

Certification Report

Certified Reference Material

BAM-S011

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Abstract

This report describes the preparation and certification of reference material BAM-S011, a niobium pentoxide powder with a certified content of fluorine, carried out in co-operation with the Committee of Chemists of GDMB Gesellschaft der Metallurgen und Bergleute. The certified mass fraction of fluorine and additional material data are listed below.

Parameter	Mass fraction ¹⁾ in mg/kg	Uncertainty ²⁾ in mg/kg
Fluorine	128	13

1) The certified value is the mean of 8 series of results obtained by different laboratories. 4 different analytical methods were used for the measurement of the parameter. Calibration was carried out with pure substances of definite stoichiometry or with 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 of $k = 2$.

Indicative values

Parameter	Mass fraction ¹⁾ in mg/kg	Uncertainty ²⁾ in mg/kg
Aluminium	0.29	0.16
Chromium	0.031	0.005
Copper	0.04	0.009
Iron	0.26	0.08
Tantalum	8	6
Molybdenum	<0.05	
Nickel	<0.3	

1) The indicative values are the means of 3 to 5 series of results (depending on the parameter) obtained by different laboratories. 2 or 3 different analytical methods were used for the measurement of one parameter.

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

Informative Values

One laboratory determined silicon to a content of 2.1 mg/kg.

Parameter		Value
Particle size	D ₁₀	0.87 μm
	D ₅₀	2.2 μm
	D ₉₀	18.1 μm
The particle size distribution (volume) was determined by laser granulometry.		

Contents

Abstract	2
1 Introduction	5
1.1 Scope	5
1.2 Certification procedure	5
2 Participating laboratories.....	5
2.1 Allocation and preparation of the material	5
2.2 Homogeneity testing.....	6
2.3 Certification analysis (certified and indicative values)	6
2.4 Determination of additional material data	6
3 Abbreviations used.....	6
4 Homogeneity investigation of the material	7
5 Time stability of the material	8
6 Characterisation study	8
6.1 Analytical methods used for certification	8
6.2 Methods used for the determination of additional material data.....	13
7 Results and discussion	13
8 Calculation of certified and indicative values and their uncertainties	15
8.1 Mass fractions	15
8.2 Uncertainties.....	15
9 Instructions for use.....	16
9.1 Area of application.....	16
9.2 Recommendations for correct sampling and sample preparation	16
9.3 Recommendations for correct storage	16
9.4 Safety guidelines	16
10 References	17
11 Appendices.....	17
Appendix 1: Homogeneity testing (ANOVA).....	18
Appendix 2: Statistical evaluation of all results of interlaboratory comparison for certification of BAM-S011	19

1 Introduction

1.1 Scope

Niobium pentoxide (Nb_2O_5) increases both the refractive index of optical glasses and the capacity of multi-layered ceramic capacitors (MLCCs). In contrast to lead oxide, niobium pentoxide poses no health risks.

When niobium pentoxide is added to the glass during the production of optical lenses, the lenses are lighter, thinner and demonstrate greater resilience. In addition, niobium pentoxide in interchangeable lenses makes them lighter while enabling better performance in digital cameras and mirrorless system cameras. Adding niobium pentoxide to spherical lenses allows the number of lenses in optical elements to be reduced, which makes the components lighter and smaller. When niobium pentoxide is used as a dopant in the production of multi-layered ceramic capacitors (MLCCs), the Curie temperature of the barium titanate substrate can be increased, this enables the best possible temperature stability to optimize capacity [1].

As a substrate for surface acoustic wave filters, also known as SAW filters, lithium niobates are found in mobile end devices such as smartphones, tablet PCs, ultrabooks, GPS applications and smart meters. These niobium containing radio frequency filters, ensure precise frequency control, optimized selectivity and reduced distortion.

The purity of the material is of high importance for its practical value, especially the content of fluorine, if the niobium oxide is used for the production of lithium niobates. Fluorine produces imperfections in the structure which influence the piezoelectric effect. Therefore the content of fluorine is of major importance.

The certification of reference material BAM-S011 was carried out on the basis of the relevant ISO-Guides [2-4] and the „Guidelines for the production of BAM Reference Materials“ [5].

1.2 Certification procedure

Niobium oxide powder material was taken from the customary production line of a specialized producer and was bottled into 340 bottles each containing 50 g of the material. After homogeneity testing one bottle was distributed to each of the 9 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.

Statistical evaluation of all analytical results was performed using the software program SoftCRM 1.2.2. [6]. The certified and indicative values were calculated as means of the laboratory means reported from the participating laboratories after testing for statistical outliers. No outlying values were removed. Uncertainties were calculated taking into account the contributions from the characterization study and, in case of fluorine, from inhomogeneity of the material.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was produced by H.C. Starck GmbH & Co. KG, Goslar, Germany
- The material was bottled by BAM Bundesanstalt für Materialforschung und -prüfung

2.2 Homogeneity testing

- The analytical investigations for the homogeneity testing of F were carried out by H.C. Starck GmbH & Co. KG, Goslar, Germany. No homogeneity testing was carried out for the other elements.
- All statistical evaluations for homogeneity testing were carried out by BAM.

2.3 Certification analysis (certified and indicative values)

The nine laboratories listed below participated in the certification intercomparison. These laboratories were either involved in daily analysis of such a kind of material or already participated successfully in the certification interlaboratory comparisons of other ceramic materials. Therefore no qualification interlaboratory comparison test was performed.

Analytik Jena AG, Jena (Germany)

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

ESK Ceramics GmbH Co. KG, Kempten (Germany)

Evans Analytical Group, Syracuse (USA)

H.C. Starck GmbH & Co. KG, Goslar (Germany)

Leibniz - Institut für Analytische Wissenschaften – ISAS – e.V., Berlin (Germany)

Osram AG, München (Germany)

Treibacher Industrie AG, Treibach-Althofen (Austria)

Wolfram Bergbau- und Hütten GmbH, St. Martin (Austria)

2.4 Determination of additional material data

The particle size distribution was determined by BAM, Division 5.5 "Advanced Technical Ceramics".

