**BAM Federal Institute for Materials Research and Testing**

in co-operation with the

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

# The Certification of Mass Fractions of Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, Ti, V, Zr, N, O, $C_{total}$, and $C_{free}$ in Silicon Carbide Powder (transparent 200/F)

# BAM-S008

## Certification report

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## Abstract

This report describes the preparation and certification of reference material BAM-S008, a silicon carbide powder (transparent 200/F) with certified impurity contents, carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additional determined data are listed below.

| Parameter | Mass fraction [1] in mg/kg | Uncertainty [2] in mg/kg |
|---|---|---|
| Aluminium | 47 | 7 |
| Boron | 3.0 | 1.2 |
| Calcium | 0.25 | 0.06 |
| Chromium | 0.16 | 0.05 |
| Copper | 0.10 | 0.05 |
| Iron | 4.8 | 0.8 |
| Magnesium | 0.07 | 0.07 |
| Manganese | 0.05 | 0.02 |
| Sodium | 0.17 | 0.09 |
| Nickel | 0.9 | 0.5 |
| Titanium | 67 | 6 |
| Vanadium | 275 | 18 |
| Zirconium | 4.4 | 1.2 |
| Nitrogen | 18 | 4 |
| Oxygen | 146 | 36 |
| | **Mass fraction [1] in %** | **Uncertainty [2] in %** |
| $Carbon_{total}$ | 29.9 | 0.1 |
| $Carbon_{free}$ | 0.045 | 0.010 |

1) The certified values are the means of 6-17 series of results (depending on the parameter) obtained by different laboratories. 2 up to 8 different analytical methods were used for the measurement of one parameter. The methods applied for determination of element mass fractions were calibrated using pure substances of definite stoichiometry or solutions prepared from them, thus achieving traceability to SI unit.

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

## Indicative values

| Parameter | Mass fraction [1] in mg/kg |
|---|---|
| Silicon dioxide | < 0.01 |
| $Silicon_{free}$ | < 0.03 |

1) The indicative values are estimated from 3 series of results each obtained by different laboratories.

## Informative values

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

| Parameter | | Mass fraction in % | Uncertainty in mass % |
|---|---|---|---|
| Phases: | SiC-6H | 99.7 [1] | 0.2 [2] |
| | SiC-15R | 0.23[1] | 0.2 [2] |
| | SiC-4H | 0.06[1] | 0.2 [2] |
| Particle size distribution | | **Size distribution in µm** | |
| | $d_{10}$ | 24.3 [3] | |
| | $d_{50}$ | 65.4 [3] | |
| | $d_{90}$ | 125.3 [3] | |

1) The analyses were carried out by high resolution powder diffraction using synchrotron radiation (λ= 0.08 nm) and Rietveld method for evaluation.
2) The calculation of the standard uncertainty is based on the evaluation of ten specimens by the Rietveld method.
3) The particle size distribution was determined by laser light diffraction method.

Contents

# 1 Introduction

## 1.1 Scope

Silicon carbide is a material of extreme hardness and therefore very wear-resistant. This is because of the tight covalent bond of Si and C atoms, which is also the reason for the high thermal conductivity, high elasticity modulus, the low thermal expansion and the very high chemical durability. The high oxidation resistance is based on thin layers of oxides which are formed in some seconds on fresh surfaces after breaking or forming the material.
In the early field of application, SiC was used as abrading medium. Today SiC is of additional wide technical importance because of its outstanding properties, such as hardness, thermal conductivity, refractoriness and chemical durability as well as special semiconductor properties useful for opto- and micro-electronic applications.
Silicon carbide is normally produced from quartz sand and coke as starting materials. At temperatures above 2000°C silicon dioxide and carbon are chemically converted to SiC and carbon monoxide.
The worldwide production of SiC at present is about 900,000 tons per year (t/a). The larger part (ca. 660,000 t/a) is used in metallurgy sector as aggregate, the other part (ca. 240,000 t/a) is the so-called crystalline SiC. It is used as abrading medium (ca. 96,000 t/a), as refractory ceramics (ca. 96,000 t/a) or for other applications (ca. 48.000 t/a), such as for formed components or opto- or micro-electronics components.
The purity of the material is of high importance for its practical value, especially in the high tech applications, such as power current and high frequency technology or opto- and micro electronics. This is the reason why so many traces in the material have to be routinely checked by chemical analysis and consequently have to be certified in a certified reference material for the chemical composition of silicon carbide. But also the fraction of silicon carbide itself is of high importance for the properties, the practical value and the price of the material. It is determined by measuring the total as well as the free carbon content. Another important information is the oxygen content, indicating the aging process of the material. Therefore all these parameters were certified: The prominent metallic traces (additionally boron), the content of total and of free carbon as well as the oxygen and nitrogen content. Besides these the following contents are of interest, which therefore have been determined and given as indicative values: free silicon dioxide and free silicon.
The eminent importance of the certified carbon values are additionally based on the fact, that this certified reference material can be used to validate methods and results of carbon determination in other refractory materials with high carbon content.
Certification of reference materials is carried out on the basis of the relevant ISO-Guides [1-3] and the „Guidelines for the production of BAM Reference Materials“ [4]

## 1.2 Certification procedure

The silicon carbide powder material (quality transparent 200/F) was taken from the customary production line of the producer and was bottled into 320 bottles each containing 50 g of the material. After homogeneity and stability testing one bottle was distributed to each of the 24 participants of the certification interlaboratory comparison. A technical discussion on analytical methods and on the results of the certification interlaboratory comparison took place during the biannual sessions of the working group "Special Materials" of GDMB.
All participating laboratories were asked to carry out six independent determinations using an analytical method of their own choice.
The statistical evaluation of all analytical results was performed using the software program SoftCRM 1.2.2. [5]. After removal of technical and statistical outliers the certified values were calculated as means of the laboratory means reported from the participating laboratories of the interlaboratory comparison. The certified uncertainties were calculated taking into account the contributions from interlaboratory comparison and from inhomogeneity of the material.

# 2 Participating laboratories

## 2.1 Allocation and preparation of the material

- The material was produced by ESK Ceramics, Kempten, Germany
- The material was bottled by BAM Bundesanstalt für Materialforschung und -prüfung
- Preparation of a highly homogenized sample was performed by BAM

## 2.2 Homogeneity testing

- The analytical investigations for the homogeneity testing Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, Ti, V, Zr were carried out by BAM
- The analytical investigations for the homogeneity testing of $C_{free}$, O, $C_{total}$, N, $Si_{free}$ and $SiO_2$ were carried out by ESK Ceramics, Kempten, Germany.
- All statistical evaluations for homogeneity testing were carried out by BAM.

## 2.3 Certification analysis (certified and indicative values)

To achieve a high international acceptance of the CRM prominent laboratories located worldwide were asked to participate. These laboratories were either involved in daily SiC analysis or had well known ability to analyse difficult materials by adequate analytical methods. Most of them already participated successfully in the certification interlaboratory comparison of BAM-S003. Totally 24 laboratories from five different countries participated in the interlaboratory comparison for certification:

BAM Bundesanstalt für Materialforschung und -prüfung Berlin (Germany)
- Laboratory: Activation Analysis; Gas Analysis
- Laboratory: Inorganic Chemical Analysis; Reference Materials

Chinese Academy of Sciences, Shanghai Institute of Ceramics, Shanghai (PR China)
ESK Ceramics GmbH Co. KG, Kempten (Germany)
ESK-SiC GmbH, Frechen (Germany)
Forschungszentrum Jülich GmbH, Jülich (Germany)
H.C. Starck GmbH & Co. KG; Goslar (Germany)
H.C. Starck GmbH & Co. KG; Laufenburg (Germany)
Horiba Ltd., Tokyo (Japan)
Japan Fine Ceramics Center, Atsuta-ku Nagoya (Japan)
JEF Refractories, Ako-City, Hyougo (Japan)
Johannes Gutenberg Universität, Institut für Kernchemie, Mainz (Germany)
Krosaki Harima Corp. Ltd., Kitakyusyu (Japan)
Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden (Germany)
Leibniz-Institut für Kristallzüchtung, Berlin (Germany)
Max-Plank-Institut für Metallforschung, Stuttgart (Germany)
NGK Insulators, LTD., Chemical analysis materials research lab., Nagayo (Japan)
OSRAM GmbH, München (Germany)
Rigaku Industrial Corp., Takasuki-shi, Osaka (Japan)
Shiva Technologies Inc., Evans Analytical Group, Tournefeuille (France)
SGL Carbon GmbH, Bonn (Germany)
SGL Carbon GmbH, Meitlingen (Germany)
TYK Corp., Research and Development Center, Tajimi-City (Japan)
Umicore Precious Metals Refining, Hoboken (Belgium)

## 2.4 Determination of additional material data

- The determination of phases was organised by BAM, laboratory "X-ray structure and phase analysis". Measurements were carried out by European Synchrotron Radiation Facility (ESRF) Grenoble.
- The particle size distribution was determined by BAM, division "Materials Technology of Advanced Ceramics and Composites".

# 3 Abbreviations used

| | |
|---|---|
| CGHE | Carrier gas hot extraction |
| Comb./coul. | Combustion of free carbon followed by coulometric determination |
| Comb.-IR | Combustion method with infrared detection |
| DCarc-OES | Direct current arc optical emission spectrometry |
| ET AAS | Atomic absorption spectrometry with electrothermal atomization |
| ETV-ICP-OES | Inductively coupled plasma optical emission spectrometry with electrothermal vaporisation |
| F AAS | Flame atomic absorption spectrometry |
| F AES | Flame atomic emission spectrometry |
| GRAV | Gravimetry |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| INAA | Instrumental neutron activation analysis |
| Method M1 | Coulometric determination of free carbon after wet chemical oxidation with hot chromic sulfuric acid, (described in Appendix 1) |
| Method M3 | Oxidation in pure oxygen followed by IR-detection; (CO2)-“Combustion method“, (described in Appendix 2) |
| Method M4 | Carrier gas hot extraction in inert gas atmosphere (He) with infra-red detection (CO2) and heat conductivity measurement (N2) (described in Appendix 3) |
| SS ET AAS | Solid sampling electrothermal atomic absorption spectrometry |
| TITR | Titrimetry |
| Vol. | Gas volumetric determination |
| $s_b$ | standard deviation of homogeneity investigation "between the bottles" |
| $s_w$ | standard deviation of homogeneity investigation "within the bottles" |
| $s_{HS}$ | standard deviation of homogeneity investigation of "homogeneous sample" |
| $u_c$ | combined uncertainty of certified mass fraction |
| $s_M$ | standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification |
| $n$ | number of accepted laboratory mean values of interlaboratory comparison for certification |
| $s_{inhom}$ | standard deviation resulting from inhomogeneity of the samples |

# 4 Homogeneity investigation of the material

## 4.1 Distribution of sub-samples; homogenized sample

For homogeneity testing 22 bottles were representatively taken from the totality of 320 bottles by a combination of random access and systematic selection (see Table 1). Each bottle contained 50 g of candidate material. From each of the N = 22 bottles four appropriate sample masses were filled into vials with masses of the taken material depending on the needs of the corresponding methods used for the homogeneity testing of different analytes. The vials were distributed to the two laboratories, where the measurements for homogeneity testing were carried out.

Tab. 1: Selected bottles analysed for homogeneity testing of BAM-S008

| BAM[1)] | 12 | 35 | 66 | 99 | 116 | 143 | 161 | 195 | 237 | 258 | 287 | 294 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ESK[2)] | 21 | 51 | 92 | 116 | 157 | 189 | 223 | 237 | 287 | 310 | | |

[1)]Homogeneity testing Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, Ti, V, Zr

[2)]Homogeneity testing of $C_{free}$, O, $C_{total}$, N and $SiO_2$

For comparison a thoroughly homogenized sample was produced (Bottle 31). For this purpose 20 g of the material were highly homogenized in the “Mixer/Mill” (Spex. Ind., USA) for 15 min. (3 x 5 min.) using polypropylene vessels and balls.
Partial masses of this sample were distributed to the laboratories, in which the measurements for homogeneity testing were carried out.

### 4.2 Homogeneity investigations for Al, Ca, Cr, Cu, Mg, Na, Ni, Ti, V, Zr

The measurements were carried out by using an ICP-OES spectrometer “IRIS-AP” (Thermo Elemental) combined with electrothermal evaporation (ETV) for the analysis of sub-samples. Aqueous calibration solutions were used for calibration. Resulting lack of trueness of results or of metrological traceability is not relevant, because a high precision is the only necessity in case of homogeneity investigation.
Since only very small sub-sample masses of about 3 mg – which is much less than normally used in wet chemical analysis - could be used with ETV-ICP-OES three measurements were summarised to a virtual value representing a higher sub-sample mass (ca. 10 mg). For the elements Al, Ca, Cr, Cu, Mg, Na, Ni, Ti, V, Zr three series of measurements were carried out on three different days.

### 4.3 Homogeneity investigations for B, Fe, Mn

The three analytes B, Fe and Mn could not be determined by ETV-ICP-OES precisely enough. Therefore DCArc-OES was used. The measurements were carried out by using a DCArc system.
For the same reasons as for ETV-ICP-OES in case of DCArc measurements four measurements were summarised to a virtual value representing a higher sub-sample mass (ca. 14 mg). For the elements B, Fe and Mn four series of measurements were carried out on four different days.

### 4.4 Homogeneity investigations of non-metallic analytes

Homogeneity investigations for the non-metallic parameters $C_{total}$, $C_{free}$, N, O, $SiO_{2\,free}$ and $Si_{free}$ were carried out by ESK Kempten. Different methods were applied for the determination of different analytes.
The content of $C_{total}$ was determined by combustion of sub-samples of 18 mg in a high frequency furnace WC200 (LECO) in an oxygen stream. The generated $CO_2$ gas was collected in a C-trap and was measured by an infrared measuring cell after release.
$C_{free}$ was determined coulometrically using the Behr C30HT + TS30 after oxidation of the free carbon with chromic sulfuric iodic acid at 120 °C for 90 min (according to Method M1, see Appendix 1). The oxidation product $CO_2$ was absorbed in $Ba(ClO_4)_2$-solution. The sample intake was 200 mg.
Oxygen was determined using about 100 mg sub-samples in a resistance heated furnace TC436 (LECO) in a helium carrier gas stream using tin as flux. CO was catalytically oxidized to $CO_2$. The total concentration of $CO_2$ was measured by an infrared measuring cell.

Nitrogen was determined by carrier gas hot extraction in a resistance heated furnace TC436 (LECO) using helium as carrier gas and a thermal conductivity measuring cell. Sub-samples of about 100 mg were used.
$SiO_{2\ free}$ was determined by distillation after chemical reaction. The sub-sample was treated with HF, distilled as $SiF_4$ and determined as Si after absorption in NaOH using ICP-OES. The sample intake was 500 mg.
$Si_{free}$ was determined using a homemade gas volumetric instrument after reaction of the free Si with NaOH and formation of hydrogen. Sub-samples of about 500 mg were used.

The contents of $SiO_{2\ free}$ and $Si_{free}$ were below the limit of determination. Therefore no statement on the homogeneity of these parameters is possible.

### 4.5 Conclusion

The results of the measurements and the homogeneity testing are listed in Appendix 4.
Below the results of measurement data and their summary two tables are arranged for homogeneity testing. One homogeneity test (Anova, F-test) was made for comparing variances “between the bottles” and “within the bottles”. In the other test (F-test) the standard deviation within the samples was compared with the standard deviation of the homogeneous sample.
It could be concluded from the F-tests (“between” and “within”) that for all investigated analytes no significant contribution by an inhomogeneity “between the bottles” could be found (“No significant inhomogeneity” and “Not very strong Inhomogeneity”). A significant inhomogeneity contribution “within the bottles” was only found for the elements Cr and Ni. This inhomogeneity contribution was taken into account in the calculation of the uncertainty of the certified values.
Independent from the results of the statistical tests carried out, the contributions from the between bottle standard deviations and the within-bottle standard deviations were corrected for by the standard deviation of the homogeneous samples (if determined) and both corrected contributions were (together with the contribution from the round robin test for certification) included into the calculation of the final measurement uncertainties of the certified values (see § 8.2).

## 5 Time stability of the material

During the certification of BAM-S003 (SiC green) the time stability of SiC was tested by measuring the oxygen content as the most sensitive parameter to indicate the aging of the material at the beginning and at the end of a period of three years (from October 2000 till September 2003). Since no changes could be detected a high stability of the material can be concluded for both BAM-S003 as well as BAM-S008. Therefore no specific stability test was performed for BAM-S008.

## 6 Characterisation study

### 6.1 Analytical methods used for certification

24 laboratories participated in the certification interlaboratory comparison. For some elements part of the laboratories used more than one analytical method reporting more than one dataset.
The laboratories were asked to analyse six subsamples. They were free to choose any suitable analytical method for analysis. Tables 2 to 20 show the analytical methods used by the participating laboratories.
All participating laboratories were asked to use only calibrants prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Tab. 2: Analytical methods used for the determination of aluminium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 3 | **Alkaline fusion**<br>- M: 0.5 g;<br>- 5g $Na_2CO_3$ were added to the sample and it was heated at 1000℃.<br>- After cooling 12 mL $H_2SO_4$ (1+1) and 8 mL HCl (1+1) were added to the samples and distilled water were filled up to 100 mL. | **1000 mg/L Al** 99.9%; Metal powder from RARE METALLIC Co., Ltd.<br>- Calibration solution: 0, 0.1, 0.5, 1.0 mg/L Al<br>- Acid of same quantity as sample solution was added to standard solution.<br>5 mg/L Sr as internal standard | ICP-OES |
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 ℃<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Al** Merck, Certipur<br>- Calibration: 8, 16, 24, 32, 40 µg/L Al;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 ℃;<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Al** Merck, Certipur<br>- Calibration: 0, 100, 150, 200, 250 µg/L Al;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ICP-OES |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 ℃<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Al** Merck, Certipur<br>- Calibration: 20, 40, 60 µg/L Al;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 23 | **Acid decomposition**<br>- M: 0.25 g; 3 mL HF + 3 mL $HNO_3$ + 3 mL$H_2SO_4$<br>- 16h at 230℃<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Al**<br>- Calibration: 0.1, 0.2, 0.3, 0.5 mg/L Al | ICP-OES |
| 28 | **Acid decomposition**<br>M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240℃ in a 25 mL PTFE vessel. | - Calibration: 0, 0.2, 0.4, 0.6, 0.8 mg/L Al | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 ℃<br>- Evaporated to dryness in Pt-vessel<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL | **1000 mg/L Al** Spex Certiprep Inc. | ICP-OES |
| 2 | **No sample preparation**<br>The sample was pressed at a pressure of 150 KN.<br>Semi-quantitative analysis was carried out. | No standard used | XRF |
| 4 | **No sample preparation**<br>- M: 5 mg | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | DC ARC OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.611)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |

| | | | |
|---|---|---|---|
| 7 | **No sample preparation**<br>M: 60 mg; additionally 24 mg graphite powder and 6 mg $BaCl_2$.<br>graphite electrodes: rod shape with 6 mm diameter | Matrix matched synthetic standards of **pure elemental oxides**.<br>Calibration:<br>1, 3, 10, 30, 100, 300, 1000 mg/kg | DC ARC OES |
| 9 | **No sample preparation**<br>- M: 5 mg; DCA 301 (Spectral Systems) | **High purity $Al_2O_3$** (Alfa)<br>Synthetic calibration standard prepared by dilution of $Al_2O_3$ with high purity graphite powder | DC ARC OES |
| 19 | **No sample preparation**<br>- M: 1.6 - 3.4 mg<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19 s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas | **1000 mg/L Al** (Bernd Kraft GmbH) checked against 1000 mg/L Al (Spetec GmbH)<br>- Calibration:<br>0, 30, 60, 90, 120, 150 ng Al | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer),<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Al** Merck<br><br>- Calibration solution: 1 mg/L Al | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000. | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 3: Analytical methods used for the determination of boron

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask | **1000 mg/L B** Merck, Certipur<br>- Calibration:<br>2, 4, 6 µg/L B<br>- Standard addition<br>- 20 µg/L Sc as internal standard were used | ICP-MS |
| 4 | **No sample preparation**<br>M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>SiC + ca. 20% Ga<br>(7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.293)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>M: 5 mg; DCA 301 (Spectral Systems) | **High purity $H_3BO_3$** (Alfa)<br>Synthetic calibration standard prepared by dilution of $H_3BO_3$ with high purity graphite powder. | DC ARC OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L B** Merck<br><br>- Calibration solution 1 mg/L B | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000. | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 4: Analytical methods used for the determination of calcium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **994.3 mg/L Ca** (Alfa J.M. 5N $CaCO_3$ in 10% v/v $HNO_3$)<br>- Calibration: 0.5, 1.0, 1.5, 2.0, 2.5 µg/L Ca;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ca** Merck, Certipur<br>- Calibration: 0.1, 0.2, 0.3 µg/L Ca<br>- Standard addition<br>- 20 µg/L Sc as internal standard were used | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2 mg/L Ca | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Ca** Spex Certiprep Inc. | ICP-MS |
| 4 | **No sample preparation**<br>- M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (0.871)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | **1000 mg/L Ca**<br>($Ca(NO_3)_3$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.5 mg/L Ca 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng | ETV-ICP-OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg; ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas | **1000 mg/L Ca** (Bernd Kraft GmbH) checked against 1000 mg/L Ca (Ultra Scientific Solutions, USA)<br>- Calibration: 0, 0.2, 0.4, 0.6, 0.8, 1.0 ng Ca | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Ca** Merck<br>- Calibration solution 0.5 mg/L Ca | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 5: Analytical methods used for the determination of chromium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Cr** Merck, Certipur<br>- Calibration: 0.2, 0.4, 0.6, 0.8, 1.0 µg/L Cr;<br>- Standard addition technique | ET AAS |
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 °C;<br>- Resulting solution diluted to 50 mL in PFA flask. | **9992.6 mg/L Cr** (Alfa J.M. 4Nm5 Cr in 28 % v/v HCl, 0.4% v/v $HNO_3$)<br>- Calibration: 0, 5, 10, 15, 20 µg/L Cr<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ | ICP-OES |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Cr** Merck, Certipur<br>- Calibration: 0.1, 0.2, 0.3 µg/L Cr<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Cr | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Cr** Spex Certiprep Inc. | ICP-MS |
| 4 | **No sample preparation**<br>- M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (2.210)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | **1000 mg/L Cr**<br>($Cr(NO_3)_3$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.5 mg/L Cr 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng | ETV-ICP-OES |
| 11 | **No sample preparation**<br>- M: 150 - 175 mg in quartz ampoules.<br>- Irradiation time: 14 days,<br>- thermal neutron flux 1.3e14 $s^{-1}$ $cm^{-2}$;<br>- 3 measurement cycles with measuring time 4h + 7h + 7h for each sample.<br>-. The blank of the quartz ampoule for Cr (0.015 mg/kg) has been subtracted. | **0.9994 mg/g Cr**<br>Self made stock solution from Cr metal 4N8;<br>- diluted 1:34 = 0.029 mg/g | INAA |
| 14 | **No sample preparation**<br>- M: 7 mg; ETV oven (O. Schuierer),<br>- program: 500 °C = 30s, 2700 °C, 25 s; RT = 60 s;<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min | **9992.6 mg/L Cr**<br>(Alfa J.M. 4Nm5 Cr in 28 % v/v HCl, 0.4% v/v $HNO_3$)<br>- Calibration: 0.2, 0.4, 0.6, 0.8 ng Cr | ETV-ICP-OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg; ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Cr** (Bernd Kraft GmbH) checked against 1000 mg/L Cr (LGC Promochem GmbH)<br>- Calibration: 0, 0.4, 0.8, 1.2, 1.6, 2.0 ng Cr | ETV-ICP-OES |

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| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Cr** Merck<br>- Calibration solution 1 mg/L Cr | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 6: Analytical methods used for the determination of copper

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Cu** Merck, Certipur<br>- Calibration: 0.25, 0.50, 0.75, 1.00 µg/L Cu;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Cu** Merck, Certipur<br>- Calibration: 0.05, 0.10, 0.15 µg/L Cu;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Cu | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Cu** Spex Certiprep | ICP-MS |
| 4 | **No sample preparation**<br>- M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (5.144)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | **1000 mg/L Cu**<br>($Cu(NO_3)_2$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.5 mg/L Cu 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng | ETV-ICP-OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg; ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Cu** (Bernd Kraft GmbH) checked against 1000 mg/L Cu (LGC Promochem GmbH)<br>- Calibration: 0, 0.4, 0.8, 1.2, 1.6, 2.0 ng Cu | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer )<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Cu** Merck<br>- Calibration solution 1 mg/L Cu | ETV-ICP-OES |

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| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000. | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 7: Analytical methods used for the determination of iron

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 3 | **Alkaline fusion**<br>- M: 0.5 g;<br>- 5g $Na_2CO_3$ were added to the sample and it was heated at 1000°C.<br>- After cooling 12 mL $H_2SO_4$ (1+1) and 8 mL HCl (1+1) were added to the samples and distilled water were filled up to 100 mL. | **1000 mg/L Fe** 99.9% (Metal powder from RARE METALLIC Co., Ltd.<br>- Calibration: 0.0-0.1-0.5-1.0 mg/L Fe<br>- Acid of same quantity as sample solution was added to standard solution.<br>5 mg/L Sr as internal standard | ICP-OES |
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Fe** Merck, Certipur<br>- Calibration: 2, 4, 6, 7, 10 µg/L Fe;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 °C;<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Fe** Merck, Certipur<br>- Calibration: 0, 10, 20, 30, 40 µg/L Fe;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ICP-OES |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Fe** Merck, Certipur<br>- Calibration: 1.6, 3.2, 4.8 µg/L Fe;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1875, 0.375, 0.5625, 0.75 mg/L Fe | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100. | **1000 mg/L Fe** Spex Certiprep Inc. | ICP-MS |
| 2 | **No sample preparation**<br>- The sample was pressed at a pressure of 150 KN.<br>Semi-quantitative analysis was carried out. | No standard used | XRF |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.301)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | **1000 mg/L Fe**<br>($Fe(NO_3)_3$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 5 mg/L Fe 5, 10, 15, 20, 30, 40 ng | ETV-ICP-OES |
| 9 | **No sample preparation**<br>- M: 5 mg; DCA-301 | **High purity $Fe_2O_3$** (Alfa)<br>Synthetic calibration standard prepared by dilution of $Fe_2O_3$ with high purity graphite powder. | DC ARC OES |

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| 11 | **No sample preparation**<br>- M: 150 - 175 mg in quartz ampoules<br>- Irradiation time: 14 days<br>- thermal neutron flux 1.3e14 $s^{-1}$ $cm^{-2}$;<br>- 3 measurement cycles with measuring time 4h + 7h + 7h for each sample.<br>- The blank of the quartz ampoule for Fe (0.089 mg/kg) have been subtracted. | **1.0024 mg/g Fe**<br>Self made stock solution from pure Fe metal | INAA |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg;<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 reaction gas. | **1000 mg/L Fe** (Bernd Kraft GmbH) checked against 1000 mg/L Fe (LGC Promochem GmbH)<br>- Calibration:<br>0, 3, 6, 9, 12, 15 ng Fe | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Fe** Merck<br>- Calibration solution 1 mg/L Fe | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 8: Analytical methods used for the determination of magnesium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1002.7 mg/L Mg** (Alfa J.M. m3N8 Mg in 5% v/v HCl)<br>- Calibration: 0.08, 0.16, 0.24, 0.32, 0.40 µg/L Mg;<br>- Standard addition technique | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Mg** Merck, Certipur<br>- Calibration:<br>0.05, 0.10, 0.15 µg/L Mg;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Mg | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Mg** Spex Certiprep Inc. | ICP-MS |
| 4 | **No sample preparation**<br>- M: 2 mg;<br>ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga<br>(7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.541)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |

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|---|---|---|---|
| 9 | **No sample preparation**<br>- M: 5 mg;<br>ETV-4000 (Spectral Systems) | **1000 mg/L Mg**<br>($Mg(NO_3)_2$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.2 mg/L Mg<br>0.2, 0.4, 0.6, 0.8, 1.2, 1.6 ng | ETV-ICP-OES |
| 14 | **No sample preparation**<br>- M: 7 mg; ETV oven (O. Schuierer),<br>- program: 500 °C = 30s, 2700 °C, 25 s;<br>RT = 60 s;<br>- bypass and carrier gas = 300 mL/min Ar,<br>Freon R12 = 3 mL/min | **1002.7 mg/L Mg**<br>(Alfa J.M. 99.98 Mg pieces)<br>- Calibration:<br>0.06, 0.1, 0.15, 0.2 ng | ETV-ICP-OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg;<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Mg** (Bernd Kraft GmbH) checked against 1000 mg/L Mg (LGC Promochem GmbH)<br>- Calibration:<br>0, 0.1, 0.2, 0.3, 0.4, 0.5 ng Mg | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer )<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar<br>Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Mg** Merck<br><br>- Calibration solution 0.1 mg/L Mg | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000. | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 9: Analytical methods used for the determination of manganese

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **10252.2 mg/L Mn** (Alfa J.M. m4N Mn in 8% v/v HCl)<br>- Calibration:<br>0.1, 0.2, 0.3, 0.4, 0.5 µg/L Mn;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Mn** Merck, Certipur<br>- Calibration:<br>0.05, 0.10, 0.15 µg/L Mn;<br>- Standard addition<br>20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Mn | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Mn** Spex Certiprep Inc. | ICP-MS |
| 6 | **No sample preparation**<br>- M: 500 mg;<br>- SiC powder was weighted and filled in PE capsules.<br>- Irradiation time: 1 h, thermal neutron flux 7 x $10^{14}$ $s^{-1}$ $cm^{-2}$; cooling time 1.5 h measuring time 0.5 h for each sample. | Self made solution from **$MnSO_4$ * $4H_2O$** p.A. | INAA |

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|---|---|---|---|
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga<br>(7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.834)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg;<br>ETV-4000 (Spectral Systems) | **1000 mg/L Mn**<br>($Mn(NO_3)_2$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.2 mg/L Mn<br>0.2, 0.4, 0.6, 0.8, 1.2, 1.6 ng | ETV-ICP-OES |
| 11 | **No sample preparation**<br>- M: 150 - 175 mg in quartz ampoules<br>- Irradiation time: 14 days<br>- thermal neutron flux 1.3e14 $s^{-1}$ $cm^{-2}$;<br>- 3 measurement cycles with measuring time 4h + 7h + 7h for each sample. | **0.96996 mg/g Mn**<br>Self made stock solution from pure Mn metal | INAA |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg;<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Mn** (Bernd Kraft GmbH) checked against 1000 mg/L Mn (LGC Promochem GmbH)<br>- Calibration:<br>0, 0.1, 0.2, 0.3, 0.4, 0.5 ng Mn | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar,<br>Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Mn** Merck<br><br>Calibration solution 0.5 mg/L Mn | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000. | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 10: Analytical methods used for the determination of sodium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Na** Merck, Certipur<br>- Calibration:<br>0.2, 0.4, 0.6, 0.8, 1.0 µg/L Na;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Na** Merck, Certipur<br>- Calibration:<br>0.1, 0.2, 0.3 µg/L Na;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Na | ET AAS |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water<br>- Resulting solution diluted to 100 mL | **1000 mg/L Na** Spex Certiprep Inc. | ICP-MS |
| 7 | **No sample preparation**<br>M: 5 mg; AAS **5EA** | CRM SiC (**BAM-S003**)<br>- 11 calibration points<br>0.004 - 0.1 mg SiC<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | SS ET AAS |

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| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | **1000 mg/L Na**<br>($NaNO_3$ Merck in 0.5 mol $HNO_3$)<br>- Calibration solution 0.5 mg/L Na 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng | ETV-ICP-OES |
| 11 | **No sample preparation**<br>- M: 150 - 175 mg in quartz ampoules<br>- Irradiation time: 14 days<br>- thermal neutron flux 1.3e14 $s^{-1}$ $cm^{-2}$;<br>- 3 measurement cycles with measuring time 4h + 7h + 7h for each sample.<br>- The blank of the quartz ampoule for Na (0.060 mg/kg) have been subtracted. | **0.72023 mg/g Na**<br>Self made stock solution from pure NaCl | INAA |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Na** Merck<br>- Calibration solution 0.2 mg/L Na | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standard were used: for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 11: Analytical methods used for the determination of nickel

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ni** Merck, Certipur<br>- Calibration: 1.6, 3.2, 4.8, 6.4, 8.0 µg/L Ni;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ni** Merck, Certipur<br>- Calibration: 0.5, 1.0, 1.5 µg/L Ni;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- for 16 h at 240°C in a 25 mL PTFE vessel | - 0, 0.1, 0.2, 0.4, 0.5 mg/L Ni | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Ni** Spex Certiprep Inc. | ICP-MS |
| 4 | **No sample preparation**<br>M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM no. 359, in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (2..160)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 9 | **No sample preparation**<br>- M: 5 mg; ETV-4000 (Spectral Systems) | $Ni(NO_3)_2$ Merck in 0.5 mol $HNO_3$ = **1000 mg/L Ni**<br>- Calibration solution 0.5 mg/L Ni 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 ng | ETV-ICP-OES |

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| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg;<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas | **1000 mg/L Ni** (Bernd Kraft GmbH) checked against 1000 mg/L Ni (LGC Promochem GmbH)<br>- Calibration:<br>0, 0.4, 0.8, 1.2, 1.6, 2.0 ng Ni | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar,<br>Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Ni** Merck<br>- Calibration solution 1 mg/L Ni | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standard were used: for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 12: Analytical methods used for the determination of titanium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 3 | **Alkaline fusion**<br>- M: 0.5 g;<br>- 5g $Na_2CO_3$ were added to the sample and it was heated at 1000°C.<br>- After cooling 12 mL $H_2SO_4$ (1+1) and 8 mL HCl (1+1) were added to the samples and distilled water were filled up to 100 mL. | **1000 mg/L Ti** 99.9% (Metal powder from WAKO Pure Chemical Corp.)<br>- Calibration:<br>0.0, 0.1, 0.5, 1.0 mg/L Ti<br>- Acid of quantity same as sample solution was added to standard solution.<br>- 5 mg/L Sr as internal standard | ICP-OES |
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ti** Merck, Certipur<br>- Calibration:<br>10, 20, 30, 40, 50 µg/L Ti;<br>- Standard addition technique. | ET AAS |
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 °C;<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ti** Merck, Certipur<br>- Calibration:<br>0, 100, 200, 300, 400 µg/L Ti;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ICP-OES |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Ti** Merck, Certipur<br>- Calibration:<br>20, 40, 60 µg/L Ti;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 23 | **Acid decomposition**<br>- M: 0.25 g; 3 mL HF + 3 mL $HNO_3$ + 3 mL $H_2SO_4$ -<br>- 16h at 230°C<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Ti**<br>- Calibration:<br>0.1, 0.2, 0.3, 0.5 mg/L Ti | ICP-OES |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel. | - 0, 0.125, 0.250, 0.375, 0.500 mg/L Ti | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) - + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Ti** Spex Certiprep Inc. | ICP-OES |
| 2 | **No sample preparation**<br>- The sample was pressed at a pressure of 150 KN.<br>Semi-quantitative analysis was carried out. | No standard used | XRF |

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| 4 | **No sample preparation**<br>- M: 5 mg; DCA-301 (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | DC ARC OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga<br>(7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (0.709)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 7 | **No sample preparation**<br>- M: 60 mg; additionally 24 mg graphite powder<br>- and 6 mg $BaCl_2$.<br>- graphite electrodes: rod shape with<br>- 6 mm diameter | Matrix matched synthetic standards of **pure elemental oxides**.<br>- Calibration:<br>1, 3, 10, 30, 100, 300, 1000 mg/kg | DC ARC OES |
| 9 | **No sample preparation**<br>- M: 5 mg; DCA 301 (Spectral Systems) | **High purity $TiO_2$** (Alfa)<br>Synthetic calibration standard prepared by dilution of $TiO_2$ with high purity graphite powder. | DC ARC OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg;<br>ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Ti** (Bernd Kraft GmbH) checked against 1000 mg/L Ti (Spetec GmbH)<br>- Calibration:<br>0, 30, 60, 90, 120, 150 ng Ti | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s,<br>no. 1-3 = 2700 °C, 10 s;<br>no. 4-6 = 2400 °C, 15 s,<br>- bypass and carrier gas = 300 mL/min Ar,<br>Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Ti** Merck<br><br>- Calibration solution 25 mg/L Ti | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 13: Analytical methods used for the determination of vanadium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 3 | **Alkaline fusion**<br>- M: 0.5 g;<br>- 5g $Na_2CO_3$ were added to the sample and it was heated at 1000°C.<br>- After cooling 12 mL $H_2SO_4$ (1+1) and 8 mL HCl (1+1) were added to the samples and distilled water were filled up to 100 mL. | **1000 mg/L V** 99.9% (Metal powder from WAKO Pure Chemical Corp.)<br>- Calibration:<br>0.0-0.5-1.0-2.0 mg/L V<br>- Acid of quantity same as sample solution was added to standard solution.<br>- 5 mg/L Sr as internal standard | ICP-OES |
| 13 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L V** Merck, Certipur<br>- Calibration:<br>20, 40, 60, 80, 100 µg/L V;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ET AAS |
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 °C;<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L V** Merck, Certipur<br>- Calibration:<br>0, 400, 800, 1200, 1600 µg/L V;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ICP-OES |
| 23 | **Acid decomposition**<br>- M: 0.25 g; 3 mL HF + 3 mL $HNO_3$ + 3 mL $H_2SO_4$ 16h at 230°C<br>- Resulting solution diluted to 100 mL. | **1000 mg/L V**<br>- Calibration:<br>0.2, 0.4, 0.6, 1.0 mg/L V | ICP-OES |

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| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel. | - 0, 0.125, 0.250, 0.375, 0.500 mg/L V | ICP-OES |
| 2 | **No sample preparation**<br>- The sample was pressed at a pressure of 150 KN.<br>Semi-quantitative analysis was carried out. | No standard used | XRF |
| 4 | **No sample preparation**<br>M: 5 mg; DCA-301, Spectral Systems | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | DC ARC OES |
| 6 | **No sample preparation**<br>- M: 500 mg;<br>- SiC powder was weighted and filled in PE capsules.<br>- Irradiation time: 1 h, thermal neutron flux 7 x $10^{14}$ $s^{-1}$ $cm^{-2}$; cooling time 1.5 h measuring time 0.5 h for each sample. | Self made solution from **$V_2O_5$** p.A. | INAA |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (0.827)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 7 | **No sample preparation**<br>- M: 60 mg; additionally 24 mg graphite powder and 6 mg $BaCl_2$.<br>- graphite electrodes: rod shape with<br>- 6 mm diameter | Matrix matched synthetic standards of **pure elemental oxides**.<br>- Calibration: 1, 3, 10, 30, 100, 300, 1000 mg/kg | DC ARC OES |
| 9 | **No sample preparation**<br>M: 5 mg; DCA 301 (Spectral Systems) | **High purity $V_2O_5$** (Alfa)<br>Synthetic calibration standard prepared by dilution of $V_2O_5$ with high purity graphite powder. | DC ARC OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg; ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C;<br>- Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L V** (Bernd Kraft GmbH) checked against 1000 mg/L V (LGC Promochem GmbH)<br>- Calibration: 0, 150, 300, 450, 600, 750, ng V | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s, bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L V** Merck<br>- Calibration solution 25 mg/L V | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 14: Analytical methods used for the determination of zirconium

| Lab code | Sample Preparation (M = mass of sub-samples) | Calibration | Final Determination |
|---|---|---|---|
| 3 | **Alkaline fusion**<br>- M: 0.5 g;<br>- 5g $Na_2CO_3$ were added to the sample and it was heated at 1000°C.<br>- After cooling 12 mL $H_2SO_4$ (1+1) and 8 mL HCl (1+1) were added to the samples and distilled water were filled up to 100 mL. | **1000 mg/L Zr** prepared from $ZrO_2$<br>- Calibration: 0.0-0.5-1.0-2.0 mg/L Zr<br>- Acid of quantity same as sample solution was added to standard solution.<br>- 5 mg/L Sr as internal standard | ICP-OES |

