Mean of means	14.96
95% H.W. Confidence Interval	1.71
95% H.W. Tolerance Interval	8.71

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**

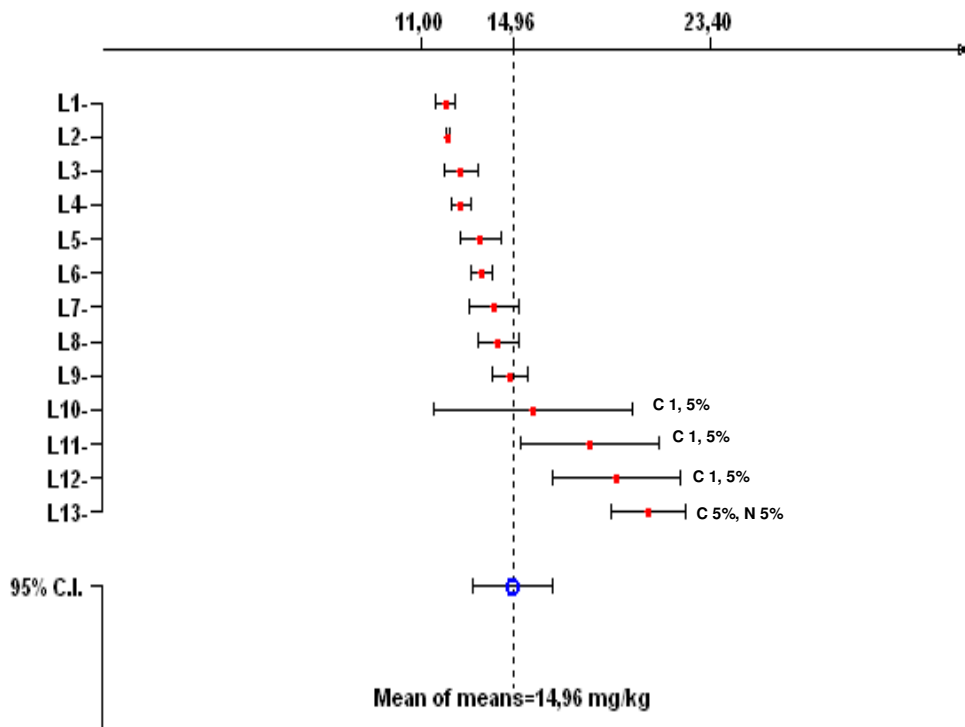**Diagram of means and 95% confidence intervals (to Tab. 4e1**

Table 4f1: Magnesium evaluation in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	17 XRF 2	40.00	1.26	1.33	40.00	39.00	39.00	41.00	42.00	39.00
L 2	24 F AAS 3	52.64	0.75	0.79	53.35	52.62	51.83	53.71	52.35	51.99
L 3	21 ETV-ICP OES 3	52.77	0.99	1.04	54.00	52.70	53.00	51.40	53.60	51.90
L 4	15 ICP OES 2	54.67	2.16	2.27	54.00	55.00	56.00	58.00	52.00	53.00
L 5	20 ICP OES 1	54.75	1.97	2.07	57.50	53.20	53.60	55.00	56.60	52.60
L 6	2 ICP OES 2	55.75	0.35	0.37	55.80	55.40	55.70	55.50	55.70	56.40
L 7	25 ICP OES 3	56.33	2.94	3.09	56.00	53.00	59.00	60.00	57.00	53.00
L 8	16 ICP OES 3	57.38	1.31	1.38	55.30	58.82	58.60	57.84	56.94	56.80
L 9	11 ICP OES 1	59.35	2.41	2.53	58.40	58.90	62.00	55.30	60.20	61.30
L 10	26 F AAS (3)	59.42	2.49	2.61	61.10	59.40	60.30	57.20	55.90	62.60
L 11	4 ICP-SF-MS 3	59.98	0.73	0.76	59.00	60.50	60.10	59.20	60.80	60.30
L 12	9 ICP OES 2	82.38	5.81	6.10	91.20	83.00	83.60	76.00	75.80	84.70

Range [min..max]	[39.00 .. 91.20]
	Case of No Pooling
Mean of means	57.12
95% H.W. Confidence Interval	6.07
95% H.W. Tolerance Interval	30.19

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**

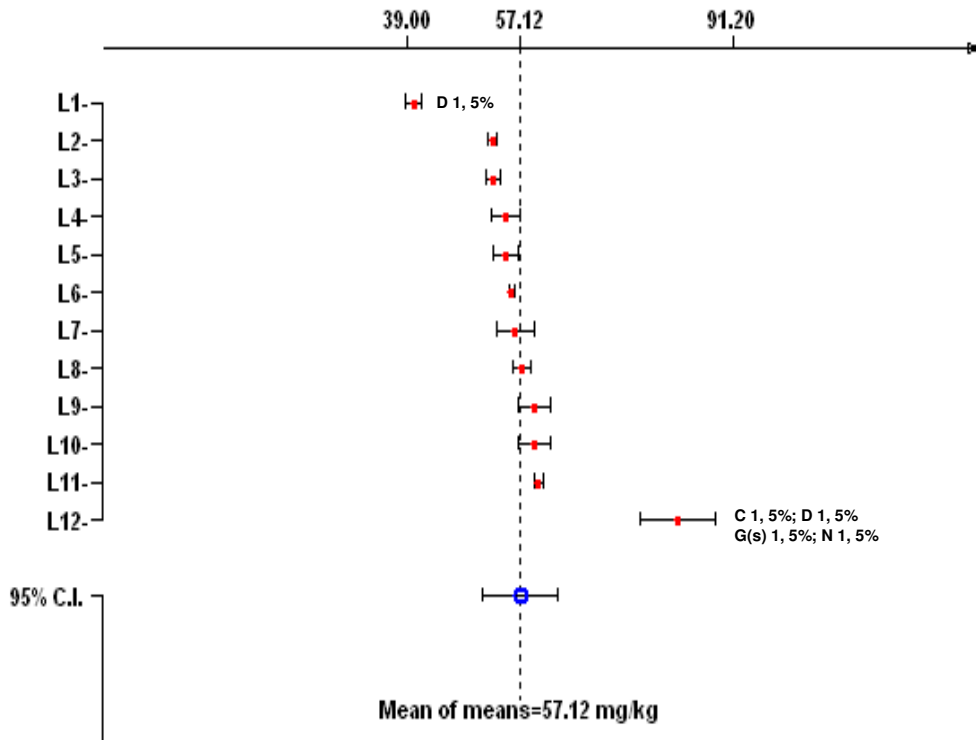**Diagram of means and 95% confidence intervals (to Tab. 4f1**