3 Abbreviations used

GD-MS	Glow discharge mass spectrometry
GF-CS AAS	Graphite furnace continuum source atomic absorption spectrometry
GF-CS MAS	Graphite furnace continuum source molecular absorption spectrometry
GF-SS-CSMAS	Graphite furnace solid sampling continuum source molecular absorption spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ISE	Ion sensitive electrode
M	mean value of the accepted laboratory means of interlaboratory comparison for certification
RSF	relative sensitivity factor
u_c	combined uncertainty of certified mass fraction
s_M	standard deviation of the accepted laboratory means of interlaboratory comparison for certification
n	number of accepted laboratory means of interlaboratory comparison for certification
SD	standard deviation
RSD	relative standard deviation

4 Homogeneity testing of the material

For homogeneity testing 10 bottles were representatively taken from the totality of 340 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 = 10 bottles three appropriate sample masses were analysed for their fluorine content on two different days.

Tab. 1: Results of homogeneity testing of BAM-S011

Sample-No.	Day 1	Day 2	Mean [mg/kg]	Mean of means [mg/kg]	SD of means [mg/kg]
	F [mg/kg]	F [mg/kg]			
44-1	123	125	124		
44-2	124	120	122		
44-3	128	127	127.5	124.5	2.78
56-1	125	124	124.5		
56-2	124	125	124.5		
56-3	124	124	124	124.3	0.29
100-1	125	125	125		
100-2	126	125	125.5		
100-3	125	125	125	125.2	0.29
132-1	124	124	124		
132-2	126	126	126		
132-3	126	124	125	125.0	1.00
165-1	127	125	126		
165-2	127	126	126.5		
165-3	126	124	125	125.8	0.76
171-1	126	124	125		
171-2	126	127	126.5		
171-3	126	124	125	125.5	0.87
209-1	125	126	125.5		
209-2	121	124	122.5		
209-3	126	126	126	124.7	1.89
241-1	127	125	126		
241-2	127	125	126		
241-3	126	125	125.5	125.8	0.29
268-1	125	126	125.5		
268-2	128	126	127		
268-3	127	125	126	126.2	0.76
310-1	125	125	125		
310-2	122	126	124		
310-3	124	125	124.5	124.5	0.50
				125.2	
				0.655	
			RSD (%)	0.5	

The measurements were carried out using a fluoride sensitive electrode (Metrohm) after pyrohydrolysis with SiO₂/V₂O₅. 1 g of Nb₂O₅ was taken for analysis. Therefore the minimum sample intake for analysis as indicated in the certificate is 1 g.

Fluorine was the only element which was tested for homogeneity. All other analytes of interest were not tested. This is one of the reasons why there are no certified values for these elements.

The estimate of inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [4] using Eq. (1) and Eq. (2):

$$s_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \quad (1)$$

$$u_{bb}^* = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

where:

- MS_{among} mean of squared deviations between bottles (from 1-way ANOVA, see Appendix 1)
- MS_{within} mean of squared deviations within bottles (from 1-way ANOVA)
- n number of replicate sub-samples per bottle
- N number of bottles selected for homogeneity study

s_{bb} signifies the between-bottle standard deviation, whereas u_{bb}^* denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). The larger of the two values was used as u_{bb} . Eq. (1) does not apply if MS_{within} is larger than MS_{among} .

The calculated values of s_{bb} , $u_{bb,r}^*$, and $u_{bb,r}$ are given in the following Table 2.

Table 2: Relative uncertainty contribution due to possible sample inhomogeneity

Element	$s_{bb,r}$ (%)	$u_{bb,r}^*$ (%)	$u_{bb,r}$ (%)
F	$MS_{among} < MS_{within}$	0.394	0.394

5 Stability of the material

Niobium oxide is known to be stable. Therefore no contribution of long-term stability to the total uncertainty has been taken into account.

6 Characterisation study

6.1 Analytical methods used for certification

Nine laboratories participated in the certification interlaboratory comparison. Some of the laboratories did not analyse all elements of interest (F, Al, Cr, Cu, Fe, Ta, Mo, Ni, Si).

The laboratories were requested to analyse six subsamples. They were free to choose any suitable analytical method for analysis. Tables 3 to 11 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. 3: Analytical methods used for the determination of fluorine