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|---|---|---|---|
| 14 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 60 h at 250 °C;<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Zr** Merck, Certipur,<br>- Calibration: 0, 10, 20, 30, 40 µg/L Zr;<br>- Matrix matching using Si (6N Alfa J.M.) $HNO_3$, HF, $H_2SO_4$ in sub boiling quality. | ICP-OES |
| 15 | **Acid decomposition**<br>- M: 0.25 g; 3 mL $HNO_3$ (65%) + 3 mL HF (48%) + 6 mL $H_2SO_4$ (95%) in sub boiling quality<br>- DAB-III, Berghof (150 mL TFM-liners)<br>- 75 h at 250 °C<br>- Resulting solution diluted to 50 mL in PFA flask. | **1000 mg/L Zr** Merck, Certipur<br>- Calibration: 20, 40, 60 µg/L Zr;<br>- Standard addition<br>- 20 µg/L Sc as internal standard | ICP-MS |
| 28 | **Acid decomposition**<br>- M: 0.5 g; 5 mL HF + 8 mL $HNO_3$ + 5 mL $H_2SO_4$<br>- 16 h at 240°C in a 25 mL PTFE vessel. | - 0, 0.125, 0.250, 0.375, 0.500 mg/L Zr | ICP-OES |
| 29 | **Acid decomposition**<br>- M: 0.25 g; 6 mL $HNO_3$ (60%) + 8 mL HF (48%) - + 5 mL $H_2SO_4$ (96%) in sub boiling quality<br>- in pressure decomposition vessels<br>- 136 h at 250 °C.<br>- Evaporated to dryness in Pt-vessel.<br>- Dissolution with 5 mL $HNO_3$ (1+1) and 20 mL water.<br>- Resulting solution diluted to 100 mL. | **1000 mg/L Zr** Spex Certiprep Inc. | ICP-OES |
| 4 | **No sample preparation**<br>M: 2 mg; ETV (Spectral Systems) | Following SiC standards were used: **BAM-S003**; CRM 359; in-house standard (NMP 1; NMP 2)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | ETV-ICP-OES |
| 7 | **No sample preparation**<br>- Powder pellets (25 x 5 mm),<br>- SiC + ca. 20% Ga (7N; PPM Pure Metals GmbH) | CRM SiC (**BAM-S003**)<br>4 samples analysed 25 times, mean of means used for calculation of RSF (1.267)<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | GD-MS |
| 7 | **No sample preparation**<br>- M: 60 mg; additionally 24 mg graphite powder and 6 mg $BaCl_2$.<br>- graphite electrodes: rod shape with<br>- 6 mm diameter | Matrix matched synthetic standards of **pure elemental oxides**.<br>Calibration:<br>1, 3, 10, 30, 100, 300, 1000 mg/kg | DC ARC OES |
| 9 | **No sample preparation**<br>M: 5 mg; DCA 301 (Spectral Systems) | $ZrOCl_2$ Merck in 2 mol $HNO_3$<br>= **1000 mg/L Zr**<br>- Calibration solution 5 mg/L Zr 5, 10, 15, 20, 30, 40 ng | ETV-ICP-OES |
| 19 | **No sample preparation**<br>- M: 1.4 - 3.9 mg; ETV-4000 (Spectral Systems)<br>- Pre-treatment 19s at 450 °C; Vaporization 30 s at 2300 °C<br>- 2.3 mL/min Freon R12 as reaction gas. | **1000 mg/L Zr** (Bernd Kraft GmbH) checked against 1000 mg/L Zr (LGC Promochem GmbH)<br>- Calibration: 0, 3, 6, 9, 12, 15 ng Zr | ETV-ICP-OES |
| 21 | **No sample preparation**<br>- M: 20 mg; ETV oven (O. Schuierer)<br>- program: 800 °C = 15s, 3000 °C = 1 s, no. 1-3 = 2700 °C, 10 s; no. 4-6 = 2400 °C, 15 s, bypass and carrier gas = 300 mL/min Ar, Freon R12 = 3 mL/min, $O_2$ = 5 mL/min | **1000 mg/L Zr** Merck<br>- Calibration solution 1 mg/L Zr | ETV-ICP-OES |
| 27 | **No sample preparation**<br>- Powder pellets with Indium as binder;<br>- Measurement in minimum mass resolution of 3000 | Following Si standards were used for calculation of RSF: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | GD-MS |

Tab. 15: Analytical methods used for the determination of carbon total

| Lab-code | Sample preparation (M = mass of sub-samples) | Calibration | Final determination |
|---|---|---|---|
| 1 | **Measurement procedure**<br>- M: 50 mg<br>- Cu - addition, no oxygen dilution | 1. **$BaCO_3$** primary substance<br>2. **$Na_2C_2O_4$** primary substance<br>Both substance from Riedel de Häen | Comb.-IR |
| 3 | **Measurement procedure**<br>- M: 50 mg<br>- Addition of 2.0 g Cu and 1.5 g W; Crucibles were pre-burned.<br>- Measurement conditions: step 1: 40 sec 300 mA; purge time 10 sec. Blank was analysed and was subtracted. | NBS 112b<br>29.43 mass % C | Comb.-IR |
| 4 | **Measurement procedure**<br>- M: 40 mg<br>- Combustion in an $O_2$ stream and - Addition of lead borate as flux. Furnace temperature: 1050 °C | **$CaCO_3$**<br>dried at 280 °C | Comb.-IR |
| 7 | **Measurement procedure**<br>- M: 60 mg<br>- Addition of 3 g Cu + 1.5 g W as flux. Combustion time 75 s | BAM-RS3 **$CaCO_3$** (99.79%) | Comb.-IR |
| 7 | **Measurement procedure**<br>- M: 20 mg<br>- Addition of 2.5 g Copper oxide wire (annealed 2 h at 900 °C)<br>- Furnace temperature: 1250 °C. | BAM-RS3 **$CaCO_3$** (99.79%) | Comb.-Coulom. |
| 8 | **Measurement procedure**<br>- M: 30 mg<br>- Addition of 1.5 g Lecocel PL and 1.0 g Iron chips Alpha AR673 | **$Na_2CO_3$**<br>dried 6 h at 105 °C | Comb.-IR |
| 9 | **Measurement procedure**<br>- M: 18 mg<br>- combustion of sample with oxygen in Al crucibles (induction furnace);<br>- Accelerator: Fe/W.<br>- Instrument procedures: purge time = 15s, delay time = 15 s, collect time = 120 s, trap purge = 55 s, minimum time = 45 s. | **$CaCO_3$** | Comb.-IR |
| 10 | **Measurement procedure**<br>- M: 29 - 40 mg<br>- instrument procedures: gas split according DIN 51075/3 | BAM-RS3 **$CaCO_3$** (99.79%) | Comb.-Coulom.. |
| 12 | **Measurement procedure**<br>- M: 18 mg<br>- combustion of sample with oxygen in ceramic crucibles (induction furnace)<br>- accelerator: 1 g Fe/ 1,5 g W/100 mg $PbBO_x$. | **$BaCO_3$** (> 99 %; Fluka) | Comb.-IR |
| 16 | **Measurement procedure**<br>- M: 100 mg<br>- Addition of 2g Sn as flux.<br>- Furnace temperature 1350 °C; Combustion time 70s. | **$CaCO_3$** (99.99%) | Comb.-IR |
| 17 | **Measurement procedure**<br>- M: 40 mg<br>- Sn-caps, accelerator W-Cu-CuO,<br>- HF furnace and preheated ceramic crucible with cover were used. | **$CaCO_3$** | Comb.-IR |
| 18 | **Measurement procedure**<br>- M: 50 mg<br>- Addition of 2.0 g Cu and 1.5 g W; Crucibles were pre-burned.<br>- Measurement conditions: 40 sec 300 mA; purge time 10 sec. Blank was analysed and subtracted. | NBS 112b<br>29.43 mass % C | Comb.-IR |

| | | | |
|---|---|---|---|
| 22 | **Measurement procedure (Method M3)**<br>- M: 25 mg<br>- Samples were weighted in Ni capsules. - Addition of 0.5 g Fe and 1 g W. Crucibles with cover were pre-burned. | **High purity carbon** (Ringsdorf) | Comb.-IR |
| 23 | **Measurement procedure**<br>- M: 100 mg<br>- Addition of 2 g Sn.<br>- instrument procedure 1350 °C x 10 min. | **Ultra carbon** (grade: 99.999%) | Comb.-IR |
| 27 | **Measurement procedure**<br>- M: 100 - 200 mg; | Following Si standards were used: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | Comb.-IR |
| 28 | **Measurement procedure**<br>- M: 100 mg<br>- Addition of 2 g Sn as flux.<br>- Furnace temperature 1350 °C; combustion time 90 s. | 30 mg **Ultra Carbon**<br>250 mg **$CaCO_3$** (4N grade) | Comb.-IR |
| 29 | **Measurement procedure**<br>- M: 50 mg<br>- Weigh the sample in a ceramic boat (Carbon free).<br>- Addition of 2 g Sn powder<br>- Furnace temperature 1350 °C; combustion time 5 min under $O_2$ gas flow. | **$CaCO_3$**<br>Dried at 525 °C for 2 h | Comb.-IR |

Tab. 16: Analytical methods used for the determination of carbon (free)

| Lab-code | Sample preparation (M = mass of sub-samples) | Calibration | Final determination |
|---|---|---|---|
| 3 | **Measurement procedure**<br>- M: 30 mg<br>- Combustion boat and cover pre-burned.<br>- Measurement conditions: 40 sec 300 mA; purge time 10 sec. Blank was analysed and was subtracted | **Ultra Carbon**<br>***the graphite specialists***<br>UCP-2-200 (100 mass%) | Comb.-IR |
| 4 | **Measurement procedure**<br>- M: 200 mg;<br>- Combustion in an oxygen stream | **$CaCO_3$**<br>dried at 280 °C | Comb.-IR |
| 7 | **Measurement procedure**<br>- M: 500-900 mg;<br>- Bath temperature 120 °C;<br>- Furnace temperature 1200 °C according to EN 12698 part 2 | **$CaCO_3$** checked against BAM-RS3 **$CaCO_3$** (99.79%) | Coulom. following wet chem. oxidation |
| 9 | **Measurement procedure (Method M1)**<br>- M: 200 mg;<br>- oxid. sol.: chromic sulphuric iodic acid, - Temperature = 120 °C,<br>- Oxidation time 90 min; $CO_2$ Absorption solution: $Ba(ClO_4)_2$ 20 wt%, Temperature = 40 °C, pH = 9.98; according to EN 12698 part 2 | **$CaCO_3$** | Coulom. following wet chem. oxidation |
| 10 | **Measurement procedure**<br>- M: 200 mg;<br>- Instrument procedures: without gas split; according DIN 51075/2 | SiC BAM-S003<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | Comb.-Coulom. |
| 18 | **Measurement procedure**<br>- M: 30 mg<br>- Combustion boat and cover pre-burned.<br>- Measurement conditions: 40 sec 300 mA; purge time 10 sec. Blank was analysed and subtracted | **Ultra Carbon**<br>***the graphite specialists***<br>UCP-2-200 (100 mass%) | Comb.-IR |
| 28 | **Measurement procedure**<br>- M: 500 mg; -<br>- Resistance heating<br>- Furnace temperature 900 °C; Combustion time 600 s. | 100 mg **$CaCO_3$** (4N grade)<br>Rare Metallic Co. Ltd. | Comb.-IR |

Tab. 17: Analytical methods used for the determination of nitrogen

| Lab-code | Sample preparation (M = mass of sub-samples) | Calibration | Final determination |
|---|---|---|---|
| 1 | **Measurement procedure**<br>- M: 50 mg<br>- high temperature crucibles, 4000-5000 W, ramp rate 30 W / s | **$KNO_3$** solution, Evaporatedd | CGHE-TC |
| 3 | **Measurement procedure**<br>- M: 50 mg<br>- Measurement conditions: 5000 W, 45 sec. Blank was analysed and was subtracted. | JSS 602-9; M: 1.0 g<br>0.0103 mass% N | CGHE-TC |
| 8 | **Measurement procedure**<br>- M: 50 mg<br>- high temperature crucibles,<br>- weigh in Sn capsules + 1.0 g Ni as flux ramp 720 A - 920 A / s; measurement time 50 s | **Gas calibration with $N_2$** | CGHE-TC |
| 9 | **Measurement procedure**<br>- M: 100 mg;<br>- Decomposition of sample in inert-gas in graphite crucibles; Sn-capsules for weighing of samples.<br>- Instrument procedures: purge time = 15 s; outgas low = 800 A, high = 980 A, ramp rate = 20 A/s; analysis: low = 920 A, high = 950 A, ramp rate = 10 A/s. | **$KNO_3$** | CGHE-TC |
| 12 | **Measurement procedure**<br>- M: 540-570 mg<br>- Sn-capsules used for weighing of samples. Addition of 8 pieces Cu à 100 mg as flux.<br>- Instrument procedures: outgas low = 1150 A, Analyse low 1050 A Integrations time 70 s | **$KNO_3$** (Merck, > 99%)<br>External calibration | CGHE-TC |
| 17 | **Measurement procedure**<br>- M: 50 mg<br>- powder in Sn-caps, compacted in Ni-caps, impulse heating 4500 W | **$KNO_3$** solution | CGHE-TC |
| 22 | **Measurement procedure**<br>- M: 140-206 mg<br>- sample weighed in Ni-capsules + 60 mg Sn as flux Heating 4500 W | **Gas calibration** with gas mixture ($He$, $H_2$, $CO_2$, $N_2$) 484 µl = 29 µg $N_2$ | CGHE-TC |
| 27 | **Measurement procedure**<br>- M: 100-200 mg | Following Si standard were used: ECISS 780-1; IPT 134; IPT 135; SRM 057A. | CGHE-TC |
| 28 | **Measurement procedure**<br>- M: 100 mg<br>- Sample weighed in Sn-capsules. Measurement procedures: 30 s outgas time; 50 s analysis delay; 20 s cool time; 6000 W outgas power; 5500 W analyse power. | 10 mg **$KNO_3$** (4N5 grade)<br>Rare Metallic Co. Ltd. | CGHE-TC |

Tab. 18: Analytical methods used for the determination of oxygen

| Lab-code | Sample preparation (M = mass of sub-samples) | Calibration | Final determination |
|---|---|---|---|
| 1 | **Measurement procedure**<br>- M: 50 mg<br>- High temperature crucibles, 4000-5000 W, ramp rate 30 W / s | **$KNO_3$** solution, evaporated | CGHE-IR |
| 3 | **Measurement procedure**<br>- M: 50 mg<br>- Measurement conditions: 5000 W, 35 sec. Blank was analysed and was subtracted. | SS-2-61; M: 0.0108 mass% O | CGHE-IR |

| | | | |
|---|---|---|---|
| 5 | **Measurement procedure**<br>- M: 120 mg;<br>- Sn capsules, high temperature crucibles;<br>- Measurement conditions: 5450 W, | **$KNO_3$** solution | CGHE-IR |
| 8 | **Measurement procedure**<br>- M: 50 mg;<br>- high temperature crucibles<br>- Sn capsules + 1.0 g Ni as flux<br>- ramp 720 A - 920 A / s;<br>measurement time 50 s | **$Na_2CO_3$**<br>dried 6 h at 105 °C | CGHE-IR |
| 9 | **Measurement procedure**<br>- M: 100 mg;<br>- decomposition of sample in inert-gas<br>- in graphite crucibles; Sn-capsules<br>- Instrument procedures:<br>15 s purge time; outgas low = 800 A, high = 980 A, ramp rate = 20 A/s; analysis: low = 920 A, high = 950 A, ramp rate = 10 A/s. | **$CaCO_3$** | CGHE-IR |
| 12 | **Measurement procedure**<br>- M: 400-440 mg<br>- Sn-capsules; Addition of 400 mg Ni (Fa. Leco) as flux.<br>- Instrument procedures:<br>outgas low = 1150 A, Analyse low 950 A<br>Integrations time 70 s | **$Fe_2O_3$** (Fa. Sidmar > 99%)<br>External calibration | CGHE-TC |
| 17 | **Measurement procedure**<br>- M: 50 mg<br>- powder in Sn-caps, compacted in Ni-caps, Impulse heating 4500 W | **$KNO_3$** solution | CGHE-IR |
| 22 | **Measurement procedure**<br>- M: 50 - 100 mg<br>- sample weighed in Ni-capsules + 60 mg Sn as flux; heating 4500 W | **Gas calibration** with gas mixture (He, $H_2$, $CO_2$, $N_2$) 484 µl = 30 µg $O_2$ | CGHE-IR |
| 27 | **Measurement procedure**<br>- M: 100-200 mg; | Following Si standard were used:<br>ECISS 780-1; IPT 134; IPT 135;<br>SRM 057A. | CGHE-IR |
| 28 | **Measurement procedure**<br>- M: 100 mg;<br>- Sample weighed in Sn-capsules. - Measurement procedures:<br>30 s outgas time; 50 s analysis delay;<br>20 s cool time; 6000 W outgas power;<br>5500 W analyse power. | 5 mg **$Y_2O_3$** (5N grade)<br>Rare Metallic Co. Ltd. | CGHE-IR |
| 30 | **Measurement procedure**<br>- M: 280-320 mg; | NIST RM 8983 Silicon Nitride Powder<br>(O 1.20%±0.14%) | CGHE-IR |

Tab. 19: Analytical methods used for the determination of free silicon dioxide

| Lab-code | Sample preparation | Calibration | Final determination |
|---|---|---|---|
| 4 | **Acid decomposition**<br>- M: 0.53 - 0.57g;<br>- HF-distillation following by ICP-OES determination. | **1000 mg/L Si** Merck, Titrisol (traceability to NIST)<br>- Calibration in NaOH/HF (matrix designed) | ICP-OES |
| 9 | **Acid decomposition**<br>- M: 500 mg<br>- Reaction of free $SiO_2$ with HF to $SiF_4$, distillation of $SiF_4$ and absorption in NaOH solution,<br>- Determination of Si in resulting sample solution by ICP-OES. | **$(NH_4)_2SiF_6$** Merck in $H_20$<br>c = 1000 mg/L<br>- Calibration: 0.5, 1.0 mg/L<br>Accuracy of method was checked with high purity $SiO_2$. | ICP-OES |
| 10 | **Acid decomposition**<br>- M: 2 g; HF-distillation<br>- Distillation steps:<br>50 °C / 15 min; 100 °C / 45 min; 150 °C 5 min following by ICP-OES determination. | **1000 mg/L Si** Merck<br>- Calibration in NaOH/HF (matrix designed) | ICP-OES |

Tab. 20: Analytical methods used for the determination of free silicon

| Lab-code | Sample preparation | Calibration | Final determination |
|---|---|---|---|
| 4 | **Acid decomposition**<br>- M: 3 g<br>- Reaction of free Si with NaOH,<br>- Formation and determination of hydrogen According to DIN/ISO 9286: 1998-1 | SiC with well known Si value<br>Check to leak tightness | Vol. |
| 9 | **Acid decomposition**<br>- M: 5 g;<br>- Reaction of free Si with NaOH,<br>- Formation and determination of hydrogen | High purity Si powder | Vol. |
| 10 | **Acid decomposition**<br>- M: 5 g<br>according DIN 51075/4 | SiC **BAM-S003**<br>***BAM-S003 is a certified reference material. By a round robin test the standard was verified.*** | Vol. |

## 6.2 Methods used for the determination of additional material data

The quantitative phase analysis was based on high resolution X-ray powder diffraction data collected at the European Synchrotron Radiation Facility (ESRF) Grenoble. The data were obtained using the diffraction geometry with an extremely fast rotating capillary and short wavelengths of $\lambda$~0.08 nm. The evaluation of the diffraction data and the quantification was carried out using the Rietveld method at BAM. The given results are based on the evaluation of the diffraction data of ten specimes. Detailed information can be found in [7].
The particle size distribution was determined by laser light diffraction method.

# 7 Results and discussion

The analytical results of the certification interlaboratory comparison are listed in Tables A6.1 to A6.17 in Appendix 5. These tables show the single results ($M_i$) of each laboratory, the resp. laboratories' mean values (M) together with the intralaboratory standard deviation (s) and the half width of confidence intervals of the laboratory mean values (C95%).
In the second column of the tables the laboratory code number in this interlaboratory comparison together with the abbreviation of the analytical method used and a number 1, 2 or 3, which is the self- declaration of the laboratory concerning their experience to determine this analyte in SiC ("1" stands for no experience; "2" stands for medium experience and "3" stands for high experience) is given. The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [6], the results are shown below the resp. tables. A summary of the results of the statistical evaluation is given in Table 22.

Table 21 shows all laboratories' mean values. All results which were excluded from the calculation of the certified values for technical or statistical reasons are marked. Especially in case of aluminium there are the four lowest results which were removed for technical reasons. The lowest result was measured with ICP-OES after decomposition for 16 h which could be shown to be not complete. Detailed investigations showed that the decomposition time had to be at least 56 h to deliberate Al completely from the SiC-matrix (see Fig. 2).

The results obtained with ETV-ICP-OES were also too low. The reason was that the temperature (ca. 2200 °C) was too low to deliberate Al from the matrix. Al is nearly completely part of the crystal lattice of SiC and therefore deliberable with temperatures above 3700 °C which could be reached in DCArc analysis.
All data were technically discussed at several meetings of the Working Group "Special Materials" of the Committee of Chemists of the GDMB where some of the participating laboratories were present. Some of the laborartories withdrew their results after the technical discussion (see Table 21).

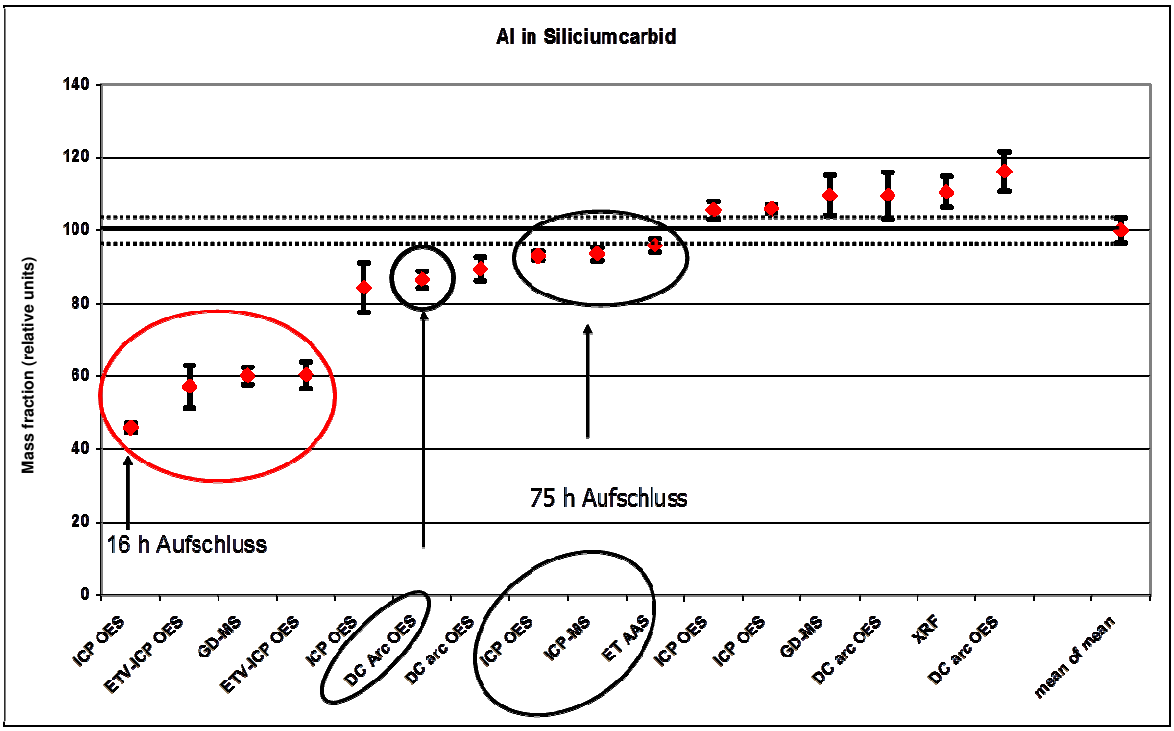


Figure 1: Results of interlaboratory comparison for aluminium (Aufschluss – decomposition)

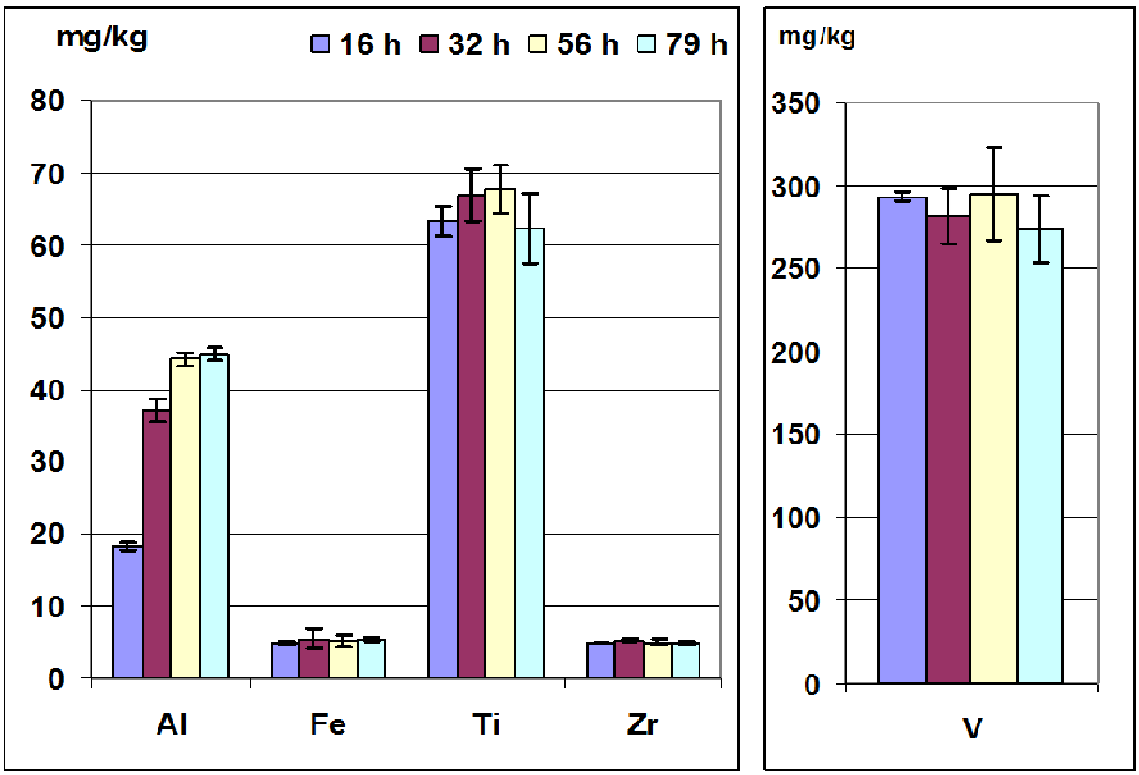


Figure 2: Recovery of different elements after different decompositions times (T = 250 °C, 0.25 g SiC +3 ml $HNO_3$ + 3 ml HF (50%) + 6 ml $H_2SO_4$)

Tab. 21: Means of the series of measurements for the analytical procedure of one laboratory (Laboratory means) before removing outliers

| Line No. | Al [mg/kg] | B [mg/kg] | Ca [mg/kg] | Cr [mg/kg] | Cu [mg/kg] | Fe [mg/kg] | Mg [mg/kg] | Mn [mg/kg] | Na [mg/kg] | Ni [mg/kg] | Ti [mg/kg] | V [mg/kg] | Zr [mg/kg] | $C_{total}$ [%] | N [mg/kg] | $C_{free}$ [%] | O [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.53 | 1.43 | 0.126 | 0.088 | 0.065 | 3.89 | 0.028 | 0.033 | 0.102 | 0.495 | 11.3 | 210 | 2.58 | 29.57 | 12.7 | 0.035 | 78.2 |
| 2 | 21.83 | 2.40 | 0.143 | 0.121 | 0.078 | 4.35 | 0.029 | 0.045 | 0.107 | 0.495 | 46.3 | 232 | 2.65 | 29.65 | 15.7 | 0.036 | 92.3 |
| 3 | 28.67 | 2.95 | 0.237 | 0.125 | 0.091 | 4.63 | 0.039 | 0.047 | 0.127 | 0.532 | 53.3 | 249 | 3.00 | 29.72 | 18.0 | 0.036 | 100.0 |
| 4 | 28.76 | 3.33 | 0.265 | 0.127 | 0.095 | 4.72 | 0.055 | 0.047 | 0.163 | 0.577 | 54.5 | 265 | 3.83 | 29.73 | 18.5 | 0.040 | 104.0 |
| 5 | 40.2 | 3.96 | 0.289 | 0.149 | 0.097 | 4.72 | 0.056 | 0.050 | 0.167 | 0.863 | 61.2 | 269 | 4.18 | 29.82 | 19.8 | 0.044 | 121.7 |
| 6 | 41.3 | 4.18 | 0.290 | 0.152 | 0.103 | 4.77 | 0.110 | 0.052 | 0.213 | 0.908 | 63.7 | 271 | 4.20 | 29.86 | 22.5 | 0.061 | 124.4 |
| 7 | 42.6 | | 0.317 | 0.155 | 0.150 | 4.78 | 0.167 | 0.055 | 0.229 | 0.940 | 70.0 | 273 | 4.40 | 29.91 | | 0.062 | 163.2 |
| 8 | 44.3 | | 0.332 | 0.233 | | 4.94 | 0.222 | 0.064 | 0.262 | 1.044 | 70.8 | 286 | 4.71 | 29.94 | | | 168.2 |
| 9 | 44.6 | | | 0.282 | | 5.05 | | 0.064 | | 1.200 | 71.4 | 288 | 5.24 | 29.94 | | | 194.3 |
| 10 | 45.7 | | | 0.437 | | 5.13 | | 0.102 | | 1.667 | 72.7 | 291 | 5.37 | 29.95 | | | 219.0 |
| 11 | 50.2 | | | 1.000 | | 5.17 | | 0.133 | | | 73.8 | 295 | 5.42 | 29.98 | | | 245.5 |
| 12 | 50.4 | | | | | 5.33 | | | | | 73.8 | 298 | 5.44 | 30.00 | | | |
| 13 | 50.5 | | | | | 10.00 | | | | | 74.4 | 308 | 5.64 | 30.00 | | | |
| 14 | 52.2 | | | | | 14.83 | | | | | 76.0 | 317 | | 30.01 | | | |
| 15 | 52.7 | | | | | 18.70 | | | | | 76.5 | 428 | | 30.03 | | | |
| 16 | 55.3 | | | | | | | | | | 123.2 | | | 30.04 | | | |
| 17 | | | | | | | | | | | | | | 30.15 | | | |
| 18 | | | | | | | | | | | | | | 30.87 | | | |
| M: | 40.7 | 3.04 | 0.250 | 0.159 | 0.097 | 6.73 | 0.088 | 0.063 | 0.171 | 0.872 | 67.1 | 285 | 4.36 | 29.95 | 17.9 | 0.045 | 146.4 |
| $s_M$: | 14.2 | 1.02 | 0.077 | 0.061 | 0.027 | 4.36 | 0.072 | 0.030 | 0.059 | 0.374 | 22.4 | 49 | 1.08 | 0.27 | 3.4 | 0.012 | 55.5 |

Note: The line number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
$s_M$: Standard deviation of the laboratory means

| | |
|---|---|
| 21.83 | Technical outlier, removed before statistical evaluation |
| 10.00 | Statistical outlier, removed resp. (laboratory informed) |
| 123.2 | Statistical outlier, withdrawn by the resp laboratory |

Tab. 22: Summary of results of statistical evaluation (the following abbreviations were used: b - Outlier at 1% significance; c - Outlier at 5% significance)

| Element<br>run of evaluation program | Al<br>run 1 | B<br>run 1 | Ca<br>run 1 | Cr<br>run 1 | Cr<br>run 2 | Cr<br>run 3 |
|---|---|---|---|---|---|---|
| Number of data sets | 12 | 6 | 8 | 11 | 10 | 9 |
| Total number of replicate measurements | 72 | 36 | 47 | 66 | 60 | 54 |
| Mean of means (in mg/kg) | 47.49 | 3.04 | 0.2497 | 0.2608 | 0.1869 | 0.1591 |
| St. Dev of means (in mg/kg) | 4.98 | 1.02 | 0.0770 | 0.2645 | 0.1047 | 0.0606 |
| Outlying or straggling mean values | | | | | | |
| ▪ Dixon test | no | no | no | b, c | no | no |
| ▪ Grubbs test (single and pair test) | no | no | c | b, c | c | no |
| ▪ Nalimov t-test | no | no | no | b, c | b, c | 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 | no | no | b, c | c | c | c |
| Variances homogeneous | | | | | | |
| ▪ Bartlett test | no | b | no | out of test range | no | no |
| St. Dev. within laboratories (in mg/kg) | 3.85 | 0.86 | 0.0614 | 0.0421 | 0.0442 | 0.0389 |
| St. Dev. between laboratories (in mg/kg) | 4.73 | 0.96 | 0.0733 | 0.2640 | 0.1032 | 0.0585 |
| Half-width of the 95% confidence interval (in mg/kg) | 3.16 | 1.07 | 0.0644 | 0.1777 | 0.0749 | 0.0466 |

| Element<br>run of evaluation program | Cu<br>run 1 | Fe<br>run 1 | Fe<br>run 2 | Fe<br>run 3 | Fe<br>run 4 |
|---|---|---|---|---|---|
| Number of data sets | 7 | 15 | 14 | 13 | 12 |
| Total number of replicate measurements | 42 | 90 | 84 | 78 | 72 |
| Mean of means (in mg/kg) | 0.0970 | 6.735 | 5.880 | 5.191 | 4.791 |
| St. Dev of means (in mg/kg) | 0.0268 | 4.363 | 2.949 | 1.492 | 0.391 |
| Outlying or straggling mean values | | | | | |
| ▪ Dixon test | no | c | b, c | b, c | c |
| ▪ Grubbs test (single and pair test) | c | b, c | b, c | b, c | c |
| ▪ Nalimov t-test | c | b, c | b, c | b, c | b, c |
| Differences between labs statistically significant? | | | | | |
| ▪ Snedecor F-test | b, c | b, c | b, c | b, c | c |
| Outlying or straggling variances | | | | | |
| ▪ Cochran test | no | b, c | c | b, c | b, c |
| Variances homogeneous | | | | | |
| ▪ Bartlett test | no | no | no | no | no |
| St. Dev. within laboratories (in mg/kg) | 0.0336 | 2.435 | 0.743 | 0.699 | 0.603 |
| St. Dev. between laboratories (in mg/kg) | 0.0230 | 4.248 | 2.933 | 1.465 | 0.304 |
| Half-width of the 95% confidence interval (in mg/kg) | 0.0247 | 2.416 | 1.703 | 0.902 | 0.248 |

| Element<br>run of evaluation program | Mg<br>run 1 | Mg<br>run 2 | Mn<br>run 1 | Mn<br>run 2 | Mn<br>run 3 | Na<br>run 1 |
|---|---|---|---|---|---|---|
| Number of data sets | 8 | 7 | 11 | 10 | 9 | 8 |
| Total number of replicate measurements | 48 | 42 | 66 | 60 | 54 | 48 |
| Mean of means (in mg/kg) | 0.0882 | 0.0691 | 0.0628 | 0.0557 | 0.0506 | 0.1711 |
| St. Dev of means (in mg/kg) | 0.0719 | 0.0513 | 0.0293 | 0.0185 | 0.0096 | 0.0590 |
| Outlying or straggling mean values | | | | | | |
| ▪ Dixon test | no | no | b, c | b, c | no | no |
| ▪ Grubbs test (single and pair test) | no | no | c | b, c | no | no |
| ▪ Nalimov t-test | c | c | b, c | b, c | c | no |
| 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 | b, c | b, c | b, c | b, c | b, c |
| Variances homogeneous | | | | | | |
| ▪ Bartlett test | no | no | no | no | no | no |
| St. Dev. within laboratories (in mg/kg) | 0.0792 | 0.0383 | 0.0185 | 0.0104 | 0.0065 | 0.0570 |
| St. Dev. between laboratories (in mg/kg) | 0.0642 | 0.0489 | 0.0283 | 0.0180 | 0.0092 | 0.0543 |
| Half-width of the 95% confidence interval (in mg/kg) | 0.0601 | 0.0475 | 0.0197 | 0.0132 | 0.0074 | 0.0494 |

| Element<br>run of evaluation program | Ni<br>run 1 | Ti<br>run 1 | Ti<br>run 2 | V<br>run 1 | V<br>run 2 | Zr<br>run 1 |
|---|---|---|---|---|---|---|
| Number of data sets<br>Total number of replicate measurements | 10<br>60 | 16<br>96 | 14<br>84 | 15<br>90 | 14<br>84 | 13<br>78 |
| Mean of means (in mg/kg)<br>St. Dev of means (in mg/kg) | 0.8721<br>0.3744 | 67.05<br>22.30 | 67.03<br>9.64 | 258.2<br>48.5 | 275.05<br>29.34 | 4.36<br>1.08 |
| Outlying or straggling mean values | | | | | | |
| ▪ Dixon test | no | b, c | no | b, c | no | no |
| ▪ Grubbs test (single and pair test) | no | c | no | b, c | no | no |
| ▪ Nalimov t-test | c | b, c | c | b, c | c | no |
| 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 | b, c | b, c | b, c | b, c | b, c |
| Variances homogeneous | | | | | | |
| ▪ Bartlett test | no | no | no | no | no | no |
| St. Dev. within laboratories (in mg/kg)<br>St. Dev. between laboratories (in mg/kg) | 0.2112<br>0.3644 | 7.68<br>22.08 | 7.75<br>9.11 | 34.8<br>46.4 | 35.29<br>25.56 | 1.09<br>0.99 |
| Half-width of the 95% confidence interval (in mg/kg) | 0.2678 | 11.88 | 5.57 | 26.9 | 16.94 | 0.65 |

| Element<br>run of evaluation program | Total C<br>run 1 | Total C<br>run 2 | Free C<br>run 1 |
|---|---|---|---|
| Number of data sets<br>Total number of replicate measurements | 18<br>107 | 17<br>102 | 7<br>42 |
| Mean of means (in %)<br>St. Dev of means (in %) | 29.955<br>0.275 | 29.900<br>0.155 | 0.0451<br>0.0122 |
| Outlying or straggling mean values | | | |
| ▪ Dixon test | b, c | no | no |
| ▪ Grubbs test (single and pair test) | b, c | no | c |
| ▪ Nalimov t-test | b, c | c | no |
| Differences between labs statistically significant? | | | |
| ▪ Snedecor F-test | b, c | b, c | b, c |
| Outlying or straggling variances | | | |
| ▪ Cochran test | b, c | b, c | no |
| Variances homogeneous | | | |
| ▪ Bartlett test | no | no | out of test range |
| St. Dev. within laboratories (in %)<br>St. Dev. between laboratories (in %) | 0.205<br>0.246 | 0.174<br>0.138 | 0.0027<br>0.0121 |
| Half-width of the 95% confidence interval (in %) | 0.137 | 0.080 | 0.0113 |

| Element<br>run of evaluation program | N<br>run 1 | O<br>run 1 |
|---|---|---|
| Number of data sets<br>Total number of replicate measurements | 6<br>36 | 11<br>66 |
| Mean of means (in mg/kg)<br>St. Dev of means (in mg/kg) | 17.9<br>3.4 | 146.4<br>55.5 |
| Outlying or straggling mean values | | |
| ▪ Dixon test | no | no |
| ▪ Grubbs test (single and pair test) | no | no |
| ▪ Nalimov t-test | no | no |
| Differences between labs statistically significant? | | |
| ▪ Snedecor F-test | b, c | b, c |
| Outlying or straggling variances | | |
| ▪ Cochran test | no | b, c |
| Variances homogeneous | | |
| ▪ Bartlett test | b, c | out of test range |
| St. Dev. within laboratories (in mg/kg)<br>St. Dev. between laboratories (in mg/kg) | 3.6<br>3.1 | 9.6<br>55.3 |
| Half-width of the 95% confidence interval (in mg/kg) | 3.6 | 37.3 |

# 8 Calculation of certified and indicative values and their uncertainties

## 8.1 Mass fractions

The certified and indicative values were calculated as the mean values "*M*" of all accepted means from the participating laboratories of the interlaboratory comparison (see § 7, Tab. 21).

## 8.2 Uncertainties

The combined uncertainties of the certified mass fractions were calculated taking into account contributions from the certification interlaboratory comparison and from the homogeneity tests (see Table 23). A contribution from an uncertainty caused by the possible aging of the material was not included, because no evidence was found that there is any detectable aging of the material (see paragraph 5).
The following parameters deriving from the homogeneity investigations were used for the calculation of the inhomogeneity contribution to the combined uncertainty:

$s_b$ = standard deviation of homogeneity investigation "between the bottles" (see Appendix 4) (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 4) (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 4). The value of $s_{HS}$ is assumed to represent the standard deviation of the analytical procedure used for the homogeneity investigation.

The following symbols and abbreviations are used additionally:

$u_c$ = combined uncertainty of certified mass fraction

$s_M$ = standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 23)

$n$ = number of accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 23)

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

whereas

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

In equation (1) from each of the variances $s^2_b$ (between the bottles) and $s^2_w$ (within the bottles) the variance $s^2_{HS}$ of the homogeneous sample (i.e. the variance of the analytical procedure) was subtracted. Thus an effective contribution of the inhomogeneity (without the contribution of the analytical procedure) was calculated. It is possible that the sum under the square root becomes less than “0”. In this case $s_{inhom}$ cannot be calculated and equation (6) combined with equation (4) are used for uncertainty calculation.