Mean of means=57.12 mg/kg

Table 4f2: Magnesium evaluation in run 2 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	17 XRF 2	40.00	1.26	1.33	40.00	39.00	39.00	41.00	42.00	39.00
L 2	24 F AAS 3	52.64	0.75	0.79	53.35	52.62	51.83	53.71	52.35	51.99
L 3	21 ETV-ICP OES 3	52.77	0.99	1.04	54.00	52.70	53.00	51.40	53.60	51.90
L 4	15 ICP OES 2	54.67	2.16	2.27	54.00	55.00	56.00	58.00	52.00	53.00
L 5	20 ICP OES 1	54.75	1.97	2.07	57.50	53.20	53.60	55.00	56.60	52.60
L 6	2 ICP OES 2	55.75	0.35	0.37	55.80	55.40	55.70	55.50	55.70	56.40
L 7	25 ICP OES 3	56.33	2.94	3.09	56.00	53.00	59.00	60.00	57.00	53.00
L 8	16 ICP OES 3	57.38	1.31	1.38	55.30	58.82	58.60	57.84	56.94	56.80
L 9	11 ICP OES 1	59.35	2.41	2.53	58.40	58.90	62.00	55.30	60.20	61.30
L 10	26 F AAS (3)	59.42	2.49	2.61	61.10	59.40	60.30	57.20	55.90	62.60
L 11	4 ICP-SF-MS 3	59.98	0.73	0.76	59.00	60.50	60.10	59.20	60.80	60.30

Range [min..max]	[39.00 .. 62.60]
	Case of No Pooling
Mean of means	54.82
95% H.W. Confidence Interval	3.72
95% H.W. Tolerance Interval	18.05

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**

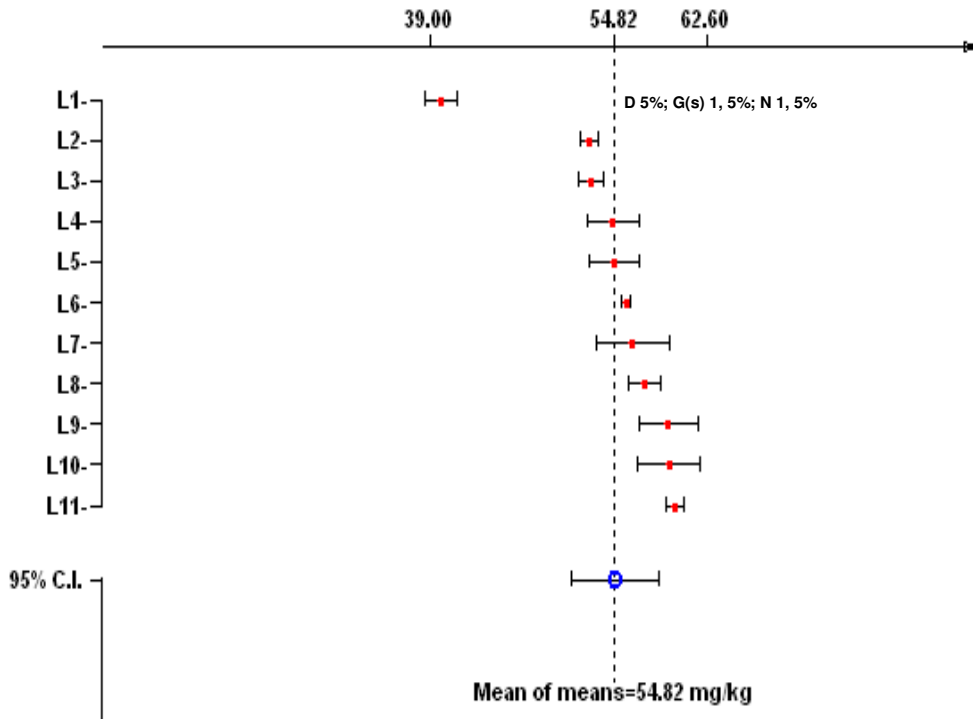**Diagram of means and 95% confidence intervals (to Tab. 4f2**

Mean of means=54.82 mg/kg

Table 4f3: Magnesium accepted results in run 3 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	24 F AAS 3	52.64	0.75	0.79	53.35	52.62	51.83	53.71	52.35	51.99
L 2	21 ETV-ICP OES 3	52.77	0.99	1.04	54.00	52.70	53.00	51.40	53.60	51.90
L 3	15 ICP OES 2	54.67	2.16	2.27	54.00	55.00	56.00	58.00	52.00	53.00
L 4	20 ICP OES 1	54.75	1.97	2.07	57.50	53.20	53.60	55.00	56.60	52.60
L 5	2 ICP OES 2	55.75	0.35	0.37	55.80	55.40	55.70	55.50	55.70	56.40
L 6	25 ICP OES 3	56.33	2.94	3.09	56.00	53.00	59.00	60.00	57.00	53.00
L 7	16 ICP OES 3	57.38	1.31	1.38	55.30	58.82	58.60	57.84	56.94	56.80
L 8	11 ICP OES 1	59.35	2.41	2.53	58.40	58.90	62.00	55.30	60.20	61.30
L 9	26 F AAS (3)	59.42	2.49	2.61	61.10	59.40	60.30	57.20	55.90	62.60
L 10	4 ICP-SF-MS 3	59.98	0.73	0.76	59.00	60.50	60.10	59.20	60.80	60.30

Range [min..max]	[51.40 .. 62.60]
	Case of No Pooling
Mean of means	56.30
95% H.W. Confidence Interval	1.92
95% H.W. Tolerance Interval	9.08

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**

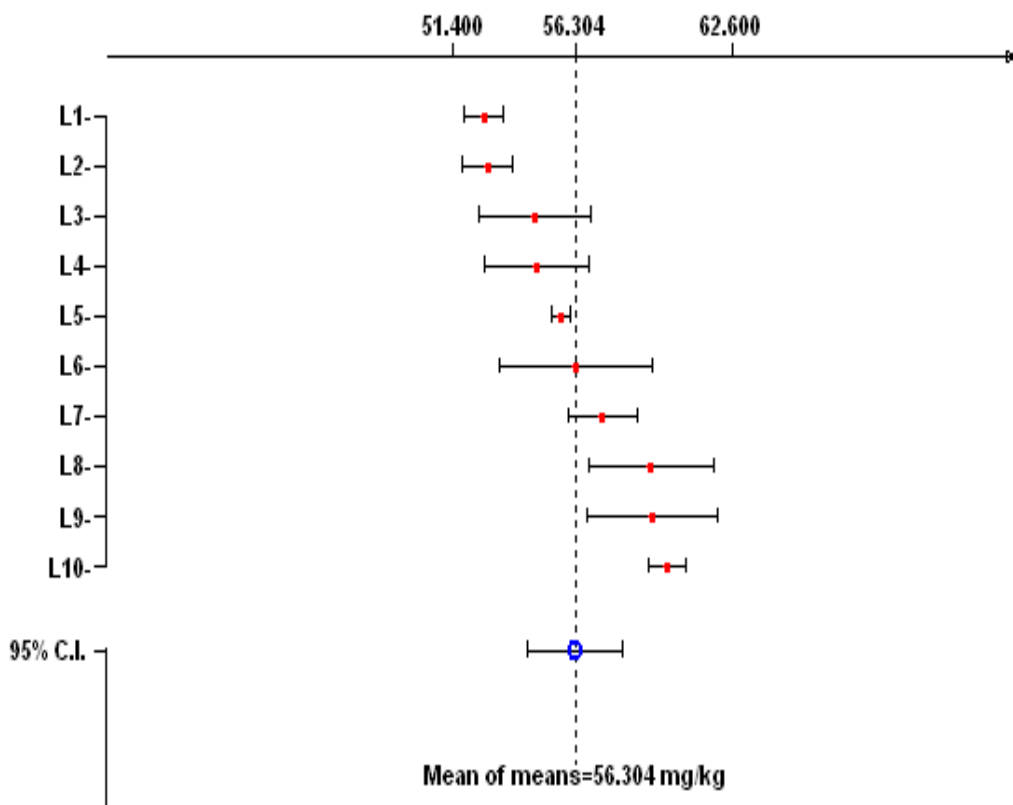**Diagram of means and 95% confidence intervals (to Tab. 4f3**

