Bundesanstalt für Materialforschung und -prüfung (BAM)

in co-operation with the WG 'Special Materials' of the Chemists' Committee of GDMB
Gesellschaft der Metallurgen und Bergleute e.V.

-

Certification Report

Certified Reference Material

BAM-S012

Titanium Diboride Powder

H.-J. Heinrich, J. Roik, W. Bremser

May 2019

Co-ordination: H.-J. Heinrich
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 "Inorganic Reference Materials"
Richard-Willstätter-Str. 11
12489 Berlin, Germany
Phone: ++49 30 8104-5988
Fax: ++49 30 8104-75988
E-mail: hans-joachim.heinrich@bam.de

Summary

This report describes the preparation and certification of the reference material BAM-S012, a titanium diboride powder with 13 certified mass fractions of main components and impurities. The certification work was carried out by Bundesanstalt für Materialforschung und -prüfung (BAM) in co-operation with the working group "Special Materials" of the Chemists' Committee of GDMB.

The following mass fractions and uncertainties have been certified:

Parameter	Mass fraction [1] in %	Uncertainty [2] in %
Ti	68.3	0.8
B	30.71	0.15
B_2O_3 [3]	0.359	0.024
	in mg/kg	**in mg/kg**
Al	12.0	1.3
Ca	44	4
Cr	97	4
Fe	640	40
Mg	1.6	0.4
Mn	3.8	0.4
Mo	11.7	0.7
Ni	23.5	1.1
V	10.2	0.8
Zr	121	4

[1] Unweighted mean value of the means of accepted sets of data (consisting of at least 5 but usually 6 single results), each set being obtained by a different laboratory and/or a different method of measurement.

[2] Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

[3] The conventional “Method M1” described in the attachment can be used for the determination of total mass fraction of boron oxide.

The following mass fractions and uncertainties are given as values for information:

Parameter	Mass fraction [1] in %	Uncertainty [2] in mg/kg
C	0.169	0.008
N	0.120	0.006
O	0.480	0.08
R_{acid} [3]	0.22	0.03
	in mg/kg	**in mg/kg**
Si	11	5
Na	< 10	
Nb [4]	1700	
S [4]	2	
W [4]	114	

[1] Values were not certified, but given for information, when the number of accepted data sets was too low (< 5) or when the uncertainty from the inter-laboratory certification was considerably larger than the expected range.

[2] Estimated expanded uncertainty *U* with a coverage factor of *k* = 2, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

[3] R_{acid}: acid insoluble residue. The conventional "Method M2" described in the attachment shall be used.

[4] Mean value of the dataset from one laboratory.

Validity of the Certificate: Until May 2034.

This report contains detailed information on the preparation of the CRMs as well as on homogeneity investigations and on the analytical methods used for certification analysis.

The certified values are based on the results of 15 laboratories which participated in the certification inter-laboratory comparison.

Contents

List of abbreviations
(if not explained elsewhere)

ANOVA	Analysis of variance
CGHE-IR	Carrier gas hot extraction method with infrared detection
CGHE-TC	Carrier gas hot extraction method with thermal conductivity detection
Comb-IR	Combustion method with infrared detection
CRM	Certified reference material
df	Degrees of freedom
ET AAS	Electrothermal atomic absorption spectrometry
F AAS	Flame atomic absorption spectrometry
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ILC	Inter-laboratory comparison
MS	Mean sum of squares from an ANOVA
n	Number of replicates per unit
r	Index denoting relative figures (uncertainties etc.)
R_{acid}	Acid insoluble residue
RSD	Relative standard deviation
s_{bb}	Between-bottle standard deviation
SD	Standard deviation
s_i	Intra-laboratory standard deviation
SS	Sum of squares from an ANOVA
SS-ET AAS	Solid sampling electrothermal atomic absorption spectrometry
u^*_{bb}	Standard uncertainty related to a maximum between-unit homogeneity that could be hidden by method repeatability; an additional index "r" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit homogeneity; an additional index "r" is added as appropriate
XRF	X-ray fluorescence spectrometry
α	Significance level

1 Introduction

Titanium Diboride (TiB_2) is the most stable of several titanium-boron compounds. The material does not occur in nature but may be synthesised by carbothermal reduction of TiO_2 and B_2O_3.
Titanium diboride is a hard refractory material with a high melting point (> 2900 °C), low electrical resistivity and high thermal conductivity. It is unaffected by most chemical reagents and has excellent stability and wettability in liquid metals such as zinc and aluminium.
TiB_2 is used as a high-performance ceramic for the following applications:

- Cathode material for aluminium smelting flux electrolysis
- Sputtering target for hard material coatings
- Evaporator boats
- Crucibles for non-ferrous metals
- Manufacture of cutting tools
- Ballistic protection

Certified reference materials, indispensable for the development and validation of appropriate analytical methods for the characterization of TiB_2 are still lacking. The idea for the development of a TiB_2 reference material is mainly based on discussions about the need und the importance of this special material within the GDMB Gesellschaft der Metallurgen und Bergleute e. V. and in particular in the working group "Special Materials" of the Chemists' Committee within GDMB. BAM organised an inter-laboratory comparison for certification of selected relevant parameters. Certification of the reference material BAM-S012 was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2 Companies/laboratories involved

2.1 Allocation and preparation of the material

- The material was produced by 3M Technical Ceramics, Zweigniederlassung der 3M Deutschland GmbH, Kempten (Germany).
- The material was filled into cleaned sample bottles by BAM under clean air conditions.

2.2 Homogeneity testing

- The analytical investigations for the homogeneity testing of Ti, Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr, C, N and O were carried out by Bundesanstalt für Materialforschung und –prüfung (BAM).
- The analytical investigations for the homogeneity testing of B, B_2O_3 and R_{acid} were carried out by 3M Technical Ceramics, Zweigniederlassung der 3M Deutschland GmbH, Kempten (Germany).
- All statistical evaluations for homogeneity testing were carried out by BAM.

2.3 Stability investigations

- Stress test was carried out by Bundesanstalt für Materialforschung und –prüfung (BAM).
- Long-term stability measurements were carried out by BAM.
- All succeeding calculations were carried out by BAM.

2.4 Characterisation study

Fifteen laboratories from four different countries participated in the inter-laboratory comparison for certification. These laboratories have well known ability to analyse refractory materials by adequate analytical methods. Most of them already participated successfully in certification inter-laboratory comparisons of other special materials CRMs. Therefore, no preceding qualification inter-laboratory comparison was carried out.

The participating laboratories are listed in alphabetical order:

- 3M Technical Ceramics, Zweigniederlassung der 3M Deutschland GmbH, Kempten (Germany)
- Bruker Elemental GmbH, Kalkar (Germany)
- Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin (Germany)
- Forschungszentrum Jülich GmbH, ZEA-3, Jülich (Germany)
- GFE Fremat GmbH, Freiberg (Germany)
- H.C. Starck GmbH, Goslar (Germany)
- H.C. Starck GmbH, Laufenburg (Germany)
- Karlsruher Institut für Technologie (KIT), Eggenstein-Leopoldshafen (Germany)
- Leibniz-Institut für Kristallzüchtung, Berlin (Germany)
- Lucideon, Penkhull, Stoke-on-Trent (United Kingdom)
- revierlabor Chemische Laboratorien für Industrie und Umwelt GmbH, Essen (Germany)
- Shanghai Institute of Ceramics, CAS, Shanghai (China)
- ThyssenKrupp Steel Europe AG, Duisburg (Germany)
- Treibacher Industrie AG, Althofen (Austria)
- Wolfram Bergbau- und Hütten AG, St. Martin im Sulmtal (Austria)

2.5 Determination of additional material data

- The determination of particle size distribution was carried out by 3M Technical Ceramics, Zweigniederlassung der 3M Deutschland GmbH, Kempten (Germany).

2.6 Compilation and revision of conventional analytical methods

- Method M1:
  Extraction Method for Measurement of B_2O_3 content of TiB_2 according to DIN 54387-2 [4]
- Method M2:
  Measurement of Acid Insoluble Residue of TiB_2 according to DIN 54387-2 [4]

3 Candidate material

The titanium diboride powder material was taken from the customary production line of the producer 3M Technical Ceramics, Kempten (Germany). The manufacturing process of the material involved its stabilisation by artificial ageing. TiB_2 is susceptible to oxidation over time as it is exposed to air and moisture. The entire material had the same lot number (#308V197) that had been produced under the same stable working conditions. The candidate material was bottled by BAM into 400 transparent Pyrex glass bottles each containing 50 g of the material. The bottles were filled with Ar, closed and sealed with a shrinking foil. The grain size of the material is given in Table 1.