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

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

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

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

whereas

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

is valid, with

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

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

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

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

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

$$u_c = \sqrt{\frac{s_M^2}{n} + u_{bb}^2} \qquad (6)$$

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

The expanded uncertainty "$U$" (coverage factor $k$ = 2) of the certified mass fraction was calculated according to GUM [6] as

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

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

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

Table 23: Overview on the specific contributions to the combined uncertainty:

| | M (in mg/kg) | n | $s_M$ | $s_b$ | $s_w$ | $s_{HS}$ | $s_{inhom}$ | $u_{bb}$ | $u_c$ |
|---|---|---|---|---|---|---|---|---|---|
| Aluminium | 47.5 | 12 | 4.98 | 2.795 | 2.316 | 1.729 | **2.682** | 0.326 | 3.05 |
| Boron | 3.04 | 6 | 1.024 | 0.325 | 0.304 | 0.170 | **0.374** | 0.031 | 0.561 |
| Calcium | 0.25 | 8 | 0.077 | 0.241 | 0.197 | 0.158 | **0.216** | 0.041 | 0.027 |
| Chromium | 0.16 | 9 | 0.061 | 0.068 | 0.057 | 0.014 | **0.086** | 0.0033 | 0.021 |
| Copper | 0.097 | 7 | 0.027 | 0.050 | 0.048 | 0.079 | n.d. | **0.023** | 0.0249 |
| Iron | 4.79 | 12 | 0.391 | 1.318 | 1.419 | 1.930 | n.d. | **0.342** | 0.360 |
| Magnesium | 0.069 | 7 | 0.051 | 0.028 | 0.038 | 0.012 | **0.044** | 0.0049 | 0.048 |
| Manganese | 0.051 | 9 | 0.010 | 0.033 | 0.033 | 0.054 | n.d. | **0.0096** | 0.010 |
| Sodium | 0.17 | 8 | 0.059 | 0.032 | 0.031 | 0.017 | **0.037** | 0.0044 | 0.043 |
| Nickel | 0.87 | 10 | 0.374 | 0.112 | 0.199 | 0.063 | **0.210** | 0.0076 | 0.24 |
| Titanium | 67 | 14 | 9.6 | 3.215 | 3.115 | 3.892 | n.d. | **0.69** | 2.66 |
| Vanadium | 275 | 14 | 29.4 | 18.41 | 26.03 | 22.40 | 3.56 | **3.75** | 8.7 |
| Zirconium | 4.36 | 13 | 1.084 | 0.476 | 0.422 | 0.264 | **0.515** | 0.047 | 0.596 |
| Nitrogen | 17.9 | 6 | 3.40 | 1.298 | 0.961 | 2.103 | n.d. | **0.683** | 1.545 |
| Oxygen | 146 | 11 | 55.5 | 5.64 | 3.88 | 2.65 | **5.73** | 0.58 | 17.7 |
| | M (in %) | | | | | | | | |
| $Carbon_{total}$ | 29.9 | 17 | 0.155 | 0.034 | 0.034 | 0.032 | **0.016** | 0.007 | 0.041 |
| $Carbon_{free}$ | 0.045 | 7 | 0.012 | 0.0027 | 0.0019 | 0.0018 | **0.002** | 0.0004 | 0.005 |

n.d. – not defined

All certified values and their uncertainties as well as indicative data can be seen in the abstract of this report (Page 2-3).

# 9 Instructions for use

## 9.1 Area of application

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

## 9.2 Recommendations for correct sampling and sample preparation

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. Each sub-sample has to be taken separately. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different analytes: Al, Ca, Cr, Cu, Mg, Na, Ni, Ti, V, Zr (10 mg); B, Fe, Mn (15 mg); $C_{total}$ (18 mg); $C_{free}$ (200 mg); O, N (100 mg); $Si_{free}$, $SiO_{2\ free}$ (500 mg). The opening duration of the bottle should be as short as possible. The lid of the bottle containing a special sealing gasket should be locked tightly immediately after usage.

### 9.3 Recommendations for correct storage

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

### 9.4 Safety guidelines

1. First aid measures

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

2. Accidental release measures

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

3. Handling

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

4. Exposure restriction and personal protection

   Respiratory protection: If necessary use a respirator mask with filter type P according to DIN EN 143
   Hand protection: protective gloves recommended
   Eye protection: protective safety glasses

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

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

6. Disposal considerations

   Not classified as hazardous waste; observe local bye-laws.

## 10 References


[1] ISO Guide 31, Contents of certificates of reference materials, 1981

[2] ISO Guide 34, General requirements for the competence of reference material producers, 2009

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

[4] Guidelines for the production of BAM Reference Materials, 2006

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

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

[7] Peplinski B, Fitch AN, Evans A, Ibberson RM, Többens DM, Crabswick LMD, Dörfel I, Emmerling F, Matschat R: Z. Kristallogr. Suppl. 30 (2009) 61-66

## 11 Regulatory information


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- DIN, ISO 51079-1, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 1 Soda-Borsäure-Aufschluss
- DIN, ISO 51079-2, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 2 Säure-Druck-Aufschluss
- DIN, ISO 51079-3, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 3 Aufschluß des freien Kohlenstoffs durch naßchemische Oxidation
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## 13 Appendices

- Appendix 1: Method M1: Coulometric determination of free carbon ($C_{free}$) in silicon carbide after wet-chemical oxidation with hot chromic-sulfuric acid
- Appendix 2: Method M3: Proposed method for determination of total carbon mass fraction in silicon carbide powder
- Appendix 3: Method M4: Proposed Method for the determination of oxygen and nitrogen mass fraction in silicon carbide powder
- Appendix 4: Homogeneity testing
- Appendix 5: Compilation of sample preparation procedures, calibrations and methods for final determination used in interlaboratory comparison for certification of CRM BAM-S008

**Appendix 1: Method M1**

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

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

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

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

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

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

Coulometric detection system for determination of carbon mass fraction (e.g. coulometric system of "Coulomat 702", Ströhlein, Germany)
Analytical balance,
precision ± 0,05 mg
Aluminium heating-block with temperature control to 130 ºC ± 5 ºC
Reaction vessel, with cooling device and drying trap (figure 1)
Aluminium capsules, e.g. ∅ 6 mm, L 15 mm, prepared from aluminium foil (carbon free)
External PC and plotter/printer

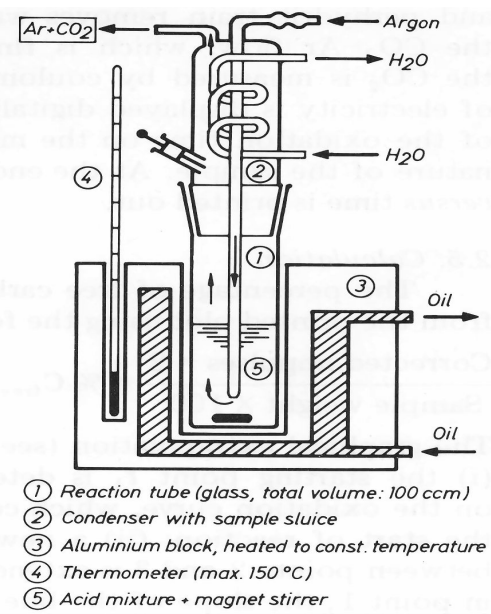


Fig.1: Aluminium heating block with reaction vessel

**Reagents and auxiliary means**

All reagents must be of known analytical grade. The used water shall be distilled water or water which has been fully demineralized by ion exchange (deionized water). Unless otherwise specified, solutions are aqueous solutions.
Calcium carbonate; $CaCO_3$ ( dried 2h/285°C )
Barium carbonate; $BaCO_3$
Barium perchlorate; $Ba(ClO_4)_2$,
$Ba(ClO_4)_2$-solution; 20% (mass%) in $H_2O$
Sodium dichromate; $Na_2Cr_2O_7$ x 2 $H_2O$
Potassium iodate; $KIO_3$
Sulfuric acid $H_2SO_4$; ρ = 1,84 g/ml
Argon; Ar, 99,998 % pure
Chromic sulfuric acid solution: prepared by dissolving 22 g of sodium dichromate in 300 ml $H_2O$, and adding 700 ml sulfuric acid.
The solution is heated for 30 min at 150 ºC ± 10 ºC. After cooling the solution is stored in a glass bottle.
Little porcelain boats, not glazed
Aluminium capsules, made from aluminium foil free of carbon

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

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

Graphical evaluation by hand:

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

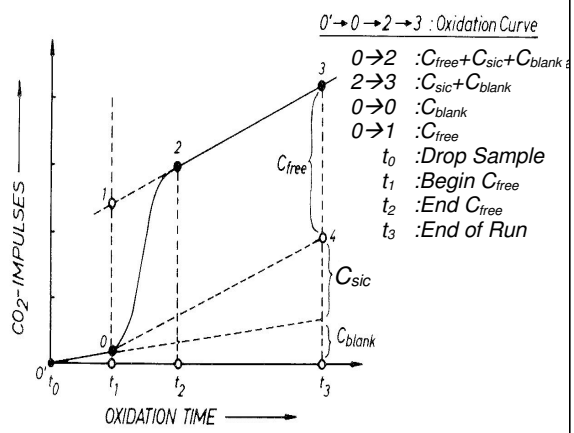


*Fig. 2. Analysis of free carbon in silicon carbide: a plot of $CO_2$ concentration vs. time with graphical extrapolation.*

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

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

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

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

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

**References:**

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DIN 51079-3 Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen
Teil 3: Aufschluss des Freien Kohlenstoffs durch nasschemische Oxidation
Norm-Entwurf Okt 1997

## Appendix 2: Method M3

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

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

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

**Preparation of measurement**

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

**Measurement**

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

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

## Appendix 3: Method M4

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

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

### Method

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

### Preparation of measurement

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

### Measurement

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

### Calibration

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

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

## Appendix 4: Homogeneity test

**Analyt Al** (ETV-ICP-OES, results were compiled over 2 lines on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 9.28 | 17.69 | 22.24 | **16.40** | **18.76** | **3.10** | **16.5** |
| | 12/2 | 12.25 | 26.55 | 31.06 | **23.29** | | | |
| | 12/3 | 10.86 | 23.61 | | **17.24** | | | |
| | 12/4 | 13.83 | 16.66 | 23.85 | **18.11** | | | |
| 2 | 35/1 | 15.18 | 26.66 | 22.81 | **21.55** | **19.24** | **1.99** | **10.3** |
| | 35/2 | 12.71 | 16.95 | 29.64 | **19.77** | | | |
| | 35/3 | 6.84 | 21.93 | 21.53 | **16.77** | | | |
| | 35/4 | 13.54 | | 24.23 | **18.88** | | | |
| 3 | 66/1 | 13.16 | 21.27 | 29.94 | **21.46** | **19.47** | **1.72** | **8.8** |
| | 66/2 | 12.67 | 17.12 | 21.99 | **17.26** | | | |
| | 66/3 | 11.10 | 25.63 | 21.60 | **19.44** | | | |
| | 66/4 | 13.11 | 19.11 | 26.97 | **19.73** | | | |
| 4 | 99/1 | 12.86 | 21.87 | 26.32 | **20.35** | **19.33** | **0.84** | **4.3** |
| | 99/2 | 13.61 | 23.45 | 21.35 | **19.47** | | | |
| | 99/3 | 12.15 | 19.62 | 25.80 | **19.19** | | | |
| | 99/4 | 11.93 | 18.76 | 24.26 | **18.32** | | | |
| 5 | 116/1 | 12.80 | 30.79 | 27.73 | **23.77** | **22.80** | **2.57** | **11.3** |
| | 116/2 | 24.83 | 20.76 | 32.36 | **25.98** | | | |
| | 116/3 | 13.42 | 20.57 | 28.41 | **20.80** | | | |
| | 116/4 | 8.19 | 19.00 | 34.70 | **20.63** | | | |
| 6 | 143/1 | 11.78 | 20.36 | 25.57 | **19.24** | **21.01** | **3.85** | **18.3** |
| | 143/2 | 12.80 | 24.84 | 24.20 | **20.61** | | | |
| | 143/3 | 34.51 | 20.02 | 24.97 | **26.50** | | | |
| | 143/4 | 8.66 | 20.85 | 23.52 | **17.68** | | | |

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | | 19.58 | 24.90 | **22.24** | **18.73** | **2.56** | **13.7** |
| | 161/2 | 9.33 | 17.30 | 26.80 | **17.81** | | | |
| | 161/3 | 9.09 | 18.93 | 20.49 | **16.17** | | | |
| | 161/4 | 9.73 | 24.80 | 21.61 | **18.72** | | | |
| 8 | 195/1 | 12.28 | 24.31 | 28.64 | **21.74** | **21.33** | **2.75** | **12.9** |
| | 195/2 | 9.64 | 24.51 | 24.68 | **19.61** | | | |
| | 195/3 | 17.62 | 20.16 | 18.98 | **18.92** | | | |
| | 195/4 | 10.80 | 24.02 | 40.27 | **25.03** | | | |
| 9 | 237/1 | 12.49 | 21.16 | 24.17 | **19.27** | **19.20** | **0.95** | **4.9** |
| | 237/2 | 8.77 | 20.79 | 24.74 | **18.10** | | | |
| | 237/3 | 10.69 | 27.25 | 23.27 | **20.40** | | | |
| | 237/4 | 11.17 | 22.50 | 23.39 | **19.02** | | | |
| 10 | 258/1 | 10.93 | 21.54 | 23.86 | **18.78** | **17.60** | **0.99** | **5.6** |
| | 258/2 | 9.39 | 18.70 | 26.10 | **18.06** | | | |
| | 258/3 | 9.72 | 18.19 | 22.23 | **16.71** | | | |
| | 258/4 | 8.84 | 18.82 | 22.87 | **16.84** | | | |
| 11 | 287/1 | 13.21 | 28.79 | 26.50 | **22.83** | **19.35** | **2.42** | **12.5** |
| | 287/2 | 10.04 | 16.84 | 30.63 | **19.17** | | | |
| | 287/3 | 12.91 | 20.15 | 19.70 | **17.59** | | | |
| | 287/4 | 11.38 | 20.43 | 21.66 | **17.82** | | | |
| 12 | 294/1 | 11.55 | 24.41 | 26.75 | **20.90** | **19.41** | **1.95** | **10.1** |
| | 294/2 | 11.91 | 20.66 | 31.01 | **21.19** | | | |
| | 294/3 | 13.97 | 16.84 | 20.77 | **17.19** | | | |
| | 294/4 | 7.85 | 27.14 | 20.04 | **18.34** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **19.69** |
| **SD of means of the sub-samples 1-4** | **1.38** |
| **RSD (%)** | **7.02** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **10.8** |

## Analyt Al

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 2 lines (12.04.11) | mean calculated from 2 lines (13.04.11) | mean calculated from 2 lines (13.04.11) | **mean** |
|---|---|---|---|---|---|
| | | | | | |
| 1 | HS 1 | 24.19 | 25.16 | 28.17 | **25.8** |
| 2 | HS 2 | 25.01 | 25.92 | 28.05 | **26.3** |
| 3 | HS 3 | 38.25 | 28.95 | 20.85 | **29.4** |
| 4 | HS 4 | 28.51 | 27.43 | 28.02 | **28.0** |
| 5 | HS 5 | 31.62 | 29.86 | 26.17 | **29.2** |
| 6 | HS 6 | 23.58 | 37.09 | 22.41 | **27.7** |
| 7 | HS 7 | 32.27 | 29.50 | 25.20 | **29.0** |
| 8 | HS 8 | 25.67 | 24.22 | 23.80 | **24.6** |
| 9 | HS 9 | 32.97 | 25.35 | 27.75 | **28.7** |
| 10 | HS 10 | 32.44 | 26.31 | 26.11 | **28.3** |
| 11 | HS 11 | 37.46 | 24.98 | 26.91 | **29.8** |
| 12 | HS 12 | 28.22 | 25.12 | 21.25 | **24.9** |
| 13 | HS 13 | 38.11 | 24.26 | 23.63 | **28.7** |
| 14 | HS 14 | 28.69 | 24.81 | 22.53 | **25.3** |
| 15 | HS 15 | 30.56 | 25.41 | 26.40 | **27.5** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **27.54** |
| **$SD_{HS}$** | **1.729** |
| **$RSD_{HS}$ (%)** | **6.28** |

## Analyt Al

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 2.316 | $M_{Ss}$ 19.69 | RSD % 7.02 |
| standard deviation between the samples $s_b$ | 2.674 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.425 | Characteristic no. for homogeneity between the samples | 0.700 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 1.729 | $M_{HS}$ 27.54 | $RSD_{HS}$ % 6.28 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 1.795 | Characteristic no. for homogeneity within the samples | 0.781 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

**Analyt B** (DC ARC OES, results were compiled over 1 line on 4 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 4.97 | 4.10 | 3.35 | 3.11 | **3.88** | **3.99** | **0.15** | **3.8** |
| | 12/2 | 4.26 | 3.56 | 3.73 | 4.16 | **3.93** | | | |
| | 12/3 | 4.67 | 3.55 | 4.00 | 4.65 | **4.22** | | | |
| | 12/4 | 4.21 | 4.33 | 3.88 | 3.36 | **3.95** | | | |
| 2 | 35/1 | 3.96 | 3.90 | 3.54 | 3.87 | **3.82** | **3.84** | **0.25** | **6.5** |
| | 35/2 | 4.42 | 3.42 | 4.82 | 3.44 | **4.02** | | | |
| | 35/3 | 3.35 | 3.46 | 3.62 | 3.53 | **3.49** | | | |
| | 35/4 | 3.76 | 5.25 | 3.91 | 3.12 | **4.01** | | | |
| 3 | 66/1 | 3.54 | 4.06 | 3.87 | 5.04 | **4.13** | **4.05** | **0.30** | **7.3** |
| | 66/2 | 4.22 | 4.94 | 3.87 | 4.01 | **4.26** | | | |
| | 66/3 | 4.17 | 3.96 | 4.41 | 4.24 | **4.20** | | | |
| | 66/4 | 3.19 | 3.87 | 3.78 | 3.62 | **3.61** | | | |
| 4 | 99/1 | 5.37 | 4.79 | 4.32 | 3.20 | **4.42** | **4.35** | **0.09** | **2.1** |
| | 99/2 | 3.88 | 4.44 | 4.01 | 5.41 | **4.44** | | | |
| | 99/3 | 5.11 | 4.09 | 3.69 | 4.05 | **4.24** | | | |
| | 99/4 | 4.41 | 3.92 | 4.01 | 4.93 | **4.32** | | | |
| 5 | 116/1 | 4.46 | 4.08 | 3.34 | 4.11 | **4.00** | **4.08** | **0.24** | **5.8** |
| | 116/2 | 3.94 | 3.05 | 4.28 | 3.85 | **3.78** | | | |
| | 116/3 | 4.75 | 4.15 | 3.86 | 4.08 | **4.21** | | | |
| | 116/4 | 4.00 | 3.75 | 3.60 | 5.91 | **4.32** | | | |
| 6 | 143/1 | 4.40 | 3.61 | 3.89 | 3.45 | **3.84** | **3.77** | **0.12** | **3.1** |
| | 143/2 | 3.80 | 3.27 | 3.32 | 4.08 | **3.62** | | | |
| | 143/3 | 3.98 | 3.53 | 2.87 | 4.54 | **3.73** | | | |
| | 143/4 | 4.55 | 4.04 | 3.91 | 3.03 | **3.88** | | | |

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 4.04 | 3.99 | 4.34 | 4.61 | **4.25** | **4.09** | **0.20** | **4.9** |
| | 161/2 | 3.97 | 3.40 | 4.16 | 5.39 | **4.23** | | | |
| | 161/3 | 4.15 | 4.58 | 2.94 | 4.51 | **4.05** | | | |
| | 161/4 | 4.06 | 3.63 | 4.14 | 3.45 | **3.82** | | | |
| 8 | 195/1 | 6.84 | 4.32 | 4.67 | 4.13 | **4.99** | **4.28** | **0.52** | **12.2** |
| | 195/2 | 3.78 | | 3.61 | 4.32 | **3.90** | | | |
| | 195/3 | 3.56 | 4.45 | 3.36 | 4.09 | **3.86** | | | |
| | 195/4 | 3.89 | 5.31 | 4.10 | 4.11 | **4.35** | | | |
| 9 | 237/1 | 4.55 | 3.67 | 2.97 | 3.51 | **3.67** | **3.98** | **0.26** | **6.4** |
| | 237/2 | 4.50 | 3.99 | 3.96 | 3.52 | **3.99** | | | |
| | 237/3 | 3.30 | 3.92 | 4.23 | 4.42 | **3.97** | | | |
| | 237/4 | 4.91 | 4.24 | 3.96 | 4.09 | **4.30** | | | |
| 10 | 258/1 | 4.89 | 3.33 | 4.41 | 4.15 | **4.20** | **4.09** | **0.36** | **8.8** |
| | 258/2 | 4.75 | 4.29 | 4.50 | 4.09 | **4.41** | | | |
| | 258/3 | 3.49 | 3.56 | 3.31 | 3.92 | **3.57** | | | |
| | 258/4 | 5.19 | 3.24 | 3.70 | 4.66 | **4.20** | | | |
| 11 | 287/1 | 3.76 | 4.32 | 4.08 | 4.46 | **4.15** | **3.95** | **0.46** | **11.7** |
| | 287/2 | 4.41 | 4.36 | 4.59 | 3.97 | **4.33** | | | |
| | 287/3 | | 3.80 | 4.10 | 4.24 | **4.05** | | | |
| | 287/4 | 3.48 | 4.31 | 2.55 | 2.80 | **3.28** | | | |
| 12 | 294/1 | 4.16 | 3.95 | 4.14 | 4.34 | **4.15** | **4.06** | **0.36** | **8.9** |
| | 294/2 | 3.38 | 3.55 | 3.57 | 3.68 | **3.54** | | | |
| | 294/3 | 4.41 | 3.75 | 3.88 | 4.64 | **4.17** | | | |
| | 294/4 | 4.58 | 3.70 | 4.07 | 5.21 | **4.39** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **4.044** |
| **SD of means of the sub-samples 1-4** | **0.16** |
| **RSD (%)** | **4.014** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **6.8** |

## Analyt B

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (16.06.11) | mean calculated from 1 line (17.03.11) | mean calculated from 1 line (22.03.11) | mean calculated from 1 line (30.03.11) | **mean** |
|---|---|---|---|---|---|---|
| 1 | HS 1 | 5.46 | 7.83 | 3.81 | 4.20 | **5.33** |
| 2 | HS 2 | 5.02 | 7.78 | 5.13 | 4.56 | **5.62** |
| 3 | HS 3 | 5.29 | 8.06 | 5.15 | 4.78 | **5.82** |
| 4 | HS 4 | 4.96 | 8.49 | 4.58 | 3.85 | **5.47** |
| 5 | HS 5 | 4.20 | 7.75 | 4.81 | 4.13 | **5.22** |
| 6 | HS 6 | 4.15 | 8.14 | 4.53 | 4.95 | **5.44** |
| 7 | HS 7 | 5.09 | 7.76 | 4.20 | 3.75 | **5.20** |
| 8 | HS 8 | 4.73 | 8.62 | 5.05 | 3.91 | **5.58** |
| 9 | HS 9 | 5.68 | 7.61 | 3.83 | 4.55 | **5.42** |
| 10 | HS 10 | 5.78 | 7.77 | 4.19 | 3.93 | **5.42** |
| 11 | HS 11 | 4.54 | 7.93 | 4.05 | 4.37 | **5.22** |
| 12 | HS 12 | 4.62 | 8.04 | 4.22 | 4.75 | **5.40** |
| 13 | HS 13 | 5.60 | 7.94 | 4.38 | 4.27 | **5.55** |
| 14 | HS 14 | 4.35 | 7.76 | 4.76 | 4.22 | **5.27** |
| 15 | HS 15 | 4.77 | 7.83 | 5.02 | 3.94 | **5.39** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **5.42** |
| **$SD_{HS}$** | **0.170** |
| **$RSD_{HS}$ (%)** | **3.14** |

## Analyt B

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.304 | $M_{Ss}$ 4.044 | RSD % 4.01 |
| standard deviation between the samples $s_b$ | 0.325 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.143 | Characteristic no. for homogeneity between the samples | 0.561 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.170 | $M_{HS}$ 5.420 | $RSD_{HS}$ % 3.14 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 3.190 | Characteristic no. for homogeneity within the samples | 1.388 |
| **Homogeneity within the samples: Not very strong inhomogeneity** | | | |

**Analyt Ca** (ETV-ICP-OES, results were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 1.70 | 1.49 | 1.00 | **1.40** | **1.02** | **0.32** | **31.1** |
| | 12/2 | 1.03 | 1.04 | 1.34 | **1.13** | | | |
| | 12/3 | 0.80 | 0.76 | 0.46 | **0.67** | | | |
| | 12/4 | 0.54 | 1.02 | 1.03 | **0.86** | | | |
| 2 | 35/1 | 1.02 | 1.57 | 1.46 | **1.35** | **1.17** | **0.23** | **20.0** |
| | 35/2 | | 1.06 | 1.04 | **1.05** | | | |
| | 35/3 | 1.83 | 0.75 | 1.58 | **1.39** | | | |
| | 35/4 | 0.91 | | 0.89 | **0.90** | | | |
| 3 | 66/1 | 0.81 | 1.02 | 1.50 | **1.11** | **1.30** | **0.18** | **13.8** |
| | 66/2 | 1.01 | 1.79 | 1.71 | **1.50** | | | |
| | 66/3 | | 0.90 | 1.50 | **1.20** | | | |
| | 66/4 | 1.71 | 1.04 | 1.44 | **1.40** | | | |
| 4 | 99/1 | 0.93 | 1.58 | 1.48 | **1.33** | **1.30** | **0.27** | **20.5** |
| | 99/2 | 1.74 | 1.87 | 0.89 | **1.50** | | | |
| | 99/3 | 0.60 | 0.96 | 1.19 | **0.91** | | | |
| | 99/4 | 1.90 | 1.00 | | **1.45** | | | |
| 5 | 116/1 | 0.70 | 1.63 | 1.15 | **1.16** | **1.27** | **0.12** | **9.2** |
| | 116/2 | 0.68 | 1.56 | 1.59 | **1.28** | | | |
| | 116/3 | 1.47 | 1.12 | 1.07 | **1.22** | | | |
| | 116/4 | 1.23 | 1.57 | 1.50 | **1.43** | | | |
| 6 | 143/1 | 0.79 | 1.06 | 1.64 | **1.16** | **1.12** | **0.19** | **17.3** |
| | 143/2 | 0.59 | 1.00 | 1.15 | **0.92** | | | |
| | 143/3 | 0.77 | 1.22 | 1.15 | **1.05** | | | |
| | 143/4 | 1.59 | 1.31 | 1.22 | **1.37** | | | |

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 1.89 | 1.02 | 1.63 | **1.51** | **1.32** | **0.18** | **13.7** |
| | 161/2 | 1.91 | 1.04 | 1.25 | **1.40** | | | |
| | 161/3 | 1.59 | 1.14 | 1.11 | **1.28** | | | |
| | 161/4 | 0.96 | 1.13 | 1.19 | **1.09** | | | |
| 8 | 195/1 | 1.74 | 1.15 | 1.07 | **1.32** | **1.32** | **0.14** | **10.2** |
| | 195/2 | 1.35 | | 1.47 | **1.41** | | | |
| | 195/3 | 0.79 | 1.99 | 0.62 | **1.13** | | | |
| | 195/4 | 1.13 | 1.82 | 1.33 | **1.43** | | | |
| 9 | 237/1 | 0.67 | 0.66 | 1.09 | **0.81** | **1.00** | **0.22** | **22.2** |
| | 237/2 | 1.69 | 1.52 | 0.71 | **1.31** | | | |
| | 237/3 | | 0.60 | 1.14 | **0.87** | | | |
| | 237/4 | 0.93 | 1.39 | 0.75 | **1.02** | | | |
| 10 | 258/1 | 0.76 | 1.30 | 1.45 | **1.17** | **1.07** | **0.14** | **13.2** |
| | 258/2 | 0.93 | 1.88 | 0.70 | **1.17** | | | |
| | 258/3 | 0.87 | 1.08 | 0.66 | **0.87** | | | |
| | 258/4 | 1.22 | 1.02 | 1.03 | **1.09** | | | |
| 11 | 287/1 | 0.81 | 1.54 | 0.78 | **1.04** | **1.09** | **0.16** | **14.5** |
| | 287/2 | 1.12 | | 0.93 | **1.03** | | | |
| | 287/3 | 0.59 | 1.35 | 0.95 | **0.96** | | | |
| | 287/4 | 0.77 | 1.63 | 1.56 | **1.32** | | | |
| 12 | 294/1 | 1.45 | 1.55 | 0.65 | **1.22** | **1.15** | **0.09** | **8.2** |
| | 294/2 | 1.06 | 1.13 | 1.19 | **1.13** | | | |
| | 294/3 | 0.62 | 0.82 | 1.63 | **1.02** | | | |
| | 294/4 | 1.02 | 1.20 | 1.45 | **1.22** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **1.179** |
| **SD of means of the sub-samples 1-4** | **0.12** |
| **RSD (%)** | **10.212** |

**mean $RSD_w$ (%) 16.2**

## Analyt Ca

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 0.92 | 0.89 | 1.81 | **1.21** |
| 2 | HS 2 | 0.62 | 1.14 | 1.01 | **0.92** |
| 3 | HS 3 | 0.84 | 1.57 | | **1.21** |
| 4 | HS 4 | 0.92 | 1.10 | 1.24 | **1.09** |
| 5 | HS 5 | 1.13 | 1.85 | 0.98 | **1.32** |
| 6 | HS 6 | 1.11 | 1.04 | 1.43 | **1.19** |
| 7 | HS 7 | 1.08 | 1.16 | 1.05 | **1.10** |
| 8 | HS 8 | 0.87 | 1.46 | 1.00 | **1.11** |
| 9 | HS 9 | 1.10 | | 1.56 | **1.33** |
| 10 | HS 10 | 1.64 | 1.67 | 0.97 | **1.43** |
| 11 | HS 11 | 1.00 | 1.27 | 0.98 | **1.08** |
| 12 | HS 12 | 0.90 | 1.25 | 0.80 | **0.98** |
| 13 | HS 13 | 0.60 | 1.27 | 0.86 | **0.91** |
| 14 | HS 14 | 0.82 | 1.75 | 1.07 | **1.21** |
| 15 | HS 15 | 1.26 | 1.57 | 1.32 | **1.38** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **1.164** |
| **$SD_{HS}$** | **0.158** |
| **$RSD_{HS}$ (%)** | **13.60** |

## Analyt Ca

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.197 | $M_{Ss}$ 1.179 | RSD % 10.21 |
| standard deviation between the samples $s_b$ | 0.241 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.497 | Characteristic no. for homogeneity between the samples | 0.735 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.158 | $M_{HS}$ 1.164 | $RSD_{HS}$ % 13.60 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 1.543 | Characteristic no. for homogeneity within the samples | 0.671 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

**Analyt Cr** (ETV-ICP-OES, results were compiled over 2 lines on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | | 0.307 | 0.287 | **0.297** | **0.319** | **0.063** | **19.9** |
| | 12/2 | 0.181 | 0.336 | 0.264 | **0.260** | | | |
| | 12/3 | 0.174 | 0.375 | 0.379 | **0.309** | | | |
| | 12/4 | | 0.366 | 0.451 | **0.409** | | | |
| 2 | 35/1 | 0.293 | 0.433 | 0.551 | **0.426** | **0.305** | **0.083** | **27.2** |
| | 35/2 | 0.214 | 0.217 | 0.299 | **0.243** | | | |
| | 35/3 | 0.284 | 0.260 | 0.234 | **0.260** | | | |
| | 35/4 | 0.138 | 0.434 | 0.307 | **0.293** | | | |
| 3 | 66/1 | 0.215 | 0.371 | | **0.293** | **0.285** | **0.084** | **29.6** |
| | 66/2 | 0.159 | 0.210 | 0.229 | **0.199** | | | |
| | 66/3 | 0.212 | 0.306 | 0.234 | **0.251** | | | |
| | 66/4 | 0.376 | 0.496 | 0.322 | **0.398** | | | |
| 4 | 99/1 | 0.396 | 0.265 | 0.318 | **0.326** | **0.283** | **0.066** | **23.1** |
| | 99/2 | 0.181 | 0.276 | 0.222 | **0.226** | | | |
| | 99/3 | 0.198 | 0.244 | 0.241 | **0.228** | | | |
| | 99/4 | 0.214 | 0.614 | 0.226 | **0.352** | | | |
| 5 | 116/1 | 0.159 | 0.299 | 0.221 | **0.227** | **0.266** | **0.036** | **13.6** |
| | 116/2 | 0.206 | 0.241 | 0.293 | **0.247** | | | |
| | 116/3 | 0.315 | 0.237 | 0.301 | **0.284** | | | |
| | 116/4 | 0.102 | 0.426 | 0.392 | **0.307** | | | |
| 6 | 143/1 | 0.109 | 0.213 | 0.206 | **0.176** | **0.238** | **0.058** | **24.3** |
| | 143/2 | 0.140 | 0.291 | 0.208 | **0.213** | | | |
| | 143/3 | 0.431 | 0.234 | 0.270 | **0.312** | | | |
| | 143/4 | 0.147 | 0.342 | 0.261 | **0.250** | | | |

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 0.277 | 0.198 | 0.211 | **0.229** | **0.222** | **0.017** | **7.7** |
| | 161/2 | 0.150 | 0.208 | 0.242 | **0.200** | | | |
| | 161/3 | 0.229 | 0.216 | 0.208 | **0.218** | | | |
| | 161/4 | 0.108 | 0.303 | 0.308 | **0.240** | | | |
| 8 | 195/1 | 0.109 | 0.227 | 0.255 | **0.197** | **0.238** | **0.034** | **14.4** |
| | 195/2 | 0.280 | 0.305 | 0.237 | **0.274** | | | |
| | 195/3 | 0.247 | 0.308 | 0.214 | **0.256** | | | |
| | 195/4 | 0.154 | 0.267 | 0.251 | **0.224** | | | |
| 9 | 237/1 | 0.141 | 0.227 | 0.228 | **0.199** | **0.238** | **0.036** | **15.2** |
| | 237/2 | 0.169 | 0.255 | 0.240 | **0.221** | | | |
| | 237/3 | 0.257 | 0.347 | 0.242 | **0.282** | | | |
| | 237/4 | 0.253 | 0.281 | 0.221 | **0.252** | | | |
| 10 | 258/1 | 0.107 | 0.245 | 0.228 | **0.193** | **0.218** | **0.021** | **9.7** |
| | 258/2 | 0.141 | 0.223 | 0.277 | **0.214** | | | |
| | 258/3 | 0.244 | 0.239 | 0.251 | **0.245** | | | |
| | 258/4 | 0.159 | 0.270 | 0.232 | **0.220** | | | |
| 11 | 287/1 | 0.198 | 0.295 | 0.227 | **0.240** | **0.237** | **0.042** | **17.9** |
| | 287/2 | 0.136 | 0.217 | 0.228 | **0.194** | | | |
| | 287/3 | 0.391 | 0.301 | 0.191 | **0.294** | | | |
| | 287/4 | 0.191 | 0.256 | 0.218 | **0.222** | | | |
| 12 | 294/1 | 0.110 | 0.235 | 0.247 | **0.198** | **0.287** | **0.080** | **27.7** |
| | 294/2 | | 0.270 | 0.301 | **0.285** | | | |
| | 294/3 | 0.283 | 0.215 | 0.328 | **0.275** | | | |
| | 294/4 | 0.427 | 0.417 | 0.330 | **0.391** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.261** |
| **SD of means of the sub-samples 1-4** | **0.034** |
| **RSD (%)** | **12.98** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **19.2** |

## Analyt Cr

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 2 lines (20.04.11) | mean calculated from 2 lines (20.04.11) | mean calculated from 2 lines (21.04.11) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 0.242 | 0.211 | 0.207 | **0.220** |
| 2 | HS 2 | 0.276 | 0.192 | 0.188 | **0.219** |
| 3 | HS 3 | 0.245 | 0.246 | 0.258 | **0.250** |
| 4 | HS 4 | 0.228 | 0.284 | 0.219 | **0.244** |
| 5 | HS 5 | 0.224 | 0.245 | 0.295 | **0.254** |
| 6 | HS 6 | 0.234 | 0.197 | 0.276 | **0.236** |
| 7 | HS 7 | 0.206 | 0.197 | 0.219 | **0.208** |
| 8 | HS 8 | 0.217 | 0.226 | 0.255 | **0.233** |
| 9 | HS 9 | 0.262 | 0.180 | 0.201 | **0.214** |
| 10 | HS 10 | 0.292 | 0.185 | 0.169 | **0.215** |
| 11 | HS 11 | 0.302 | 0.192 | 0.191 | **0.228** |
| 12 | HS 12 | 0.336 | 0.170 | 0.171 | **0.226** |
| 13 | HS 13 | 0.301 | 0.214 | 0.174 | **0.230** |
| 14 | HS 14 | 0.265 | 0.198 | 0.187 | **0.217** |
| 15 | HS 15 | 0.255 | 0.189 | 0.191 | **0.212** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **0.227** |
| **$SD_{HS}$** | **0.014** |
| **$RSD_{HS}$ (%)** | **6.248** |

## Analyt Cr

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.057 | $M_{Ss}$ 0.261 | RSD % 12.98 |
| standard deviation between the samples $s_b$ | 0.068 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.441 | Characteristic no. for homogeneity between the samples | 0.708 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.014 | $M_{HS}$ 0.227 | $RSD_{HS}$ % 6.25 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 15.888 | Characteristic no. for homogeneity within the samples | 6.914 |
| **Homogeneity within the samples: Strong inhomogeneity** | | | |

**Analyt Cu** (ETV-ICP-OES, results were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 0.35 | 0.45 | 0.18 | **0.33** | **0.38** | **0.05** | **12.1** |
| | 12/2 | 0.55 | 0.58 | 0.19 | **0.44** | | | |
| | 12/3 | 0.51 | 0.48 | 0.17 | **0.39** | | | |
| | 12/4 | 0.32 | 0.61 | 0.19 | **0.38** | | | |
| 2 | 35/1 | 0.41 | 0.32 | 0.25 | **0.33** | **0.37** | **0.05** | **13.6** |
| | 35/2 | 0.53 | 0.62 | 0.19 | **0.45** | | | |
| | 35/3 | 0.48 | 0.44 | 0.16 | **0.36** | | | |
| | 35/4 | 0.24 | 0.61 | 0.26 | **0.37** | | | |
| 3 | 66/1 | 0.24 | 0.43 | 0.24 | **0.30** | **0.40** | **0.07** | **16.8** |
| | 66/2 | 0.55 | 0.54 | 0.20 | **0.43** | | | |
| | 66/3 | 0.49 | 0.46 | 0.26 | **0.40** | | | |
| | 66/4 | 0.55 | 0.47 | 0.35 | **0.46** | | | |
| 4 | 99/1 | 0.38 | 0.49 | 0.26 | **0.38** | **0.40** | **0.02** | **5.8** |
| | 99/2 | 0.36 | 0.62 | 0.21 | **0.39** | | | |
| | 99/3 | 0.43 | 0.56 | 0.29 | **0.43** | | | |
| | 99/4 | 0.52 | 0.53 | 0.21 | **0.42** | | | |
| 5 | 116/1 | 0.33 | 0.42 | 0.20 | **0.32** | **0.44** | **0.10** | **22.7** |
| | 116/2 | 0.60 | 0.46 | 0.18 | **0.41** | | | |
| | 116/3 | 0.46 | 0.62 | 0.60 | **0.56** | | | |
| | 116/4 | 0.50 | 0.61 | 0.27 | **0.46** | | | |
| 6 | 143/1 | 0.47 | 0.45 | 0.29 | **0.40** | **0.40** | **0.01** | **3.7** |
| | 143/2 | 0.43 | 0.58 | 0.18 | **0.40** | | | |
| | 143/3 | 0.48 | 0.58 | 0.21 | **0.42** | | | |
| | 143/4 | 0.44 | 0.50 | 0.21 | **0.38** | | | |

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 0.63 | 0.40 | 0.26 | **0.43** | **0.42** | **0.02** | **4.4** |
| | 161/2 | 0.61 | 0.52 | 0.19 | **0.44** | | | |
| | 161/3 | 0.60 | 0.44 | 0.15 | **0.40** | | | |
| | 161/4 | 0.46 | 0.49 | 0.31 | **0.42** | | | |
| 8 | 195/1 | 0.46 | 0.54 | 0.24 | **0.41** | **0.45** | **0.06** | **12.8** |
| | 195/2 | 0.72 | 0.68 | 0.20 | **0.53** | | | |
| | 195/3 | 0.39 | 0.58 | 0.31 | **0.42** | | | |
| | 195/4 | 0.54 | 0.49 | 0.23 | **0.42** | | | |
| 9 | 237/1 | 0.33 | 0.65 | 0.20 | **0.39** | **0.42** | **0.02** | **5.7** |
| | 237/2 | 0.52 | 0.61 | 0.21 | **0.45** | | | |
| | 237/3 | 0.49 | 0.55 | 0.27 | **0.44** | | | |
| | 237/4 | 0.43 | 0.59 | 0.22 | **0.41** | | | |
| 10 | 258/1 | 0.45 | 0.61 | 0.32 | **0.46** | **0.46** | **0.04** | **7.8** |
| | 258/2 | 0.55 | 0.69 | 0.16 | **0.46** | | | |
| | 258/3 | 0.57 | 0.60 | 0.32 | **0.50** | | | |
| | 258/4 | 0.39 | 0.62 | 0.23 | **0.41** | | | |
| 11 | 287/1 | 0.44 | 0.53 | 0.20 | **0.39** | **0.43** | **0.03** | **6.8** |
| | 287/2 | 0.54 | 0.53 | 0.23 | **0.43** | | | |
| | 287/3 | 0.37 | 0.61 | 0.41 | **0.46** | | | |
| | 287/4 | 0.43 | 0.65 | 0.22 | **0.43** | | | |
| 12 | 294/1 | 0.44 | 0.54 | 0.19 | **0.39** | **0.42** | **0.03** | **8.3** |
| | 294/2 | 0.65 | 0.54 | 0.19 | **0.46** | | | |
| | 294/3 | 0.41 | 0.59 | 0.30 | **0.43** | | | |
| | 294/4 | 0.39 | 0.60 | 0.17 | **0.39** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.417** |
| **SD of means of the sub-samples 1-4** | **0.025** |
| **RSD (%)** | **6.038** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **10.0** |