Table 4g1: Sodium accepted results in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	17 XRF 2	10.20	1.92	2.39	9.00		13.00	8.00	10.00	11.00
L 2	25 F AAS (3)	10.87	1.40	1.47	10.00	9.50	13.00	12.00	9.70	11.00
L 3	26 F AAS 3	11.23	0.23	0.25	11.40	11.40	11.20	10.80	11.40	11.20
L 4	20 ICP OES 1	11.85	0.45	0.47	12.40	12.20	12.00	11.20	11.80	11.50
L 5	21 ETV-ICP OES 3	11.97	0.38	0.40	11.50	11.50	12.20	12.20	12.00	12.40
L 6	4 ICP-SF-MS 3	12.82	0.08	0.08	12.80	12.70	12.80	12.80	12.90	12.90
L 7	16 ICP OES 3	12.85	0.77	0.80	11.79	12.40	12.40	13.68	13.25	13.60
L 8	15 ET AAS (2)	13.00	0.89	0.94	13.00	12.00	12.00	14.00	14.00	13.00
L 9	2 F AAS (2)	13.13	0.08	0.09	13.00	13.20	13.20	13.10	13.10	13.20
L 10	24 F AAS 3	14.63	1.83	1.93	15.90	13.60	17.83	13.55	13.39	13.53

Range [min..max]	[8.00 .. 17.83]
	Case of No Pooling
Mean of means	12.26
95% H.W. Confidence Interval	0.93
95% H.W. Tolerance Interval	4.38

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**

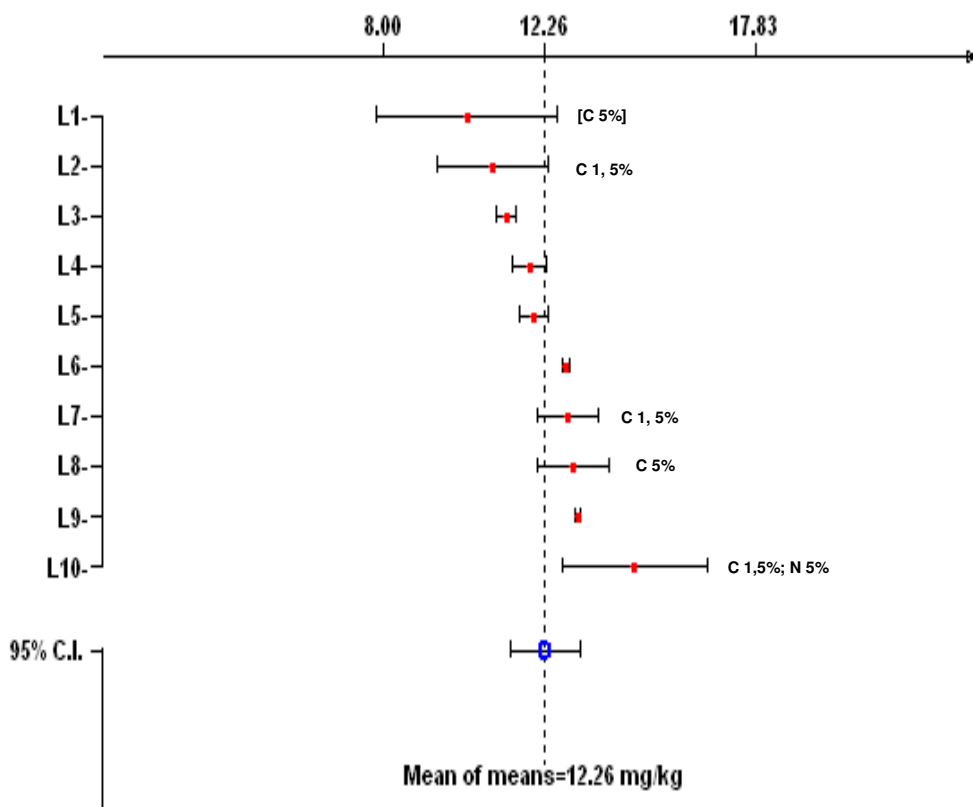**Diagram of means and 95% confidence intervals (to Tab. 4g1**

Table 4h1: Silicon accepted results in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 ICP OES 3	13.2	3.9	4.1	11.0	15.0	20.0	13.0	10.0	10.0
L 2	25 ICP OES 3	15.8	3.0	3.1	19.0	19.0	13.0	12.0	15.0	17.0
L 3	4 ICP-SF-MS 3	17.8	2.9	3.0	16.7	19.4	14.1	20.6	15.2	20.8
L 4	21 ETV-ICP OES 3	18.6	0.4	0.4	18.4	19.2	18.6	18.3	19.0	18.2
L 5	17 XRF 2	19.5	0.5	0.6	19.0	20.0	19.0	20.0	19.0	20.0

Range [min..max]	[10.0 .. 20.8]
	Case of No Pooling
Mean of means	17.0
95% H.W. Confidence Interval	3.1
95% H.W. Tolerance Interval	12.8

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. 4h1
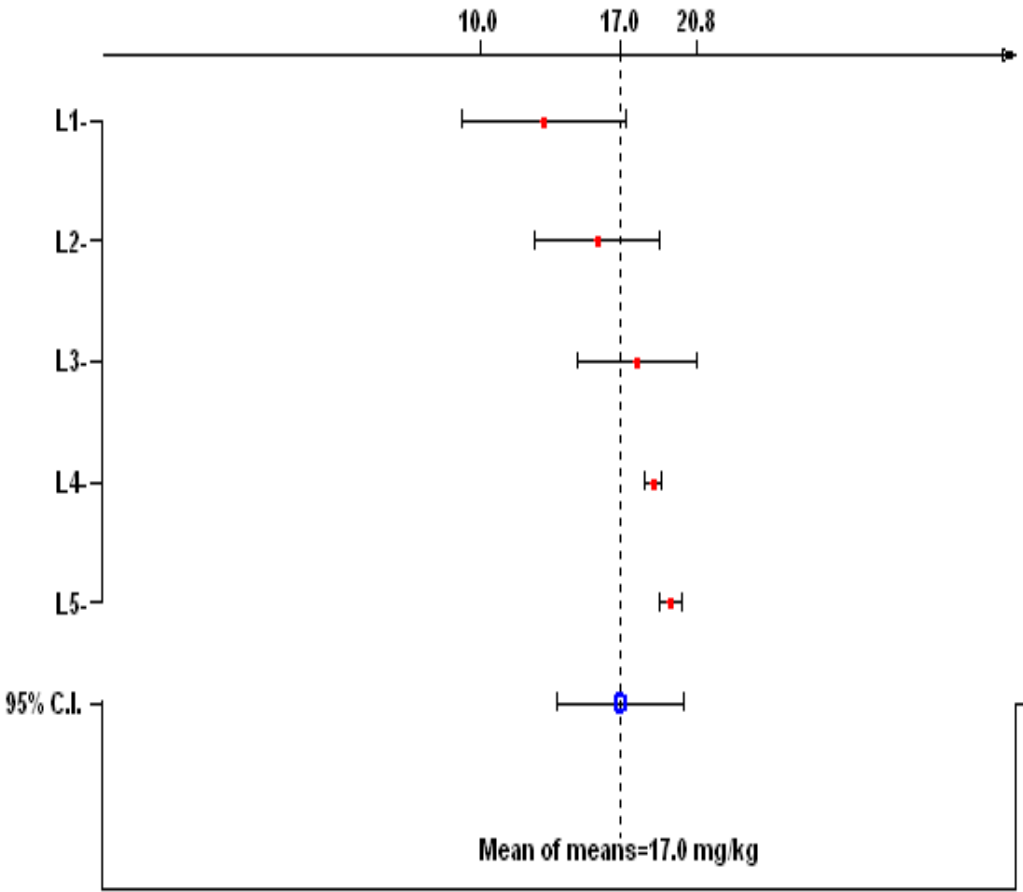
No Pooling - Lab means & CI for silicon