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
3	Fusion - Distillation: <ul style="list-style-type: none"> - M: 1g sample + 5 g K₂CO₃ (in Pt Crucible at 850°C) - cooled melt + H₂O - Solution + 75 mL H₂SO₄ (72%), receiver 5 mL NaOH (2mol/L) + 50 mL H₂O - Stream superheater 149°C (acetic acid iso-amylester) 	0.001 mol/L F⁻ standard solution (Orion, Thermo) is compared with Merck <ul style="list-style-type: none"> - Calibration: 0.19, 0.57, 0.95 mg/L - Addition calibration was used 	ISE
5	Pyrohydrolysis: <ul style="list-style-type: none"> - M: 0.1 g in alumina sample boats in a stream of O₂ and water vapour at 1200°C - Tubular furnace with quartz reaction tube - Collection of condensate in 50 mL flask filled with 20 mL water - Reaction time after insertion of sample boat = 5 min. 	1000 mg/L F (Merck, NaF in water) 99.99% v/v Oxygen <ul style="list-style-type: none"> - standard addition method with 100 mg/L F was used 	ISE
8	Pyrohydrolysis: <ul style="list-style-type: none"> - M: 1.0 g + 0.3 g SiO₂/V₂O₅ 	Selfmade: 4.4202 g NaF dissolved in 1000 mL H ₂ O <ul style="list-style-type: none"> - Calibration: 0, 0.2, 2.0, 20, 200 µg/L F 	ISE
10	Pyrohydrolysis: <ul style="list-style-type: none"> - M: 0.5 g in alumina sample boats in a stream of O₂ and water vapour at 900°C - Tubular furnace with quartz reaction tube - Collection of condensate in 100 mL flask filled with 15 mL NaOH (1mol/L) - Solution + H₂SO₄ (1 mol/L), CH₃COONa(105 g/L) + acetic acid (100 mL/L) → pH 4.3 	Self made 100.036 mg/L F (0.22111 g NaF in 1000 mL water, Swiss Primary Reference Material, <i>EMPA</i>) <ul style="list-style-type: none"> - calibration: 2.5, 5, 7.5, 10, 15, 20, 25 	Photometry
12	Fusion - Distillation: <ul style="list-style-type: none"> - M: 4 g sample + 20 g Na₂CO₃/K₂CO₃ melted in a furnace at 980°C for 2 h - cooled melt, extract with H₂O, filtrate and store in 250 ml flask. - 50 mL solution + 20 mL Tisab-solution fill to 100 mL 	1000 mg/L F⁻ (Merck, NaF in H ₂ O) <ul style="list-style-type: none"> - Calibration: 10, 20, 40, 60, 80, 130, 160, 190, 240 µg/L 	ISE
7	No sample preparation: <ul style="list-style-type: none"> - Direct sampling using 99.99999% purity In pressed in pellets 	Standard RSF = 10 was set	GD-MS
9	No sample preparation: <ul style="list-style-type: none"> - M: 0.02 - 0.04 g Nb₂O₅ - slurries were prepared in polystyrene vessels by suspending of sample in 10 mL 0.5% v/v HNO₃. - the suspension was pre-treated for 20 min in an ultrasonic bath. During the final determination the slurry were permanently homogenized by magnetic stirring. - 10 µL sample slurry+10 µL 0.5% Ca were pipetted into graphite tube. - pyrolysis temperature were 800°C - atomization temperature were 2300°C 	5457 mg/L F (self made from high purity NaF) <ul style="list-style-type: none"> - calibration solution: Standard addition method were used.0.182, 0.364 mg/L 	GF-CSMAS
20	No sample preparation: <ul style="list-style-type: none"> - M: 0.0005 – 0.0027 mg - To determination of F was composed the molecule GaF. Furnace tube was treated with 1 g/L Zr as permanent modifier. For stabilization of measurements were modifiers by drying and pyrolysis used. 7 µL 0.1%/0.05%/20 mg/L Pd/Mg/Zr 5 µL 10 g/L Ga(NO₃)₃ - pyrolysis temperature were 550°C - atomization temperature were 1650°C 	1000 mg/L F (Merck, NaF in water) <ul style="list-style-type: none"> - calibration 80, 160, 240, 320, 400 ng F 	GF-SS-CSMAS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO ₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO ₃	1000 mg/L Al (Merck) - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Al	ICP-MS
11	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 1.4 g Nb ₂ O ₅ + 5 mL HNO ₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10.	1000 mg/L Al (Merck Certipur) compared with NIST SRM 3101a - calibration by standard addition 0.5, 1, 1.5, 2 µg/L and Sc as an internal standard	ICP-MS
7	NO SAMPLE PREPARATION: - Direct sampling using 99.99999% purity In pressed to pellets	Standard RSF was set	GD-MS
8	NO SAMPLE PREPARATION: - M: 2 g + 25 ml 99.99999% Ga pressed to pellets	Standard RSF: 1.378	GD-MS
9	NO SAMPLE PREPARATION: - M: 0.06 - 0.14 g Nb ₂ O ₅ - slurries were prepared in polystyrene vessels by suspending of sample in 10 mL 0.5% v/v HNO ₃ . - 20 µL sample slurry were pipetted into graphite tube. - pyrolysis temperature were 1000°C - atomization temperature were 2600°C	1002 mg/L Al Merck - calibration solution: 0.01 mg Al	GF-CSAAS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample Digestion: - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO ₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO ₃	1000 mg/L Cr (Merck) - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Cr	ICP-MS
11	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 1.4 g Nb ₂ O ₅ + 5 mL HNO ₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10.	1000 mg/L Cr (Merck Certipur) compared with NIST SRM 3112a - calibration by standard addition 0.025, 0.05, 0.075, 0.1 µg/L and Sc as an internal standard	ICP-MS
7	NO SAMPLE PREPARATION: - Direct sampling using 99.99999% purity In pressed to pellets	Standard RSF was set	GD-MS
8	NO SAMPLE PREPARATION: - M: 2 g + 25 ml 99.99999% Ga pressed to pellets	Standard RSF: 2.933	GD-MS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample Digestion: <ul style="list-style-type: none"> - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO₃ 	1000 mg/L Cu (Merck) <ul style="list-style-type: none"> - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Cu 	ICP-MS
11	Sample decomposition: <ul style="list-style-type: none"> - Sample was dried at 130°C for 1 h - M: 1.4 g Nb₂O₅ + 5 mL HNO₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10. 	1000 mg/L Cu (Merck Certipur) compared with NIST SRM 3114 <ul style="list-style-type: none"> - calibration by standard addition 0.05, 0.1, 0.15, 0.2 µg/L and Sc as an internal standard 	ICP-MS
7	NO SAMPLE PREPARATION: <ul style="list-style-type: none"> - Direct sampling using 99.99999% purity In pressed to pellets 	Standard RSF was set	GD-MS
8	NO SAMPLE PREPARATION: <ul style="list-style-type: none"> - M: 2 g + 25 ml 99.99999% Ga pressed to pellets 	Standard RSF: 5.144	GD-MS
9	NO SAMPLE PREPARATION: <ul style="list-style-type: none"> - M: 0.1 - 0.22 g Nb₂O₅ - slurries were prepared in polystyrene vessels by suspending of sample in 10 mL 0.5% v/v HNO₃. the suspension was pre-treated for 20 min in an ultrasonic bath. During the final determination the slurry were permanently homogenized by magnetic stirring. - 20 µL sample slurry were pipetted into graphite tube. - pyrolysis temperature were 1000°C - atomization temperature were 2300°C 	1001 mg/L Cu Merck <ul style="list-style-type: none"> - calibration solution: 0.01 mg Cu 	GF-CSAAS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample decomposition: <ul style="list-style-type: none"> - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO₃ 	1000 mg/L Fe (Merck) <ul style="list-style-type: none"> - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Fe 	ICP-MS
11	Sample decomposition: <ul style="list-style-type: none"> - Sample was dried at 130°C for 1 h - M: 1.4 g Nb₂O₅ + 5 mL HNO₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10. 	1000 mg/L Fe (Merck Certipur) compared with NIST SRM 3126a <ul style="list-style-type: none"> - calibration by standard addition 0.5, 1, 1.5, 2 µg/L and Sc as an internal standard 	ICP-MS
7	No sample preparation: <ul style="list-style-type: none"> - Direct sampling using 99.99999% purity In pressed to pellets 	Standard RSF was set	GD-MS
8	No sample preparation: <ul style="list-style-type: none"> - M: 2 g + 25 ml 99.99999% Ga pressed to pellets 	Standard RSF: 1.000	GD-MS
9	No sample preparation: <ul style="list-style-type: none"> - M: 0.09 - 0.11 g Nb₂O₅ - slurries were prepared in polystyrene vessels by suspending of sample in 10 mL 0.5% v/v HNO₃. the suspension was pre-treated for 20 min in an ultrasonic bath. During the final determination the slurry were permanently homogenized by magnetic stirring. - 10 µL sample slurry were pipetted into graphite tube. - pyrolysis temperature were 1000°C - atomization temperature were 2500°C 	999 mg/L Fe Merck <ul style="list-style-type: none"> - calibration solution: 0.01, 0.02 mg/L Fe 	GF-CSAAS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO ₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO ₃	1000 mg/L Mo (Merck) - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Mo	ICP-MS
11	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 1.4 g Nb ₂ O ₅ + 5 mL HNO ₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10.	1000 mg/L Mo (Merck Certipur) compared with NIST SRM 3134 - calibration by standard addition 0.1, 0.2, 0.3, 0.4 µg/L and Sc as an internal standard	ICP-MS
7	No sample preparation: - Direct sampling using 99.99999% purity In pressed in pellets	Standard RSF was set	GD-MS
8	No sample preparation: - M: 2 g + 25 ml 99.99999% Ga pressed to pellets	Standard RSF: 1.119	GD-MS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO ₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO ₃	1000 mg/L Ni (Merck) - Calibration solution 0.25, 0.50, 1.00, 2.00 µg/L Al	ICP-MS
11	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 1.4 g Nb ₂ O ₅ + 5 mL HNO ₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10.	1000 mg/L Ni (Merck Certipur) compared with NIST SRM 3136 - calibration by standard addition 1, 2, 3, 4 µg/L and Sc as an internal standard	ICP-MS
7	No sample preparation: - Direct sampling using 99.99999% purity In pressed in pellets	Standard RSF was set	GD-MS
8	No sample preparation: - M: 2 g + 25 ml 99.99999% Ga pressed to pellets	Standard RSF: 3.969	GD-MS