## Analyt Cu

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 2 lines (Serie 1) | mean calculated from 2 lines (Serie 2) | mean calculated from 2 lines (Serie 3) | **mean** |
|---|---|---|---|---|---|
| | | | | | |
| 1 | HS 1 | 0.499 | 0.527 | 0.452 | **0.492** |
| 2 | HS 2 | 0.472 | 0.546 | 0.504 | **0.508** |
| 3 | HS 3 | 0.524 | 0.497 | 0.510 | **0.510** |
| 4 | HS 4 | 0.631 | 0.599 | 0.675 | |
| 5 | HS 5 | 0.477 | 0.553 | 0.513 | **0.514** |
| 6 | HS 6 | 0.599 | 0.533 | 0.684 | |
| 7 | HS 7 | 0.604 | 0.459 | 0.574 | **0.546** |
| 8 | HS 8 | 0.489 | 0.395 | 0.727 | **0.537** |
| 9 | HS 9 | 0.371 | 0.341 | 0.549 | **0.421** |
| 10 | HS 10 | 0.424 | 0.307 | 0.328 | **0.353** |
| 11 | HS 11 | 0.359 | 0.344 | 0.295 | **0.333** |
| 12 | HS 12 | 0.316 | 0.276 | 0.426 | **0.339** |
| 13 | HS 13 | 0.322 | 0.456 | 0.335 | **0.371** |
| 14 | HS 14 | 0.399 | 0.344 | 0.444 | **0.396** |
| 15 | HS 15 | 0.499 | 0.443 | 0.386 | **0.442** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **0.443** |
| **$SD_{HS}$** | **0.079** |
| **$RSD_{HS}$ (%)** | **17.78** |

## Analyt Cu

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.048 | $M_{Ss}$ 0.417 | RSD % 6.04 |
| standard deviation between the samples $s_b$ | 0.050 | $F_{value}$ | 2.045 |
| test value $s_b^2/s_w^2$ | 1.109 | Characteristic no. for homogeneity between the samples | 0.561 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.079 | $M_{HS}$ 0.443 | $RSD_{HS}$ % 17.78 |
| | | $F_{value}$ | 2.450 |
| test value $s_w^2/s_{HS}^2$ | 0.367 | Characteristic no. for homogeneity within the samples | 1.388 |
| **Homogeneity between the samples: Not very strong inhomogeneity** | | | |

**Analyt Fe** (DC ARC OES, results were compiled over 1 line on 4 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 20.72 | 22.56 | 17.92 | 10.89 | **18.02** | **17.19** | **0.97** | **5.6** |
| | 12/2 | 17.98 | 15.43 | 16.86 | 13.23 | **15.87** | | | |
| | 12/3 | 22.49 | 15.80 | 21.08 | 11.80 | **17.79** | | | |
| | 12/4 | 20.24 | 18.30 | 18.88 | 10.85 | **17.07** | | | |
| 2 | 35/1 | 16.81 | 17.91 | 18.56 | 12.04 | **16.33** | **18.04** | **1.77** | **9.8** |
| | 35/2 | 18.97 | 20.14 | 24.49 | 10.07 | **18.42** | | | |
| | 35/3 | 17.77 | 16.80 | 20.90 | 12.72 | **17.05** | | | |
| | 35/4 | 18.94 | 28.93 | 19.42 | 14.10 | **20.35** | | | |
| 3 | 66/1 | 19.31 | 19.28 | 19.80 | 15.97 | **18.59** | **18.06** | **1.66** | **9.2** |
| | 66/2 | 19.24 | 20.47 | 19.47 | 14.12 | **18.32** | | | |
| | 66/3 | 19.19 | 21.02 | 25.42 | 12.80 | **19.61** | | | |
| | 66/4 | 15.00 | 17.84 | 19.33 | 10.65 | **15.71** | | | |
| 4 | 99/1 | 23.37 | 24.14 | 22.29 | 8.67 | **19.62** | **19.34** | **1.28** | **6.6** |
| | 99/2 | 21.65 | 22.82 | 21.60 | 17.22 | **20.82** | | | |
| | 99/3 | 23.21 | 20.48 | 19.47 | 13.63 | **19.20** | | | |
| | 99/4 | 18.87 | 19.18 | 19.90 | 12.91 | **17.71** | | | |
| 5 | 116/1 | 20.19 | 22.07 | 16.63 | 11.69 | **17.64** | **18.77** | **1.30** | **6.9** |
| | 116/2 | 19.93 | 18.66 | 21.08 | 11.32 | **17.75** | | | |
| | 116/3 | 23.41 | 20.47 | 21.12 | 12.38 | **19.34** | | | |
| | 116/4 | 22.01 | 18.67 | 20.26 | 20.38 | **20.33** | | | |
| 6 | 143/1 | 17.38 | 16.27 | 18.18 | 11.56 | **15.85** | **16.80** | **0.64** | **3.8** |
| | 143/2 | 19.54 | 19.07 | 17.41 | 12.38 | **17.10** | | | |
| | 143/3 | 19.09 | 20.01 | 15.27 | 13.65 | **17.01** | | | |
| | 143/4 | 19.36 | 17.86 | 20.95 | 10.85 | **17.26** | | | |

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 17.43 | 15.54 | 21.23 | 14.50 | **17.18** | **17.91** | **0.75** | **4.2** |
| | 161/2 | 20.18 | 17.80 | 21.05 | 16.33 | **18.84** | | | |
| | 161/3 | 20.15 | 20.52 | 17.91 | 14.06 | **18.16** | | | |
| | 161/4 | 19.19 | 18.36 | 18.74 | 13.52 | **17.45** | | | |
| 8 | 195/1 | 17.54 | 20.11 | 14.17 | 13.11 | **16.23** | **17.56** | **1.00** | **5.7** |
| | 195/2 | 20.77 | 17.96 | 18.92 | 12.56 | **17.55** | | | |
| | 195/3 | 16.32 | 19.03 | 17.44 | 18.53 | **17.83** | | | |
| | 195/4 | 19.36 | 19.70 | 20.92 | 14.57 | **18.64** | | | |
| 9 | 237/1 | 23.22 | 18.52 | 13.53 | 10.73 | **16.50** | **18.31** | **1.32** | **7.2** |
| | 237/2 | 20.69 | 20.21 | 22.21 | 11.47 | **18.64** | | | |
| | 237/3 | 16.94 | 18.26 | 23.16 | 15.30 | **18.42** | | | |
| | 237/4 | 21.34 | 19.91 | 22.81 | 14.62 | **19.67** | | | |
| 10 | 258/1 | 18.59 | 21.03 | 21.18 | 13.26 | **18.51** | **18.06** | **1.20** | **6.6** |
| | 258/2 | 21.02 | 17.78 | 25.91 | 13.11 | **19.45** | | | |
| | 258/3 | 17.87 | 17.92 | 17.81 | 13.09 | **16.67** | | | |
| | 258/4 | 23.61 | 15.77 | 17.54 | 13.47 | **17.60** | | | |
| 11 | 287/1 | 16.71 | 20.50 | 16.85 | 14.73 | **17.20** | **17.94** | **1.76** | **9.8** |
| | 287/2 | 19.07 | 21.44 | 24.68 | 16.63 | **20.45** | | | |
| | 287/3 | | 19.41 | 20.45 | 13.24 | **17.70** | | | |
| | 287/4 | 19.14 | 19.50 | 17.92 | 9.08 | **16.41** | | | |
| 12 | 294/1 | 16.94 | 18.97 | 20.07 | 11.47 | **16.86** | **18.04** | **2.40** | **13.3** |
| | 294/2 | 13.63 | 16.41 | 19.05 | 11.81 | **15.23** | | | |
| | 294/3 | 28.10 | 17.90 | 20.20 | 14.33 | **20.13** | | | |
| | 294/4 | 21.50 | 18.22 | 23.24 | 16.78 | **19.93** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **18.00** |
| **SD of means of the sub-samples 1-4** | **0.66** |
| **RSD (%)** | **3.66** |

**mean $RSD_w$ (%) 7.4**

## Analyt Fe

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (16.06.11) | mean calculated from 1 line (17.03.11) | mean calculated from 1 line (22.03.11) | mean calculated from 1 line (30.03.11) | **mean** |
|---|---|---|---|---|---|---|
| 1 | HS 1 | 29.92 | 35.74 | 15.15 | 15.38 | **24.05** |
| 2 | HS 2 | 24.92 | 43.22 | 22.79 | 17.47 | **27.10** |
| 3 | HS 3 | 33.66 | 43.80 | 25.95 | 17.64 | **30.26** |
| 4 | HS 4 | 30.26 | 37.24 | 20.25 | 15.69 | **25.86** |
| 5 | HS 5 | 24.36 | 41.07 | 20.48 | 15.54 | **25.36** |
| 6 | HS 6 | 22.76 | 34.71 | 19.93 | 16.75 | **23.54** |
| 7 | HS 7 | 33.25 | 46.50 | 21.27 | 13.21 | **28.56** |
| 8 | HS 8 | 25.27 | 38.73 | 31.22 | 13.06 | **27.07** |
| 9 | HS 9 | 32.10 | 40.89 | 24.22 | 14.53 | **27.94** |
| 10 | HS 10 | 28.98 | 42.94 | 19.64 | 13.77 | **26.33** |
| 11 | HS 11 | 26.67 | 38.08 | 18.79 | 15.24 | **24.70** |
| 12 | HS 12 | 24.66 | 37.50 | 23.63 | 15.41 | **25.30** |
| 13 | HS 13 | 25.17 | 34.07 | 21.90 | 16.08 | **24.30** |
| 14 | HS 14 | 24.18 | 36.35 | 25.32 | 12.38 | **24.56** |
| 15 | HS 15 | 23.39 | 35.77 | 26.32 | 10.77 | **24.06** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **25.93** |
| **$SD_{HS}$** | **1.93** |
| **$RSD_{HS}$ (%)** | **7.43** |

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 1.42 | $M_{Ss}$<br>18.00 | RSD %<br>3.66 |
| standard deviation between the samples $s_b$ | 1.32 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 0.86 | Characteristic no. for homogeneity between the samples | 0.424 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 1.93 | $M_{HS}$<br>25.93 | $RSD_{HS}$ %<br>7.43 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 0.54 | Characteristic no. for homogeneity within the samples | 0.236 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

**Analyt Mg** (ETV-ICP-OES, results were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 0.186 | 0.209 | 0.154 | **0.183** | **0.161** | **0.017** | **10.6** |
| | 12/2 | 0.176 | 0.163 | 0.093 | **0.144** | | | |
| | 12/3 | 0.227 | 0.160 | 0.108 | **0.165** | | | |
| | 12/4 | 0.059 | 0.238 | 0.157 | **0.151** | | | |
| 2 | 35/1 | 0.193 | 0.192 | 0.285 | **0.223** | **0.211** | **0.010** | **4.8** |
| | 35/2 | | 0.189 | 0.222 | **0.205** | | | |
| | 35/3 | 0.227 | 0.173 | 0.242 | **0.214** | | | |
| | 35/4 | 0.125 | 0.309 | 0.167 | **0.200** | | | |
| 3 | 66/1 | 0.064 | 0.295 | 0.200 | **0.186** | **0.167** | **0.020** | **11.7** |
| | 66/2 | 0.114 | 0.180 | 0.154 | **0.149** | | | |
| | 66/3 | 0.229 | 0.168 | 0.146 | **0.181** | | | |
| | 66/4 | | | 0.151 | **0.151** | | | |
| 4 | 99/1 | 0.092 | 0.197 | 0.215 | **0.168** | **0.145** | **0.032** | **22.4** |
| | 99/2 | 0.248 | 0.238 | 0.221 | | | | |
| | 99/3 | 0.094 | 0.168 | 0.104 | **0.122** | | | |
| | 99/4 | 0.270 | 0.226 | 0.228 | | | | |
| 5 | 116/1 | 0.065 | 0.200 | 0.113 | **0.126** | **0.162** | **0.025** | **15.3** |
| | 116/2 | 0.102 | 0.155 | 0.235 | **0.164** | | | |
| | 116/3 | 0.127 | 0.220 | 0.183 | **0.177** | | | |
| | 116/4 | 0.251 | 0.131 | 0.160 | **0.181** | | | |
| 6 | 143/1 | 0.112 | 0.186 | 0.123 | **0.140** | **0.152** | **0.020** | **13.2** |
| | 143/2 | 0.101 | 0.189 | 0.104 | **0.131** | | | |
| | 143/3 | 0.165 | | 0.159 | **0.162** | | | |
| | 143/4 | 0.231 | 0.145 | 0.149 | **0.175** | | | |

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 0.139 | 0.103 | 0.200 | **0.147** | **0.175** | **0.031** | **17.6** |
| | 161/2 | 0.146 | 0.370 | 0.092 | **0.203** | | | |
| | 161/3 | 0.130 | 0.193 | 0.128 | **0.150** | | | |
| | 161/4 | 0.132 | 0.175 | 0.298 | **0.202** | | | |
| 8 | 195/1 | 0.141 | 0.117 | 0.083 | **0.114** | **0.166** | **0.036** | **21.6** |
| | 195/2 | 0.129 | 0.218 | 0.200 | **0.182** | | | |
| | 195/3 | 0.108 | 0.362 | 0.111 | **0.194** | | | |
| | 195/4 | 0.139 | 0.174 | 0.213 | **0.175** | | | |
| 9 | 237/1 | 0.084 | 0.077 | 0.110 | **0.090** | **0.148** | **0.040** | **27.2** |
| | 237/2 | 0.137 | 0.170 | 0.190 | **0.166** | | | |
| | 237/3 | 0.177 | 0.145 | 0.224 | **0.182** | | | |
| | 237/4 | 0.136 | 0.179 | 0.148 | **0.154** | | | |
| 10 | 258/1 | 0.204 | 0.147 | 0.102 | **0.151** | **0.155** | **0.017** | **11.0** |
| | 258/2 | 0.178 | 0.210 | 0.062 | **0.150** | | | |
| | 258/3 | 0.148 | 0.145 | 0.127 | **0.140** | | | |
| | 258/4 | 0.181 | 0.167 | 0.191 | **0.180** | | | |
| 11 | 287/1 | 0.211 | 0.286 | 0.230 | **0.243** | **0.201** | **0.029** | **14.3** |
| | 287/2 | 0.128 | 0.238 | 0.228 | **0.198** | | | |
| | 287/3 | 0.082 | 0.182 | 0.287 | **0.184** | | | |
| | 287/4 | 0.240 | 0.153 | 0.147 | **0.180** | | | |
| 12 | 294/1 | 0.116 | 0.163 | 0.107 | **0.128** | **0.185** | **0.040** | **21.6** |
| | 294/2 | 0.194 | | 0.202 | **0.198** | | | |
| | 294/3 | 0.123 | 0.276 | 0.268 | **0.222** | | | |
| | 294/4 | 0.241 | 0.195 | 0.135 | **0.190** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.169** |
| **SD of means of the sub-samples 1-4** | **0.0206** |
| **RSD (%)** | **12.207** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **15.9** |

## Analyt Mg

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 0.137 | 0.168 | 0.126 | **0.144** |
| 2 | HS 2 | 0.099 | 0.185 | 0.124 | **0.136** |
| 3 | HS 3 | 0.104 | 0.193 | 0.098 | **0.132** |
| 4 | HS 4 | 0.080 | 0.169 | 0.070 | **0.106** |
| 5 | HS 5 | 0.110 | 0.185 | 0.113 | **0.136** |
| 6 | HS 6 | 0.099 | 0.159 | 0.115 | **0.124** |
| 7 | HS 7 | 0.111 | 0.123 | | **0.117** |
| 8 | HS 8 | 0.101 | 0.229 | 0.091 | **0.141** |
| 9 | HS 9 | 0.112 | 0.147 | 0.090 | **0.117** |
| 10 | HS 10 | 0.223 | 0.083 | 0.132 | **0.146** |
| 11 | HS 11 | 0.111 | 0.144 | 0.085 | **0.113** |
| 12 | HS 12 | 0.197 | 0.111 | 0.068 | **0.125** |
| 13 | HS 13 | 0.175 | 0.163 | 0.093 | **0.144** |
| 14 | HS 14 | 0.102 | 0.167 | 0.120 | **0.130** |
| 15 | HS 15 | 0.104 | 0.137 | 0.142 | **0.127** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **0.129** |
| **$SD_{HS}$** | **0.0121** |
| **$RSD_{HS}$ (%)** | **9.37** |

## Analyt Mg

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.028 | $M_{Ss}$ 0.169 | RSD % 12.18 |
| standard deviation between the samples $s_b$ | 0.038 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.856 | Characteristic no. for homogeneity between the samples | 0.911 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.012 | $M_{HS}$ 0.129 | $RSD_{HS}$ % 9.37 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 5.316 | Characteristic no. for homogeneity within the samples | 2.313 |
| **Homogeneity within the samples: Not very strong inhomogeneity** | | | |

**Analyt Mn** (DC ARC OES, results were compiled over 1 line on 4 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 0.53 | 0.57 | 0.45 | 0.35 | **0.48** | **0.48** | **0.01** | **1.8** |
| | 12/2 | 0.48 | 0.48 | 0.50 | 0.46 | **0.48** | | | |
| | 12/3 | 0.54 | 0.47 | 0.58 | 0.39 | **0.49** | | | |
| | 12/4 | 0.53 | 0.57 | 0.47 | 0.39 | **0.49** | | | |
| 2 | 35/1 | 0.44 | 0.52 | 0.45 | 0.44 | **0.46** | **0.48** | **0.04** | **8.2** |
| | 35/2 | 0.49 | 0.46 | 0.64 | 0.39 | **0.50** | | | |
| | 35/3 | 0.40 | 0.49 | 0.47 | 0.39 | **0.44** | | | |
| | 35/4 | 0.51 | 0.70 | 0.52 | 0.37 | **0.53** | | | |
| 3 | 66/1 | 0.43 | 0.56 | 0.50 | 0.60 | **0.52** | **0.50** | **0.03** | **5.4** |
| | 66/2 | 0.49 | 0.60 | 0.55 | 0.44 | **0.52** | | | |
| | 66/3 | 0.48 | 0.53 | 0.58 | 0.47 | **0.52** | | | |
| | 66/4 | 0.42 | 0.50 | 0.53 | 0.41 | **0.46** | | | |
| 4 | 99/1 | 0.53 | 0.69 | 0.57 | 0.35 | **0.54** | **0.52** | **0.03** | **4.9** |
| | 99/2 | 0.42 | 0.61 | 0.56 | 0.57 | **0.54** | | | |
| | 99/3 | 0.58 | 0.52 | 0.51 | 0.45 | **0.52** | | | |
| | 99/4 | 0.34 | 0.57 | 0.52 | 0.51 | **0.48** | | | |
| 5 | 116/1 | 0.49 | 0.58 | 0.45 | 0.47 | **0.50** | **0.52** | **0.03** | **6.0** |
| | 116/2 | 0.44 | 0.44 | 0.60 | 0.44 | **0.48** | | | |
| | 116/3 | 0.56 | 0.57 | 0.55 | 0.47 | **0.54** | | | |
| | 116/4 | 0.49 | 0.52 | 0.49 | 0.69 | **0.55** | | | |
| 6 | 143/1 | 0.50 | 0.50 | 0.49 | 0.39 | **0.47** | **0.46** | **0.01** | **2.5** |
| | 143/2 | 0.43 | 0.47 | 0.45 | 0.45 | **0.45** | | | |
| | 143/3 | 0.43 | 0.49 | 0.37 | 0.51 | **0.45** | | | |
| | 143/4 | 0.47 | 0.53 | 0.53 | 0.35 | **0.47** | | | |

| Line number | Sample number | mean calculated from 1 line (23.03.11) | mean calculated from 1 line (24.03.11) | mean calculated from 1 line (28.03.11) | mean calculated from 1 line (30.03.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 0.45 | 0.50 | 0.57 | 0.53 | **0.51** | **0.50** | **0.02** | **4.7** |
| | 161/2 | 0.47 | 0.47 | 0.55 | 0.60 | **0.52** | | | |
| | 161/3 | 0.50 | 0.61 | 0.39 | 0.42 | **0.48** | | | |
| | 161/4 | 0.45 | 0.51 | 0.56 | 0.39 | **0.47** | | | |
| 8 | 195/1 | 0.48 | 0.58 | 0.42 | 0.48 | **0.49** | **0.49** | **0.02** | **4.6** |
| | 195/2 | 0.47 | 0.59 | 0.49 | 0.48 | **0.51** | | | |
| | 195/3 | 0.43 | 0.55 | 0.44 | 0.42 | **0.46** | | | |
| | 195/4 | 0.45 | 0.55 | 0.57 | 0.47 | **0.51** | | | |
| 9 | 237/1 | 0.51 | 0.46 | 0.32 | 0.38 | **0.42** | **0.48** | **0.04** | **9.0** |
| | 237/2 | 0.53 | 0.56 | 0.56 | 0.39 | **0.51** | | | |
| | 237/3 | 0.39 | 0.53 | 0.59 | 0.50 | **0.50** | | | |
| | 237/4 | 0.44 | 0.50 | 0.53 | 0.47 | **0.48** | | | |
| 10 | 258/1 | 0.49 | 0.46 | 0.59 | 0.45 | **0.50** | **0.48** | **0.03** | **6.4** |
| | 258/2 | 0.51 | 0.47 | 0.60 | 0.46 | **0.51** | | | |
| | 258/3 | 0.41 | 0.46 | 0.45 | 0.43 | **0.44** | | | |
| | 258/4 | 0.55 | 0.44 | 0.46 | 0.50 | **0.49** | | | |
| 11 | 287/1 | 0.44 | 0.62 | 0.48 | 0.50 | **0.51** | **0.49** | **0.06** | **11.8** |
| | 287/2 | 0.50 | 0.58 | 0.58 | 0.45 | **0.53** | | | |
| | 287/3 | | 0.53 | 0.55 | 0.47 | **0.52** | | | |
| | 287/4 | 0.36 | 0.59 | 0.36 | 0.31 | **0.41** | | | |
| 12 | 294/1 | 0.46 | 0.57 | 0.50 | 0.48 | **0.50** | **0.49** | **0.05** | **9.4** |
| | 294/2 | 0.33 | 0.49 | 0.48 | 0.40 | **0.42** | | | |
| | 294/3 | 0.53 | 0.48 | 0.54 | 0.52 | **0.52** | | | |
| | 294/4 | 0.45 | 0.49 | 0.58 | 0.57 | **0.52** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.491** |
| **SD of means of the sub-samples 1-4** | **0.016** |
| **RSD (%)** | **3.33** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **6.2** |

## Analyt Mn

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (16.06.11) | mean calculated from 1 line (17.03.11) | mean calculated from line (22.03.11) | mean calculated from line (30.03.11) | **mean** |
|---|---|---|---|---|---|---|
| 1 | HS 1 | 2.99 | 0.93 | 0.30 | 0.50 | **1.18** |
| 2 | HS 2 | 3.07 | 0.83 | 0.45 | 0.58 | **1.23** |
| 3 | HS 3 | 3.04 | 0.83 | 0.48 | 0.56 | **1.23** |
| 4 | HS 4 | 2.78 | 0.77 | 0.43 | 0.54 | **1.13** |
| 5 | HS 5 | 2.53 | 0.76 | 0.46 | 0.54 | **1.08** |
| 6 | HS 6 | 2.44 | 0.83 | 0.43 | 0.59 | **1.07** |
| 7 | HS 7 | 3.02 | 0.80 | 0.37 | 0.49 | **1.17** |
| 8 | HS 8 | 2.90 | 0.85 | 0.49 | 0.50 | **1.19** |
| 9 | HS 9 | 3.07 | 0.77 | 0.42 | 0.53 | **1.20** |
| 10 | HS 10 | 3.01 | 0.62 | 0.41 | 0.50 | **1.14** |
| 11 | HS 11 | 2.61 | 0.81 | 0.36 | 0.55 | **1.08** |
| 12 | HS 12 | 2.52 | 0.86 | 0.39 | 0.60 | **1.09** |
| 13 | HS 13 | 2.81 | 0.86 | 0.40 | 0.54 | **1.15** |
| 14 | HS 14 | 2.57 | 0.83 | 0.45 | 0.53 | **1.10** |
| 15 | HS 15 | 2.81 | 0.87 | 0.48 | 0.47 | **1.16** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **1.146** |
| **$SD_{HS}$** | **0.054** |
| **$RSD_{HS}$ (%)** | **4.68** |

## Analyt Mn

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.033 | $M_{Ss}$ 0.491 | RSD % 3.33 |
| standard deviation between the samples $s_b$ | 0.033 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 0.954 | Characteristic no. for homogeneity between the samples | 0.468 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.054 | $M_{HS}$ 1.146 | $RSD_{HS}$ % 4.68 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 0.398 | Characteristic no. for homogeneity within the samples | 0.169 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

**Analyt Na** (ETV-ICP-OES, results were compiled over 1 line on 3 different days

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 0.27 | 0.13 | 0.17 | **0.19** | **0.23** | **0.03** | **12.4** |
| | 12/2 | 0.31 | | 0.22 | **0.26** | | | |
| | 12/3 | 0.23 | 0.32 | 0.14 | **0.23** | | | |
| | 12/4 | 0.24 | 0.28 | 0.21 | **0.24** | | | |
| 2 | 35/1 | 0.25 | 0.22 | 0.19 | **0.22** | **0.26** | **0.03** | **10.8** |
| | 35/2 | 0.25 | 0.35 | 0.21 | **0.27** | | | |
| | 35/3 | 0.26 | 0.34 | 0.27 | **0.29** | | | |
| | 35/4 | 0.24 | 0.31 | 0.24 | **0.26** | | | |
| 3 | 66/1 | 0.30 | | 0.23 | **0.27** | **0.28** | **0.02** | **7.2** |
| | 66/2 | 0.23 | 0.42 | 0.24 | **0.30** | | | |
| | 66/3 | 0.22 | 0.40 | 0.16 | **0.26** | | | |
| | 66/4 | 0.25 | 0.26 | 0.39 | **0.30** | | | |
| 4 | 99/1 | 0.32 | 0.46 | | **0.39** | **0.29** | **0.06** | **22.2** |
| | 99/2 | 0.15 | 0.32 | 0.31 | **0.26** | | | |
| | 99/3 | 0.21 | 0.36 | 0.19 | **0.25** | | | |
| | 99/4 | 0.27 | 0.29 | 0.23 | **0.27** | | | |
| 5 | 116/1 | 0.25 | 0.31 | 0.26 | **0.27** | **0.28** | **0.03** | **9.2** |
| | 116/2 | 0.28 | 0.45 | 0.24 | **0.32** | | | |
| | 116/3 | 0.20 | 0.35 | 0.28 | **0.28** | | | |
| | 116/4 | 0.25 | 0.29 | 0.25 | **0.26** | | | |
| 6 | 143/1 | 0.26 | 0.41 | 0.27 | **0.31** | **0.29** | **0.03** | **9.2** |
| | 143/2 | 0.28 | 0.44 | 0.19 | **0.31** | | | |
| | 143/3 | 0.22 | 0.28 | 0.31 | **0.27** | | | |
| | 143/4 | 0.31 | 0.28 | 0.18 | **0.26** | | | |

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 0.25 | 0.38 | | **0.32** | **0.27** | **0.03** | **10.9** |
| | 161/2 | 0.25 | 0.36 | 0.16 | **0.26** | | | |
| | 161/3 | 0.22 | 0.28 | 0.24 | **0.25** | | | |
| | 161/4 | 0.21 | 0.28 | 0.33 | **0.27** | | | |
| 8 | 195/1 | 0.26 | 0.47 | 0.23 | **0.32** | **0.28** | **0.03** | **9.7** |
| | 195/2 | 0.21 | 0.36 | 0.24 | **0.27** | | | |
| | 195/3 | 0.22 | 0.30 | 0.27 | **0.26** | | | |
| | 195/4 | 0.29 | 0.33 | 0.21 | **0.27** | | | |
| 9 | 237/1 | 0.21 | 0.36 | 0.27 | **0.28** | **0.28** | **0.02** | **8.0** |
| | 237/2 | 0.22 | 0.34 | 0.19 | **0.25** | | | |
| | 237/3 | 0.24 | 0.27 | 0.32 | **0.27** | | | |
| | 237/4 | 0.28 | 0.36 | 0.27 | **0.30** | | | |
| 10 | 258/1 | 0.23 | 0.44 | 0.19 | **0.29** | **0.27** | **0.02** | **8.2** |
| | 258/2 | 0.30 | 0.32 | 0.14 | **0.25** | | | |
| | 258/3 | 0.33 | 0.38 | 0.18 | **0.30** | | | |
| | 258/4 | 0.23 | 0.32 | 0.22 | **0.26** | | | |
| 11 | 287/1 | 0.27 | 0.47 | 0.19 | **0.31** | **0.27** | **0.02** | **8.9** |
| | 287/2 | 0.21 | 0.35 | 0.29 | **0.28** | | | |
| | 287/3 | 0.22 | 0.31 | 0.22 | **0.25** | | | |
| | 287/4 | 0.21 | 0.27 | 0.30 | **0.26** | | | |
| 12 | 294/1 | 0.32 | 0.36 | 0.24 | **0.31** | **0.29** | **0.03** | **8.6** |
| | 294/2 | 0.26 | 0.37 | 0.23 | **0.29** | | | |
| | 294/3 | 0.22 | 0.27 | 0.27 | **0.26** | | | |
| | 294/4 | 0.45 | 0.26 | 0.22 | **0.31** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.276** |
| **SD of means of the sub-samples 1-4** | **0.02** |
| **RSD (%)** | **5.791** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **10.4** |

## Analyt Na

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 0.246 | 0.252 | 0.263 | **0.254** |
| 2 | HS 2 | 0.278 | 0.293 | 0.252 | **0.274** |
| 3 | HS 3 | 0.273 | 0.218 | 0.240 | **0.244** |
| 4 | HS 4 | 0.289 | 0.259 | 0.293 | **0.280** |
| 5 | HS 5 | 0.266 | 0.233 | 0.218 | **0.239** |
| 6 | HS 6 | 0.241 | 0.218 | 0.255 | **0.238** |
| 7 | HS 7 | 0.313 | 0.195 | 0.168 | **0.225** |
| 8 | HS 8 | 0.265 | 0.228 | 0.263 | **0.252** |
| 9 | HS 9 | 0.250 | 0.217 | 0.264 | **0.243** |
| 10 | HS 10 | 0.258 | 0.237 | 0.262 | **0.252** |
| 11 | HS 11 | 0.263 | 0.192 | 0.279 | **0.245** |
| 12 | HS 12 | 0.236 | 0.186 | 0.239 | **0.220** |
| 13 | HS 13 | 0.282 | 0.215 | 0.231 | **0.243** |
| 14 | HS 14 | 0.240 | 0.179 | 0.257 | **0.225** |
| 15 | HS 15 | 0.275 | 0.149 | 0.264 | **0.229** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **0.244** |
| **$SD_{HS}$** | **0.017** |
| **$RSD_{HS}$ (%)** | **6.93** |

## Analyt Na

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.0309 | $M_{Ss}$ 0.276 | RSD % 5.79 |
| standard deviation between the samples $s_b$ | 0.032 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.069 | Characteristic no. for homogeneity between the samples | 0.525 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.017 | $M_{HS}$ 0.244 | $RSD_{HS}$ % 6.93 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 3.328 | Characteristic no. for homogeneity within the samples | 1.388 |
| **Homogeneity within the samples: Not very strong inhomogeneity** | | | |

**Analyt Ni** (ETV-ICP-OES, results were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 1.73 | 1.72 | 1.15 | **1.53** | **1.47** | **0.10** | **6.7** |
| | 12/2 | 1.84 | 1.53 | 1.33 | **1.57** | | | |
| | 12/3 | 1.30 | 1.59 | 1.31 | **1.40** | | | |
| | 12/4 | 1.22 | 1.49 | 1.40 | **1.37** | | | |
| 2 | 35/1 | 1.63 | 1.50 | 1.39 | **1.51** | **1.56** | **0.10** | **6.6** |
| | 35/2 | 1.83 | 1.80 | 1.37 | **1.67** | | | |
| | 35/3 | 1.62 | 1.62 | 1.09 | **1.44** | | | |
| | 35/4 | 1.66 | 1.71 | 1.48 | **1.62** | | | |
| 3 | 66/1 | 1.30 | 1.15 | 1.07 | **1.17** | **1.51** | **0.26** | **17.5** |
| | 66/2 | 1.70 | 1.30 | 1.89 | **1.63** | | | |
| | 66/3 | 1.60 | 1.45 | 1.28 | **1.44** | | | |
| | 66/4 | 1.84 | 1.69 | 1.84 | **1.79** | | | |
| 4 | 99/1 | 1.67 | 1.89 | 1.11 | **1.56** | **1.49** | **0.10** | **6.8** |
| | 99/2 | 1.38 | 1.55 | 1.20 | **1.37** | | | |
| | 99/3 | 1.52 | 1.51 | 1.31 | **1.45** | | | |
| | 99/4 | 1.68 | 1.82 | 1.29 | **1.60** | | | |
| 5 | 116/1 | 1.43 | 1.38 | 1.03 | **1.28** | **1.64** | **0.48** | **29.2** |
| | 116/2 | 1.54 | 1.45 | 1.26 | **1.42** | | | |
| | 116/3 | 1.53 | 1.57 | 1.51 | **1.53** | | | |
| | 116/4 | 1.77 | 1.57 | 3.70 | **2.35** | | | |
| 6 | 143/1 | 1.71 | 1.47 | 1.73 | **1.64** | **1.55** | **0.08** | **5.1** |
| | 143/2 | 1.63 | 1.49 | 1.28 | **1.47** | | | |
| | 143/3 | 1.64 | 1.78 | 1.07 | **1.50** | | | |
| | 143/4 | 1.51 | 1.64 | 1.63 | **1.59** | | | |

| Line number | Sample number | mean calculated from 1 line (26.04.11) | mean calculated from 1 line (27.04.11) | mean calculated from 1 line (28.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 1.95 | 1.51 | 1.21 | **1.56** | **1.57** | **0.10** | **6.2** |
| | 161/2 | 1.84 | 1.35 | 1.40 | **1.53** | | | |
| | 161/3 | 1.58 | 1.47 | 1.37 | **1.47** | | | |
| | 161/4 | 1.65 | 1.70 | 1.74 | **1.70** | | | |
| 8 | 195/1 | 2.11 | 1.43 | 1.28 | **1.61** | **1.60** | **0.14** | **8.6** |
| | 195/2 | 1.52 | 1.76 | 1.15 | **1.47** | | | |
| | 195/3 | 1.46 | 1.74 | 1.38 | **1.53** | | | |
| | 195/4 | 1.93 | 1.37 | 2.06 | **1.79** | | | |
| 9 | 237/1 | 1.22 | 1.77 | 1.05 | **1.35** | **1.54** | **0.26** | **17.0** |
| | 237/2 | 1.20 | 1.50 | 1.16 | **1.28** | | | |
| | 237/3 | 2.29 | 1.86 | 1.32 | **1.82** | | | |
| | 237/4 | 1.66 | 1.79 | 1.65 | **1.70** | | | |
| 10 | 258/1 | 1.50 | 1.75 | 1.00 | **1.42** | **1.52** | **0.13** | **8.6** |
| | 258/2 | 1.54 | 2.14 | 0.92 | **1.53** | | | |
| | 258/3 | 1.21 | 1.86 | 1.19 | **1.42** | | | |
| | 258/4 | 1.76 | 1.79 | 1.54 | **1.69** | | | |
| 11 | 287/1 | 1.92 | 2.03 | 1.11 | **1.69** | **1.55** | **0.14** | **9.0** |
| | 287/2 | 1.59 | 1.59 | 1.05 | **1.41** | | | |
| | 287/3 | 1.69 | 1.58 | 1.71 | **1.66** | | | |
| | 287/4 | 1.41 | 1.62 | 1.33 | **1.45** | | | |
| 12 | 294/1 | 1.49 | 1.68 | 1.20 | **1.46** | **1.44** | **0.06** | **4.4** |
| | 294/2 | 1.54 | 1.42 | 1.09 | **1.35** | | | |
| | 294/3 | 1.53 | 1.41 | 1.55 | **1.50** | | | |
| | 294/4 | 1.36 | 1.71 | 1.29 | **1.45** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **1.536** |
| **SD of means of the sub-samples 1-4** | **0.06** |
| **RSD (%)** | **3.658** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **10.5** |

## Analyt Ni

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 1.659 | 1.965 | 1.787 | **1.804** |
| 2 | HS 2 | 1.650 | 1.665 | 1.560 | **1.625** |
| 3 | HS 3 | 1.541 | 1.777 | 1.860 | **1.726** |
| 4 | HS 4 | 1.528 | 2.203 | 1.609 | **1.780** |
| 5 | HS 5 | 1.471 | 1.641 | 1.887 | **1.666** |
| 6 | HS 6 | 1.489 | 1.647 | 2.076 | **1.737** |
| 7 | HS 7 | 1.631 | 1.676 | 1.702 | **1.669** |
| 8 | HS 8 | 1.475 | 1.751 | 1.782 | **1.669** |
| 9 | HS 9 | 1.541 | 1.525 | 2.146 | **1.737** |
| 10 | HS 10 | 1.808 | 1.652 | 1.482 | **1.647** |
| 11 | HS 11 | 1.634 | 1.637 | 1.514 | **1.595** |
| 12 | HS 12 | 1.881 | 1.577 | 1.557 | **1.672** |
| 13 | HS 13 | 1.536 | 1.730 | 1.578 | **1.615** |
| 14 | HS 14 | 1.381 | 1.730 | 1.760 | **1.624** |
| 15 | HS 15 | 1.732 | 1.842 | 1.650 | **1.741** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **1.687** |
| **$SD_{HS}$** | **0.063** |
| **$RSD_{HS}$ (%)** | **3.75** |

**Analyt Ni**

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.199 | $M_{Ss}$ 1.536 | RSD % 3.66 |
| standard deviation between the samples $s_b$ | 0.112 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 0.319 | Characteristic no. for homogeneity between the samples | 0.157 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.063 | $M_{HS}$ 1.687 | $RSD_{HS}$ % 3.75 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 9.867 | Characteristic no. for homogeneity within the samples | 4.294 |
| **Homogeneity within the samples: Strong inhomogeneity** | | | |

**Analyt Ti** (ETV-ICP-OES, results were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (14.04.11) | mean calculated from 1 line (15.04.11) | mean calculated from 1 line (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 53.89 | 60.90 | 69.31 | **61.37** | **62.15** | **1.48** | **2.4** |
| | 12/2 | 43.89 | 68.43 | 69.18 | **60.50** | | | |
| | 12/3 | 49.22 | 73.82 | 68.12 | **63.72** | | | |
| | 12/4 | 50.67 | 71.04 | 67.33 | **63.01** | | | |
| 2 | 35/1 | 49.82 | 64.71 | 69.00 | **61.18** | **59.24** | **1.46** | **2.5** |
| | 35/2 | 51.07 | 53.44 | 69.14 | **57.88** | | | |
| | 35/3 | 48.06 | 66.36 | 60.75 | **58.39** | | | |
| | 35/4 | 50.49 | 65.80 | 62.25 | **59.51** | | | |
| 3 | 66/1 | 45.57 | 72.69 | 77.97 | **65.41** | **59.77** | **4.55** | **7.6** |
| | 66/2 | 46.34 | 56.89 | 59.89 | **54.37** | | | |
| | 66/3 | 43.37 | 68.49 | 69.30 | **60.39** | | | |
| | 66/4 | 49.36 | 60.43 | 66.97 | **58.92** | | | |
| 4 | 99/1 | 50.72 | 69.12 | 72.11 | **63.98** | **61.52** | **2.14** | **3.5** |
| | 99/2 | 50.51 | 69.10 | 63.55 | **61.05** | | | |
| | 99/3 | 48.04 | 66.69 | 71.76 | **62.16** | | | |
| | 99/4 | 51.08 | 59.04 | 66.52 | **58.88** | | | |
| 5 | 116/1 | 52.83 | | 72.01 | **62.42** | **58.40** | **4.27** | **7.3** |
| | 116/2 | 46.12 | 61.90 | | **54.01** | | | |
| | 116/3 | 42.63 | 68.37 | | **55.50** | | | |
| | 116/4 | 48.91 | 64.43 | 71.69 | **61.67** | | | |
| 6 | 143/1 | 51.08 | 64.86 | 74.39 | **63.44** | **60.89** | **2.91** | **4.8** |
| | 143/2 | 57.82 | 68.92 | 63.34 | **63.36** | | | |
| | 143/3 | 45.08 | 57.93 | 72.98 | **58.66** | | | |
| | 143/4 | 45.22 | 61.12 | 67.98 | **58.11** | | | |

| Line number | Sample number | mean calculated from 1 line (14.04.11) | mean calculated from 1 line (15.04.11) | mean calculated from 1 line (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 51.08 | 60.12 | | **55.60** | **58.49** | **3.03** | **5.2** |
| | 161/2 | 57.82 | 60.31 | 68.55 | **62.22** | | | |
| | 161/3 | 45.08 | 67.41 | 56.98 | **56.49** | | | |
| | 161/4 | 45.22 | 72.43 | 61.23 | **59.63** | | | |
| 8 | 195/1 | 49.33 | 71.51 | 72.76 | **64.53** | **61.69** | **2.46** | **4.0** |
| | 195/2 | 48.82 | 65.44 | 71.57 | **61.94** | | | |
| | 195/3 | 48.43 | 68.23 | 58.90 | **58.52** | | | |
| | 195/4 | 45.11 | 68.65 | 71.50 | **61.75** | | | |
| 9 | 237/1 | 48.17 | 74.38 | 76.53 | **66.36** | **60.98** | **4.24** | **6.9** |
| | 237/2 | 46.96 | 56.23 | 70.03 | **57.74** | | | |
| | 237/3 | 46.56 | 69.63 | 70.97 | **62.39** | | | |
| | 237/4 | 49.27 | 55.27 | 67.81 | **57.45** | | | |
| 10 | 258/1 | 46.64 | 73.99 | 63.34 | **61.32** | **61.32** | **2.08** | **3.4** |
| | 258/2 | 43.35 | 62.43 | 70.20 | **58.66** | | | |
| | 258/3 | 50.48 | 64.04 | 70.15 | **61.56** | | | |
| | 258/4 | 48.99 | 69.32 | 72.89 | **63.73** | | | |
| 11 | 287/1 | 51.59 | 65.45 | 68.21 | **61.75** | **57.93** | **3.82** | **6.6** |
| | 287/2 | 53.33 | 54.65 | 66.91 | **58.30** | | | |
| | 287/3 | 45.04 | 63.98 | 48.94 | **52.65** | | | |
| | 287/4 | 47.19 | 61.35 | 68.53 | **59.02** | | | |
| 12 | 294/1 | 43.21 | 69.81 | 73.26 | **62.09** | **62.75** | **2.85** | **4.5** |
| | 294/2 | 46.25 | 70.82 | 68.45 | **61.84** | | | |
| | 294/3 | 46.41 | 63.72 | 70.60 | **60.24** | | | |
| | 294/4 | 51.73 | 73.63 | 75.17 | **66.84** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **60.428** |
| **SD of means of the sub-samples 1-4** | **1.61** |
| **RSD (%)** | **2.660** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **4.9** |