Mean of means=17.0 mg/kg

Table 4i1: Titanium accepted results in run 1 (values in mg/kg)

Line no.	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	16 ICP OES 3	3.99	0.18	0.19	3.76	4.30	3.96	4.02	3.91	3.98
L 2	15 ICP OES 2	4.00	0.00	0.00	4.00	4.00	4.00	4.00	4.00	4.00
L 3	2 ICP OES 2	4.04	0.09	0.10	3.97	4.01	3.90	4.10	4.13	4.11
L 4	3 ET AAS 3	4.46	0.14	0.15	4.32	4.46	4.49	4.42	4.37	4.72
L 5	25 ICP OES 3	4.70	0.51	0.53	4.40	4.40	4.70	4.60	4.40	5.70
L 6	4 ICP-SF-MS 3	4.74	0.12	0.13	4.59	4.87	4.84	4.76	4.58	4.77
L 7	17 XRF 2	4.80	0.45	0.56	5.00	5.00		5.00	5.00	4.00
L 8	11 ICP OES (-)	5.02	0.47	0.49	5.20	5.20	4.40	4.60	5.00	5.70
L 9	20 ICP OES 1	5.08	0.37	0.39	5.60	4.80	5.00	5.10	5.40	4.60
L 10	24 ICP OES 3	5.41	0.20	0.21	5.54	5.11	5.49	5.26	5.67	5.38
L 11	26 ICP OES 3	5.53	0.38	0.40	6.00	5.40	5.40	6.00	5.30	5.10
L 12	9 ICP OES 2	5.58	0.52	0.55	5.95	5.93	5.86	4.90	4.91	5.90
L 13	21 ETV-ICP OES 3	6.47	0.41	0.43	6.40	5.80	6.60	6.30	7.00	6.70

Range [min..max]	[3.76 .. 7.00]
	Case of No Pooling
Mean of means	4.91
95% H.W. Confidence Interval	0.44
95% H.W. Tolerance Interval	2.23

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. 4i1
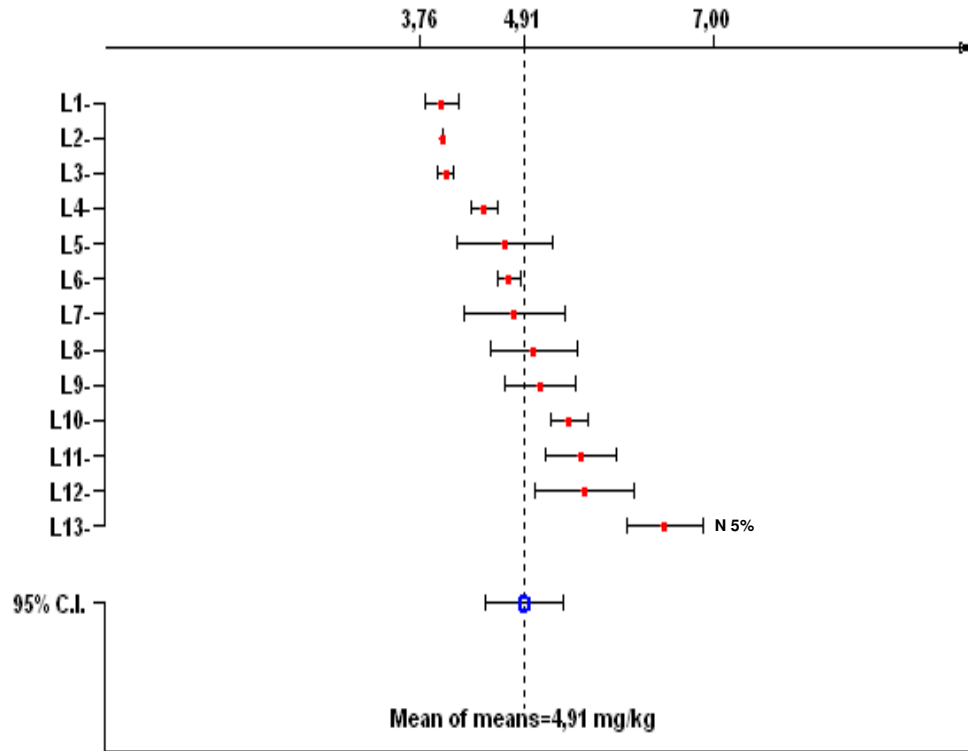
No Pooling - Lab means & CI for titanium

Appendix of certification report ERM®-ED103

Table 4j1: Total Boron accepted results in run 1 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	21 TITR 3	43,133	0,121	0,127	43,100	43,000	43,200	43,300	43,200	43,000
L 2	25 TITR 3	43,272	0,045	0,048	43,200	43,300	43,260	43,250	43,290	43,330
L 3	26 TITR 3	43,450	0,091	0,095	43,480	43,330	43,390	43,590	43,420	43,490
L 4	5 TITR 2	43,466	0,174	0,183	43,356	43,497	43,477	43,790	43,351	43,324
L 5	6 ICPOES 2	43,663	0,304	0,319	44,210	43,600	43,800	43,370	43,520	43,480
L 6	15 TITR 1	43,878	0,046	0,048	43,840	43,840	43,950	43,840	43,900	43,900

Range [min..max]	[43,000 .. 44,210]
	Case of No Pooling
Mean of means	43,477
95% H.W. Confidence Interval	0,280
95% H.W. Tolerance Interval	1,179