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
8	Sample decomposition: - M: 5 g Nb ₂ O ₅ dissolved in HF/HNO ₃ and HClO ₄ - Trace matrix separation by distillation See "Analyse der Metalle" 2. Erg. Bd., GDMB-Informationsgesellschaft, p.222-228	Self made: 1.069 g SiO₂ (annealed at 1200°C) dissolved in HF - Calibration: 0, 5 mg/L Si	ICP OES

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

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
4	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 0.2 – 0.5 g sample + 3 mL HNO ₃ + 2 mL HF in PFA-Vial - Heating at 80°C for 1 h - Diluted with definite mass of 3% HNO ₃	1000 mg/L Ta (Merck) - Calibration solution 1.00, 2.50, 5.00 µg/L Ta	ICP-MS
8	Sample decomposition: - M: 5 g Nb ₂ O ₅ dissolved in HF at 105°C - Trace matrix separation by extraction with MIBK	Self made: 0.610 g Ta₂O₅ (annealed at 1200°C) dissolved in HF/HNO ₃ by 105°C - Calibration: 0, 5 mg/L Ta	ICP OES
11	Sample decomposition: - Sample was dried at 130°C for 1 h - M: 1.4 g Nb ₂ O ₅ + 5 mL HNO ₃ + 10 mL HF in PFA flask. Heating at 80°C for 10 h in a water bath. - For measurements the digests were diluted 1:10.	1000 mg/L Ta (Alfa Aesar Specpure) compared with NIST SRM 3155 - calibration by standard addition 5, 10, 15, 20 µg/L and Sc as an internal standard	ICP-MS

6.2 Methods used for the determination of additional material data

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 A2.1 to A2.6 in Appendix 2. These tables show the single results of each laboratory, the resp. laboratories' mean values together with the intralaboratory standard deviation 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 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 12. Table 13 shows all laboratories' mean values.

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.