## Analyt Ti

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 79.192 | 68.208 | 66.907 | **71.436** |
| 2 | HS 2 | 69.312 | 64.328 | 62.268 | **65.303** |
| 3 | HS 3 | 70.289 | 63.668 | 52.649 | **62.202** |
| 4 | HS 4 | 66.914 | 78.993 | 77.340 | **74.416** |
| 5 | HS 5 | 70.138 | 73.476 | 71.528 | **71.714** |
| 6 | HS 6 | 69.068 | 72.154 | 53.069 | **64.763** |
| 7 | HS 7 | 69.100 | 60.207 | 63.207 | **64.171** |
| 8 | HS 8 | 65.390 | 66.774 | 65.799 | **65.988** |
| 9 | HS 9 | 62.534 | 77.140 | 63.914 | **67.863** |
| 10 | HS 10 | 70.707 | 67.462 | 74.204 | **70.791** |
| 11 | HS 11 | 71.914 | 63.215 | 74.263 | **69.798** |
| 12 | HS 12 | 77.957 | 57.096 | 66.273 | **67.108** |
| 13 | HS 13 | 78.868 | 69.993 | 67.870 | **72.244** |
| 14 | HS 14 | 79.120 | 74.149 | 71.798 | **75.022** |
| 15 | HS 15 | 68.466 | 70.477 | 60.852 | **66.599** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **68.628** |
| **$SD_{HS}$** | **3.892** |
| **$RSD_{HS}$ (%)** | **5.67** |

## Analyt Ti

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 3.115 | $M_{Ss}$ 60.430 | RSD % 2.66 |
| standard deviation between the samples $s_b$ | 3.215 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.066 | Characteristic no. for homogeneity between the samples | 0.523 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 3.892 | $M_{HS}$ 68.628 | $RSD_{HS}$ % 5.67 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 0.640 | Characteristic no. for homogeneity within the samples | 0.279 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

**Analyt V** (ETV-ICP-OES-results which were compiled over 1 line on 3 different days)

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 1 line (14.04.11) | mean calculated from 1 line (15.04.11) | mean calculated from 1 line (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 236.60 | 229.70 | 314.96 | **260.42** | **295.30** | **23.55** | **8.0** |
| | 12/2 | 324.71 | 249.18 | 355.13 | **309.67** | | | |
| | 12/3 | 323.52 | 242.01 | 362.90 | **309.48** | | | |
| | 12/4 | 311.18 | 264.52 | 329.23 | **301.64** | | | |
| 2 | 35/1 | 310.65 | 210.82 | 351.90 | **291.12** | **287.99** | **37.23** | **12.9** |
| | 35/2 | 288.37 | 243.15 | 317.00 | **282.84** | | | |
| | 35/3 | 189.00 | 221.74 | 320.08 | **243.61** | | | |
| | 35/4 | 365.74 | 263.79 | 373.61 | **334.38** | | | |
| 3 | 66/1 | 340.02 | 252.80 | 322.90 | **305.24** | **289.13** | **19.94** | **6.9** |
| | 66/2 | 216.94 | 237.51 | 326.33 | **260.26** | | | |
| | 66/3 | 278.75 | 262.70 | 354.04 | **298.50** | | | |
| | 66/4 | 269.40 | 227.89 | 380.31 | **292.54** | | | |
| 4 | 99/1 | 364.02 | 256.95 | 308.36 | **309.78** | **295.94** | **10.84** | **3.7** |
| | 99/2 | 266.89 | 276.79 | 325.34 | **289.67** | | | |
| | 99/3 | 323.59 | 241.13 | 332.19 | **298.97** | | | |
| | 99/4 | 273.17 | 240.07 | 342.78 | **285.34** | | | |
| 5 | 116/1 | 378.44 | 217.38 | 327.64 | **307.82** | **307.35** | **35.19** | **11.4** |
| | 116/2 | 381.26 | 232.71 | 375.76 | **329.91** | | | |
| | 116/3 | 375.07 | 242.60 | 384.84 | **334.17** | | | |
| | 116/4 | 212.70 | 241.03 | 318.76 | **257.49** | | | |
| 6 | 143/1 | 238.76 | 225.84 | 311.04 | **258.55** | **284.67** | **34.91** | **12.3** |
| | 143/2 | 350.31 | 256.68 | 354.04 | **320.35** | | | |
| | 143/3 | 290.06 | 230.03 | 405.91 | **308.67** | | | |
| | 143/4 | 227.09 | 252.96 | 273.37 | **251.14** | | | |

| Line number | Sample number | mean calculated from 1 line (14.04.11) | mean calculated from 1 line (15.04.11) | mean calculated from 1 line (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 379.26 | 235.59 | 366.86 | **327.24** | **290.11** | **26.94** | **9.3** |
| | 161/2 | 240.83 | 225.63 | 336.61 | **267.69** | | | |
| | 161/3 | 262.95 | 229.32 | 326.93 | **273.07** | | | |
| | 161/4 | 257.78 | 255.60 | 363.98 | **292.45** | | | |
| 8 | 195/1 | 229.71 | 270.78 | 340.84 | **280.44** | **283.69** | **6.06** | **2.1** |
| | 195/2 | 240.70 | 233.88 | 363.45 | **279.34** | | | |
| | 195/3 | 264.87 | 234.85 | 378.03 | **292.58** | | | |
| | 195/4 | 348.06 | 216.14 | 282.92 | **282.37** | | | |
| 9 | 237/1 | 367.10 | 213.11 | 370.49 | **316.90** | **289.14** | **33.40** | **11.6** |
| | 237/2 | 218.80 | 244.28 | 306.24 | **256.44** | | | |
| | 237/3 | 376.19 | 223.63 | 356.97 | **318.93** | | | |
| | 237/4 | 291.74 | 220.14 | 280.93 | **264.27** | | | |
| 10 | 258/1 | 219.56 | 238.92 | 304.16 | **254.21** | **294.18** | **31.33** | **10.7** |
| | 258/2 | 248.82 | 250.77 | 353.38 | **284.32** | | | |
| | 258/3 | 321.20 | 229.63 | 399.98 | **316.94** | | | |
| | 258/4 | 377.22 | 224.29 | 362.23 | **321.25** | | | |
| 11 | 287/1 | 307.07 | 263.22 | 357.79 | **309.36** | **303.33** | **5.28** | **1.7** |
| | 287/2 | 371.31 | 240.82 | 306.24 | **306.12** | | | |
| | 287/3 | 351.22 | 225.83 | 318.11 | **298.39** | | | |
| | 287/4 | 336.02 | 230.70 | 331.67 | **299.46** | | | |
| 12 | 294/1 | 368.75 | 263.58 | 375.53 | **335.95** | **313.30** | **18.08** | **5.8** |
| | 294/2 | 340.49 | 278.99 | 324.43 | **314.64** | | | |
| | 294/3 | 298.18 | 250.72 | 383.39 | **310.76** | | | |
| | 294/4 | 285.87 | 268.46 | 321.26 | **291.86** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **294.511** |
| **SD of means of the sub-samples 1-4** | **9.21** |
| **RSD (%)** | **3.126** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **8.0** |

## Analyt V

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 1 line (Serie 1) | mean calculated from 1 line (Serie 2) | mean calculated from 1 line (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 379.3 | 263.4 | 290.2 | **310.9** |
| 2 | HS 2 | 348.5 | 268.7 | 331.2 | **316.1** |
| 3 | HS 3 | 385.5 | 340.2 | 190.1 | **305.3** |
| 4 | HS 4 | 403.9 | 285.7 | 293.4 | **327.7** |
| 5 | HS 5 | 336.7 | 263.5 | | **300.1** |
| 6 | HS 6 | 304.3 | 254.3 | 186.5 | **248.4** |
| 7 | HS 7 | 443.9 | 162.1 | 219.7 | **275.2** |
| 8 | HS 8 | 418.2 | 182.5 | 252.0 | **284.3** |
| 9 | HS 9 | 383.9 | 231.8 | 244.0 | **286.6** |
| 10 | HS 10 | 422.7 | 193.9 | 262.6 | **293.1** |
| 11 | HS 11 | 390.3 | 197.0 | 292.4 | **293.2** |
| 12 | HS 12 | 390.8 | 214.6 | 230.5 | **278.6** |
| 13 | HS 13 | 432.2 | 213.3 | 239.1 | **294.9** |
| 14 | HS 14 | 394.4 | 321.6 | 257.2 | **324.4** |
| 15 | HS 15 | 437.4 | 300.0 | 258.5 | **332.0** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **298.0** |
| **$SD_{HS}$** | **22.4** |
| **$RSD_{HS}$ (%)** | **7.51** |

## Analyt V

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 26.023 | $M_{Ss}$ 294.500 | RSD % 3.13 |
| standard deviation between the samples $s_b$ | 18.412 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 0.501 | Characteristic no. for homogeneity between the samples | 0.275 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 22.400 | $M_{HS}$ 298.000 | $RSD_{HS}$ % 7.51 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 1.351 | Characteristic no. for homogeneity within the samples | 0.588 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

**Analyt Zr** (ETV-ICP-OES, results were compiled over 2 lines on 3 different days

mass fraction in mg/kg

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 1 | 12/1 | 3.16 | 4.37 | 4.48 | **4.00** | **4.06** | **0.45** | **11.0** |
| | 12/2 | 2.25 | 5.03 | 4.01 | **3.76** | | | |
| | 12/3 | 1.65 | 5.10 | 4.55 | **3.77** | | | |
| | 12/4 | | 5.85 | 3.57 | **4.71** | | | |
| 2 | 35/1 | 2.92 | 5.83 | 4.00 | **4.25** | **3.89** | **0.39** | **10.1** |
| | 35/2 | 2.11 | 4.60 | 3.76 | **3.49** | | | |
| | 35/3 | 1.87 | 5.32 | 3.63 | **3.61** | | | |
| | 35/4 | 4.09 | 4.97 | 3.52 | **4.19** | | | |
| 3 | 66/1 | 3.51 | 4.63 | 4.66 | **4.26** | **3.94** | **0.31** | **7.8** |
| | 66/2 | 3.75 | 4.32 | 4.30 | **4.13** | | | |
| | 66/3 | 2.52 | 4.83 | 3.55 | **3.64** | | | |
| | 66/4 | 2.27 | 5.05 | 3.85 | **3.72** | | | |
| 4 | 99/1 | 3.13 | 4.68 | 3.53 | **3.78** | **4.00** | **0.54** | **13.4** |
| | 99/2 | 4.17 | 5.00 | 4.44 | **4.54** | | | |
| | 99/3 | 2.06 | 4.20 | 3.82 | **3.36** | | | |
| | 99/4 | 3.89 | 5.24 | 3.89 | **4.34** | | | |
| 5 | 116/1 | 2.81 | 4.17 | 3.48 | **3.49** | **3.94** | **0.31** | **7.8** |
| | 116/2 | 3.46 | 4.37 | 4.22 | **4.02** | | | |
| | 116/3 | 3.72 | 4.86 | 3.80 | **4.13** | | | |
| | 116/4 | 2.70 | 5.33 | 4.37 | **4.13** | | | |
| 6 | 143/1 | 1.61 | 4.63 | 3.41 | **3.22** | **3.49** | **0.38** | **10.9** |
| | 143/2 | 1.06 | 4.63 | 3.69 | **3.13** | | | |
| | 143/3 | 2.98 | 4.61 | 3.59 | **3.73** | | | |
| | 143/4 | 3.41 | 4.56 | 3.75 | **3.91** | | | |

| Line number | Sample number | mean calculated from 2 lines (14.04.11) | mean calculated from 2 lines (15.04.11) | mean calculated from 2 lines (19.04.11) | **mean** | **mean of sub-samples 1-4** | **SD of sub-samples 1-4** | **$RSD_w$ (rel.%)** |
|---|---|---|---|---|---|---|---|---|
| 7 | 161/1 | 2.10 | 4.60 | 3.84 | **3.51** | **3.57** | **0.31** | **8.8** |
| | 161/2 | 1.84 | 5.05 | 3.50 | **3.46** | | | |
| | 161/3 | 1.51 | 4.65 | 3.71 | **3.29** | | | |
| | 161/4 | 3.57 | 4.89 | 3.61 | **4.02** | | | |
| 8 | 195/1 | 2.90 | 4.99 | 4.27 | **4.06** | **4.24** | **0.41** | **9.7** |
| | 195/2 | 3.81 | 5.28 | 3.55 | **4.21** | | | |
| | 195/3 | 3.70 | 4.70 | 3.20 | **3.86** | | | |
| | 195/4 | 5.29 | 4.67 | 4.49 | **4.82** | | | |
| 9 | 237/1 | 4.00 | 5.10 | 4.06 | **4.39** | **3.81** | **0.53** | **14.0** |
| | 237/2 | 2.13 | 4.26 | 3.51 | **3.30** | | | |
| | 237/3 | 4.06 | 4.72 | 3.64 | **4.14** | | | |
| | 237/4 | 2.06 | 4.53 | 3.67 | **3.42** | | | |
| 10 | 258/1 | 4.66 | 5.06 | 4.15 | **4.62** | **4.29** | **0.50** | **11.7** |
| | 258/2 | 2.34 | 4.96 | 3.33 | **3.54** | | | |
| | 258/3 | 3.70 | 4.95 | 4.89 | **4.51** | | | |
| | 258/4 | 3.32 | 5.40 | 4.68 | **4.47** | | | |
| 11 | 287/1 | 4.44 | 5.02 | 3.92 | **4.46** | **3.72** | **0.52** | **13.9** |
| | 287/2 | 2.45 | 3.94 | 3.68 | **3.36** | | | |
| | 287/3 | 1.71 | 4.91 | 4.44 | **3.69** | | | |
| | 287/4 | 1.37 | 4.92 | 3.80 | **3.36** | | | |
| 12 | 294/1 | 2.23 | 4.91 | 3.35 | **3.50** | **3.82** | **0.30** | **7.9** |
| | 294/2 | 1.65 | 5.15 | 4.30 | **3.70** | | | |
| | 294/3 | 4.10 | 5.03 | 3.52 | **4.21** | | | |
| | 294/4 | 2.38 | 4.92 | 4.30 | **3.87** | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **3.898** |
| **SD of means of the sub-samples 1-4** | **0.24** |
| **RSD (%)** | **6.104** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **10.6** |

## Analyt Zr

**HS = Homogeneous sample**

| Line number | Sample number | mean calculated from 2 lines (Serie 1) | mean calculated from 2 lines (Serie 2) | mean calculated from 2 lines (Serie 3) | **mean** |
|---|---|---|---|---|---|
| 1 | HS 1 | 3.772 | 4.614 | 4.447 | **4.278** |
| 2 | HS 2 | 4.038 | 4.176 | 4.633 | **4.282** |
| 3 | HS 3 | 3.969 | 4.424 | 4.140 | **4.177** |
| 4 | HS 4 | 3.663 | 4.104 | 3.559 | **3.775** |
| 5 | HS 5 | 4.057 | 3.742 | 3.870 | **3.889** |
| 6 | HS 6 | 4.883 | 3.752 | 3.843 | **4.159** |
| 7 | HS 7 | 3.898 | 3.677 | 3.091 | **3.555** |
| 8 | HS 8 | 3.287 | 4.095 | 3.427 | **3.603** |
| 9 | HS 9 | 3.409 | 3.939 | 3.683 | **3.677** |
| 10 | HS 10 | 4.268 | 3.827 | 4.779 | **4.292** |
| 11 | HS 11 | 4.000 | 4.530 | 4.107 | **4.212** |
| 12 | HS 12 | 3.295 | 3.963 | 3.923 | **3.727** |
| 13 | HS 13 | 3.833 | 4.010 | 3.295 | **3.713** |
| 14 | HS 14 | 3.973 | 3.972 | 3.703 | **3.883** |
| 15 | HS 15 | 3.772 | 3.991 | 3.879 | **3.881** |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **3.940** |
| **$SD_{HS}$** | **0.267** |
| **$RSD_{HS}$ (%)** | **6.77** |

## Analyt Zr

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.422 | $M_{Ss}$ 3.898 | RSD % 6.10 |
| standard deviation between the samples $s_b$ | 0.476 | $F_{value}$ | 2.036 |
| test value $s_b^2/s_w^2$ | 1.269 | Characteristic no. for homogeneity between the samples | 0.623 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.267 | $M_{HS}$ 3.940 | $RSD_{HS}$ % 6.77 |
| | | $F_{value}$ | 2.298 |
| test value $s_w^2/s_{HS}^2$ | 2.505 | Characteristic no. for homogeneity within the samples | 1.090 |
| **Homogeneity within the samples: Not very strong inhomogeneity** | | | |

## Analyt Carbon total

mass fraction in %

| Line number | Sample number | mean | mean of sub-samples 1-4 | SD of sub-samples 1-4 | $RSD_w$ (rel.%) |
|---|---|---|---|---|---|
| 1 | 21/1 | 30.00 | **30.03** | **0.02** | **0.1** |
| | 21/2 | 30.05 | | | |
| | 21/3 | 30.01 | | | |
| | 21/4 | 30.04 | | | |
| 2 | 51/1 | 29.97 | **29.99** | **0.02** | **0.1** |
| | 51/2 | 30.00 | | | |
| | 51/3 | 30.00 | | | |
| | 51/4 | 29.97 | | | |
| 3 | 92/1 | 30.03 | **30.02** | **0.04** | **0.1** |
| | 92/2 | 30.03 | | | |
| | 92/3 | 29.96 | | | |
| | 92/4 | 30.06 | | | |
| 4 | 116/1 | 29.98 | **30.00** | **0.06** | **0.2** |
| | 116/2 | 30.06 | | | |
| | 116/3 | 30.02 | | | |
| | 116/4 | 29.93 | | | |
| 5 | 157/1 | 30.00 | **29.99** | **0.02** | **0.1** |
| | 157/2 | 30.01 | | | |
| | 157/3 | 29.97 | | | |
| | 157/4 | 29.99 | | | |
| 6 | 189/1 | 30.03 | **30.00** | **0.03** | **0.1** |
| | 189/2 | 29.99 | | | |
| | 189/3 | 29.97 | | | |
| | 189/4 | 30.00 | | | |
| 7 | 223/1 | 30.00 | **29.99** | **0.02** | **0.1** |
| | 223/2 | 29.97 | | | |
| | 223/3 | 30.00 | | | |
| | 223/4 | 30.00 | | | |
| 8 | 237/1 | 30.06 | **30.04** | **0.03** | **0.1** |
| | 237/2 | 30.05 | | | |
| | 237/3 | 30.05 | | | |
| | 237/4 | 30.00 | | | |
| 9 | 287/1 | 29.99 | **30.01** | **0.04** | **0.1** |
| | 287/2 | 29.95 | | | |
| | 287/3 | 30.05 | | | |
| | 287/4 | 30.03 | | | |
| 10 | 310/1 | 29.99 | **30.01** | **0.04** | **0.1** |
| | 310/2 | 29.95 | | | |
| | 310/3 | 30.05 | | | |
| | 310/4 | 30.03 | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **30.01** |
| **SD of means of the sub-samples 1-4** | **0.02** |
| **RSD (%)** | **0.06** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **0.1** |

## Analyt Carbon total

**HS = Homogeneous sample**

| Line number | Sample number | **mean** |
|---|---|---|
| 1 | HS 1 | 30.01 |
| 2 | HS 2 | 29.97 |
| 3 | HS 3 | 30.04 |
| 4 | HS 4 | 30.03 |
| 5 | HS 5 | 29.95 |
| 6 | HS 6 | 29.98 |
| 7 | HS 7 | 29.98 |
| 8 | HS 8 | 30.05 |
| 9 | HS 9 | 30.00 |
| 10 | HS 10 | 30.01 |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **30.002** |
| **$SD_{HS}$** | **0.0322** |
| **$RSD_{HS}$ (%)** | **0.11** |

## Analyt Carbon total

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 0.034 | $M_{Ss}$<br>30.01 | RSD %<br>0.06 |
| standard deviation between the samples $s_b$ | 0.034 | $F_{value}$ | 2.210 |
| test value $s_b^2/s_w^2$ | 1.024 | Characteristic no. for homogeneity between the samples | 0.463 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 0.032 | $M_{HS}$<br>30.00 | $RSD_{HS}$ %<br>0.11 |
| | | $F_{value}$ | 2.86 |
| test value $s_w^2/s_{HS}^2$ | 1.112 | Characteristic no. for homogeneity within the samples | 0.389 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

**Analyt Carbon free**

mass fraction in %

| Line number | Sample number | mean | mean of sub-samples 1-4 | SD of sub-samples 1-4 | $RSD_w$ (rel.%) |
|---|---|---|---|---|---|
| 1 | 21/1 | 0.0380 | **0.0378** | **0.0020** | **5.18** |
| | 21/2 | 0.0401 | | | |
| | 21/3 | 0.0353 | | | |
| | 21/4 | 0.0378 | | | |
| 2 | 51/1 | 0.0350 | **0.0358** | **0.0025** | **6.99** |
| | 51/2 | 0.0390 | | | |
| | 51/3 | 0.0360 | | | |
| | 51/4 | 0.0330 | | | |
| 3 | 92/1 | 0.0360 | **0.0358** | **0.0019** | **5.30** |
| | 92/2 | 0.0330 | | | |
| | 92/3 | 0.0370 | | | |
| | 92/4 | 0.0370 | | | |
| 4 | 116/1 | 0.0360 | **0.0368** | **0.0017** | **4.65** |
| | 116/2 | 0.0370 | | | |
| | 116/3 | 0.0350 | | | |
| | 116/4 | 0.0390 | | | |
| 5 | 157/1 | 0.0350 | **0.0353** | **0.0010** | **2.72** |
| | 157/2 | 0.0360 | | | |
| | 157/3 | 0.0340 | | | |
| | 157/4 | 0.0360 | | | |
| 6 | 189/1 | 0.0390 | **0.0373** | **0.0013** | **3.38** |
| | 189/2 | 0.0370 | | | |
| | 189/3 | 0.0360 | | | |
| | 189/4 | 0.0370 | | | |
| 7 | 223/1 | 0.0331 | **0.0341** | **0.0018** | **5.17** |
| | 223/2 | 0.0363 | | | |
| | 223/3 | 0.0324 | | | |
| | 223/4 | 0.0347 | | | |
| 8 | 237/1 | 0.0360 | **0.0358** | **0.0025** | **6.99** |
| | 237/2 | 0.0350 | | | |
| | 237/3 | 0.0390 | | | |
| | 237/4 | 0.0330 | | | |
| 9 | 287/1 | 0.0370 | **0.0385** | **0.0010** | **2.60** |
| | 287/2 | 0.0390 | | | |
| | 287/3 | 0.0390 | | | |
| | 287/4 | 0.0390 | | | |
| 10 | 310/1 | 0.0370 | **0.0353** | **0.0021** | **5.85** |
| | 310/2 | 0.0330 | | | |
| | 310/3 | 0.0340 | | | |
| | 310/4 | 0.0370 | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **0.0362** |
| **SD of means of the sub-samples 1-4** | **0.0013** |
| **RSD (%)** | **3.6754** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **4.9** |

## Analyt Carbon free

**HS = Homogeneous sample**

| Line number | Sample number | **mean** |
|---|---|---|
| 1 | HS 1 | 0.0350 |
| 2 | HS 2 | 0.0358 |
| 3 | HS 3 | 0.0384 |
| 4 | HS 4 | 0.0353 |
| 5 | HS 5 | 0.0349 |
| 6 | HS 6 | 0.0329 |
| 7 | HS 7 | 0.0384 |
| 8 | HS 8 | 0.0372 |
| 9 | HS 9 | 0.0347 |
| 10 | HS 10 | 0.0341 |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **0.0357** |
| **$SD_{HS}$** | **0.0018** |
| **$RSD_{HS}$ (%)** | **5.0998** |

## Analyt Carbon free

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 1.84E-03 | $M_{Ss}$ 0.0362 | RSD % 3.6700 |
| standard deviation between the samples $s_b$ | 2.66E-03 | $F_{value}$ | 2.210 |
| test value $s_b^2/s_w^2$ | 2.104 | Characteristic no. for homogeneity between the samples | 0.444 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 1.80E-03 | $M_{HS}$ 5.11 | $RSD_{HS}$ % 7.33 |
| | | $F_{value}$ | 2.860 |
| test value $s_w^2/s_{HS}^2$ | 1.018 | Characteristic no. for homogeneity within the samples | 0.356 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

## Analyt Nitrogen

mass fraction in mg/kg

| Line number | Sample number | mean | mean of sub-samples 1-4 | SD of sub-samples 1-4 | $RSD_w$ (rel.%) |
|---|---|---|---|---|---|
| 1 | 21/1 | 21.46 | **20.87** | **1.54** | **7.4** |
| | 21/2 | 22.78 | | | |
| | 21/3 | 19.66 | | | |
| | 21/4 | 19.58 | | | |
| 2 | 51/1 | 20.04 | **19.99** | **0.50** | **2.5** |
| | 51/2 | 19.32 | | | |
| | 51/3 | 20.52 | | | |
| | 51/4 | 20.08 | | | |
| 3 | 92/1 | 23.08 | **20.94** | **1.75** | **8.4** |
| | 92/2 | 18.80 | | | |
| | 92/3 | 20.74 | | | |
| | 92/4 | 21.12 | | | |
| 4 | 116/1 | 19.38 | **20.98** | **2.69** | **12.8** |
| | 116/2 | 21.98 | | | |
| | 116/3 | 18.28 | | | |
| | 116/4 | 24.28 | | | |
| 5 | 157/1 | 18.06 | **19.57** | **1.04** | **5.3** |
| | 157/2 | 19.88 | | | |
| | 157/3 | 19.86 | | | |
| | 157/4 | 20.46 | | | |
| 6 | 189/1 | 22.66 | **20.23** | **1.75** | **8.6** |
| | 189/2 | 18.60 | | | |
| | 189/3 | 19.44 | | | |
| | 189/4 | 20.22 | | | |
| 7 | 223/1 | 22.52 | **21.93** | **1.15** | **5.2** |
| | 223/2 | 22.12 | | | |
| | 223/3 | 22.82 | | | |
| | 223/4 | 20.26 | | | |
| 8 | 237/1 | 21.90 | **20.50** | **1.47** | **7.2** |
| | 237/2 | 21.62 | | | |
| | 237/3 | 19.32 | | | |
| | 237/4 | 19.14 | | | |
| 9 | 287/1 | 25.16 | **20.50** | **3.23** | **15.8** |
| | 287/2 | 18.48 | | | |
| | 287/3 | 18.16 | | | |
| | 287/4 | 20.18 | | | |
| 10 | 310/1 | 24.20 | **20.29** | **2.73** | **13.4** |
| | 310/2 | 17.90 | | | |
| | 310/3 | 19.78 | | | |
| | 310/4 | 19.28 | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **20.58** |
| **SD of means of the sub-samples 1-4** | **0.65** |
| **RSD (%)** | **3.15** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **8.7** |

## Analyt Nitrogen

**HS = Homogeneous sample**

| Line number | Sample number | **mean** |
|---|---|---|
| 1 | HS 1 | 21.90 |
| 2 | HS 2 | 21.40 |
| 3 | HS 3 | 18.00 |
| 4 | HS 4 | 21.90 |
| 5 | HS 5 | 24.40 |
| 6 | HS 6 | 20.10 |
| 7 | HS 7 | 21.10 |
| 8 | HS 8 | 23.70 |
| 9 | HS 9 | 20.70 |
| 10 | HS 10 | 25.00 |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **21.820** |
| **$SD_{HS}$** | **2.1033** |
| **$RSD_{HS}$ (%)** | **9.64** |

## Analyt Nitrogen

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 1.961 | $M_{Ss}$ 20.58 | RSD % 3.15 |
| standard deviation between the samples $s_b$ | 1.298 | $F_{value}$ | 2.210 |
| test value $s_b^2/s_w^2$ | 0.438 | Characteristic no. for homogeneity between the samples | 0.198 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 2.103 | $M_{HS}$ 21.82 | $RSD_{HS}$ % 9.64 |
| | | $F_{value}$ | 2.860 |
| test value $s_w^2/s_{HS}^2$ | 0.869 | Characteristic no. for homogeneity within the samples | 0.304 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

**Analyt Oxygen**

mass fraction in mg/kg

| Line number | Sample number | mean | mean of sub-samples 1-4 | SD of sub-samples 1-4 | $RSD_w$ (rel.%) |
|---|---|---|---|---|---|
| 1 | 21/1 | 156.70 | **157.56** | **5.93** | **3.8** |
| | 21/2 | 151.28 | | | |
| | 21/3 | 165.60 | | | |
| | 21/4 | 156.64 | | | |
| 2 | 51/1 | 162.74 | **157.46** | **4.21** | **2.7** |
| | 51/2 | 154.32 | | | |
| | 51/3 | 153.82 | | | |
| | 51/4 | 158.96 | | | |
| 3 | 92/1 | 156.02 | **157.24** | **3.12** | **2.0** |
| | 92/2 | 153.66 | | | |
| | 92/3 | 160.94 | | | |
| | 92/4 | 158.34 | | | |
| 4 | 116/1 | 153.36 | **153.97** | **3.63** | **2.4** |
| | 116/2 | 149.38 | | | |
| | 116/3 | 155.04 | | | |
| | 116/4 | 158.08 | | | |
| 5 | 157/1 | 151.26 | **153.33** | **3.39** | **2.2** |
| | 157/2 | 151.10 | | | |
| | 157/3 | 152.66 | | | |
| | 157/4 | 158.30 | | | |
| 6 | 189/1 | 155.76 | **160.58** | **5.31** | **3.3** |
| | 189/2 | 157.50 | | | |
| | 189/3 | 161.30 | | | |
| | 189/4 | 167.74 | | | |
| 7 | 223/1 | 153.28 | **153.46** | **0.83** | **0.5** |
| | 223/2 | 152.58 | | | |
| | 223/3 | 154.58 | | | |
| | 223/4 | 153.40 | | | |
| 8 | 237/1 | 163.74 | **160.52** | **2.70** | **1.7** |
| | 237/2 | 157.14 | | | |
| | 237/3 | 160.42 | | | |
| | 237/4 | 160.76 | | | |
| 9 | 287/1 | 161.50 | **160.05** | **4.88** | **3.0** |
| | 287/2 | 160.94 | | | |
| | 287/3 | 153.14 | | | |
| | 287/4 | 164.60 | | | |
| 10 | 310/1 | 153.78 | **155.87** | **1.81** | **1.2** |
| | 310/2 | 157.82 | | | |
| | 310/3 | 156.84 | | | |
| | 310/4 | 155.04 | | | |

| | |
|---|---|
| **$M_{ss}$ - mean of means of the sub-samples 1-4** | **157.00** |
| **SD of means of the sub-samples 1-4** | **2.82** |
| **RSD (%)** | **1.79** |

| | |
|---|---|
| **mean $RSD_w$ (%)** | **2.3** |

## Analyt Oxygen

**HS = Homogeneous sample**

| Line number | Sample number | **mean** |
|---|---|---|
| | | |
| 1 | HS 1 | 160.10 |
| 2 | HS 2 | 162.60 |
| 3 | HS 3 | 158.30 |
| 4 | HS 4 | 160.00 |
| 5 | HS 5 | 160.30 |
| 6 | HS 6 | 161.40 |
| 7 | HS 7 | 154.00 |
| 8 | HS 8 | 163.50 |
| 9 | HS 9 | 159.00 |
| 10 | HS 10 | 158.40 |

| | |
|---|---|
| **$M_{HS}$ - mean of homogeneous sample** | **159.760** |
| **$SD_{HS}$** | **2.645** |
| **$RSD_{HS}$ (%)** | **1.66** |

## Analyt Oxygen

| Homogeneity between the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation within the samples $s_w$ | 3.880 | $M_{Ss}$ 157.00 | RSD % 1.79 |
| standard deviation between the samples $s_b$ | 5.636 | $F_{value}$ | 2.210 |
| test value $s_b^2/s_w^2$ | 2.110 | Characteristic no. for homogeneity between the samples | 0.955 |
| **Homogeneity between the samples: No significant inhomogeneity** | | | |

| Homogeneity within the samples | | | |
|---|---|---|---|
| | | | |
| Analysis of variance: $\alpha = 0.05$ | | | |
| standard deviation of homogeneous sample $s_{HS}$ | 2.645 | $M_{HS}$ 5.11 | $RSD_{HS}$ % 7.33 |
| | | $F_{value}$ | 2.860 |
| test value $s_w^2/s_{HS}^2$ | 2.152 | Characteristic no. for homogeneity within the samples | 0.753 |
| **Homogeneity within the samples: No significant inhomogeneity** | | | |

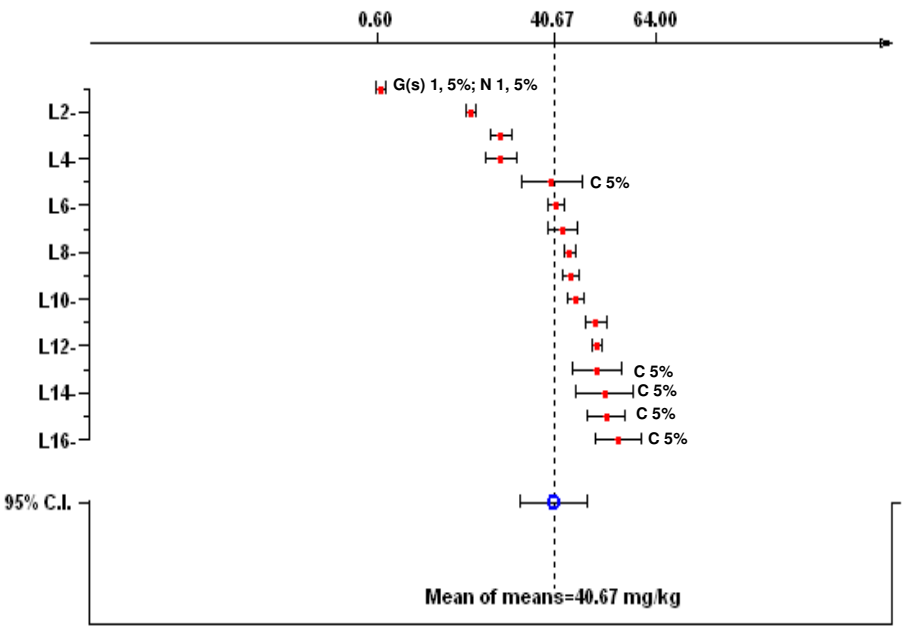
## Appendix 5: Statistical evaluation of all results of interlaboratory comparison for certification of BAM-S008

### Tab. A6.1.1: Aluminium (values in mg/kg)

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 21 ETV-ICP OES 2 | 1.53 | 1.03 | 1.08 | 2.70 | 2.40 | 2.30 | 0.60 | 0.60 | 0.60 |
| L 2 | 28 ICP OES 2 | 21.83 | 1.17 | 1.23 | 20.00 | 22.00 | 23.00 | 22.00 | 21.00 | 23.00 |
| L 3 | 27 GD-MS 3 | 28.67 | 2.25 | 2.36 | 25.00 | 27.00 | 31.00 | 30.00 | 30.00 | 29.00 |
| L 4 | 19 ETV-ICP OES 3 | 28.76 | 3.53 | 3.70 | 23.91 | 34.38 | 28.39 | 30.02 | 26.52 | 29.33 |
| L 5 | 23 ICP OES 3 | 40.18 | 6.48 | 6.80 | 39.20 | 38.60 | 49.90 | 45.70 | 34.70 | 33.00 |
| L 6 | 14 DC Arc OES 1 | 41.30 | 1.75 | 1.84 | 43.20 | 43.30 | 38.60 | 40.80 | 40.90 | 41.00 |
| L 7 | 9 DC Arc OES 3 | 42.62 | 3.20 | 3.36 | 46.50 | 38.70 | 41.00 | 39.90 | 44.00 | 45.60 |
| L 8 | 14 ICP OES 2 | 44.32 | 1.10 | 1.16 | 43.00 | 43.00 | 45.40 | 45.30 | 45.00 | 44.20 |
| L 9 | 15 ICP-SF-MS 3 | 44.55 | 1.70 | 1.79 | 47.30 | 44.10 | 44.20 | 45.30 | 42.10 | 44.30 |
| L 10 | 13 ET AAS 3 | 45.67 | 1.75 | 1.83 | 48.60 | 44.40 | 45.10 | 46.60 | 43.70 | 45.60 |
| L 11 | 3 ICP OES 2 | 50.23 | 2.30 | 2.42 | 54.30 | 51.70 | 49.20 | 48.60 | 48.70 | 48.90 |
| L 12 | 29 ICP OES 3 | 50.40 | 1.03 | 1.08 | 49.81 | 50.66 | 50.93 | 51.28 | 48.59 | 51.14 |
| L 13 | 7 GD-MS 3 | 50.50 | 5.32 | 5.58 | 45.00 | 50.00 | 47.00 | 56.00 | 47.00 | 58.00 |
| L 14 | 7 DC Arc OES3 | 52.17 | 6.18 | 6.48 | 57.00 | 56.00 | 44.00 | 45.00 | 58.00 | 53.00 |
| L 15 | 2 XRF 2 | 52.67 | 4.08 | 4.28 | 53.00 | 53.00 | 48.00 | 50.00 | 52.00 | 60.00 |
| L 16 | 4 DC Arc OES 3 | 55.33 | 5.05 | 5.30 | 55.00 | 64.00 | 49.00 | 56.00 | 52.00 | 56.00 |

The results L1 to L4 were withdrawn by the resp. laboratories as technical outliers after discussion. Therefore a statistical evaluation was only carried out with the remaining results. Therefore these results don't appear on the certificate.