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**

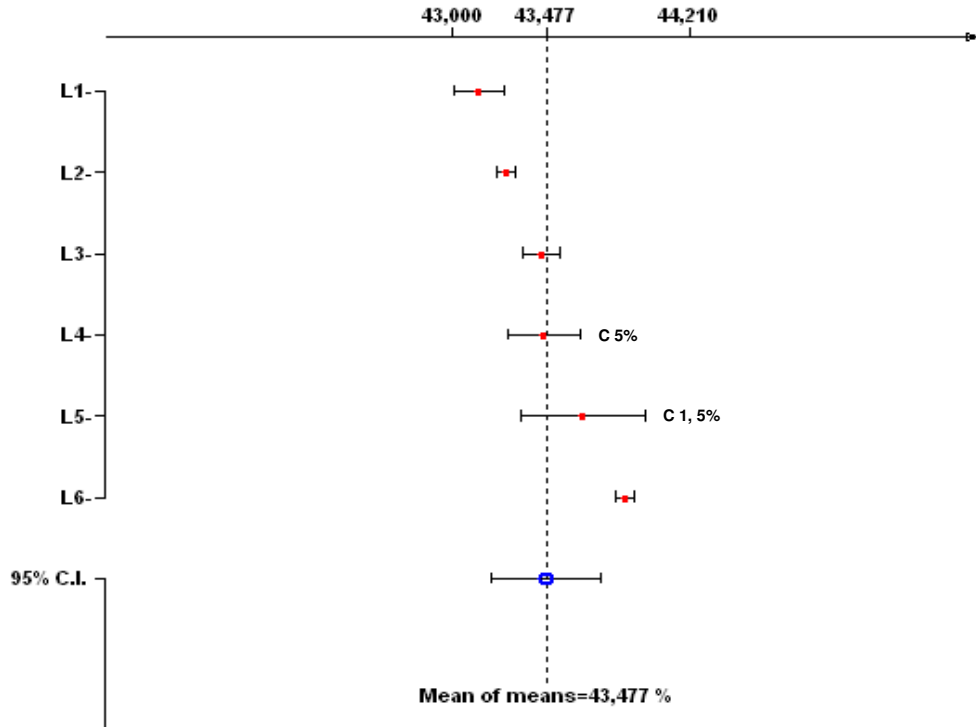**Diagram of means and 95% confidence intervals (to Tab. 4j1**

Table 4k1: Adherent Boron Oxide accepted results in run 1 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	20 ICP OES 1	0.0662	0.0020	0.0021	0.0634	0.0651	0.0652	0.0667	0.0685	0.0685
L 2	25 ICP OES (2)	0.0678	0.0034	0.0036	0.0670	0.0660	0.0640	0.0690	0.0740	0.0670
L 3	2 ICP OES (-)	0.0698	0.0020	0.0021	0.0713	0.0670	0.0716	0.0682	0.0690	0.0715
L 4	21 TITR 3	0.0717	0.0012	0.0013	0.0730	0.0700	0.0710	0.0720	0.0710	0.0730
L 5	5 TITR 2	0.0753	0.0021	0.0022	0.0724	0.0759	0.0763	0.0753	0.0737	0.0783

Range [min..max]	[0.0634 .. 0.0783]
	Case of No Pooling
Mean of means	0.0702
95% H.W. Confidence Interval	0.0044
95% H.W. Tolerance Interval	0.0179

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**

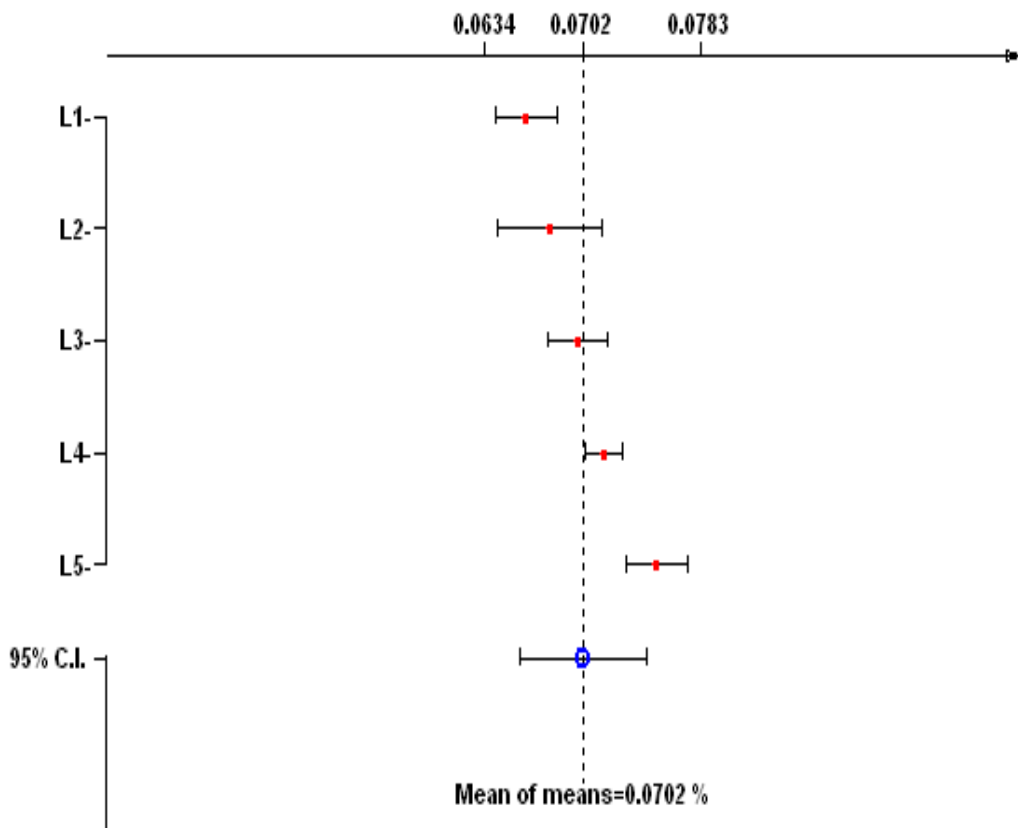**Diagram of means and 95% confidence intervals (to Tab. 4k1**

Table 4I1: Carbon evaluation in run 1 (values in%)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 Comb.-IR 3	0.01470	0.00060	0.00063	0.01500	0.01450	0.01530	0.01360	0.01480	0.01500
L 2	22 Comb.-IR 3	0.01570	0.00179	0.00188	0.01511	0.01710	0.01739	0.01719	0.01317	0.01421
L 3	21 Comb.-IR 3	0.01607	0.00057	0.00060	0.01680	0.01570	0.01650	0.01640	0.01540	0.01560
L 4	9 Comb.-IR 2	0.01637	0.00064	0.00067	0.01580	0.01590	0.01570	0.01700	0.01670	0.01710
L 5	10 Comb.-IR 2	0.01733	0.00052	0.00054	0.01700	0.01700	0.01800	0.01700	0.01800	0.01700
L 6	24 Comb.-IR 3	0.01798	0.00192	0.00202	0.01780	0.02110	0.01550	0.01660	0.01880	0.01810
L 7	25 Comb.-IR 3	0.01850	0.00048	0.00051	0.01940	0.01820	0.01820	0.01810	0.01850	0.01860
L 8	18 Comb.-IR 2	0.01872	0.00113	0.00119	0.01880	0.01800	0.02060	0.01940	0.01770	0.01780
L 9	20 Comb.-IR 1	0.02075	0.00173	0.00182	0.02000	0.01820	0.02160	0.02240	0.01970	0.02260
L 10	16 Comb.-IR 3	0.02182	0.00046	0.00049	0.02230	0.02160	0.02210	0.02100	0.02200	0.02190
L 11	6 Comb.-IR 2	0.02967	0.00929	0.00975	0.03100	0.02000	0.02600	0.02900	0.02500	0.04700
L 12	15 Comb.-IR 3	0.11167	0.01169	0.01227	0.09000	0.12000	0.11000	0.11000	0.12000	0.12000