Table 1: Particle size distribution of BAM-S012

D_{97}	33.8 µm
D_{50}	12.3 µm
D_{06}	2.3 µm

4 Homogeneity investigation of the material

For homogeneity testing 15 bottles were representatively taken from a total of 400 bottles by a combination of random access and systematic selection (see Table 2). From each of the N = 15 bottles four sub-samples were taken for analysis.

Table 2: Selected bottles analysed for homogeneity of BAM-S012

15	34	69	99	119	150	170	198	219	257	270	296	318	342	383

The methods used for homogeneity testing are given in Table 3. For all parameters well established methods also applied for certification inter-laboratory comparison were used.

Table 3: Analytical methods used for homogeneity testing

Parameter	Analytical method	Sub-sample mass
Ti	ICP OES after microwave assisted acid decomposition with HF/HCl/HNO_3	100 mg
Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr	ICP OES after microwave assisted acid decomposition with HF/HCl/HNO_3	500 mg
B	Titrimetry (mannitoboric acid procedure) after fusion with $NaKCO_3$	150 mg
B_2O_3	Method M1 (Annex D)	5 g
R_{acid}	Method M2 (Annex E)	2.5 g
C	Comb-IR	200 mg
N	CGHE-TC	50 mg
O	CGHE-IR	50mg

Between-unit inhomogeneity was quantified using one-way analysis of variance (ANOVA).
All measurement results (raw data) with data analysis are summarised in Annex 1.
In case of Mg an additional correction for trend was made as described in ISO Guide 35 [3]. The initial results obtained from ICP OES showed a modest downward trend, attributable to instrument drift. Statistical treatment was therefore used to remove the adverse effects of the trend. The linear trend from the data was subtracted. The results are shown as the residuals in a new table. One-way analysis of variance (ANOVA) was then applied to the residuals.

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budget were calculated according to ISO Guide 35 [3] using Eq. (1) and Eq. (2):

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

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

with:

$MS_{between}$	mean of squared deviations between bottles (from one-way ANOVA)
MS_{within}	mean of squared deviations within bottles (from one-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). In any case the larger of the two values was used as u_{bb}. Eq. (1) does not apply if MS_{within} is larger than $MS_{between}$.
The ANOVA results together with the calculated values of s_{bb}, u^*_{bb}, and u_{bb} are listed in Table 4.

Table 4: Results from one-way ANOVA and relative uncertainty contributions due to possible inhomogeneity

Element	$MS_{between}$[a] ($mg^2\ kg^{-2}$)	MS_{within}[b] ($mg^2\ kg^{-2}$)	F_{obs}[c]	F_{crit}[d]	$s_{bb,r}$ (%)	$u^*_{bb,r}$ (%)	$u_{bb,r}$ (%)
Ti	2.8771439	2.4558669	1.1715	1.9182	0.47	0.52	0.52
B	0.0044650	0.0039374	1.1340	1.9182	0.04	0.05	0.05
B_2O_3	4.9542E-06	2.2597E-06	2.1924	1.9182	0.23	0.10	0.23
R_{acid}	2.0238E-05	2.9444E-05	0.6873	1.9182	$MS_{between} < MS_{within}$	0.62	0.62
C	3.2005E-06	1.8154E-06	1.7629	1.9182	0.35	0.18	0.35
N	1.6405E-05	1.2287E-05	1.3351	1.9182	0.89	0.71	0.89
O	0.0010395	0.0005525	1.8817	1.9182	2.56	1.25	2.56
Al	1.2656655	1.0262843	1.2333	1.9182	1.75	1.67	1.75
Ca	2.2400188	1.8219186	1.2295	1.9182	0.81	0.78	0.81
Cr	0.9243463	0.4287985	2.1557	1.9182	0.38	0.16	0.38
Fe	63.331050	34.320421	1.8453	1.9182	0.42	0.21	0.42
Mg	0.0025194	0.0013531	1.9043	1.9182	1.02	0.50	1.02
Mn	0.0016591	0.0010346	1.6037	1.9182	0.36	0.21	0.36
Mo	0.0263938	0.0185340	1.4241	1.9182	0.38	0.27	0.38
Ni	0.0514505	0.0383183	1.3427	1.9182	0.25	0.20	0.25
V	0.0200552	0.0104960	1.9108	1.9182	0.51	0.25	0.51
Zr	1.6512623	0.5716796	2.8884	1.9182	0.42	0.14	0.42

[a] Mean Square between bottles from one-way ANOVA
[b] Mean Square within bottles from one-way ANOVA
[c] Observed F-value: $MS_{between}/MS_{within}$
[d] Critical F-value $F_{0.05}(14,45)$

The results of this study indicate that the material is sufficiently homogeneous for the use as reference material.