**Diagram of means and 95% confidence intervals (to Tab. A1)**



### Tab. A6.1.2: Aluminium accepted results in run 1 (values in mg/kg)

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 23 ICP OES 3 | 40.18 | 6.48 | 6.80 | 39.20 | 38.60 | 49.90 | 45.70 | 34.70 | 33.00 |
| L 2 | 14 DC Arc OES 1 | 41.30 | 1.75 | 1.84 | 43.20 | 43.30 | 38.60 | 40.80 | 40.90 | 41.00 |
| L 3 | 9 DC Arc OES 3 | 42.62 | 3.20 | 3.36 | 46.50 | 38.70 | 41.00 | 39.90 | 44.00 | 45.60 |
| L 4 | 14 ICP OES 2 | 44.32 | 1.10 | 1.16 | 43.00 | 43.00 | 45.40 | 45.30 | 45.00 | 44.20 |
| L 5 | 15 ICP-SF-MS 3 | 44.55 | 1.70 | 1.79 | 47.30 | 44.10 | 44.20 | 45.30 | 42.10 | 44.30 |
| L 6 | 13 ET AAS 3 | 45.67 | 1.75 | 1.83 | 48.60 | 44.40 | 45.10 | 46.60 | 43.70 | 45.60 |
| L 7 | 3 ICP OES 2 | 50.23 | 2.30 | 2.42 | 54.30 | 51.70 | 49.20 | 48.60 | 48.70 | 48.90 |
| L 8 | 29 ICP OES 3 | 50.40 | 1.03 | 1.08 | 49.81 | 50.66 | 50.93 | 51.28 | 48.59 | 51.14 |
| L 9 | 7 GD-MS 3 | 50.50 | 5.32 | 5.58 | 45.00 | 50.00 | 47.00 | 56.00 | 47.00 | 58.00 |
| L 10 | 7 DC Arc OES 3 | 52.17 | 6.18 | 6.48 | 57.00 | 56.00 | 44.00 | 45.00 | 58.00 | 53.00 |
| L 11 | 2 XRF 2 | 52.67 | 4.08 | 4.28 | 53.00 | 53.00 | 48.00 | 50.00 | 52.00 | 60.00 |
| L 12 | 4 DC Arc OES 3 | 55.33 | 5.05 | 5.30 | 55.00 | 64.00 | 49.00 | 56.00 | 52.00 | 56.00 |

| | |
|---|---|
| Range [min..max] | [ 33.00 .. 64.00 ] |
| | Case of No Pooling |
| Mean of means | 47.49 |
| 95% H.W. Confidence Interval | 3.16 |

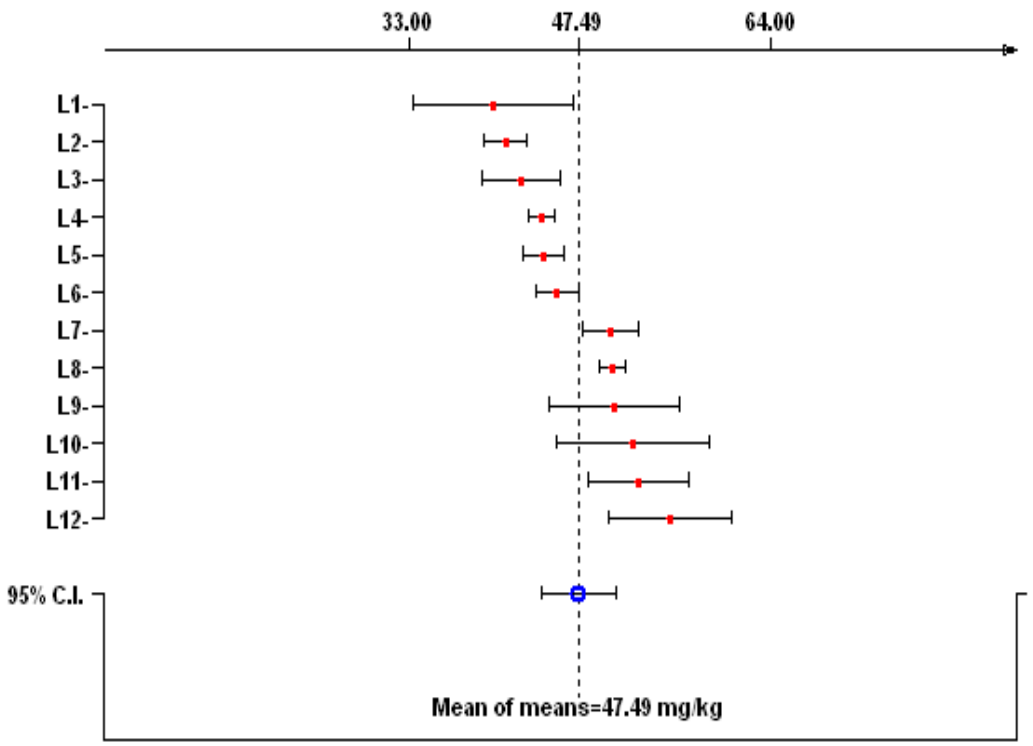
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

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. A2)



**Tab. A6.2: Boron accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 21 ETV-ICP OES 2 | 1.43 | 0.34 | 0.36 | 1.20 | 1.80 | 1.40 | 1.20 | 1.10 | 1.90 |
| L 2 | 27 GD-MS 3 | 2.40 | 0.61 | 0.64 | 2.60 | 3.50 | 2.40 | 2.10 | 1.90 | 1.90 |
| L 3 | 9 DC Arc OES 3 | 2.95 | 0.50 | 0.53 | 3.30 | 3.50 | 2.50 | 3.40 | 2.40 | 2.60 |
| L 4 | 4 ETV-ICP OES 3 | 3.33 | 0.52 | 0.54 | 4.00 | 3.00 | 3.00 | 3.00 | 3.00 | 4.00 |
| L 5 | 15 ICP-SF-MS 3 | 3.96 | 1.32 | 1.39 | 3.12 | 5.70 | 3.59 | 3.34 | 2.51 | 5.51 |
| L 6 | 7 GD-MS 3 | 4.18 | 1.32 | 1.38 | 2.80 | 4.70 | 3.10 | 5.50 | 3.20 | 5.80 |

| | |
|---|---|
| Range [min..max] | [ 1.10 .. 5.80 ] |
| | Case of No Pooling |
| Mean of means | 3.04 |
| 95% H.W. Confidence Interval | 1.07 |

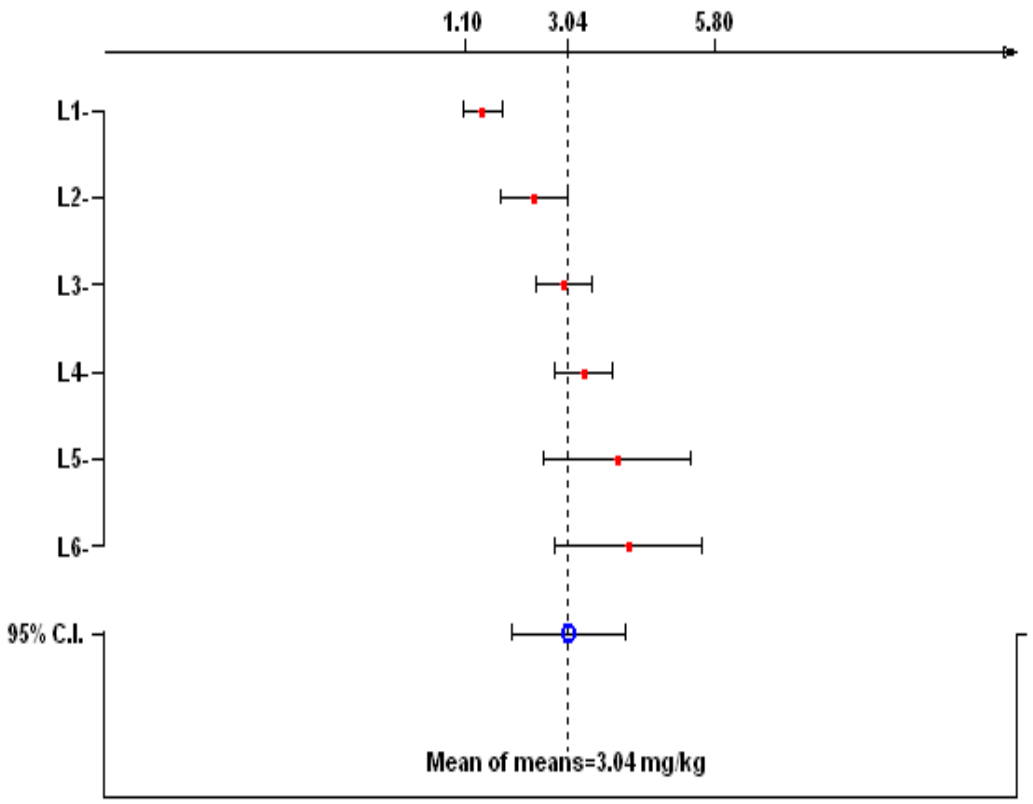
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
- C = Cochran test
- D = Dixon test
- $G_{(s)}$ = Grubbs test
- 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. B1)**



**Tab. A6.3: Calcium accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.1261 | 0.0478 | 0.0501 | 0.1350 | 0.1850 | 0.1001 | 0.0651 | 0.0952 | 0.1762 |
| L 2 | 9 ETV-ICP OES 3 | 0.1427 | 0.0076 | 0.0079 | 0.1390 | 0.1450 | 0.1320 | 0.1430 | 0.1420 | 0.1550 |
| L 3 | 29 ICP-MS 3 | 0.2368 | 0.0182 | 0.0191 | 0.2260 | 0.2240 | 0.2480 | 0.2140 | 0.2470 | 0.2620 |
| L 4 | 21 ETV-ICP OES 2 | 0.2650 | 0.0505 | 0.0530 | 0.2300 | 0.2300 | 0.2100 | 0.3200 | 0.2700 | 0.3300 |
| L 5 | 13 ET AAS 3 | 0.2887 | 0.0549 | 0.0576 | 0.2460 | 0.2840 | 0.2830 | 0.3230 | 0.2210 | 0.3750 |
| L 6 | 15 ICP-SF-MS 3 | 0.2900 | 0.0374 | 0.0465 | 0.2800 | 0.3400 | 0.2400 | 0.2800 | | 0.3100 |
| L 7 | 28 ICP OES 2 | 0.3167 | 0.1169 | 0.1227 | 0.3000 | 0.4000 | 0.2000 | 0.5000 | 0.2000 | 0.3000 |
| L 8 | 27 GD-MS 3 | 0.3317 | 0.0801 | 0.0841 | 0.4000 | 0.3000 | 0.2000 | 0.3000 | 0.4000 | 0.3900 |

| | |
|---|---|
| Range [min..max] | [ 0.0651 .. 0.5000 ] |
| | Case of No Pooling |
| Mean of means | 0.2497 |
| 95% H.W. Confidence Interval | 0.0644 |

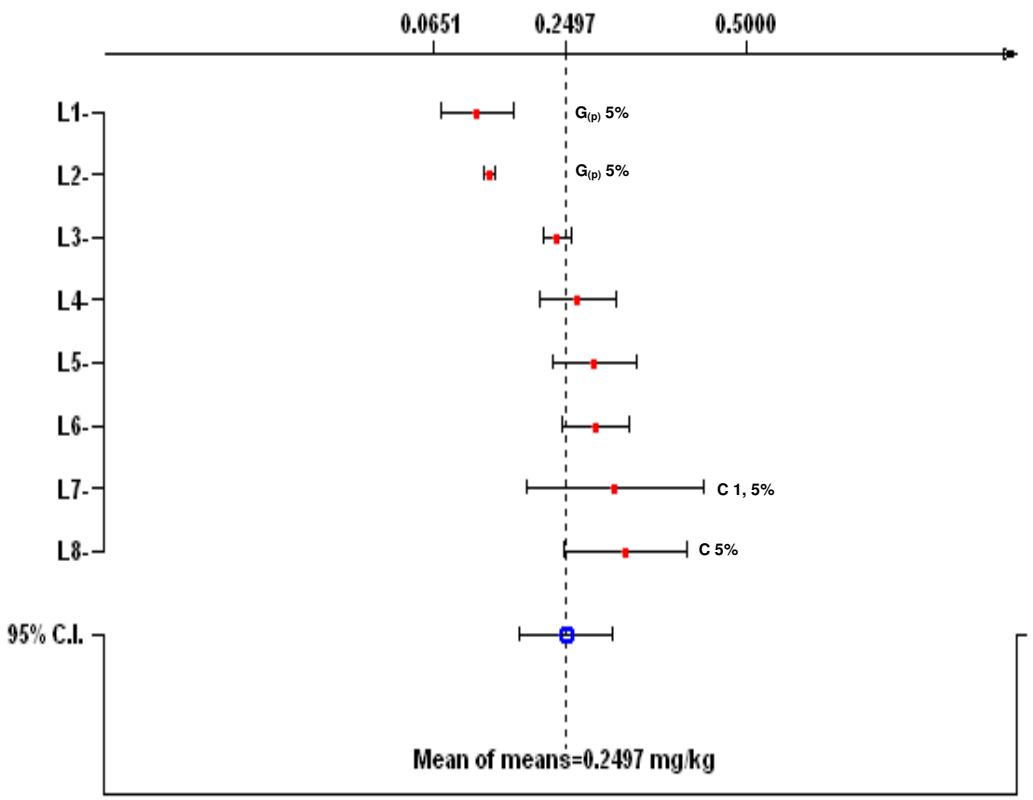
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. C1)**



**Tab. A6.4.1: Chromium evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 11 INAA 3 | 0.0879 | 0.0127 | 0.0133 | 0.0772 | 0.0854 | 0.0708 | 0.1013 | 0.0905 | 0.1021 |
| L 2 | 15 ICP-SF-MS 3 | 0.1208 | 0.0427 | 0.0448 | 0.1210 | 0.1490 | 0.0950 | 0.1050 | 0.0670 | 0.1880 |
| L 3 | 13 ET AAS 3 | 0.1252 | 0.0431 | 0.0452 | 0.1370 | 0.1530 | 0.1120 | 0.0920 | 0.0690 | 0.1880 |
| L 4 | 19 ETV-ICP OES 3 | 0.1274 | 0.0415 | 0.0435 | 0.1112 | 0.1410 | 0.0900 | 0.1271 | 0.2020 | 0.0930 |
| L 5 | 14 ETV-ICP OES 2 | 0.1490 | 0.0181 | 0.0189 | 0.1460 | 0.1230 | 0.1750 | 0.1380 | 0.1610 | 0.1510 |
| L 6 | 9 ETV-ICP OES 3 | 0.1518 | 0.0082 | 0.0086 | 0.1590 | 0.1630 | 0.1480 | 0.1450 | 0.1540 | 0.1420 |
| L 7 | 21 ETV-ICP OES 2 | 0.1550 | 0.0197 | 0.0207 | 0.1700 | 0.1600 | 0.1300 | 0.1700 | 0.1300 | 0.1700 |
| L 8 | 28 ICP OES 2 | 0.2333 | 0.0516 | 0.0542 | 0.2000 | 0.3000 | 0.2000 | 0.2000 | 0.3000 | 0.2000 |
| L 9 | 7 GD-MS 3 | 0.2817 | 0.0677 | 0.0710 | 0.3100 | 0.2100 | 0.3300 | 0.3700 | 0.2700 | 0.2000 |
| L 10 | 27 GD-MS 3 | 0.4367 | 0.0771 | 0.0809 | 0.4400 | 0.3000 | 0.4000 | 0.5000 | 0.4900 | 0.4900 |
| L 11 | 4 ETV-ICP OES 3 | 1.0000 | 0.0000 | 0.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |

| | |
|---|---|
| Range [min..max] | [ 0.0670 .. 1.0000 ] |
| | Case of No Pooling |
| Mean of means | 0.2608 |
| 95% H.W. Confidence Interval | 0.1777 |

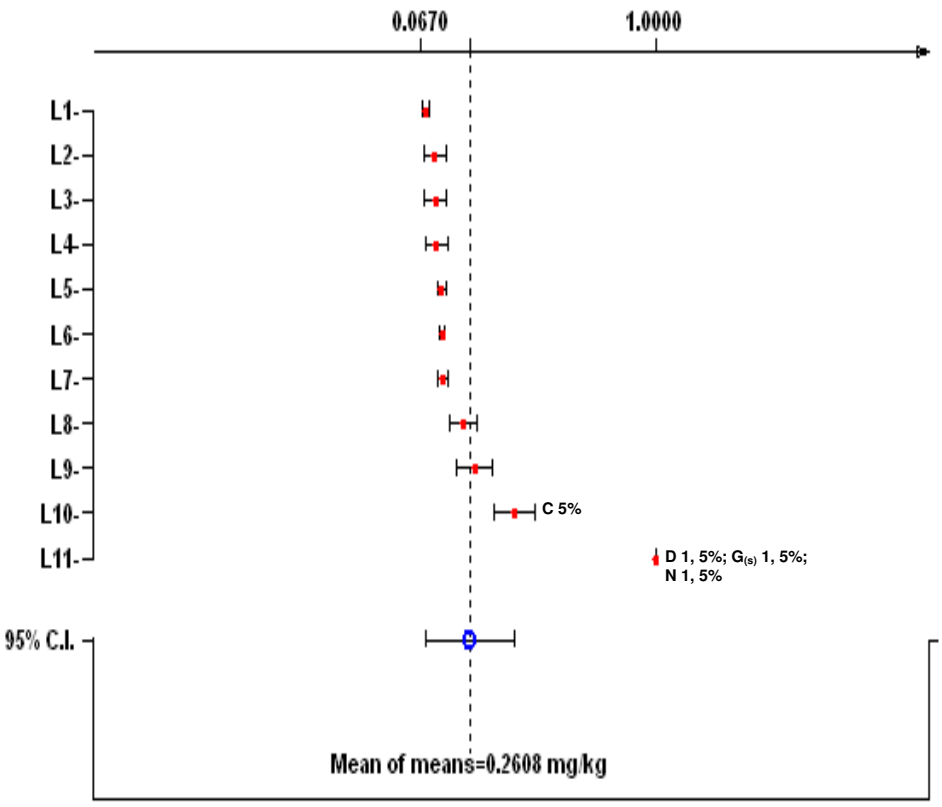
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. D1)**



**Tab. A6.4.2: Chromium evaluation in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 11 INAA 3 | 0.0879 | 0.0127 | 0.0133 | 0.0772 | 0.0854 | 0.0708 | 0.1013 | 0.0905 | 0.1021 |
| L 2 | 15 ICP-SF-MS 3 | 0.1208 | 0.0427 | 0.0448 | 0.1210 | 0.1490 | 0.0950 | 0.1050 | 0.0670 | 0.1880 |
| L 3 | 13 ET AAS 3 | 0.1252 | 0.0431 | 0.0452 | 0.1370 | 0.1530 | 0.1120 | 0.0920 | 0.0690 | 0.1880 |
| L 4 | 19 ETV-ICP OES 3 | 0.1274 | 0.0415 | 0.0435 | 0.1112 | 0.1410 | 0.0900 | 0.1271 | 0.2020 | 0.0930 |
| L 5 | 14 ETV-ICP OES 2 | 0.1490 | 0.0181 | 0.0189 | 0.1460 | 0.1230 | 0.1750 | 0.1380 | 0.1610 | 0.1510 |
| L 6 | 9 ETV-ICP OES 3 | 0.1518 | 0.0082 | 0.0086 | 0.1590 | 0.1630 | 0.1480 | 0.1450 | 0.1540 | 0.1420 |
| L 7 | 21 ETV-ICP OES 2 | 0.1550 | 0.0197 | 0.0207 | 0.1700 | 0.1600 | 0.1300 | 0.1700 | 0.1300 | 0.1700 |
| L 8 | 28 ICP OES 2 | 0.2333 | 0.0516 | 0.0542 | 0.2000 | 0.3000 | 0.2000 | 0.2000 | 0.3000 | 0.2000 |
| L 9 | 7 GD-MS 3 | 0.2817 | 0.0677 | 0.0710 | 0.3100 | 0.2100 | 0.3300 | 0.3700 | 0.2700 | 0.2000 |
| L 10 | 27 GD-MS 3 | 0.4367 | 0.0771 | 0.0809 | 0.4400 | 0.3000 | 0.4000 | 0.5000 | 0.4900 | 0.4900 |

| | |
|---|---|
| Range [min..max] | [ 0.0670 .. 0.5000 ] |
| | Case of No Pooling |
| Mean of means | 0.1869 |
| 95% H.W. Confidence Interval | 0.0749 |

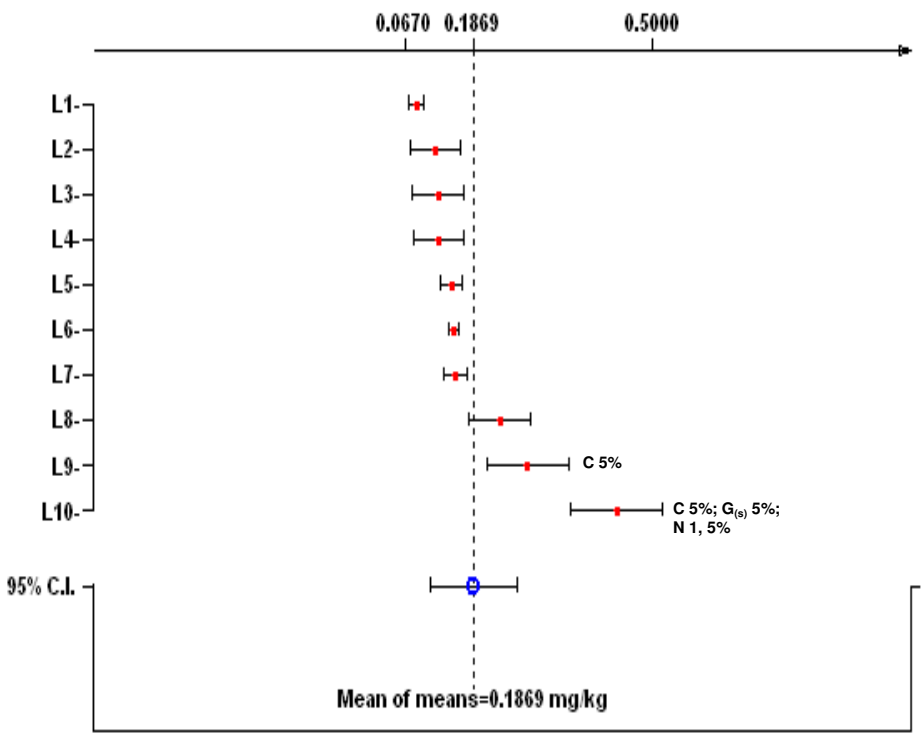
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. D2)**



**Tab. A6.4.3: Chromium accepted results in run 3 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 11 INAA 3 | 0.0879 | 0.0127 | 0.0133 | 0.0772 | 0.0854 | 0.0708 | 0.1013 | 0.0905 | 0.1021 |
| L 2 | 15 ICP-SF-MS 3 | 0.1208 | 0.0427 | 0.0448 | 0.1210 | 0.1490 | 0.0950 | 0.1050 | 0.0670 | 0.1880 |
| L 3 | 13 ET AAS 3 | 0.1252 | 0.0431 | 0.0452 | 0.1370 | 0.1530 | 0.1120 | 0.0920 | 0.0690 | 0.1880 |
| L 4 | 19 ETV-ICP OES 3 | 0.1274 | 0.0415 | 0.0435 | 0.1112 | 0.1410 | 0.0900 | 0.1271 | 0.2020 | 0.0930 |
| L 5 | 14 ETV-ICP OES 2 | 0.1490 | 0.0181 | 0.0189 | 0.1460 | 0.1230 | 0.1750 | 0.1380 | 0.1610 | 0.1510 |
| L 6 | 9 ETV-ICP OES 3 | 0.1518 | 0.0082 | 0.0086 | 0.1590 | 0.1630 | 0.1480 | 0.1450 | 0.1540 | 0.1420 |
| L 7 | 21 ETV-ICP OES 2 | 0.1550 | 0.0197 | 0.0207 | 0.1700 | 0.1600 | 0.1300 | 0.1700 | 0.1300 | 0.1700 |
| L 8 | 28 ICP OES 2 | 0.2333 | 0.0516 | 0.0542 | 0.2000 | 0.3000 | 0.2000 | 0.2000 | 0.3000 | 0.2000 |
| L 9 | 7 GD-MS 3 | 0.2817 | 0.0677 | 0.0710 | 0.3100 | 0.2100 | 0.3300 | 0.3700 | 0.2700 | 0.2000 |

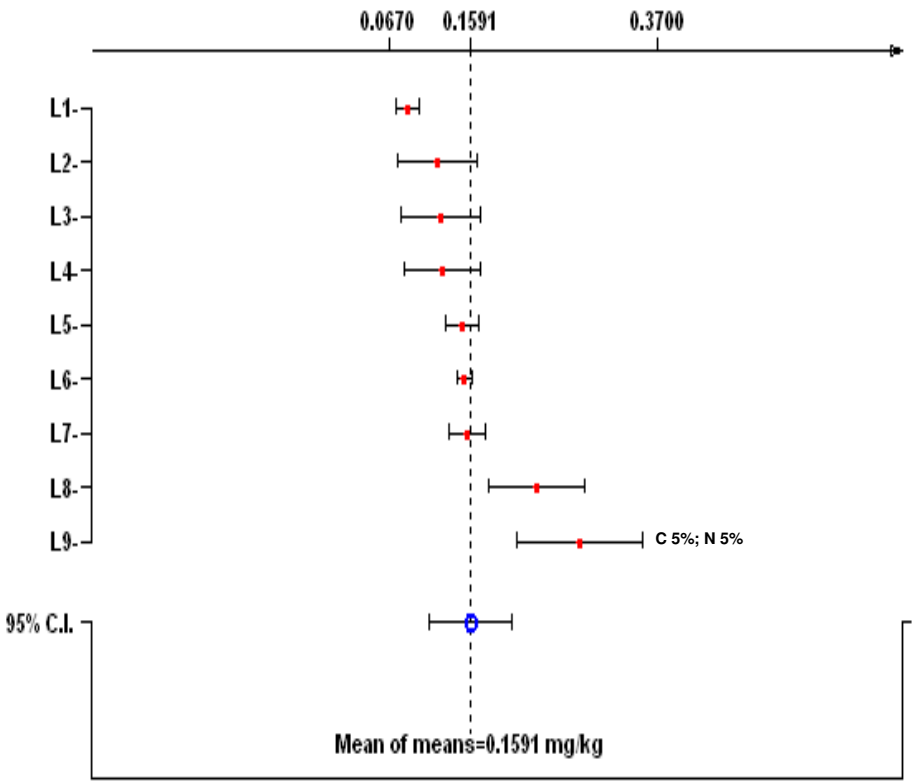
| | |
|---|---|
| Range [min..max] | [ 0.0670 .. 0.3700 ] |
| | Case of No Pooling |
| Mean of means | 0.1591 |
| 95% H.W. Confidence Interval | 0.0466 |

**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. D3)**



**Tab. A6.5: Copper accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 0.0645 | 0.0047 | 0.0049 | 0.0730 | 0.0610 | 0.0660 | 0.0600 | 0.0640 | 0.0630 |
| L 2 | 7 GD-MS 3 | 0.0783 | 0.0286 | 0.0300 | 0.0500 | 0.1300 | 0.0600 | 0.0700 | 0.0700 | 0.0900 |
| L 3 | 13 ET AAS 3 | 0.0910 | 0.0163 | 0.0171 | 0.0800 | 0.1070 | 0.0830 | 0.1150 | 0.0740 | 0.0870 |
| L 4 | 15 ICP-SF-MS 3 | 0.0947 | 0.0212 | 0.0223 | 0.0780 | 0.1010 | 0.0810 | 0.1330 | 0.0780 | 0.0970 |
| L 5 | 19 ETV-ICP OES 3 | 0.0973 | 0.0193 | 0.0202 | 0.1063 | 0.1040 | 0.0889 | 0.1270 | 0.0851 | 0.0722 |
| L 6 | 27 GD-MS 2 | 0.1033 | 0.0547 | 0.0574 | 0.1000 | 0.2000 | 0.0700 | 0.0600 | 0.0600 | 0.1300 |
| L 7 | 28 ICP OES 2 | 0.1500 | 0.0548 | 0.0575 | 0.1000 | 0.1000 | 0.2000 | 0.1000 | 0.2000 | 0.2000 |

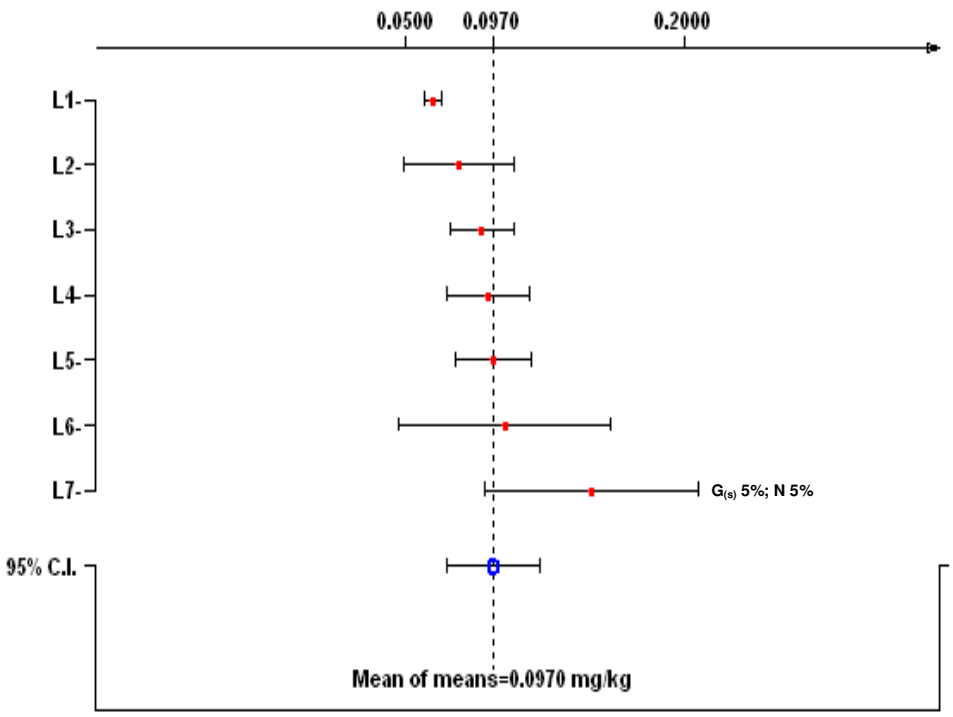
| | |
|---|---|
| Range [min..max] | [ 0.0500 .. 0.2000 ] |
| | Case of No Pooling |
| Mean of means | 0.0970 |
| 95% H.W. Confidence Interval | 0.0247 |

**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. E1)**



**Tab. A6.6.1: Iron evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 3.893 | 0.157 | 0.164 | 3.760 | 3.710 | 4.000 | 4.060 | 4.040 | 3.790 |
| L 2 | 21 ETV-ICP OES 2 | 4.350 | 1.169 | 1.227 | 4.600 | 4.000 | 3.800 | 3.500 | 3.600 | 6.600 |
| L 3 | 27 GD-MS 3 | 4.633 | 1.117 | 1.172 | 3.500 | 3.200 | 4.500 | 5.000 | 5.700 | 5.900 |
| L 4 | 7 GD-MS 3 | 4.717 | 0.773 | 0.811 | 4.400 | 6.100 | 4.000 | 4.200 | 4.500 | 5.100 |
| L 5 | 9 DC Arc OES (3) | 4.717 | 0.445 | 0.467 | 4.700 | 4.200 | 4.300 | 5.000 | 5.400 | 4.700 |
| L 6 | 19 ETV-ICP OES 3 | 4.770 | 0.439 | 0.461 | 5.500 | 4.400 | 4.290 | 4.790 | 4.990 | 4.650 |
| L 7 | 11 INAA 2 | 4.780 | 0.315 | 0.331 | 5.108 | 4.769 | 4.301 | 4.540 | 4.880 | 5.082 |
| L 8 | 15 ICP-SF-MS 3 | 4.942 | 0.292 | 0.307 | 5.080 | 5.120 | 4.780 | 4.830 | 4.510 | 5.330 |
| L 9 | 14 ICP OES 2 | 5.053 | 0.372 | 0.391 | 4.660 | 4.760 | 4.820 | 5.090 | 5.550 | 5.440 |
| L 10 | 13 ET AAS 3 | 5.127 | 0.270 | 0.284 | 5.250 | 5.420 | 5.100 | 5.070 | 4.640 | 5.280 |
| L 11 | 29 ICP-MS (3) | 5.173 | 0.260 | 0.273 | 4.780 | 5.500 | 5.270 | 5.310 | 5.220 | 4.960 |
| L 12 | 4 ETV-ICP OES 3 | 5.333 | 0.516 | 0.542 | 5.000 | 5.000 | 6.000 | 5.000 | 6.000 | 5.000 |
| L 13 | 28 ICP OES 2 | 10.000 | 1.414 | 1.484 | 10.000 | 8.000 | 11.000 | 12.000 | 9.000 | 10.000 |
| L 14 | 2 XRF 2 | 14.833 | 1.169 | 1.227 | 15.000 | 13.000 | 16.000 | 15.000 | 14.000 | 16.000 |
| L 15 | 3 ICP OES 2 | 18.700 | 9.014 | 9.459 | 11.700 | 9.900 | 32.000 | 27.400 | 13.600 | 17.600 |

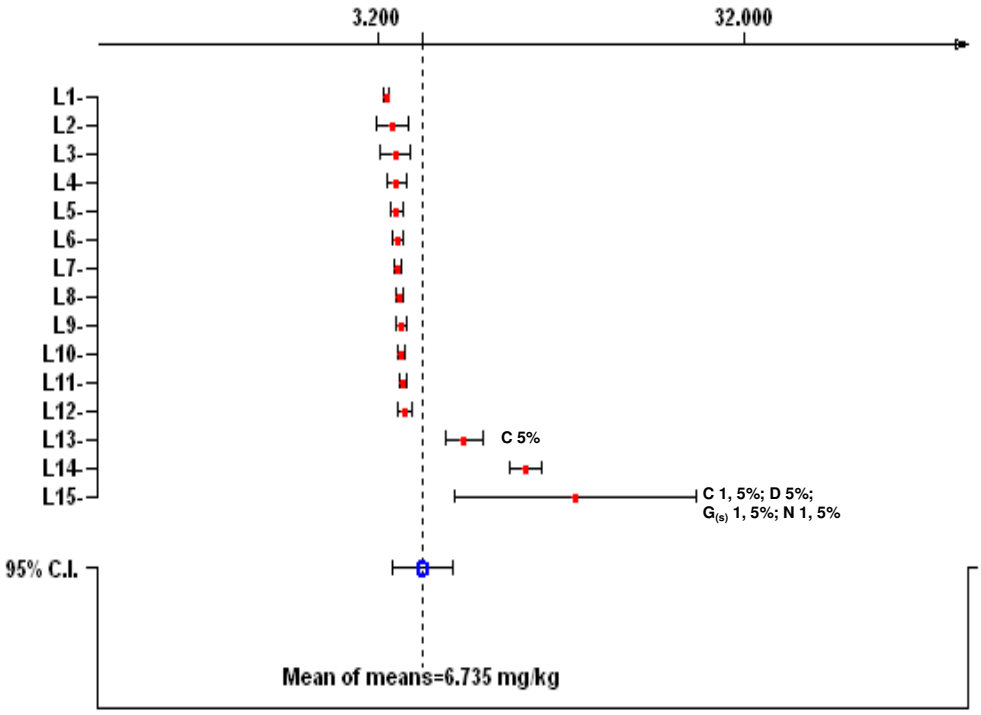
| | |
|---|---|
| Range [min..max] | [ 3.200 .. 32.000 ] |
| | Case of No Pooling |
| Mean of means | 6.735 |
| 95% H.W. Confidence Interval | 2.416 |

**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. F1)**



**Tab. A6.6.2: Iron evaluation in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 3.893 | 0.157 | 0.164 | 3.760 | 3.710 | 4.000 | 4.060 | 4.040 | 3.790 |
| L 2 | 21 ETV-ICP OES 2 | 4.350 | 1.169 | 1.227 | 4.600 | 4.000 | 3.800 | 3.500 | 3.600 | 6.600 |
| L 3 | 27 GD-MS 3 | 4.633 | 1.117 | 1.172 | 3.500 | 3.200 | 4.500 | 5.000 | 5.700 | 5.900 |
| L 4 | 7 GD-MS 3 | 4.717 | 0.773 | 0.811 | 4.400 | 6.100 | 4.000 | 4.200 | 4.500 | 5.100 |
| L 5 | 9 DC Arc OES (3) | 4.717 | 0.445 | 0.467 | 4.700 | 4.200 | 4.300 | 5.000 | 5.400 | 4.700 |
| L 6 | 19 ETV-ICP OES 3 | 4.770 | 0.439 | 0.461 | 5.500 | 4.400 | 4.290 | 4.790 | 4.990 | 4.650 |
| L 7 | 11 INAA 2 | 4.780 | 0.315 | 0.331 | 5.108 | 4.769 | 4.301 | 4.540 | 4.880 | 5.082 |
| L 8 | 15 ICP-SF-MS 3 | 4.942 | 0.292 | 0.307 | 5.080 | 5.120 | 4.780 | 4.830 | 4.510 | 5.330 |
| L 9 | 14 ICP OES 2 | 5.053 | 0.372 | 0.391 | 4.660 | 4.760 | 4.820 | 5.090 | 5.550 | 5.440 |
| L 10 | 13 ET AAS 3 | 5.127 | 0.270 | 0.284 | 5.250 | 5.420 | 5.100 | 5.070 | 4.640 | 5.280 |
| L 11 | 29 ICP-MS (3) | 5.173 | 0.260 | 0.273 | 4.780 | 5.500 | 5.270 | 5.310 | 5.220 | 4.960 |
| L 12 | 4 ETV-ICP OES 3 | 5.333 | 0.516 | 0.542 | 5.000 | 5.000 | 6.000 | 5.000 | 6.000 | 5.000 |
| L 13 | 28 ICP OES 2 | 10.000 | 1.414 | 1.484 | 10.000 | 8.000 | 11.000 | 12.000 | 9.000 | 10.000 |
| L 14 | 2 XRF 2 | 14.833 | 1.169 | 1.227 | 15.000 | 13.000 | 16.000 | 15.000 | 14.000 | 16.000 |

| | |
|---|---|
| Range [min..max] | [ 3.200 .. 16.000 ] |
| | Case of No Pooling |
| Mean of means | 5.880 |
| 95% H.W. Confidence Interval | 1.703 |

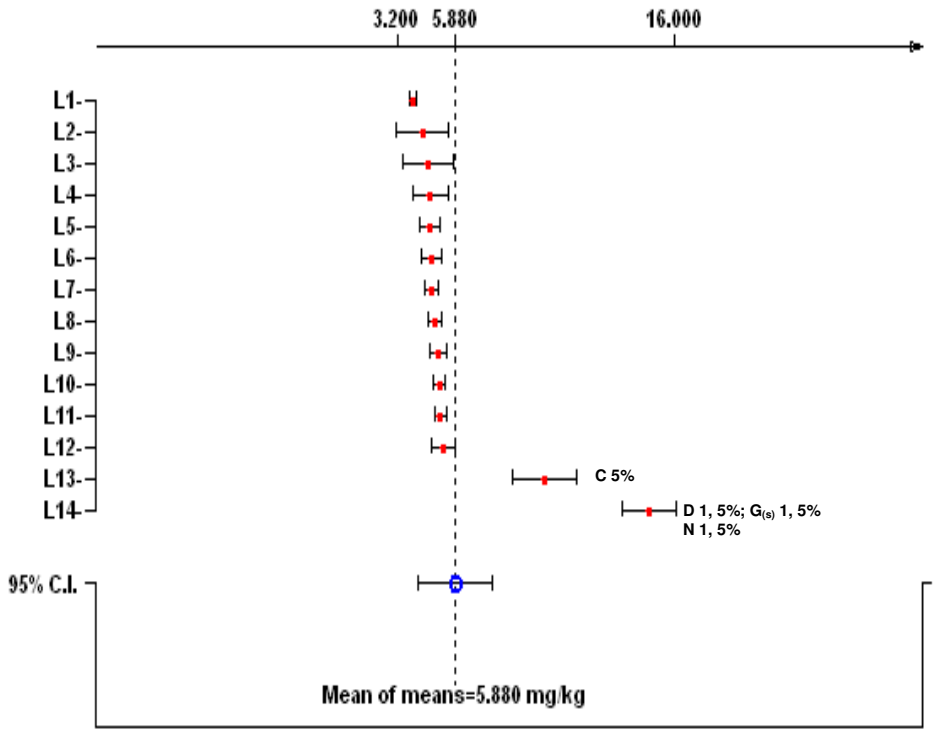
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. F2)**



**Tab. A6.6.3: Iron evaluation in run 3 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 3.893 | 0.157 | 0.164 | 3.760 | 3.710 | 4.000 | 4.060 | 4.040 | 3.790 |
| L 2 | 21 ETV-ICP OES 2 | 4.350 | 1.169 | 1.227 | 4.600 | 4.000 | 3.800 | 3.500 | 3.600 | 6.600 |
| L 3 | 27 GD-MS 3 | 4.633 | 1.117 | 1.172 | 3.500 | 3.200 | 4.500 | 5.000 | 5.700 | 5.900 |
| L 4 | 7 GD-MS 3 | 4.717 | 0.773 | 0.811 | 4.400 | 6.100 | 4.000 | 4.200 | 4.500 | 5.100 |
| L 5 | 9 DC Arc OES (3) | 4.717 | 0.445 | 0.467 | 4.700 | 4.200 | 4.300 | 5.000 | 5.400 | 4.700 |
| L 6 | 19 ETV-ICP OES 3 | 4.770 | 0.439 | 0.461 | 5.500 | 4.400 | 4.290 | 4.790 | 4.990 | 4.650 |
| L 7 | 11 INAA 2 | 4.780 | 0.315 | 0.331 | 5.108 | 4.769 | 4.301 | 4.540 | 4.880 | 5.082 |
| L 8 | 15 ICP-SF-MS 3 | 4.942 | 0.292 | 0.307 | 5.080 | 5.120 | 4.780 | 4.830 | 4.510 | 5.330 |
| L 9 | 14 ICP OES 2 | 5.053 | 0.372 | 0.391 | 4.660 | 4.760 | 4.820 | 5.090 | 5.550 | 5.440 |
| L 10 | 13 ET AAS 3 | 5.127 | 0.270 | 0.284 | 5.250 | 5.420 | 5.100 | 5.070 | 4.640 | 5.280 |
| L 11 | 29 ICP-MS (3) | 5.173 | 0.260 | 0.273 | 4.780 | 5.500 | 5.270 | 5.310 | 5.220 | 4.960 |
| L 12 | 4 ETV-ICP OES 3 | 5.333 | 0.516 | 0.542 | 5.000 | 5.000 | 6.000 | 5.000 | 6.000 | 5.000 |
| L 13 | 28 ICP OES 2 | 10.000 | 1.414 | 1.484 | 10.000 | 8.000 | 11.000 | 12.000 | 9.000 | 10.000 |

| | |
|---|---|
| Range [min..max] | [ 3.200 .. 12.000 ] |
| | Case of No Pooling |
| Mean of means | 5.191 |
| 95% H.W. Confidence Interval | 0.902 |