Range [min..max]	[0.01317 .. 0.12000]
	Case of No Pooling
Mean of means	0.02661
95% H.W. Confidence Interval	0.01721
95% H.W. Tolerance Interval	0.08563

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. 4I1

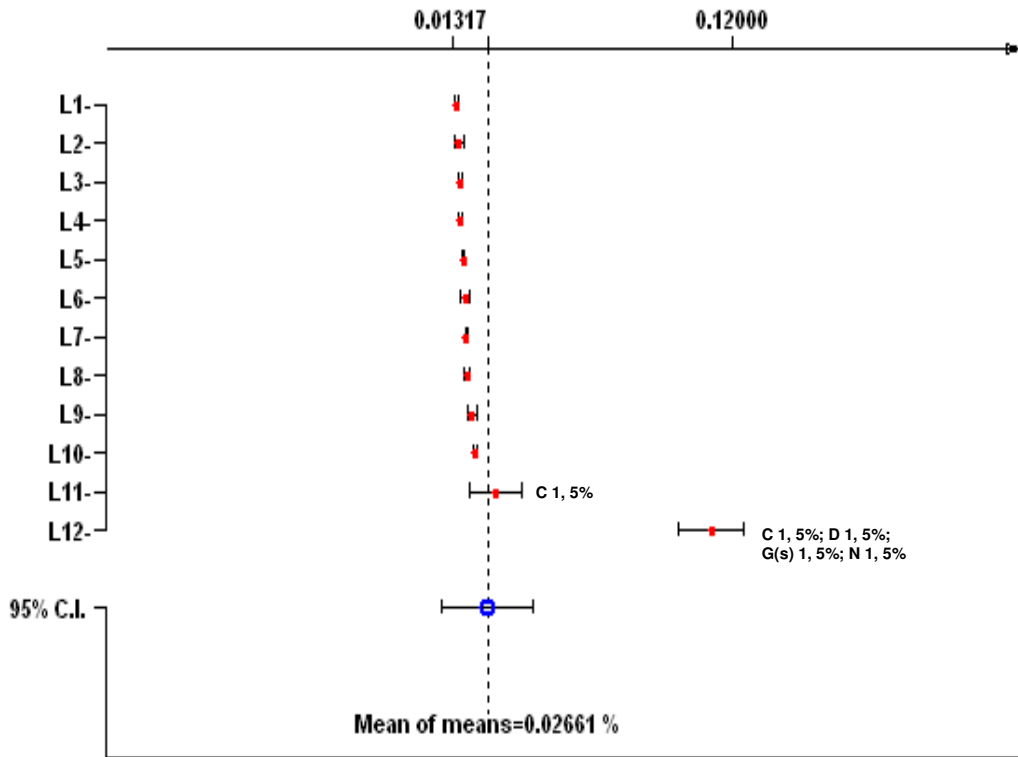# No Pooling - Lab means & CI for carbon

Appendix of certification report ERM®-ED103

Table 4I2: Carbon evaluation in run 2 (values in%)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 Comb.,-IR 3	0.01470	0.00060	0.00063	0.01500	0.01450	0.01530	0.01360	0.01480	0.01500
L 2	22 CGHE-IR 3	0.01570	0.00179	0.00188	0.01511	0.01710	0.01739	0.01719	0.01317	0.01421
L 3	21 CGHE-IR 3	0.01607	0.00057	0.00060	0.01680	0.01570	0.01650	0.01640	0.01540	0.01560
L 4	9 Comb.,-IR 2	0.01637	0.00064	0.00067	0.01580	0.01590	0.01570	0.01700	0.01670	0.01710
L 5	10 Comb.,-IR 2	0.01733	0.00052	0.00054	0.01700	0.01700	0.01800	0.01700	0.01800	0.01700
L 6	24 Comb.,-IR 3	0.01798	0.00192	0.00202	0.01780	0.02110	0.01550	0.01660	0.01880	0.01810
L 7	25 Comb.,-IR 3	0.01850	0.00048	0.00051	0.01940	0.01820	0.01820	0.01810	0.01850	0.01860
L 8	18 Comb.,-IR 2	0.01872	0.00113	0.00119	0.01880	0.01800	0.02060	0.01940	0.01770	0.01780
L 9	20 Comb.,-IR 1	0.02075	0.00173	0.00182	0.02000	0.01820	0.02160	0.02240	0.01970	0.02260
L 10	16 Comb.,-IR 3	0.02182	0.00046	0.00049	0.02230	0.02160	0.02210	0.02100	0.02200	0.02190
L 11	6 Comb.,-IR 2	0.02967	0.00929	0.00975	0.03100	0.02000	0.02600	0.02900	0.02500	0.04700

Range [min..max]	[0.01317 .. 0.04700]
	Case of No Pooling
Mean of means	0.01887
95% H.W. Confidence Interval	0.00280
95% H.W. Tolerance Interval	0.01358

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**

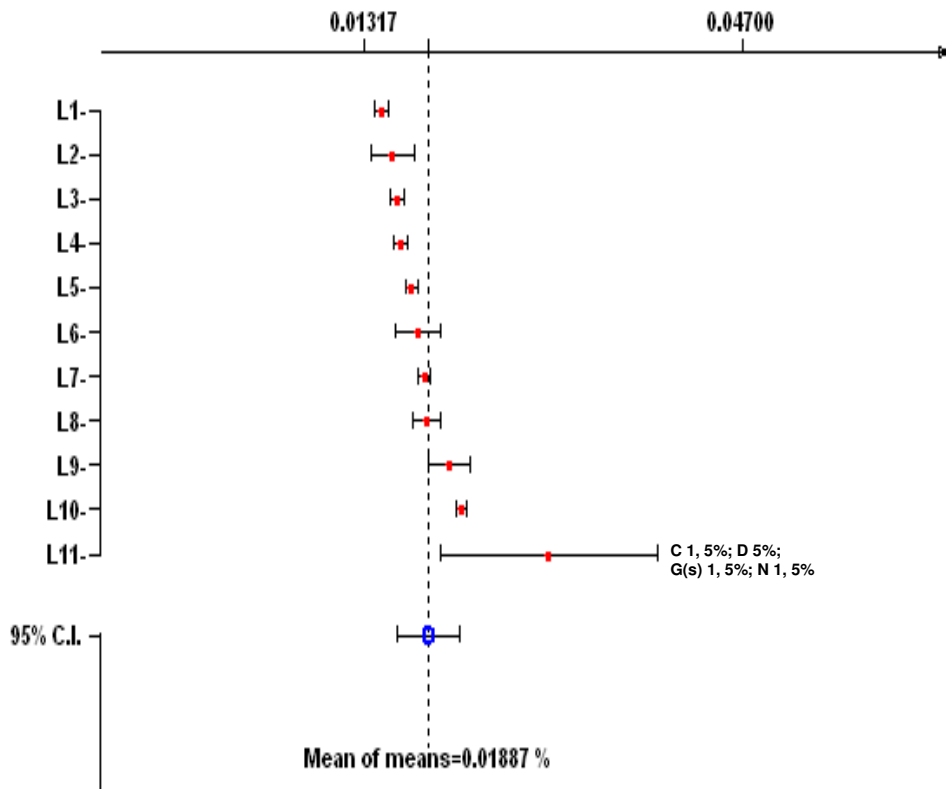**Diagram of means and 95% confidence intervals (to Tab. 4I2**