5 Stability of the material

TiB_2 as a refractory ceramic material is known to be stable. Because of its chemical inertness and its stability at high temperatures no comprehensive stability test involving all parameters was performed. If at all, the non-metal contents were the most sensitive parameters to indicate an aging of the material. Therefore, the mass fractions of C, N and O in selected units of the candidate material were followed after an additional accelerated ageing over several weeks at temperatures at 40 °C and 80 °C (so-called "stress test") and up to 48 months (long-term study).

5.1 Stress test

In each case 4 sub-samples from three bottles were analysed for C, N and O after exposition of the following stress levels in an isochronous study [5]:

ref: Reference level, 4 weeks at 4 °C (refrigerator)
4_40: 4 weeks at 40 °C
2_80: 2 weeks at 80 °C, then 2 weeks at 4 °C (refrigerator)

Mass fractions of C, N and O were determined using the methods described in the homogeneity study. For evaluation chi-square test was used under the assumption that the value is constant over all stress levels. It assesses the compatibility of the constant average with the results taken at different times and stress levels within their analytical uncertainties.

Individual results and the related test are summarised in Annex B1.

The test results assess good stability under ambient conditions.

5.2 Long-term study

Samples were stored in addition to the stress test for 36 and 48 months for the long-term stability study. According to the same scheme also samples filled in bottles without Ar (only under air) were measured. All data used for the evaluation of stability are summarised in Annexes B2 – B7. The data points were plotted against time and the regression line was calculated. The slope of the regression lines was then tested for statistical significance (loss/increase) due to storage conditions.

For mass fractions of C and O in the bottles filled under Ar an insignificant change over time was found. A slightly significant change towards lower N values was observed. For bottles without Ar only C values were insignificant while N and O values show a significant change over time.

It was decided to include the apparent degradation for O (positive coefficient) in the uncertainty of stability. The standard error from the regression statistics was used as uncertainty of stability u_{lts} of the materials.

Following from the stability investigations, the mass fractions of the non-metals C, N and O were taken as informative values only. The material will be subjected to post-certification stability monitoring after 24 months to control its further stability.

6 Inter-laboratory comparison for characterisation

6.1 Analytical methods used

Fifteen laboratories participated in the certification inter-laboratory comparison. The laboratories were asked to analyse six subsamples after drying at (110 ± 5) °C for one hour to achieve defined starting conditions for subsequent analysis. They were free to choose any suitable method of analysis, except for the conventional methods for B_2O_3 and the acid insoluble residue (R_{acid}).

All participating laboratories were instructed to use only calibrants prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 5 summarises the analytical procedures used by the participating laboratories. The laboratory code is a random number and does not correspond to the order of laboratories in Section 2.4.

Table 5: Summary of analytical procedures used by the participating laboratories

Lab code	Element	Sub-sample mass	Sample pre-treatment/ decomposition	Calibrants	Analytical method
1	Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr	250 mg	Dissolution in a mixture of HF, HCl and HNO_3	1 g/L Merck Certipur	ICP-MS
2	Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr	500 mg	Dissolution in a mixture of HF, HCl and HNO_3	1 g/L Merck Certipur	ICP OES
	Na, Si	6.4 - 11.6 mg	Solid sampling technique	1 g/L Merck Certipur	SS-ET AAS
	C	200 mg		Na_2CO_3	Comb-IR
	N	50 mg		KNO_3	CGHE-TC
	O	50 mg		Fe_2O_3	CGHE-IR
4	Ca, Cr, Fe, Mo, Ni, Zr	100 mg	Dissolution in a mixture of HF and HNO_3	1 mg/L single element standard solutions (National Analysis Center for Iron&Steel, China)	ICP OES

(continued)