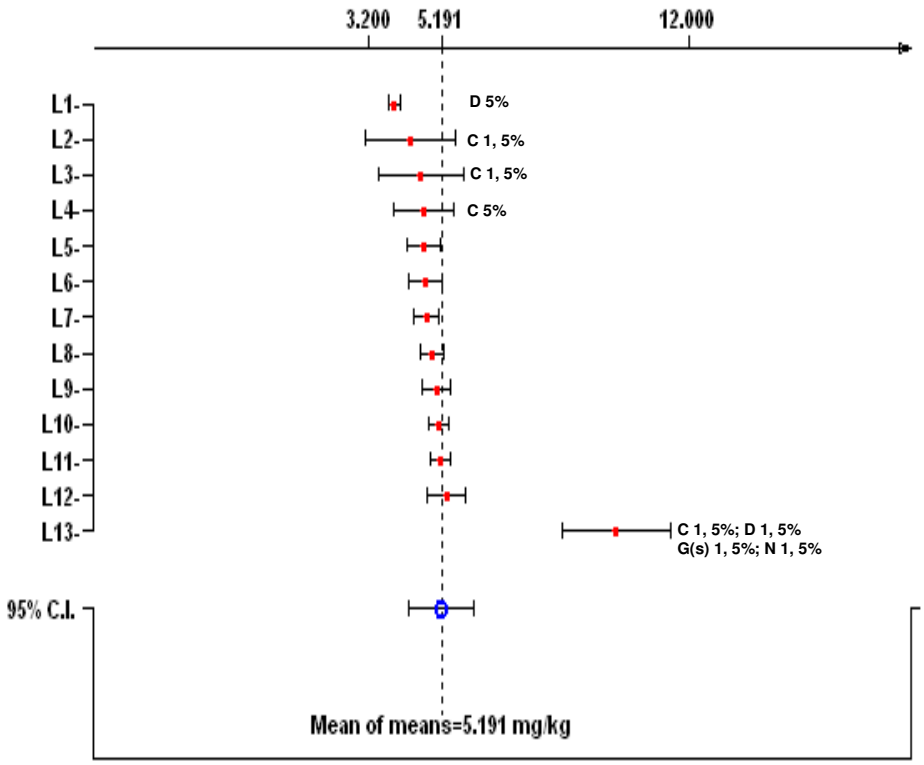
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. F3)**



**Tab. A6.6.4: Iron accepted results in run 4 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 3.893 | 0.157 | 0.164 | 3.760 | 3.710 | 4.000 | 4.060 | 4.040 | 3.790 |
| L 2 | 21 ETV-ICP OES 2 | 4.350 | 1.169 | 1.227 | 4.600 | 4.000 | 3.800 | 3.500 | 3.600 | 6.600 |
| L 3 | 27 GD-MS 3 | 4.633 | 1.117 | 1.172 | 3.500 | 3.200 | 4.500 | 5.000 | 5.700 | 5.900 |
| L 4 | 7 GD-MS 3 | 4.717 | 0.773 | 0.811 | 4.400 | 6.100 | 4.000 | 4.200 | 4.500 | 5.100 |
| L 5 | 9 DC Arc OES (3) | 4.717 | 0.445 | 0.467 | 4.700 | 4.200 | 4.300 | 5.000 | 5.400 | 4.700 |
| L 6 | 19 ETV-ICP OES 3 | 4.770 | 0.439 | 0.461 | 5.500 | 4.400 | 4.290 | 4.790 | 4.990 | 4.650 |
| L 7 | 11 INAA 2 | 4.780 | 0.315 | 0.331 | 5.108 | 4.769 | 4.301 | 4.540 | 4.880 | 5.082 |
| L 8 | 15 ICP-SF-MS 3 | 4.942 | 0.292 | 0.307 | 5.080 | 5.120 | 4.780 | 4.830 | 4.510 | 5.330 |
| L 9 | 14 ICP OES 2 | 5.053 | 0.372 | 0.391 | 4.660 | 4.760 | 4.820 | 5.090 | 5.550 | 5.440 |
| L 10 | 13 ET AAS 3 | 5.127 | 0.270 | 0.284 | 5.250 | 5.420 | 5.100 | 5.070 | 4.640 | 5.280 |
| L 11 | 29 ICP-MS (3) | 5.173 | 0.260 | 0.273 | 4.780 | 5.500 | 5.270 | 5.310 | 5.220 | 4.960 |
| L 12 | 4 ETV-ICP OES 3 | 5.333 | 0.516 | 0.542 | 5.000 | 5.000 | 6.000 | 5.000 | 6.000 | 5.000 |

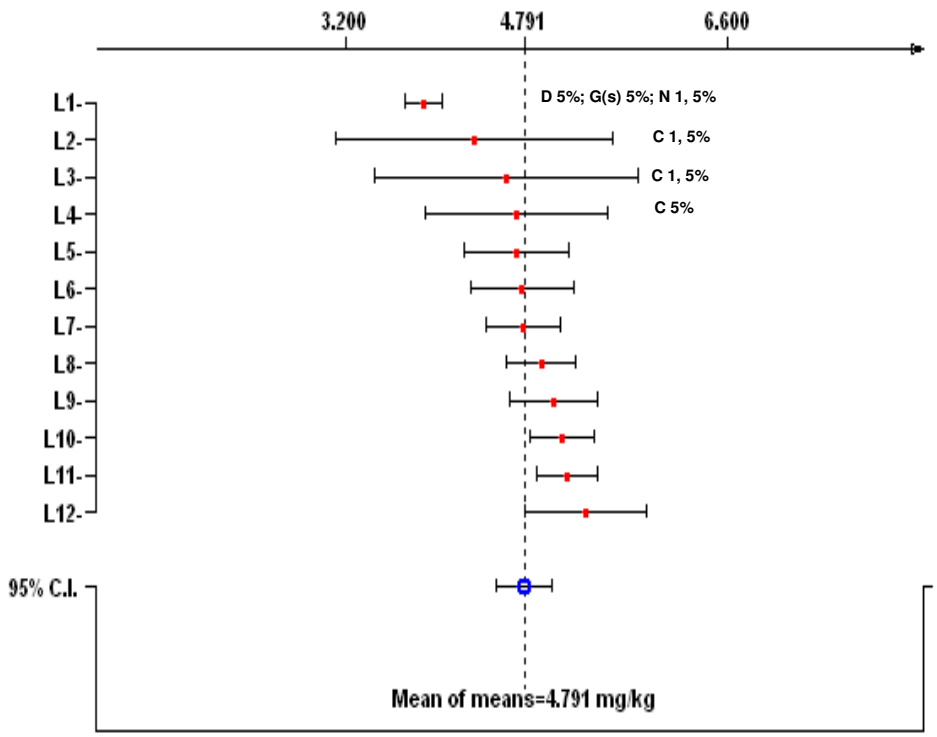
| | |
|---|---|
| Range [min..max] | [ 3.200 .. 6.600 ] |
| | Case of No Pooling |
| Mean of means | 4.791 |
| 95% H.W. Confidence Interval | 0.248 |

**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. F4)**



**Tab. A6.7.1: Magnesium evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.0280 | 0.0082 | 0.0086 | 0.0413 | 0.0166 | 0.0243 | 0.0304 | 0.0301 | 0.0251 |
| L 2 | 13 ET AAS 3 | 0.0288 | 0.0048 | 0.0050 | 0.0290 | 0.0240 | 0.0310 | 0.0230 | 0.0300 | 0.0360 |
| L 3 | 9 ETV-ICP OES 3 | 0.0385 | 0.0035 | 0.0037 | 0.0340 | 0.0420 | 0.0390 | 0.0360 | 0.0430 | 0.0370 |
| L 4 | 14 ETV-ICP OES 2 | 0.0553 | 0.0208 | 0.0218 | 0.0860 | 0.0680 | 0.0650 | 0.0410 | 0.0390 | 0.0330 |
| L 5 | 21 ETV-ICP OES 2 | 0.0563 | 0.0225 | 0.0236 | 0.0490 | 0.0320 | 0.0400 | 0.0550 | 0.0950 | 0.0670 |
| L 6 | 7 GD-MS 3 | 0.1100 | 0.0506 | 0.0531 | 0.0400 | 0.0900 | 0.1000 | 0.1400 | 0.1900 | 0.1000 |
| L 7 | 28 ICP OES 2 | 0.1667 | 0.0816 | 0.0857 | 0.1000 | 0.2000 | 0.1000 | 0.3000 | 0.1000 | 0.2000 |
| L 8 | 27 GD-MS 3 | 0.2217 | 0.1999 | 0.2098 | 0.0500 | 0.5000 | 0.0500 | 0.4400 | 0.1000 | 0.1900 |

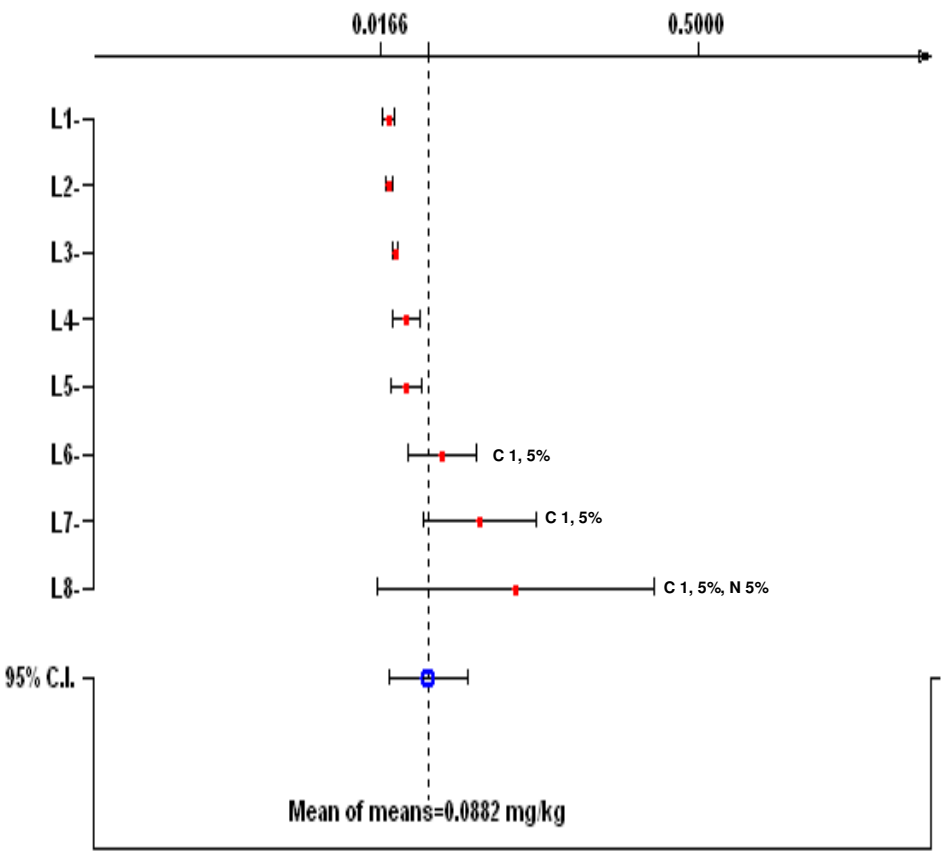
| | |
|---|---|
| Range [min..max] | [ 0.0166 .. 0.5000 ] |
| | Case of No Pooling |
| Mean of means | 0.0882 |
| 95% H.W. Confidence Interval | 0.0601 |

**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. G1)**



**Tab. A6.7.2: Magnesium accepted results in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.0280 | 0.0082 | 0.0086 | 0.0413 | 0.0166 | 0.0243 | 0.0304 | 0.0301 | 0.0251 |
| L 2 | 13 ET AAS 3 | 0.0288 | 0.0048 | 0.0050 | 0.0290 | 0.0240 | 0.0310 | 0.0230 | 0.0300 | 0.0360 |
| L 3 | 9 ETV-ICP OES 3 | 0.0385 | 0.0035 | 0.0037 | 0.0340 | 0.0420 | 0.0390 | 0.0360 | 0.0430 | 0.0370 |
| L 4 | 14 ETV-ICP OES 2 | 0.0553 | 0.0208 | 0.0218 | 0.0860 | 0.0680 | 0.0650 | 0.0410 | 0.0390 | 0.0330 |
| L 5 | 21 ETV-ICP OES 2 | 0.0563 | 0.0225 | 0.0236 | 0.0490 | 0.0320 | 0.0400 | 0.0550 | 0.0950 | 0.0670 |
| L 6 | 7 GD-MS 3 | 0.1100 | 0.0506 | 0.0531 | 0.0400 | 0.0900 | 0.1000 | 0.1400 | 0.1900 | 0.1000 |
| L 7 | 28 ICP OES 2 | 0.1667 | 0.0816 | 0.0857 | 0.1000 | 0.2000 | 0.1000 | 0.3000 | 0.1000 | 0.2000 |

| | |
|---|---|
| Range [min..max] | [ 0.0166 .. 0.3000 ] |
| | Case of No Pooling |
| Mean of means | 0.0691 |
| 95% H.W. Confidence Interval | 0.0475 |

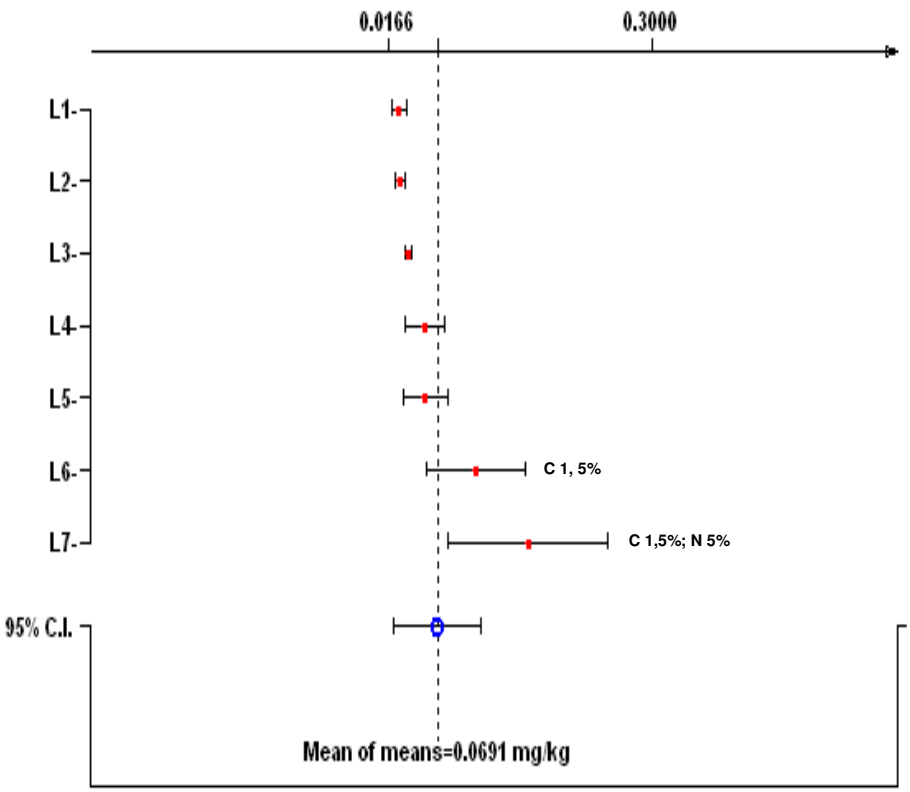
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. G2)**



**Tab. A6.8.1: Manganese evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.0329 | 0.0044 | 0.0046 | 0.0348 | 0.0401 | 0.0303 | 0.0343 | 0.0282 | 0.0295 |
| L 2 | 7 GD-MS 3 | 0.0450 | 0.0084 | 0.0088 | 0.0400 | 0.0400 | 0.0400 | 0.0500 | 0.0600 | 0.0400 |
| L 3 | 11 INAA 2 | 0.0468 | 0.0012 | 0.0013 | 0.0487 | 0.0452 | 0.0458 | 0.0472 | 0.0472 | 0.0468 |
| L 4 | 9 ETV-ICP OES 3 | 0.0472 | 0.0044 | 0.0046 | 0.0530 | 0.0450 | 0.0420 | 0.0450 | 0.0520 | 0.0460 |
| L 5 | 27 GD-MS 3 | 0.0500 | 0.0141 | 0.0148 | 0.0400 | 0.0500 | 0.0300 | 0.0700 | 0.0600 | 0.0500 |
| L 6 | 13 ET AAS 3 | 0.0517 | 0.0053 | 0.0055 | 0.0510 | 0.0520 | 0.0520 | 0.0490 | 0.0450 | 0.0610 |
| L 7 | 15 ICP-SF-MS 3 | 0.0545 | 0.0040 | 0.0042 | 0.0540 | 0.0570 | 0.0570 | 0.0540 | 0.0470 | 0.0580 |
| L 8 | 6 INAA 2 | 0.0637 | 0.0037 | 0.0039 | 0.0580 | 0.0600 | 0.0660 | 0.0660 | 0.0670 | 0.0650 |
| L 9 | 29 ICP-MS 3 | 0.0640 | 0.0039 | 0.0041 | 0.0600 | 0.0700 | 0.0660 | 0.0660 | 0.0610 | 0.0610 |
| L 10 | 21 ETV-ICP OES 2 | 0.1017 | 0.0264 | 0.0277 | 0.1400 | 0.1100 | 0.0900 | 0.0600 | 0.1000 | 0.1100 |
| L 11 | 28 ICP OES 2 | 0.1333 | 0.0516 | 0.0542 | 0.2000 | 0.2000 | 0.1000 | 0.1000 | 0.1000 | 0.1000 |

| | |
|---|---|
| Range [min..max] | [ 0.0282 .. 0.2000 ] |
| | Case of No Pooling |
| Mean of means | 0.0628 |
| 95% H.W. Confidence Interval | 0.0197 |

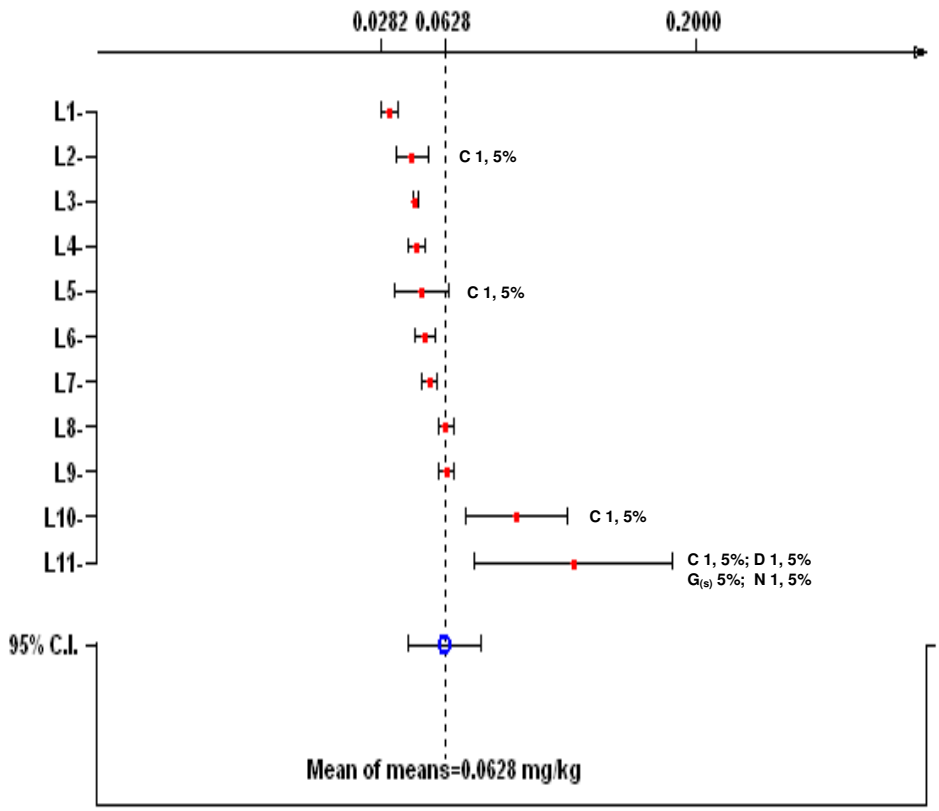
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. H1)**



**Tab. A6.8.2: Manganese evaluation in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.0329 | 0.0044 | 0.0046 | 0.0348 | 0.0401 | 0.0303 | 0.0343 | 0.0282 | 0.0295 |
| L 2 | 7 GD-MS 3 | 0.0450 | 0.0084 | 0.0088 | 0.0400 | 0.0400 | 0.0400 | 0.0500 | 0.0600 | 0.0400 |
| L 3 | 11 INAA 2 | 0.0468 | 0.0012 | 0.0013 | 0.0487 | 0.0452 | 0.0458 | 0.0472 | 0.0472 | 0.0468 |
| L 4 | 9 ETV-ICP OES 3 | 0.0472 | 0.0044 | 0.0046 | 0.0530 | 0.0450 | 0.0420 | 0.0450 | 0.0520 | 0.0460 |
| L 5 | 27 GD-MS 3 | 0.0500 | 0.0141 | 0.0148 | 0.0400 | 0.0500 | 0.0300 | 0.0700 | 0.0600 | 0.0500 |
| L 6 | 13 ET AAS 3 | 0.0517 | 0.0053 | 0.0055 | 0.0510 | 0.0520 | 0.0520 | 0.0490 | 0.0450 | 0.0610 |
| L 7 | 15 ICP-SF-MS 3 | 0.0545 | 0.0040 | 0.0042 | 0.0540 | 0.0570 | 0.0570 | 0.0540 | 0.0470 | 0.0580 |
| L 8 | 6 INAA 2 | 0.0637 | 0.0037 | 0.0039 | 0.0580 | 0.0600 | 0.0660 | 0.0660 | 0.0670 | 0.0650 |
| L 9 | 29 ICP-MS 3 | 0.0640 | 0.0039 | 0.0041 | 0.0600 | 0.0700 | 0.0660 | 0.0660 | 0.0610 | 0.0610 |
| L 10 | 21 ETV-ICP OES 2 | 0.1017 | 0.0264 | 0.0277 | 0.1400 | 0.1100 | 0.0900 | 0.0600 | 0.1000 | 0.1100 |

| | |
|---|---|
| Range [min..max] | [ 0.0282 .. 0.1400 ] |
| | Case of No Pooling |
| Mean of means | 0.0557 |
| 95% H.W. Confidence Interval | 0.0132 |

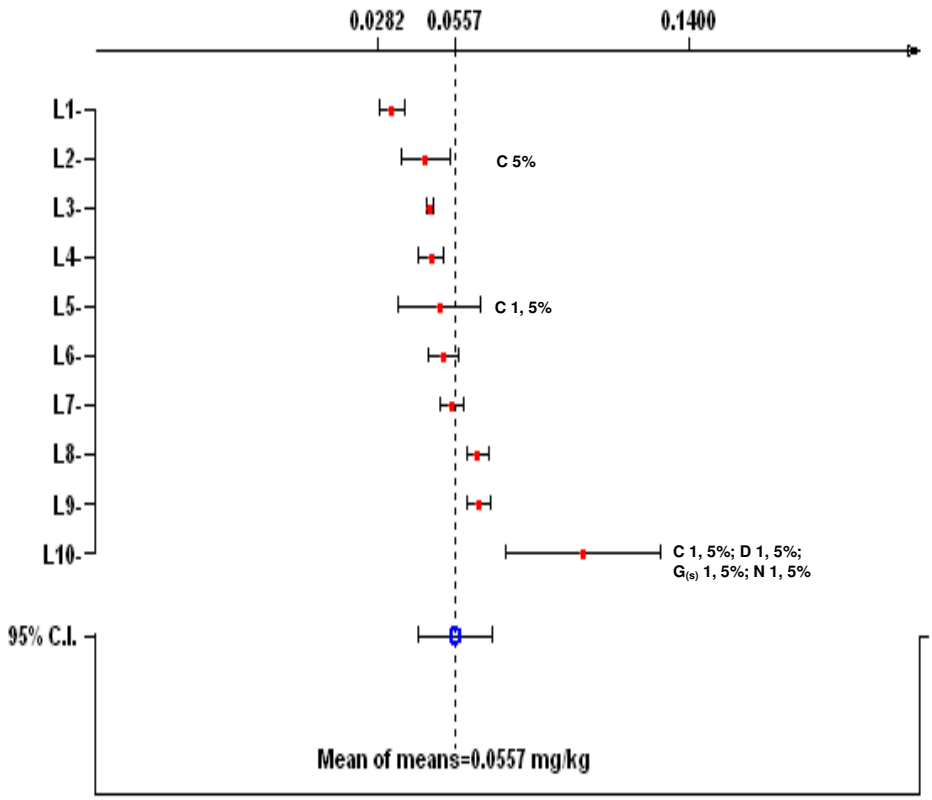
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. H2)**



**Tab. A6.8.3: Manganese accepted results in run 3 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 19 ETV-ICP OES 3 | 0.0329 | 0.0044 | 0.0046 | 0.0348 | 0.0401 | 0.0303 | 0.0343 | 0.0282 | 0.0295 |
| L 2 | 7 GD-MS 3 | 0.0450 | 0.0084 | 0.0088 | 0.0400 | 0.0400 | 0.0400 | 0.0500 | 0.0600 | 0.0400 |
| L 3 | 11 INAA 2 | 0.0468 | 0.0012 | 0.0013 | 0.0487 | 0.0452 | 0.0458 | 0.0472 | 0.0472 | 0.0468 |
| L 4 | 9 ETV-ICP OES 3 | 0.0472 | 0.0044 | 0.0046 | 0.0530 | 0.0450 | 0.0420 | 0.0450 | 0.0520 | 0.0460 |
| L 5 | 27 GD-MS 3 | 0.0500 | 0.0141 | 0.0148 | 0.0400 | 0.0500 | 0.0300 | 0.0700 | 0.0600 | 0.0500 |
| L 6 | 13 ET AAS 3 | 0.0517 | 0.0053 | 0.0055 | 0.0510 | 0.0520 | 0.0520 | 0.0490 | 0.0450 | 0.0610 |
| L 7 | 15 ICP-SF-MS 3 | 0.0545 | 0.0040 | 0.0042 | 0.0540 | 0.0570 | 0.0570 | 0.0540 | 0.0470 | 0.0580 |
| L 8 | 6 INAA 2 | 0.0637 | 0.0037 | 0.0039 | 0.0580 | 0.0600 | 0.0660 | 0.0660 | 0.0670 | 0.0650 |
| L 9 | 29 ICP-MS 3 | 0.0640 | 0.0039 | 0.0041 | 0.0600 | 0.0700 | 0.0660 | 0.0660 | 0.0610 | 0.0610 |

| | |
|---|---|
| Range [min..max] | [ 0.0282 .. 0.0700 ] |
| | Case of No Pooling |
| Mean of means | 0.0506 |
| 95% H.W. Confidence Interval | 0.0074 |

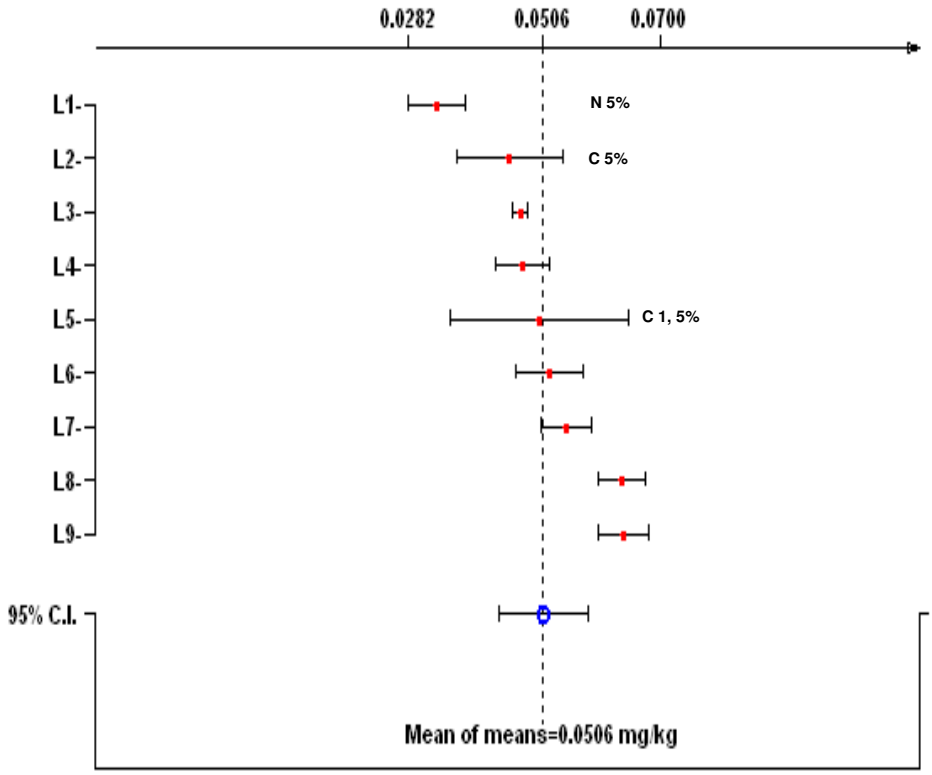
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. H3)**



**Tab. A6.9: Sodium accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 15 ICP-SF-MS 3 | 0.1015 | 0.0148 | 0.0156 | 0.0820 | 0.1020 | 0.1120 | 0.1240 | 0.0960 | 0.0930 |
| L 2 | 13 ET AAS 3 | 0.1070 | 0.0153 | 0.0161 | 0.0980 | 0.1270 | 0.0900 | 0.1230 | 0.0950 | 0.1090 |
| L 3 | 7 SS ET AAS 3 | 0.1267 | 0.0216 | 0.0227 | 0.1400 | 0.1100 | 0.1200 | 0.1600 | 0.1300 | 0.1000 |
| L 4 | 11 INAA 2 | 0.1631 | 0.0412 | 0.0432 | 0.1413 | 0.1467 | 0.1241 | 0.1696 | 0.1553 | 0.2413 |
| L 5 | 28 ET AAS 2 | 0.1667 | 0.0516 | 0.0542 | 0.1000 | 0.2000 | 0.2000 | 0.2000 | 0.1000 | 0.2000 |
| L 6 | 27 GD-MS 3 | 0.2133 | 0.0804 | 0.0844 | 0.2000 | 0.2900 | 0.1400 | 0.2600 | 0.2900 | 0.1000 |
| L 7 | 9 ETV-ICP OES 3 | 0.2293 | 0.0195 | 0.0204 | 0.2390 | 0.2550 | 0.2100 | 0.2250 | 0.2050 | 0.2420 |
| L 8 | 21 ETV-ICP OES 2 | 0.2617 | 0.1175 | 0.1234 | 0.2500 | 0.2800 | 0.2400 | 0.4700 | 0.1100 | 0.2200 |

| | |
|---|---|
| Range [min..max] | [ 0.0820 .. 0.4700 ] |
| | Case of No Pooling |
| Mean of means | 0.1712 |
| 95% H.W. Confidence Interval | 0.0493 |

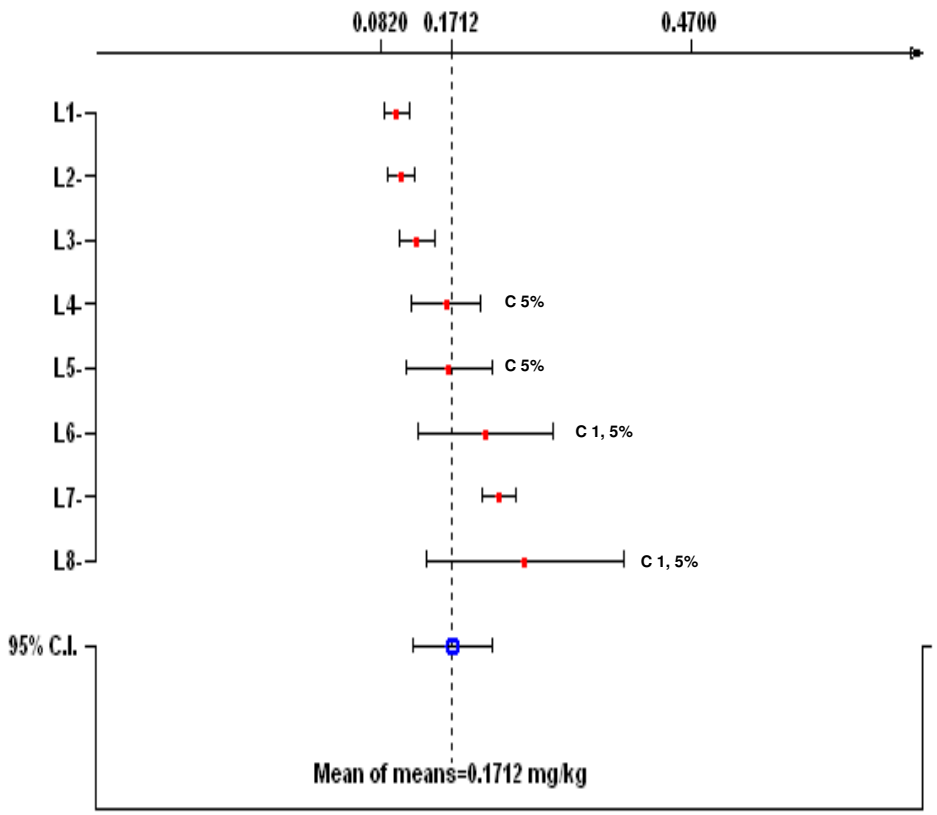
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. I1)**



**Tab. A6.10: Nickel accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 0.4950 | 0.0291 | 0.0305 | 0.5080 | 0.4850 | 0.4930 | 0.5460 | 0.4670 | 0.4710 |
| L 2 | 19 ETV-ICP OES 3 | 0.4952 | 0.1645 | 0.1727 | 0.5511 | 0.7215 | 0.4773 | 0.4262 | 0.5663 | 0.2290 |
| L 3 | 21 ETV-ICP OES 2 | 0.5317 | 0.0691 | 0.0725 | 0.5100 | 0.4600 | 0.4900 | 0.6600 | 0.5300 | 0.5400 |
| L 4 | 27 GD-MS 3 | 0.5767 | 0.2682 | 0.2814 | 0.3000 | 1.0000 | 0.5000 | 0.4800 | 0.3800 | 0.8000 |
| L 5 | 15 ICP-SF-MS 3 | 0.8633 | 0.1005 | 0.1055 | 0.9000 | 0.9400 | 0.7600 | 0.8900 | 0.7200 | 0.9700 |
| L 6 | 7 GD-MS 3 | 0.9083 | 0.2049 | 0.2150 | 0.7400 | 0.9000 | 0.8400 | 0.8700 | 0.7900 | 1.3100 |
| L 7 | 13 ET AAS 3 | 0.9400 | 0.1055 | 0.1107 | 0.9500 | 1.0200 | 0.8100 | 0.9700 | 0.8200 | 1.0700 |
| L 8 | 29 ICP-MS 3 | 1.0438 | 0.0603 | 0.0633 | 0.9620 | 1.0850 | 1.0640 | 1.1000 | 1.0790 | 0.9730 |
| L 9 | 28 ICP OES 2 | 1.2000 | 0.0894 | 0.0939 | 1.3000 | 1.1000 | 1.3000 | 1.2000 | 1.2000 | 1.1000 |
| L 10 | 4 ETV-ICP OES 3 | 1.6667 | 0.5164 | 0.5419 | 1.5000 | 2.5000 | 1.5000 | 1.0000 | 1.5000 | 2.0000 |

| | |
|---|---|
| Range [min..max] | [ 0.2290 .. 2.5000 ] |
| | Case of No Pooling |
| Mean of means | 0.8721 |
| 95% H.W. Confidence Interval | 0.2678 |

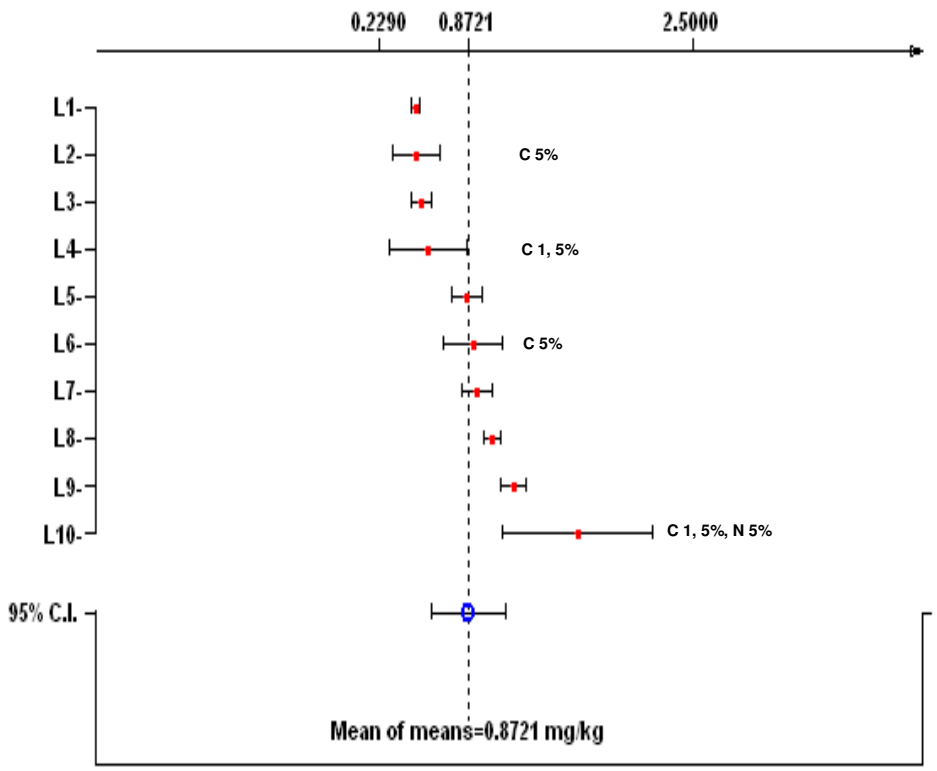
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. J1)**



**Tab. A6.11.1: Titanium evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 21 ETV-ICP OES 2 | 11.33 | 5.42 | 5.68 | 9.40 | 10.40 | 8.20 | 5.70 | 13.10 | 21.20 |
| L 2 | 27 GD-MS 3 | 46.33 | 12.09 | 12.69 | 60.00 | 30.00 | 38.00 | 48.00 | 42.00 | 60.00 |
| L 3 | 19 ETV-ICP OES 3 | 53.32 | 9.59 | 10.06 | 59.70 | 41.08 | 48.46 | 53.03 | 68.44 | 49.20 |
| L 4 | 28 ICP OES 2 | 54.50 | 1.05 | 1.10 | 53.00 | 54.00 | 56.00 | 55.00 | 55.00 | 54.00 |
| L 5 | 14 DC Arc OES (-) | 61.23 | 6.83 | 7.17 | 61.80 | 59.00 | 57.30 | 51.70 | 70.70 | 66.90 |
| L 6 | 7 DC Arc OES 3 | 63.67 | 3.56 | 3.73 | 60.00 | 61.00 | 61.00 | 66.00 | 65.00 | 69.00 |
| L 7 | 4 DC Arc OES (3) | 70.00 | 12.46 | 13.07 | 68.00 | 83.00 | 47.00 | 77.00 | 70.00 | 75.00 |
| L 8 | 13 ET AAS 3 | 70.75 | 4.00 | 4.20 | 77.00 | 71.50 | 69.10 | 65.60 | 68.30 | 73.00 |
| L 9 | 14 ICP OES 2 | 71.35 | 3.01 | 3.16 | 70.50 | 76.60 | 72.50 | 70.60 | 70.30 | 67.60 |
| L 10 | 3 ICP OES 2 | 72.68 | 2.73 | 2.86 | 74.90 | 76.10 | 72.70 | 73.30 | 70.10 | 69.00 |
| L 11 | 15 ICP-SF-MS (-) | 73.83 | 5.36 | 5.63 | 80.90 | 74.60 | 71.20 | 67.60 | 69.50 | 79.20 |
| L 12 | 9 DC Arc OES 3 | 73.83 | 7.01 | 7.36 | 77.30 | 62.40 | 69.90 | 81.20 | 79.50 | 72.70 |
| L 13 | 29 ICP OES 3 | 74.41 | 1.04 | 1.09 | 73.89 | 73.24 | 74.86 | 75.97 | 73.50 | 74.99 |
| L 14 | 7 GD-MS 3 | 76.00 | 16.35 | 17.15 | 84.00 | 56.00 | 102.00 | 70.00 | 80.00 | 64.00 |
| L 15 | 23 ICP OES 2 | 76.47 | 3.02 | 3.17 | 72.80 | 74.80 | 80.20 | 79.20 | 77.80 | 74.00 |
| L 16 | 2 XRF 2 | 123.17 | 8.52 | 8.94 | 131.00 | 118.00 | 110.00 | 125.00 | 122.00 | 133.00 |

| | |
|---|---|
| Range [min..max] | [ 5.70 .. 133.00 ] |
| | Case of No Pooling |
| Mean of means | 67.05 |
| 95% H.W. Confidence Interval | 11.88 |

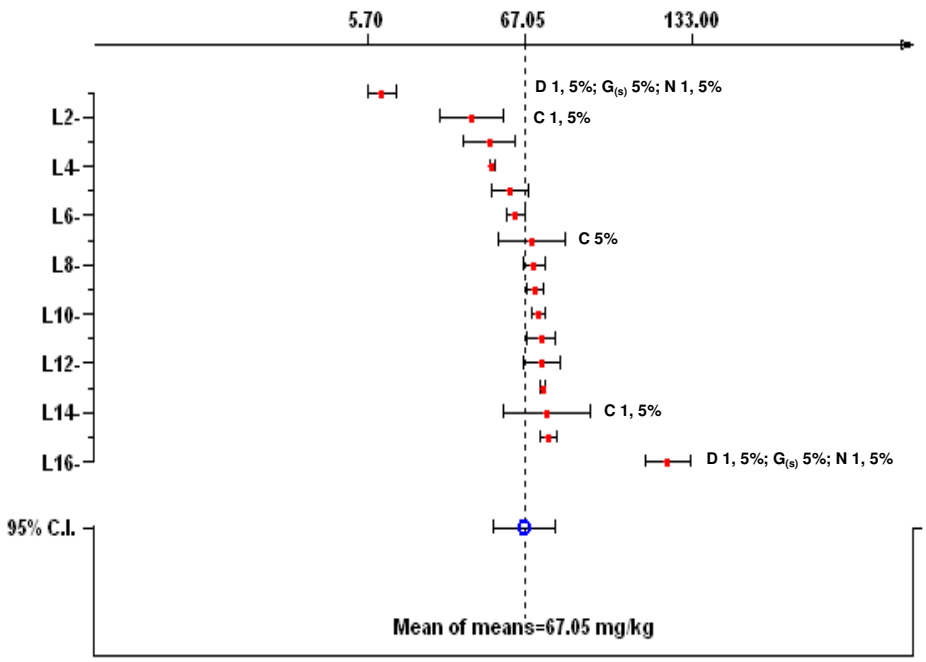
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. K1)**