Table 4l3: Carbon accepted results in run 3 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 Comb.,-IR 3	0.01470	0.00060	0.00063	0.01500	0.01450	0.01530	0.01360	0.01480	0.01500
L 2	22 CGHE-IR 3	0.01570	0.00179	0.00188	0.01511	0.01710	0.01739	0.01719	0.01317	0.01421
L 3	21 CGHE-IR 3	0.01607	0.00057	0.00060	0.01680	0.01570	0.01650	0.01640	0.01540	0.01560
L 4	9 Comb.,-IR 2	0.01637	0.00064	0.00067	0.01580	0.01590	0.01570	0.01700	0.01670	0.01710
L 5	10 Comb.,-IR 2	0.01733	0.00052	0.00054	0.01700	0.01700	0.01800	0.01700	0.01800	0.01700
L 6	24 Comb.,-IR 3	0.01798	0.00192	0.00202	0.01780	0.02110	0.01550	0.01660	0.01880	0.01810
L 7	25 Comb.,-IR 3	0.01850	0.00048	0.00051	0.01940	0.01820	0.01820	0.01810	0.01850	0.01860
L 8	18 Comb.,-IR 2	0.01872	0.00113	0.00119	0.01880	0.01800	0.02060	0.01940	0.01770	0.01780
L 9	20 Comb.,-IR 1	0.02075	0.00173	0.00182	0.02000	0.01820	0.02160	0.02240	0.01970	0.02260
L 10	16 Comb.,-IR 3	0.02182	0.00046	0.00049	0.02230	0.02160	0.02210	0.02100	0.02200	0.02190

Range [min..max]	[0.01317 .. 0.02260]
	Case of No Pooling
Mean of means	0.01779
95% H.W. Confidence Interval	0.00161
95% H.W. Tolerance Interval	0.00760

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**
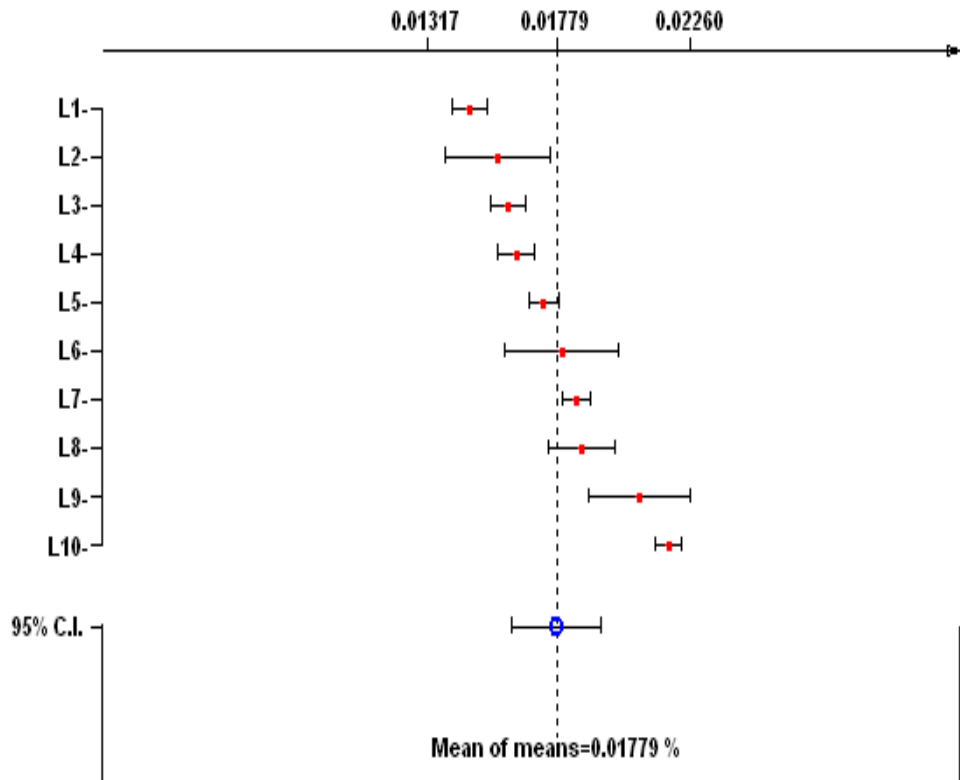
Diagram of means and 95% confidence intervals (to Tab. 4l3

Table 4m1: Nitrogen accepted results in run 1 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	18 CGHE-TC (3)	54.492	0.231	0.242	54.660	54.850	54.260	54.290	54.370	54.520
L 2	15 CGHE-TC 1	54.938	0.057	0.060	54.890	55.030	54.910	54.970	54.950	54.880
L 3	21 CGHE-TC 3	55.217	0.141	0.148	55.250	55.180	55.040	55.100	55.300	55.430
L 4	16 CGHE-TC 3	55.260	0.073	0.077	55.220	55.130	55.320	55.290	55.280	55.320
L 5	22 CGHE-TC 3	55.484	0.097	0.101	55.363	55.570	55.513	55.428	55.418	55.612
L 6	21 TITR (3)	55.593	0.077	0.080	55.480	55.640	55.700	55.560	55.620	55.560
L 7	9 CGHE-TC 2	55.695	0.244	0.256	56.070	55.850	55.770	55.440	55.500	55.540
L 8	26 CGHE-TC 3	55.713	0.151	0.159	55.560	55.800	55.950	55.750	55.660	55.560
L 9	25 TITR 3	55.728	0.214	0.225	55.850	55.850	55.750	55.920	55.330	55.670
L 10	1 CGHE-TC 2	55.917	0.719	0.755	56.400	54.700	56.700	56.300	55.600	55.800
L 11	20 CGHE-TC 1	56.470	0.224	0.235	56.220	56.190	56.580	56.680	56.700	56.450
L 12	24 CGHE-TC 3	56.847	0.380	0.399	56.260	56.980	56.620	57.290	57.170	56.760

Range [min..max]	[54.260 .. 57.290]
	Case of No Pooling
Mean of means	55.613
95% H.W. Confidence Interval	0.401
95% H.W. Tolerance Interval	1.998