Tab. 12: Summary of results of statistical evaluation (the following abbreviations were used: b - Outlier at 1% significance; c - Outlier at 5% significance)

Element	Al	Cr	Cu	F	Fe	Ta
Number of data sets	5	4	4	8	5	3
Total number of replicate measurements	30	24	24	46	30	18
Mean of means (mg/kg)	0.29	0.031	0.040	128.1	0.256	7.57
St. Dev. of means (mg/kg)	0.18	0.005	0.009	17.9	0.084	4.35
Outlying or straggling mean values						
▪ Dixon test	no	no	no	no	no	no
▪ Grubbs test (single and pair test)	no	no	no	no	no	no
▪ Nalimov t-test	no	no	no	c	no	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	no	no	no	b, c	no	b, c
Variances homogeneous						
▪ Bartlett test	no	b	b, c	no	b, c	no
St. Dev. within – laboratories (mg/kg)	0.07	0.005	0.005	12.0	0.033	1.61
St. Dev. between laboratories (mg/kg)	0.17	0.004	0.008	17.4	0.083	4.30
Half-width of the 95% confidence interval	0.22	0.008	0.004	15.0	0.104	10.81

Tab. 13: Means of the series of measurements (Laboratory means in mg/kg)

Line-No.	F		<i>Al</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Ta</i>	<i>Mo</i>	<i>Ni</i>
1	102		0.09	0.025	0.033	0.162	3.62	< 0.01	< 0.01
2	113		0.24	0.030	0.034	0.197	6.87	< 0.01	0.026
3	121		0.25	0.031	0.041	0.242	12.2	0.012	< 0.3
4	124		0.33	0.037	0.052	0.315		< 0.05	
5	126		0.56	< 0.1		0.365			
6	139								
7	140								
8	160								
<i>M</i>	128		0.29	0.031	0.040	0.256	7.57		
<i>s_M</i>	18		0.18	0.005	0.009	0.084	4.36		

Note: The line number should not be mistaken for the laboratory code number.

M: Arithmetic mean of the laboratory means (rounded)

s_M: Standard deviation of the laboratory means (rounded)

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 Chapter 7, Tab. 13). No outlying results were removed.

8.2 Uncertainties

The combined uncertainty of the certified mass fraction for fluorine was calculated taking into account contributions from the certification interlaboratory comparison and from the homogeneity test (see Table 13). A contribution from an uncertainty caused by the possible aging of the material was not included, because this was negligible compared with the contribution from the certification interlaboratory comparison (see paragraph 5).

Uncertainty estimation for the other elements was done using the spread from the certification interlaboratory comparison only.

The following Equation (3) was used to calculate the combined uncertainty

$$u_c = \sqrt{\frac{s_M^2}{n} + u_{bb}^2} \quad (3)$$

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

$$U = 2 u_c. \quad (4)$$

Table 14: Overview on the specific contributions to the combined uncertainty:

	M (in mg/kg)	n	s_M	u_{bb}	u_c
Fluorine	128.1	8	17.96	0.394	6.362
Aluminium	0.293	5	0.175		0.0783
Chromium	0.031	4	0.0050		0.0025
Copper	0.040	4	0.0086		0.0043
Iron	0.256	5	0.084		0.0374
Tantalum	7.57	3	4.352		2.512
Molybdenum	< 0.05	4			
Nickel	< 0.3	3			

The certified mass fraction for fluorine and its uncertainty as well as indicative data for other elements are given 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 or indicative parameters in niobium oxide material are determined by a laboratory. Based on own results and on the certified value of fluorine the uncertainty of own measurements can be calculated.

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 sub-sample mass for the homogeneity testing a minimum sub-sample mass of 1000 mg has to be taken for analysis. The opening duration of the bottle should be as short as possible. The screw cap 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 an appropriate filter
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] http://www.hcstarck.com/niobium_oxide_niobium_pentoxide_nb2o5
- [2] ISO Guide 31, Contents of certificates of reference materials, 1981
- [3] ISO Guide 34, General requirements for the competence of reference material producers, 2009
- [4] ISO Guide 35, Reference materials - General and statistical principles for certification. Third edition, 2006
- [5] Guidelines for the production of BAM Reference Materials, 2006
- [6] Bonas G, Zervou M, Papaeoannou T, Lees M: Accred Qual Assur (2003) 8:101-107
- [7] Guide to the Expression of Uncertainty in measurement (1995), International Organization for Standardization, ISBN 92-67-10188-9

11 Appendices

- Appendix 1: Homogeneity testing (ANOVA)
- Appendix 2: Statistical evaluation of all results of interlaboratory comparison for certification of BAM-S011

Appendix 1: Homogeneity testing (ANOVA)

Tab. A1: Results of ANOVA

ANOVA						
Summary						
<i>Groups</i>	<i>Number</i>	<i>Sum</i>	<i>Mean value</i>	<i>Variance</i>		
Bottle 44	3	373.5	124.50	7.75		
Bottle 56	3	373	124.33	0.08		
Bottle 100	3	375.5	125.17	0.08		
Bottle 132	3	375	125.00	1.00		
Bottle 165	3	377.5	125.83	0.58		
Bottle 171	3	376.5	125.50	0.75		
Bottle 209	3	374	124.67	3.58		
Bottle 241	3	377.5	125.83	0.08		
Bottle 268	3	378.5	126.17	0.58		
Bottle 310	3	373.5	124.50	0.25		
ANOVA						
<i>Source of variation</i>	<i>sums of squares (SS)</i>	<i>degrees of freedom (df)</i>	<i>Mean squares (MS)</i>	<i>F-value</i>	<i>P-value</i>	<i>critical F-value</i>
Between groups	11.575	9	1.2861	0.8719	0.5645	2.3928
Within groups	29.5	20	1.475			
Total	41.075	29				
(sbb) ²	-0.06296296					
ubb	0.394307813					
ubb ²	0.155478652					

Appendix 2: Statistical evaluation of all results of interlaboratory comparison for certification of BAM-S011