**Tab. A6.11.2: Titanium accepted results in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 27 GD-MS 3 | 46.33 | 12.09 | 12.69 | 60.00 | 30.00 | 38.00 | 48.00 | 42.00 | 60.00 |
| L 2 | 19 ETV-ICP OES 3 | 53.32 | 9.59 | 10.06 | 59.70 | 41.08 | 48.46 | 53.03 | 68.44 | 49.20 |
| L 3 | 28 ICP OES 2 | 54.50 | 1.05 | 1.10 | 53.00 | 54.00 | 56.00 | 55.00 | 55.00 | 54.00 |
| L 4 | 14 DC Arc OES (-) | 61.23 | 6.83 | 7.17 | 61.80 | 59.00 | 57.30 | 51.70 | 70.70 | 66.90 |
| L 5 | 7 DC Arc OES 3 | 63.67 | 3.56 | 3.73 | 60.00 | 61.00 | 61.00 | 66.00 | 65.00 | 69.00 |
| L 6 | 4 DC Arc OES (3) | 70.00 | 12.46 | 13.07 | 68.00 | 83.00 | 47.00 | 77.00 | 70.00 | 75.00 |
| L 7 | 13 ET AAS 3 | 70.75 | 4.00 | 4.20 | 77.00 | 71.50 | 69.10 | 65.60 | 68.30 | 73.00 |
| L 8 | 14 ICP OES 2 | 71.35 | 3.01 | 3.16 | 70.50 | 76.60 | 72.50 | 70.60 | 70.30 | 67.60 |
| L 9 | 3 ICP OES 2 | 72.68 | 2.73 | 2.86 | 74.90 | 76.10 | 72.70 | 73.30 | 70.10 | 69.00 |
| L 10 | 15 ICP-SF-MS (-) | 73.83 | 5.36 | 5.63 | 80.90 | 74.60 | 71.20 | 67.60 | 69.50 | 79.20 |
| L 11 | 9 DC Arc OES 3 | 73.83 | 7.01 | 7.36 | 77.30 | 62.40 | 69.90 | 81.20 | 79.50 | 72.70 |
| L 12 | 29 ICP OES 3 | 74.41 | 1.04 | 1.09 | 73.89 | 73.24 | 74.86 | 75.97 | 73.50 | 74.99 |
| L 13 | 7 GD-MS 3 | 76.00 | 16.35 | 17.15 | 84.00 | 56.00 | 102.00 | 70.00 | 80.00 | 64.00 |
| L 14 | 23 ICP OES 2 | 76.47 | 3.02 | 3.17 | 72.80 | 74.80 | 80.20 | 79.20 | 77.80 | 74.00 |

| | |
|---|---|
| Range [min..max] | [ 30.00 .. 102.00 ] |
| | Case of No Pooling |
| Mean of means | 67.03 |
| 95% H.W. Confidence Interval | 5.57 |

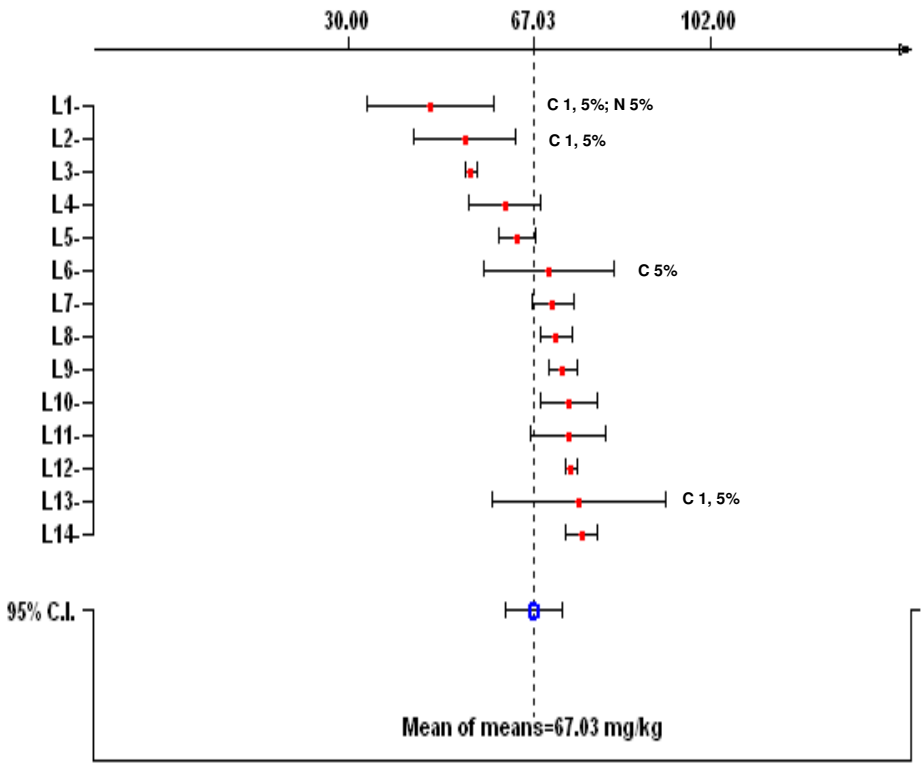
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. K2)**



**Tab. A6.12.1: Vanadium evaluation in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 27 GD-MS 3 | 210.0 | 36.9 | 38.7 | 200.0 | 200.0 | 170.0 | 280.0 | 200.0 | 210.0 |
| L 2 | 21 ETV-ICP OES 2 | 231.8 | 26.5 | 27.8 | 248.0 | 246.0 | 220.0 | 212.0 | 197.0 | 268.0 |
| L 3 | 19 ETV-ICP OES 3 | 249.3 | 76.3 | 80.1 | 192.7 | 178.5 | 274.1 | 347.8 | 178.5 | 324.0 |
| L 4 | 6 INAA (-) | 264.9 | 12.4 | 13.0 | 253.3 | 264.7 | 250.6 | 269.3 | 285.2 | 266.3 |
| L 5 | 14 DC Arc OES (-) | 268.8 | 32.4 | 34.0 | 246.0 | 267.0 | 275.0 | 223.0 | 317.0 | 285.0 |
| L 6 | 7 DC Arc OES 3 | 270.8 | 14.1 | 14.8 | 270.0 | 277.0 | 260.0 | 295.0 | 255.0 | 268.0 |
| L 7 | 9 DC Arc OES 3 | 273.3 | 21.0 | 22.0 | 289.0 | 253.0 | 295.0 | 249.0 | 292.0 | 262.0 |
| L 8 | 14 ICP OES 2 | 285.7 | 18.5 | 19.4 | 282.0 | 314.0 | 301.0 | 263.0 | 278.0 | 276.0 |
| L 9 | 4 DC Arc OES (3) | 288.0 | 21.6 | 22.7 | 270.0 | 277.0 | 326.0 | 281.0 | 301.0 | 273.0 |
| L 10 | 13 ET AAS 3 | 290.7 | 26.6 | 27.9 | 320.0 | 305.0 | 278.0 | 282.0 | 248.0 | 311.0 |
| L 11 | 3 ICP OES 2 | 294.5 | 11.0 | 11.5 | 301.0 | 308.0 | 297.0 | 298.0 | 278.0 | 285.0 |
| L 12 | 23 ICP OES 2 | 297.7 | 10.5 | 11.0 | 294.0 | 307.0 | 280.0 | 306.0 | 305.0 | 294.0 |
| L 13 | 7 GD-MS 3 | 308.3 | 77.0 | 80.9 | 340.0 | 214.0 | 434.0 | 287.0 | 324.0 | 251.0 |
| L 14 | 28 ICP OES 2 | 316.8 | 4.7 | 4.9 | 309.0 | 320.0 | 319.0 | 322.0 | 317.0 | 314.0 |
| L 15 | 2 XRF 2 | 427.8 | 27.0 | 28.3 | 456.0 | 448.0 | 380.0 | 426.0 | 420.0 | 437.0 |

| | |
|---|---|
| Range [min..max] | [ 170.0 .. 456.0 ] |
| | Case of No Pooling |
| Mean of means | 285.2 |
| 95% H.W. Confidence Interval | 26.9 |

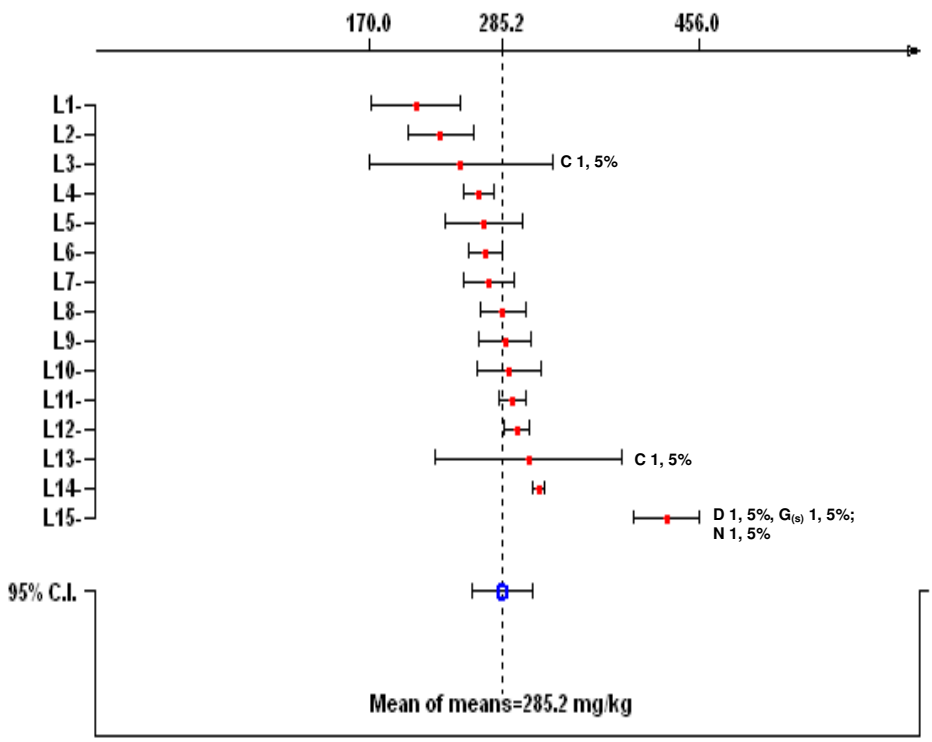
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. L1)**



**Tab. A6.12.2: Vanadium accepted results in run 2 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 27 GD-MS 3 | 210.00 | 36.88 | 38.70 | 200.00 | 200.00 | 170.00 | 280.00 | 200.00 | 210.00 |
| L 2 | 21 ETV-ICP OES 2 | 231.83 | 26.52 | 27.83 | 248.00 | 246.00 | 220.00 | 212.00 | 197.00 | 268.00 |
| L 3 | 19 ETV-ICP OES 3 | 249.27 | 76.32 | 80.10 | 192.70 | 178.50 | 274.10 | 347.80 | 178.50 | 324.00 |
| L 4 | 6 INAA (-) | 264.90 | 12.43 | 13.04 | 253.30 | 264.70 | 250.60 | 269.30 | 285.20 | 266.30 |
| L 5 | 14 DC Arc OES (-) | 268.83 | 32.39 | 33.99 | 246.00 | 267.00 | 275.00 | 223.00 | 317.00 | 285.00 |
| L 6 | 7 DC Arc OES 3 | 270.83 | 14.13 | 14.83 | 270.00 | 277.00 | 260.00 | 295.00 | 255.00 | 268.00 |
| L 7 | 9 DC Arc OES 3 | 273.33 | 20.96 | 22.00 | 289.00 | 253.00 | 295.00 | 249.00 | 292.00 | 262.00 |
| L 8 | 14 ICP OES 2 | 285.67 | 18.53 | 19.45 | 282.00 | 314.00 | 301.00 | 263.00 | 278.00 | 276.00 |
| L 9 | 4 DC Arc OES (3) | 288.00 | 21.60 | 22.66 | 270.00 | 277.00 | 326.00 | 281.00 | 301.00 | 273.00 |
| L 10 | 13 ET AAS 3 | 290.67 | 26.59 | 27.91 | 320.00 | 305.00 | 278.00 | 282.00 | 248.00 | 311.00 |
| L 11 | 3 ICP OES 2 | 294.50 | 11.00 | 11.55 | 301.00 | 308.00 | 297.00 | 298.00 | 278.00 | 285.00 |
| L 12 | 23 ICP OES 2 | 297.67 | 10.48 | 11.00 | 294.00 | 307.00 | 280.00 | 306.00 | 305.00 | 294.00 |
| L 13 | 7 GD-MS 3 | 308.33 | 77.05 | 80.86 | 340.00 | 214.00 | 434.00 | 287.00 | 324.00 | 251.00 |
| L 14 | 28 ICP OES 2 | 316.83 | 4.71 | 4.94 | 309.00 | 320.00 | 319.00 | 322.00 | 317.00 | 314.00 |

| | |
|---|---|
| Range [min..max] | [ 170.00 .. 434.00 ] |
| | Case of No Pooling |
| Mean of means | 275.05 |
| 95% H.W. Confidence Interval | 16.94 |

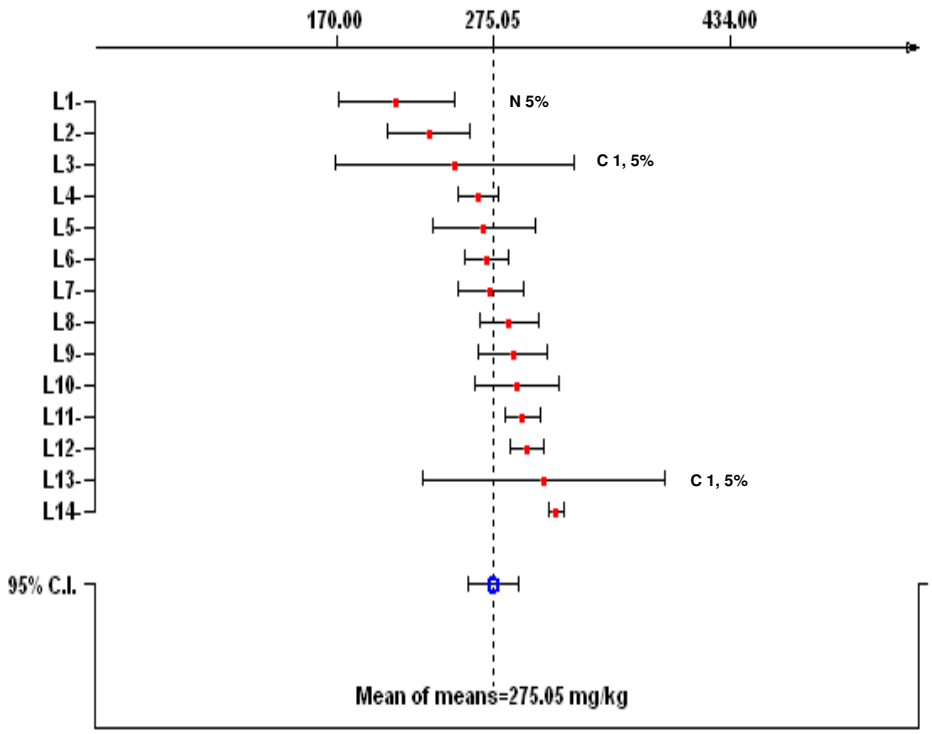
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. L2)**



**Tab. A6.13: Zirconium accepted results in run 1 (values in mg/kg)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 9 ETV-ICP OES 3 | 2.58 | 0.10 | 0.11 | 2.55 | 2.56 | 2.46 | 2.71 | 2.70 | 2.50 |
| L 2 | 19 ETV-ICP OES 3 | 2.65 | 0.75 | 0.79 | 2.59 | 2.86 | 2.17 | 4.02 | 2.38 | 1.89 |
| L 3 | 4 ETV-ICP OES 3 | 3.00 | 0.89 | 0.94 | 3.00 | 2.00 | 2.00 | 4.00 | 4.00 | 3.00 |
| L 4 | 28 ICP OES 2 | 3.83 | 0.41 | 0.43 | 4.00 | 3.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| L 5 | 21 ETV-ICP OES 2 | 4.18 | 2.93 | 3.07 | 2.80 | 2.30 | 2.70 | 1.70 | 6.60 | 9.00 |
| L 6 | 27 GD-MS 3 | 4.20 | 0.58 | 0.61 | 3.30 | 4.40 | 4.50 | 4.10 | 3.90 | 5.00 |
| L 7 | 7 DC Arc OES 3 | 4.40 | 0.65 | 0.69 | 5.00 | 4.20 | 3.40 | 4.10 | 4.50 | 5.20 |
| L 8 | 3 ICP OES 2 | 4.71 | 1.43 | 1.50 | 6.18 | 6.29 | 5.46 | 3.44 | 3.12 | 3.77 |
| L 9 | 14 DC Arc OES (-) | 5.24 | 0.72 | 0.75 | 4.79 | 4.55 | 5.16 | 5.27 | 5.04 | 6.60 |
| L 10 | 15 ICP-SF-MS 3 | 5.37 | 0.41 | 0.43 | 5.90 | 5.41 | 5.16 | 4.86 | 5.08 | 5.80 |
| L 11 | 7 GD-MS 3 | 5.42 | 1.27 | 1.34 | 6.50 | 3.70 | 6.50 | 4.80 | 6.60 | 4.40 |
| L 12 | 14 ICP OES 2 | 5.44 | 0.37 | 0.39 | 5.06 | 5.88 | 5.80 | 4.97 | 5.48 | 5.44 |
| L 13 | 29 ICP OES 3 | 5.64 | 0.14 | 0.14 | 5.48 | 5.55 | 5.54 | 5.77 | 5.69 | 5.81 |

| | |
|---|---|
| Range [min..max] | [ 1.70 .. 9.00 ] |
| | Case of No Pooling |
| Mean of means | 4.36 |
| 95% H.W. Confidence Interval | 0.65 |

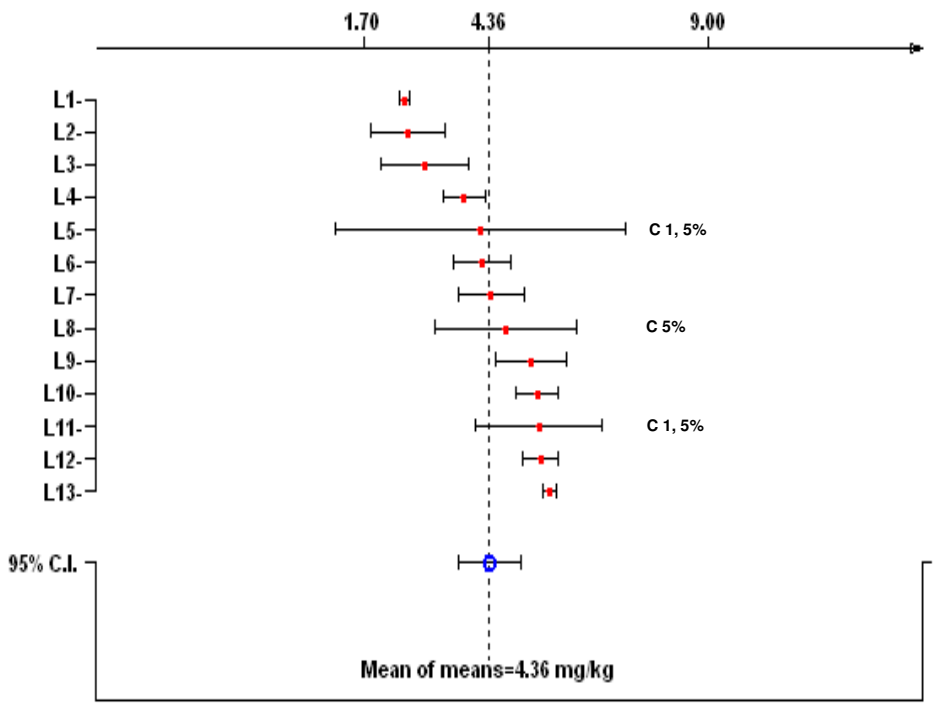
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. M1)**



**Tab. A6.14.1: Carbon total evaluation in run 1 (values in %)**

| Line no. | Lab Abbreviation | Mean ( % ) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 3 Comb.-IR (-) | 29.573 | 0.044 | 0.046 | 29.560 | 29.630 | 29.530 | 29.590 | 29.520 | 29.610 |
| L 2 | 27 Comb.-IR 3 | 29.650 | 0.609 | 0.639 | 30.100 | 28.700 | 29.400 | 29.400 | 30.400 | 29.900 |
| L 3 | 23 Comb.-IR 2 | 29.717 | 0.070 | 0.073 | 29.690 | 29.790 | 29.740 | 29.590 | 29.750 | 29.740 |
| L 4 | 18 Comb.-IR 3 | 29.730 | 0.056 | 0.059 | 29.680 | 29.740 | 29.710 | 29.740 | 29.680 | 29.830 |
| L 5 | 8 Comb.-IR 1 | 29.823 | 0.127 | 0.133 | 29.850 | 29.870 | 29.570 | 29.920 | 29.880 | 29.850 |
| L 6 | 29 Comb.-IR (-) | 29.860 | 0.094 | 0.099 | 29.910 | 29.970 | 29.820 | 29.700 | 29.850 | 29.910 |
| L 7 | 10 Comb. / Coul. 3 | 29.908 | 0.113 | 0.118 | 30.110 | 29.950 | 29.870 | 29.810 | 29.900 | 29.810 |
| L 8 | 1 Comb.-IR (3) | 29.943 | 0.058 | 0.060 | 29.910 | 29.920 | 30.020 | 29.970 | 29.980 | 29.860 |
| L 9 | 16 Comb.-IR 3 | 29.943 | 0.016 | 0.017 | 29.940 | 29.950 | 29.940 | 29.920 | 29.940 | 29.970 |
| L 10 | 22 Comb.-IR 3 | 29.952 | 0.031 | 0.032 | 29.970 | 29.980 | 29.950 | 29.920 | 29.980 | 29.910 |
| L 11 | 4 Comb.-IR 1 | 29.977 | 0.010 | 0.011 | 29.980 | 29.980 | 29.960 | 29.980 | 29.990 | 29.970 |
| L 12 | 9 Comb.-IR 3 | 30.000 | 0.070 | 0.074 | 29.930 | 29.960 | 29.930 | 30.070 | 30.090 | 30.020 |
| L 13 | 28 Comb.-IR 3 | 30.002 | 0.059 | 0.062 | 30.080 | 30.050 | 29.960 | 29.980 | 29.920 | 30.020 |
| L.14 | 12 Comb.-IR 3 | 30.010 | 0.055 | 0.057 | 30.000 | 30.110 | 30.030 | 29.960 | 29.990 | 29.970 |
| L 15 | 7 Comb.-IR 3 | 30.031 | 0.035 | 0.036 | 30.049 | 30.044 | 30.001 | 30.085 | 30.014 | 29.993 |
| L 16 | 7 Comb. / Coul. 3 | 30.036 | 0.029 | 0.031 | 30.009 | 30.017 | 30.042 | 30.031 | 30.091 | 30.025 |
| L 17 | 17 Comb.-IR 3 | 30.152 | 0.276 | 0.289 | 29.863 | 29.953 | 29.931 | 30.232 | 30.425 | 30.508 |
| L 18 | 26 Comb.-IR 2 | 30.876 | 0.544 | 0.675 | 31.725 | 30.985 | 30.800 | 30.270 | 30.600 | |

| | |
|---|---|
| Range [min..max] | [ 28.700 .. 31.725 ] |
| | Case of No Pooling |
| Mean of means | 29.955 |
| 95% H.W. Confidence Interval | 0.137 |

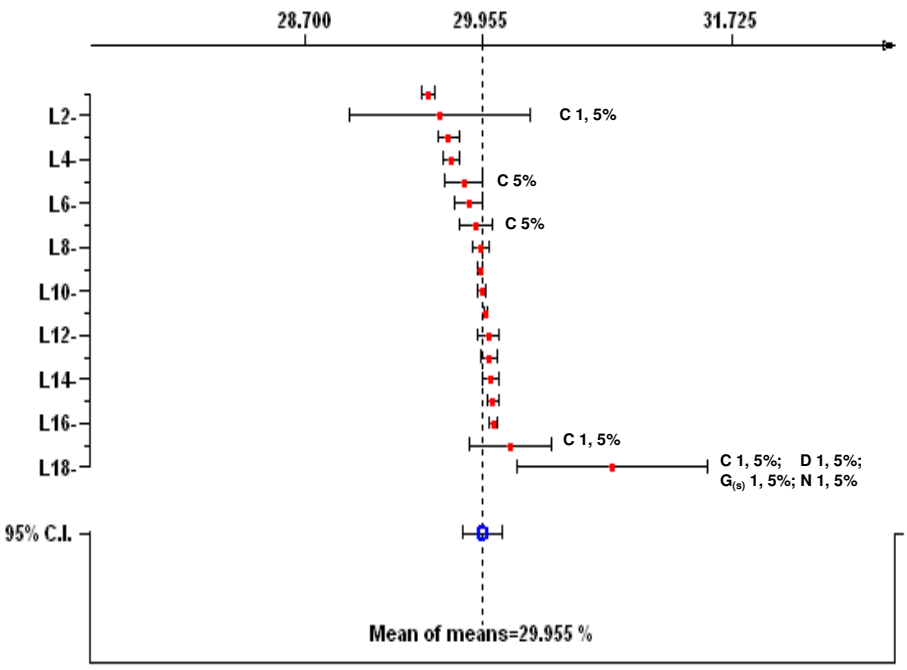
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. N1)**



**Tab. A6.14.2: Carbon total accepted results in run 2 (values in %)**

| Line no. | Lab Abbreviation | Mean ( % ) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 3 Comb.-IR (-) | 29.573 | 0.044 | 0.046 | 29.560 | 29.630 | 29.530 | 29.590 | 29.520 | 29.610 |
| L 2 | 27 Comb.-IR 3 | 29.650 | 0.609 | 0.639 | 30.100 | 28.700 | 29.400 | 29.400 | 30.400 | 29.900 |
| L 3 | 23 Comb.-IR 2 | 29.717 | 0.070 | 0.073 | 29.690 | 29.790 | 29.740 | 29.590 | 29.750 | 29.740 |
| L 4 | 18 Comb.-IR 3 | 29.730 | 0.056 | 0.059 | 29.680 | 29.740 | 29.710 | 29.740 | 29.680 | 29.830 |
| L 5 | 8 Comb.-IR 1 | 29.823 | 0.127 | 0.133 | 29.850 | 29.870 | 29.570 | 29.920 | 29.880 | 29.850 |
| L 6 | 29 Comb.-IR (-) | 29.860 | 0.094 | 0.099 | 29.910 | 29.970 | 29.820 | 29.700 | 29.850 | 29.910 |
| L 7 | 10 Comb. / Coul. 3 | 29.908 | 0.113 | 0.118 | 30.110 | 29.950 | 29.870 | 29.810 | 29.900 | 29.810 |
| L 8 | 1 Comb.-IR (3) | 29.943 | 0.058 | 0.060 | 29.910 | 29.920 | 30.020 | 29.970 | 29.980 | 29.860 |
| L 9 | 16 Comb.-IR 3 | 29.943 | 0.016 | 0.017 | 29.940 | 29.950 | 29.940 | 29.920 | 29.940 | 29.970 |
| L 10 | 22 Comb.-IR 3 | 29.952 | 0.031 | 0.032 | 29.970 | 29.980 | 29.950 | 29.920 | 29.980 | 29.910 |
| L 11 | 4 Comb.-IR 1 | 29.977 | 0.010 | 0.011 | 29.980 | 29.980 | 29.960 | 29.980 | 29.990 | 29.970 |
| L 12 | 9 Comb.-IR 3 | 30.000 | 0.070 | 0.074 | 29.930 | 29.960 | 29.930 | 30.070 | 30.090 | 30.020 |
| L 13 | 28 Comb.-IR 3 | 30.002 | 0.059 | 0.062 | 30.080 | 30.050 | 29.960 | 29.980 | 29.920 | 30.020 |
| L.14 | 12 Comb.-IR 3 | 30.010 | 0.055 | 0.057 | 30.000 | 30.110 | 30.030 | 29.960 | 29.990 | 29.970 |
| L 15 | 7 Comb.-IR 3 | 30.031 | 0.035 | 0.036 | 30.049 | 30.044 | 30.001 | 30.085 | 30.014 | 29.993 |
| L 16 | 7 Comb. / Coul. 3 | 30.036 | 0.029 | 0.031 | 30.009 | 30.017 | 30.042 | 30.031 | 30.091 | 30.025 |
| L 17 | 17 Comb.-IR 3 | 30.152 | 0.276 | 0.289 | 29.863 | 29.953 | 29.931 | 30.232 | 30.425 | 30.508 |

| | |
|---|---|
| Range [min..max] | [ 28.700 .. 30.508 ] |
| | Case of No Pooling |
| Mean of means | 29.900 |
| 95% H.W. Confidence Interval | 0.080 |

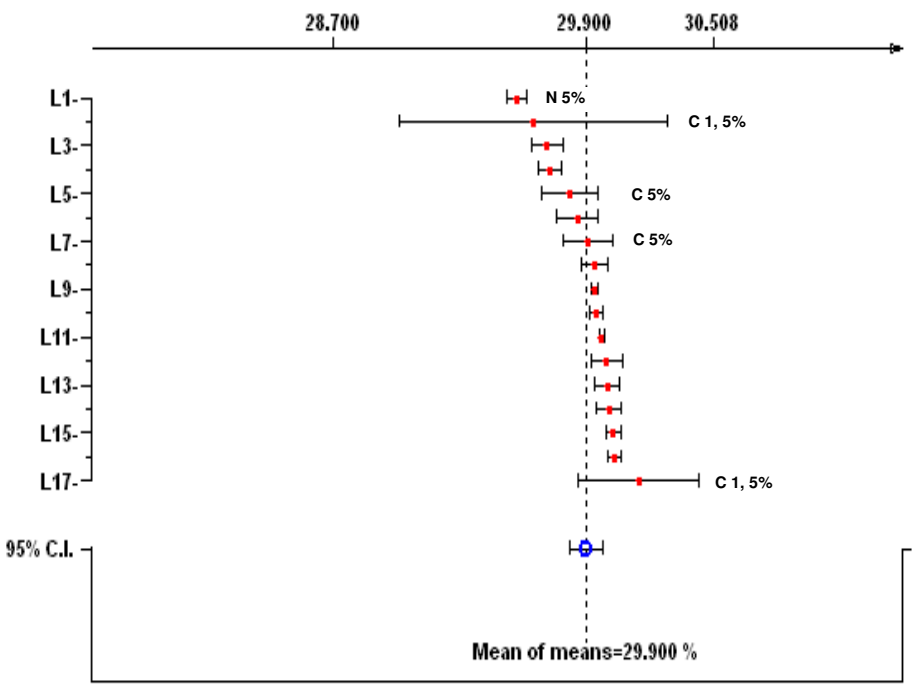
**Outliers detected by different statistical tests at a = 1% level and at a = 5% level.**

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. N2)**



**Tab. A6.15: Carbon free accepted results in run 1 (values in %)**

| Line no. | Lab Abbreviation | Mean ( % ) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 3 Comb.-IR2 | 0.0345 | 0.0023 | 0.0025 | 0.0310 | 0.0340 | 0.0340 | 0.0380 | 0.0360 | 0.0340 |
| L 2 | 7 wet chem. Oxidation – Coul. 3 | 0.0361 | 0.0018 | 0.0019 | 0.0389 | 0.0366 | 0.0352 | 0.0340 | 0.0370 | 0.0347 |
| L 3 | 9 wet chem. Oxidation – Coul. 3 | 0.0362 | 0.0028 | 0.0029 | 0.0330 | 0.0370 | 0.0380 | 0.0360 | 0.0400 | 0.0330 |
| L 4 | 28 Comb.-IR 3 | 0.0400 | | 0.0000 | 0.0400 | 0.0400 | 0.0400 | 0.0400 | 0.0400 | 0.0400 |
| L 5 | 18 Comb.-IR 3 | 0.0442 | 0.0013 | 0.0014 | 0.0420 | 0.0440 | 0.0450 | 0.0440 | 0.0460 | 0.0440 |
| L 6 | 10 Comb. / Coul. 3 | 0.0613 | 0.0023 | 0.0024 | 0.0590 | 0.0590 | 0.0610 | 0.0620 | 0.0620 | 0.0650 |
| L 7 | 4 Comb.-IR 3 | 0.0617 | 0.0041 | 0.0043 | 0.0600 | 0.0700 | 0.0600 | 0.0600 | 0.0600 | 0.0600 |

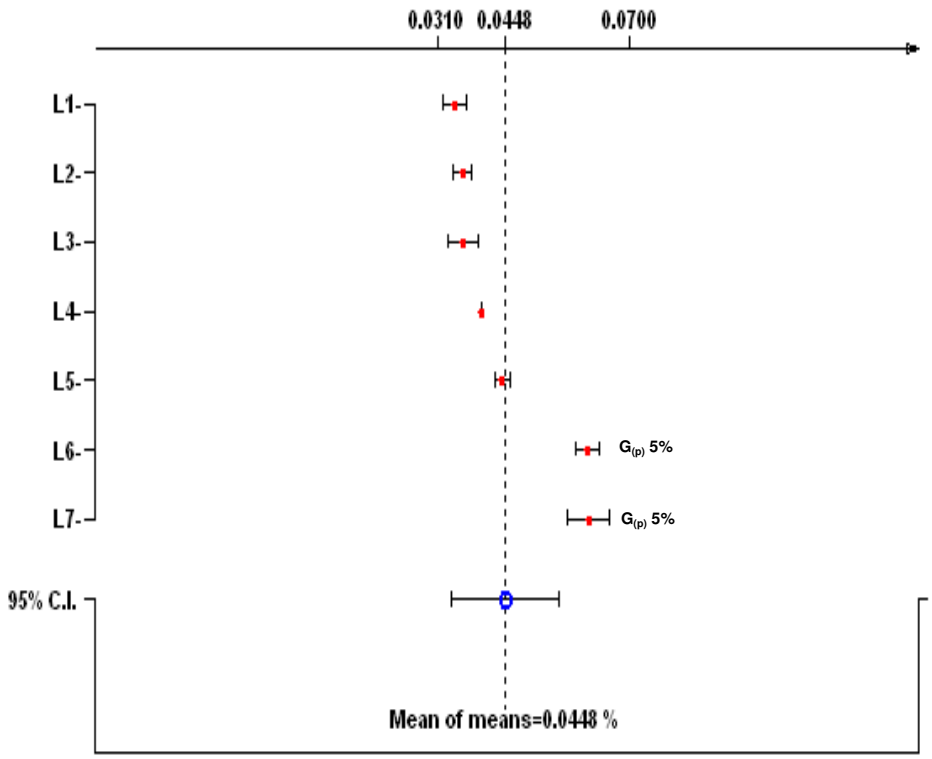
| | |
|---|---|
| Range [min..max] | [ 0.0310 .. 0.0700 ] |
| | Case of No Pooling |
| Mean of means | 0.0448 |
| 95% H.W. Confidence Interval | 0.0109 |

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

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

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

**Diagram of means and 95% confidence intervals (to Tab. O1)**



**Tab. A6.16: Nitrogen accepted results in run 1 (values in %)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 17 CGHE-TC 3 | 12.7 | 4.4 | 4.6 | 13.0 | 8.0 | 9.0 | 20.0 | 11.0 | 15.0 |
| L 2 | 3 CGHE-TC 2 | 15.7 | 1.8 | 1.8 | 14.0 | 17.0 | 17.0 | 16.0 | 13.0 | 17.0 |
| L 3 | 1 CGHE-TC 2 | 18.0 | 3.5 | 3.7 | 20.6 | 23.9 | 15.7 | 15.6 | 17.1 | 15.3 |
| L 4 | 8 CGHE-TC 1 | 18.5 | 4.3 | 4.5 | 13.0 | 18.0 | 17.0 | 16.0 | 25.0 | 22.0 |
| L 5 | 22 CGHE-TC 3 | 19.8 | 2.3 | 2.4 | 20.0 | 18.0 | 22.0 | 19.0 | 23.0 | 17.0 |
| L 6 | 9 CGHE-TC 3 | 22.5 | 4.1 | 4.3 | 17.0 | 24.0 | 18.0 | 23.0 | 27.0 | 26.0 |

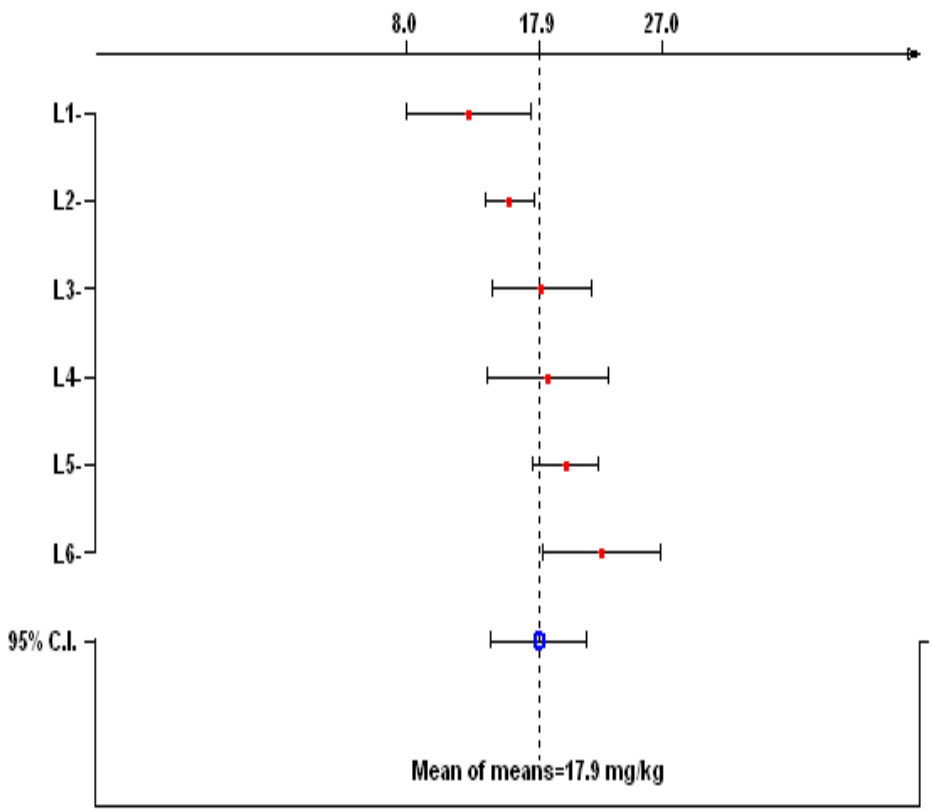
| | |
|---|---|
| Range [min..max] | [ 8.0 .. 27.0 ] |
| | Case of No Pooling |
| Mean of means | 17.9 |
| 95% H.W. Confidence Interval | 3.6 |

**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. P1)**



**Tab. A6.17: Oxygen accepted results in run 1 (values in %)**

| Line no. | Lab Abbreviation | Mean (mg/kg) | STDev | H.W. CI (95%) | Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 | Sample #6 |
|---|---|---|---|---|---|---|---|---|---|---|
| L 1 | 27 CGHE-IR 3 | 78.2 | 8.5 | 8.9 | 65.0 | 89.0 | 79.0 | 81.0 | 72.0 | 83.0 |
| L 2 | 12 CGHE-IR 3 | 92.3 | 7.3 | 7.7 | 87.0 | 96.0 | 81.0 | 94.0 | 102.0 | 94.0 |
| L 3 | 28 CGHE-IR 1 | 100.0 | 0.0 | 0.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| L 4 | 5 CGHE-IR 2 | 104.0 | 3.6 | 3.8 | 99.0 | 110.0 | 103.0 | 105.0 | 104.0 | 103.0 |
| L 5 | 8 CGHE-IR 1 | 121.7 | 8.8 | 9.2 | 123.0 | 111.0 | 134.0 | 113.0 | 128.0 | 121.0 |
| L 6 | 1 CGHE-IR 2 | 124.4 | 8.9 | 9.3 | 136.1 | 120.7 | 129.9 | 118.0 | 112.2 | 129.4 |
| L 7 | 9 CGHE-IR 3 | 163.2 | 11.3 | 11.8 | 152.0 | 161.0 | 150.0 | 165.0 | 179.0 | 172.0 |
| L 8 | 17 CGHE-IR 3 | 168.2 | 20.4 | 21.4 | 190.0 | 146.0 | 142.0 | 173.0 | 188.0 | 170.0 |
| L 9 | 22 CGHE-IR 3 | 194.3 | 4.5 | 4.7 | 190.0 | 198.0 | 191.0 | 201.0 | 195.0 | 191.0 |
| L 10 | 30 CGHE-IR 2 | 219.0 | 7.2 | 7.6 | 233.0 | 212.0 | 217.0 | 216.0 | 217.0 | 219.0 |
| L 11 | 3 CGHE-IR 2 | 245.5 | 10.4 | 10.9 | 236.0 | 243.0 | 237.0 | 240.0 | 259.0 | 258.0 |

| | |
|---|---|
| Range [min..max] | [ 65.0 .. 259.0 ] |
| | Case of No Pooling |
| Mean of means | 146.4 |
| 95% H.W. Confidence Interval | 37.3 |

**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. Q1)**