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**

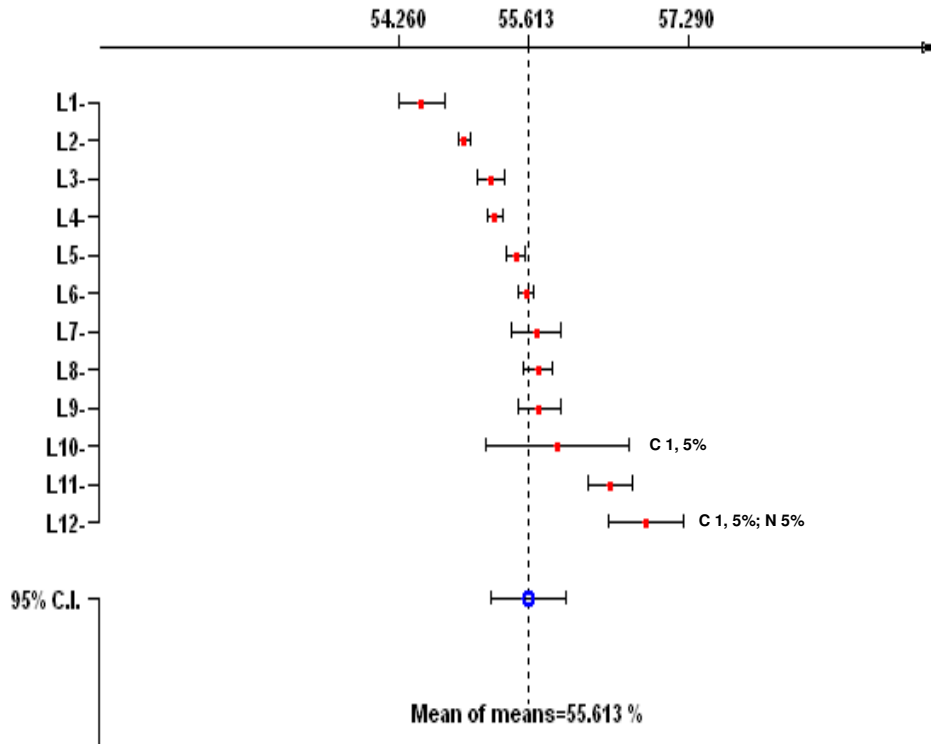**Diagram of means and 95% confidence intervals (to Tab. 4m1**

Table 4n1: Oxygen accepted results in run 1 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	26 CGHE-IR 3	0.4995	0.0097	0.0102	0.4960	0.4870	0.4940	0.5000	0.5150	0.5050
L 2	20 CGHE-IR 1	0.5689	0.0097	0.0102	0.5794	0.5774	0.5615	0.5575	0.5618	0.5760
L 3	9 CGHE-IR 2	0.6180	0.0052	0.0054	0.6230	0.6180	0.6200	0.6140	0.6100	0.6230
L 4	18 CGHE-IR (3)	0.6350	0.0086	0.0090	0.6260	0.6350	0.6410	0.6380	0.6460	0.6240
L 5	22 CGHE-IR 3	0.6374	0.0165	0.0174	0.6610	0.6475	0.6457	0.6251	0.6277	0.6175
L 6	1 CGHE-IR 2	0.6800	0.0268	0.0282	0.6700	0.7300	0.6800	0.6800	0.6700	0.6500
L 7	24 CGHE-IR 3	0.6917	0.0172	0.0181	0.6800	0.6900	0.7000	0.7200	0.6900	0.6700
L 8	21 CGHE-IR 3	0.7370	0.0061	0.0064	0.7450	0.7320	0.7390	0.7420	0.7350	0.7290
L 9	15 CGHE-IR 1	0.8667	0.0344	0.0362	0.9200	0.8900	0.8500	0.8600	0.8600	0.8200
L 10	16 CGHE-IR 3	0.8685	0.0056	0.0059	0.8650	0.8760	0.8700	0.8600	0.8720	0.8680

Range [min..max]	[0.4870 .. 0.9200]
	Case of No Pooling
Mean of means	0.6803
95% H.W. Confidence Interval	0.0848
95% H.W. Tolerance Interval	0.4004

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
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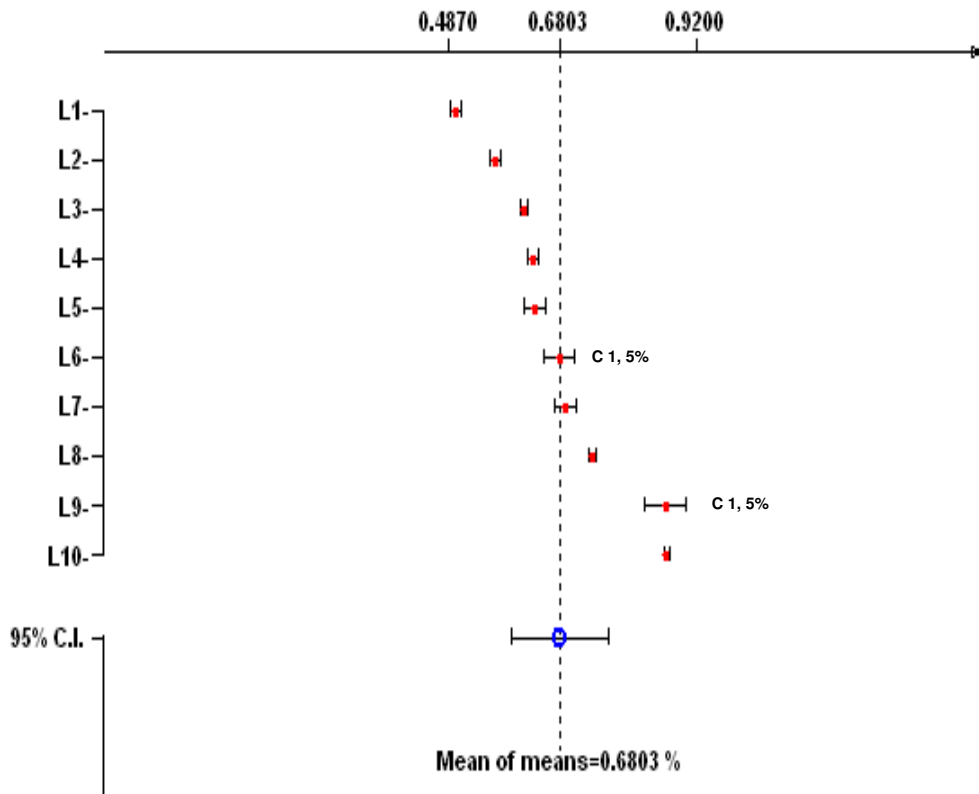**Diagram of means and 95% confidence intervals (to Tab. 4n1**

Table 4o1: Water accepted results in run 1 (values in %)

Line no.	Lab Abbreviation	Mean (%)	STDev	H.W. C.I. (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	16 GRAV	0.035	0.008	0.076	0.041	0.029				
L 2	26 GRAV	0.046	0.005	0.005	0.045	0.039	0.046	0.054	0.047	0.046
L 3	25 TITR	0.048	0.005	0.005	0.040	0.049	0.046	0.050	0.054	0.050
L 4	24 GRAV	0.085	0.021	0.022	0.111	0.059	0.104	0.094	0.073	0.069
L 5	21 El.CHEM	0.143	0.008	0.009	0.150	0.150	0.140	0.150	0.140	0.130

Range [min..max]	[0.029 .. 0.150]
	Case of No Pooling
Mean of means	0.072
95% H.W. Confidence Interval	0.055
95% H.W. Tolerance Interval	0.225

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. 4o1