Tab. A2.1: Fluorine (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
12 ISE	102.1	3.7	3.9	105.9	104.0	104.9	102.9	97.9	97.2
10 ISE	112.9	4.1	5.1	114.5	113.7	110.4	118.3	107.5	
5 ISE	121.0	2.1	2.2	125.0	121.0	120.0	121.0	119.0	120.0
3 ISE	123.8	5.9	6.2	124.0	129.0	116.0	120.0	132.0	122.0
8 ISE	126.2	2.5	2.6	124.0	129.0	128.0	125.0	123.0	128.0
20 GF-CSMAS	138.6	22.1	27.4	127.0	120.0	169.0	155.0	122.0	
9 GF-CSMAS	140.1	9.0	9.4	135.8	151.2	148.0	143.5	127.8	134.2
7 GD-MS	160.0	23.7	24.8	200.0	170.0	150.0	160.0	150.0	130.0

Range [min..max]	[97.2 .. 200.0]
Mean of means	128.1
95% H.W. Confidence Interval	15.0
95% H.W. Tolerance Interval	66.9

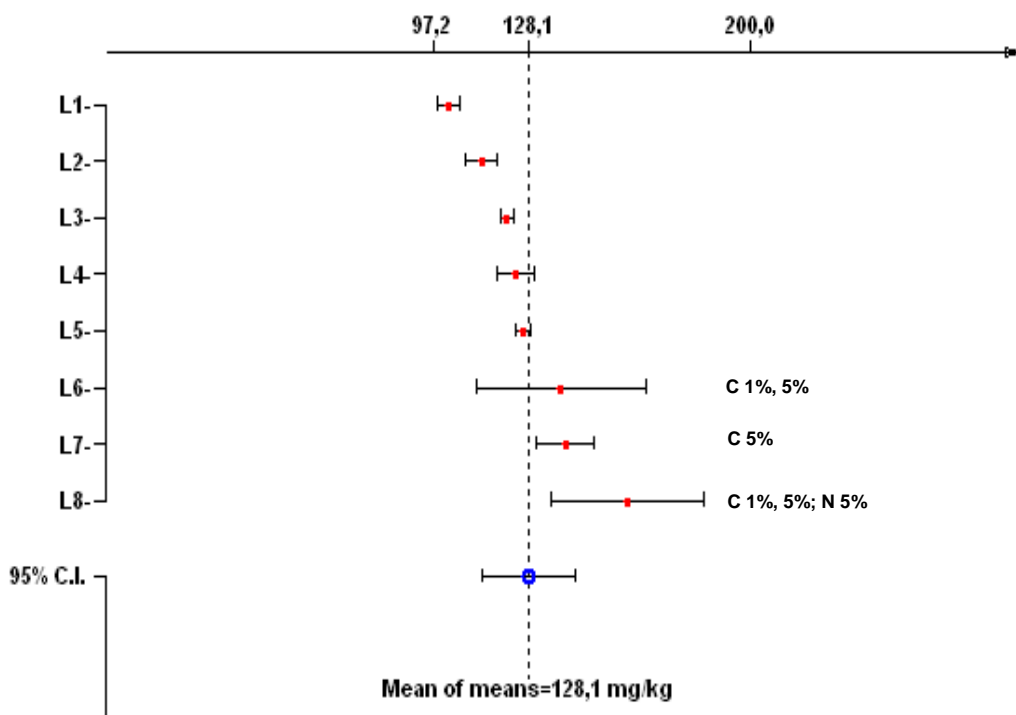
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

- Abbreviations: C = Cochran test
 D = Dixon test
 G_(s) = Grubbs test (single test)
 N = Nalimov 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. A2.1)



Tab. A2.2: Aluminium (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
7 GD-MS	0.09	0.06	0.07	0.09	0.04	0.04	0.20	0.10	0.04
4 ICP-MS	0.24	0.02	0.02	0.25	0.23	0.24	0.25	0.27	0.22
11 ICP-MS	0.25	0.11	0.12	0.47	0.20	0.21	0.15	0.25	0.19
8 GD-MS	0.33	0.10	0.10	0.27	0.27	0.37	0.29	0.51	0.28
9 GF-CSAAS	0.56	0.03	0.04	0.59	0.62	0.53	0.55	0.55	0.54

Range [min..max]	[0.04 .. 0.62]
Mean of means	0.29
95% H.W. Confidence Interval	0.22
95% H.W. Tolerance Interval	0.89

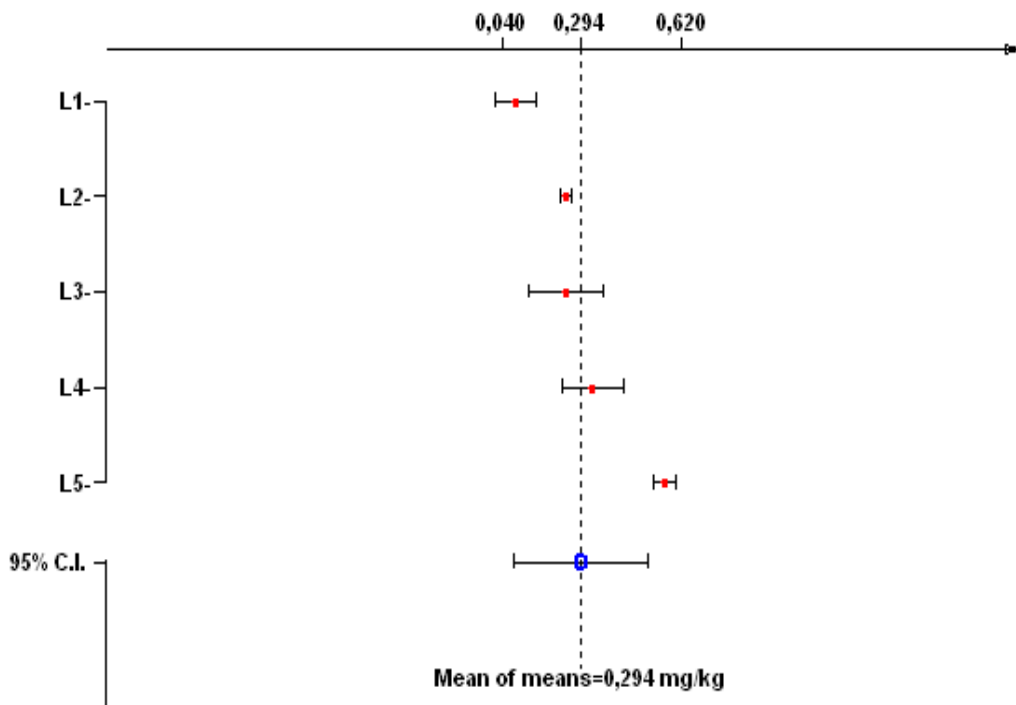
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
 D = Dixon test
 G_(s) = Grubbs test (single test)
 N = Nalimov 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. A2.2)