Lab code	Element	Sub-sample mass	Sample pre-treatment/ decomposition	Calibrants	Analytical method
5	Al, Ca, Cr, Fe, Mg, Mn, Mo, Na, Ni, Si, V, Zr	500 mg	Dissolution in a mixture of HF, HCl and HNO_3; final volume 100 mL	1 g/L Merck Certipur single element standard solutions; matrix-matched with Ti, H_3BO_3, HF, HCl and HNO_3	ICP OES
	B	150 mg	Fusion with 5 g $NaKCO_3$, Pt crucible with Pt lid, Bunsen burner, dissolution of the melt cake with diluted HCl. Precipitation of TiO_2 by addition of $BaCO_3$ and boiling. Filtration.		Titrimetry (mannitoboric acid procedure)
	Ti	75 mg	Sample decomposition: melt fusion with 5 g Na_2CO_3, Pt crucible with Pt lid, Bunsen burner, dissolution of the melt cake with diluted H_2SO_4. Formation of $H_2[TiO_2(SO_4)_2]$ by addition of diluted H_2O_2 solution	1 g/L Merck Certipur; exact matrix matching	Photometry
	B_2O_3	5 g	According to the conventional method M1		Titrimetry (mannitoboric acid procedure)
	R_{acid}	2.5 g	According to the conventional method M2		Gravimetry
	C	150 mg	Weighing of sub-samples into alumina crucibles	$BaCO_3$	Comb-IR
	N	50 mg	Weighing of sub-samples into tin capsules	KNO_3	CGHE-TC
	O	50 mg	Weighing of sub-samples into tin capsules	$BaCO_3$	CGHE-IR
6	C	100 mg	Weighing of sub-samples into ceramic crucibles	Steel Standard CRM 286-1 (C=0.100%)	Comb-IR
	N	50 mg	Weighing of sub-samples into tin capsules	Steel Standard AR 656 (N=0.0225%)	CGHE-TC
	O	50 mg	Weighing of sub-samples into tin capsules	Iron oxide Standard JK 47 (O=1.09%),	CGHE-IR
7	Al, Ca, Cr, Fe, Mg, Mn, Mo, Na, Ni, V, Zr	500 mg	Microwave assisted acid decomposition with $HF/HNO_3/HCl$ (240 °C, 60 bar)	10 g/L single element Alfa Aesar plasma standards; matrix-matched with Ti	ICP OES
	Si	500 mg	Fusion with K_2CO_3, 850 °C	10 g/L Alfa Aesar plasma standard; matrix-matched with Ti	ET AAS
	C			BCS-CRM352	Comb-IR
	O			WO_3	CGHE-TC
8	Al, Ca, Cr, Fe, Mn, Mo, Ni, V, Zr	500 mg	Dissolution in a mixture of HF, HCl and HNO_3	1 g/L certified standard solutions; addition method	ICP OES
	Ti	300 mg	HNO_3/HF digestion, $Na_2B_4O_7$ flux	matrix-matched	XRF
	C	250 mg		Steel CRM	Comb-IR
	N	50 mg		Steel CRM	CGHE-TC
	O	50 mg		Steel CRM	CGHE-IR

(continued)

Lab code	Element	Sub-sample mass	Sample pre-treatment/ decomposition	Calibrants	Analytical method
9	Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr	250 mg	Dissolution in a mixture of HF, HCl and HNO_3	1 g/L single element Alfa Aesar plasma standards; matrix-matched with Ti, H_3BO_3	ICP OES
	Cr, Mn, Mo, Ni, Zr	250 mg	Dissolution in a mixture of HF, HCl and HNO_3	1 g/L single element Alfa Aesar plasma standards; matrix-matched with Ti, H_3BO_3	ICP-MS
	N			AR646 (FeNiCr pins, Alpha Recources)	CGHE-TC
	O			JK 47 (Fe powder, Swerim)	CGHE-IR
10	Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Si, V, Zr	1 g	Dissolution in a mixture of HF and HNO_3, 2 h/105 °C	10 g/L Spetec, matrix-matched with TiO_2, H_3BO_3	ICP OES
	Na	1 g	Dissolution in a mixture of HF and HNO_3, 2 h/105 °C	10 g/L Spetec, matrix-matched with TiO_2, H_3BO_3	F AAS
	Ti	90 mg	fusion with $Na_2CO_3/Na_2B_2O_4$	TiO_2 (1150 °C / 2h)	Photometry
	B	200 mg	fusion with Na_2CO_3	Potassium hydrogen phthalate (120 °C / 2 h)	Titrimetry
	B_2O_3	3 – 5 g	According to the conventional method M1	Potassium hydrogen phthalate (120 °C / 2 h)	Titrimetry
	R_{acid}	2.5 g	According to the conventional method M2		Gravimetry
	C	100 mg		Na_2CO_3	Comb-IR
11	B, Al, Ca, Cr, Fe, Mg, Mn, Mo, Na, Ni, V, Zr, (Nb, S, W)*	100 mg	Microwave assisted acid decomposition with HF/HNO_3	1 g/L Merck standard solutions	ICP OES
	B_2O_3		According to the conventional method M1	0.1 mol/L NaOH, oxalic acid dihydrate	Titrimetry
	R_{acid}	15 g	According to the conventional method M2		Gravimetry
	C	200 mg		LECO Std 501-503 (steel)	Comb-IR
	N	200 mg		BCS-CRM 361 (Cr metal, BAS)	CGHE-TC
	O	200 mg		BCS-CRM 361 (Cr metal, BAS)	CGHE-IR
12	Al, Cr, Mn, Mo, Si, V, Zr	1 g	Dissolution in a mixture of HF, HCl and HNO_3, 105 °C	1 g/L standard solutions (Bernd Kraft); standard addition	ICP OES
	Ca, Fe, Mg, Na, Ni	1 g	Dissolution in a mixture of HF, HCl and HNO_3, 105 °C	1 g/L standard solutions (Bernd Kraft); standard addition	F AAS
	Ti	86 - 89 mg	Fusion with $NaKCO_3/Na_2B_2O_4$, stained with H_2O_2	TiO_2	Photometry
	B	250 mg	Fusion with $NaKCO_3/KNO_3$	1 g/L B standard solution (Bernd Kraft)	Titrimetry