Tab. A2.3: Chromium (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
7 GD-MS	0.025	0.005	0.006	0.020	0.020	0.030	0.020	0.030	0.030
4 ICP-MS	0.030	0.002	0.002	0.029	0.033	0.030	0.031	0.029	0.029
11 ICP-MS	0.031	0.005	0.005	0.031	0.037	0.027	0.028	0.035	0.026
8 GD-MS	0.037	0.008	0.008	0.031	0.037	0.052	0.034	0.039	0.030

Range [min..max]	[0.020 .. 0.052]
Case of No Pooling	
Mean of means	0.031
95% H.W. Confidence Interval	0.008
95% H.W. Tolerance Interval	0.032

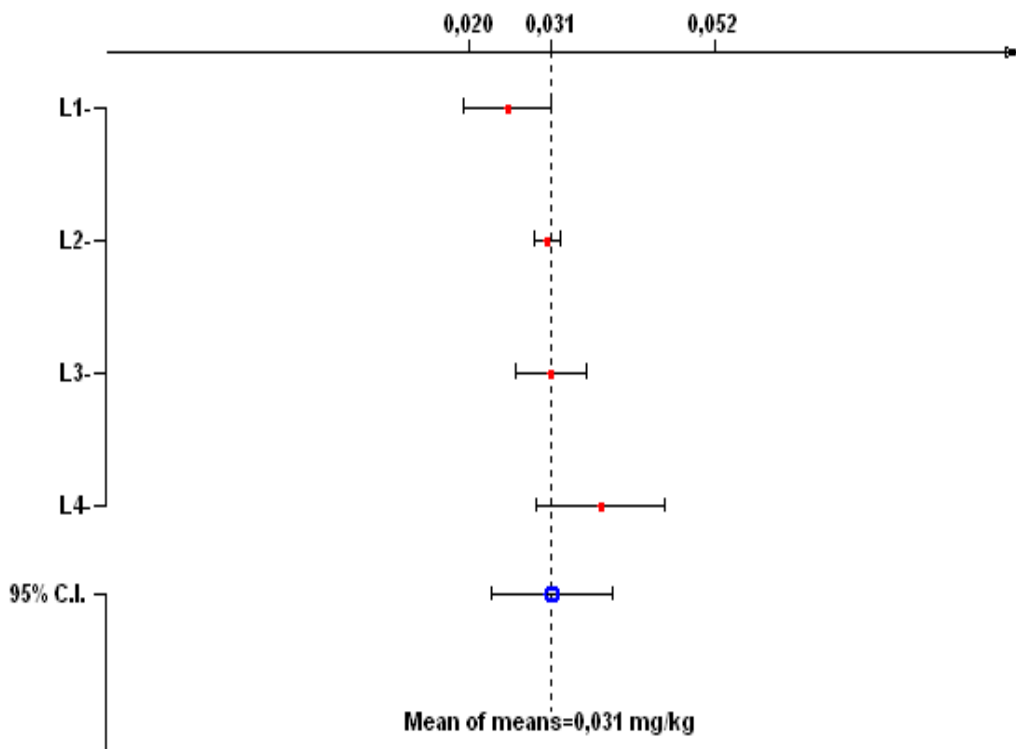
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
 D = Dixon test
 G_(s) = Grubbs test (single test)
 N = Nalimov 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. A2.3)



Tab. A2.4 Copper (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
7 GD-MS	0.033	0.005	0.005	0.030	0.030	0.030	0.030	0.040	0.040
4 ICP-MS	0.034	0.005	0.006	0.036	0.035	0.024	0.038	0.039	0.033
8 GD-MS	0.041	0.007	0.007	0.037	0.032	0.043	0.038	0.050	0.048
9 GF-CSAAS	0.052	0.003	0.003	0.052	0.050	0.047	0.052	0.055	0.056

Range [min..max]	[0.024 .. 0.056]
Mean of means	0.040
95% H.W. Confidence Interval	0.014
95% H.W. Tolerance Interval	0.055

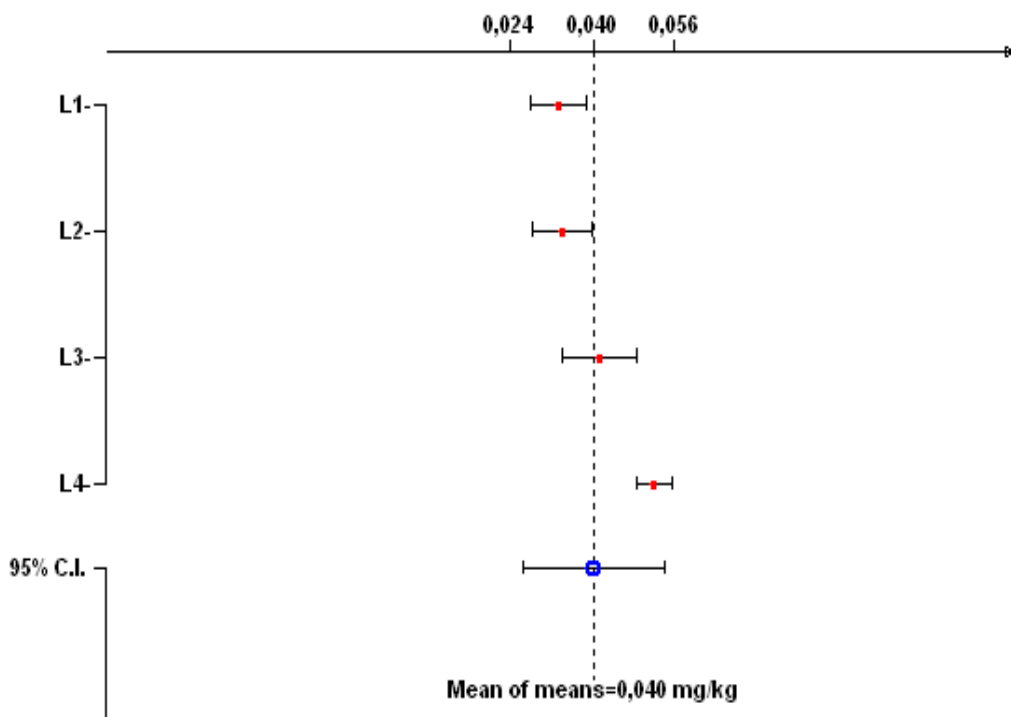
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
 D = Dixon test
 G_(s) = Grubbs test (single test)
 N = Nalimov 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. A2.4)



Tab. A2.5: Iron (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
8 GD-MS	0.162	0.014	0.015	0.143	0.165	0.186	0.156	0.155	0.164
7 GD-MS	0.197	0.023	0.024	0.220	0.210	0.170	0.180	0.180	0.220
4 ICP-MS	0.242	0.027	0.028	0.240	0.290	0.230	0.250	0.210	0.230
11 ICP-MS	0.315	0.042	0.044	0.390	0.330	0.270	0.310	0.290	0.300
9 GF-CSAAS	0.365	0.048	0.050	0.390	0.370	0.320	0.430	0.300	0.380

Range [min..max]	[0.143 .. 0.430]
Mean of means	0.256
95% H.W. Confidence Interval	0.104
95% H.W. Tolerance Interval	0.425

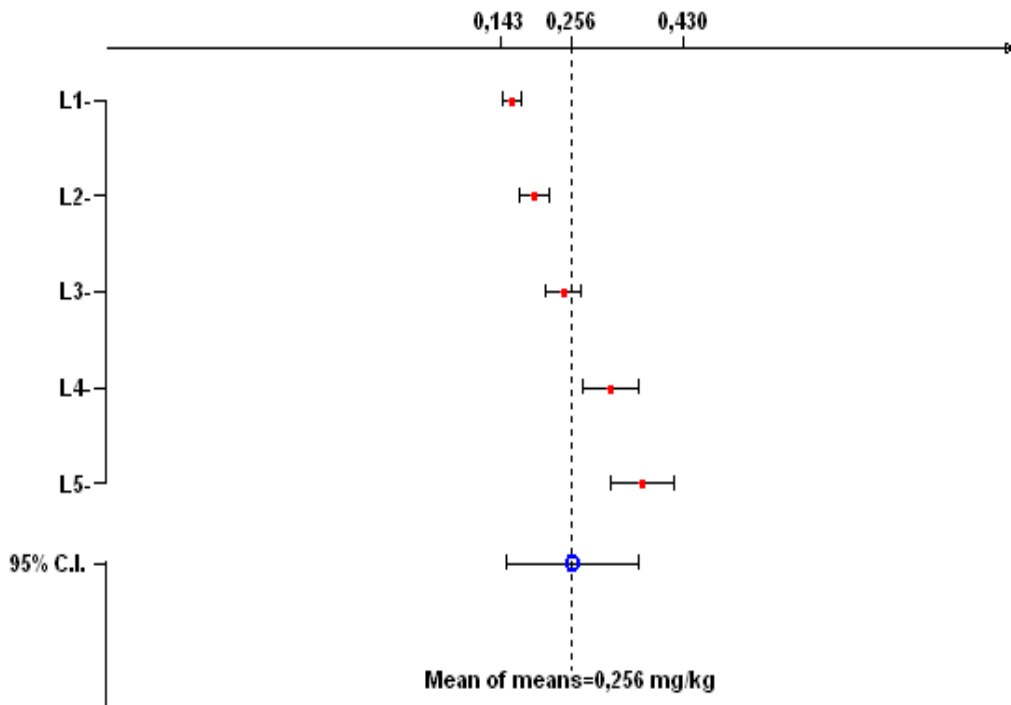
Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
 D = Dixon test
 G_(s) = Grubbs test (single test)
 N = Nalimov 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. A2.5)



Tab. A2.6: Tantalum (values in mg/kg)

Lab Abbreviation	M (mg/kg)	S _M	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
4 ICP-MS	3.62	0.22	0.23	3.50	3.49	3.94	3.86	3.44	3.47
8 ICP OES	6.87	0.84	0.88	6.04	5.71	7.22	6.85	7.64	7.73
11 ICP-MS	12.23	2.76	2.90	10.10	14.70	8.00	12.30	15.20	13.10

Range [min..max]	[3.44 .. 15.20]
Mean of means	7.57
95% H.W. Confidence Interval	10.81
95% H.W. Tolerance Interval	43.15

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 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. A2.6)