(continued)

Lab code	Element	Sub-sample mass	Sample pre-treatment/ decomposition	Calibrants	Analytical method
12	B_2O_3	2 g	According to the conventional method M1		
	R_{acid}	3 g	According to the conventional method M2		Gravimetry
	C	300 mg	Addition of 1 g W/Sn (30% Sn) + 1 g Fe with known blank	$CaCO_3$	Comb-IR
	N	30 mg	Addition of 1 g Ni pin and Sn capsule with known blank	KNO_3	CGHE-TC
	O	30 mg	Addition of 1 g Ni pin and Sn capsule with known blank	KNO_3	CGHE-IR
14	B, Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Ti, V, Zr	36 - 49 mg	HF + HNO_3, room temperature, 1.2 µm ultrafiltration	1 g/L standard solutions (Bernd Kraft); matrix matching with HNO_3, HF, Ti, B	ICP OES
	B, Ti	4.2 – 6.3 mg	HF + HNO_3, room temperature, 1.2 µm ultrafiltration	1 g/L standard solutions (Bernd Kraft); matrix matching with HNO_3, HF	ICP OES
15	Cr, Fe, Mn, Mo, Ni, Zr	100 mg	digested in a mixture of 2 mL HF + 2 mL HCl + 6 mL HNO_3 and neutralized with 20 mL of 4% boric acid solution	1 g/L commercial mono-element solutions	ICP OES
	B	50 mg	fused with Na_2CO_3 over a Bunsen burner and made up to 500 mL	1 g/L B prepared in house from pure B_2O_3 powder	ICP OES
	Ti	435 mg	mixed with Lithium Borate flux and fused over a Bunsen burner until complete decomposition	Pure TiO_2 powder	XRF
16	Ca, Cr, Fe, Zr	250 mg	Fusion with 4g Na_2CO_3/K_2CO_3 mixture + 4 g Na_2O_2, melt dissolved in HCl	1 g/L Merck Certipur single element standard solutions	ICP OES
	Fe				F AAS
	B, Ti	100 mg	Fusion with 2g Na_2CO_3/K_2CO_3 mixture + 2 g Na_2O_2, melt dissolved in HCl	1 g/L Merck Certipur,	ICP OES
	Si		distillation	1 g/L Merck Certipur	Photometry
	C	80 mg		Commercial steel samples St 145 (ASMW), 42400-3050 and 42400-3040 (Eltra)	Comb-IR
	N	70 - 100 mg	in Ni capsule + 3.3 g Ni flux	Commercial standards from LECO, Ti matrix	CGHE-TC
	O	70 - 100 mg	in Ni capsule + 3.3 g Ni flux	Commercial standards from LECO, Ti matrix	CGHE-IR

(continued)

Lab code	Element	Sub-sample mass	Sample pre-treatment/ decomposition	Calibrants	Analytical method
17	Al, B, Ca, Cr, Fe, Mg, Mn, Mo, Na, Ni, Si, Ti, V, Zr	1 g	Dissolution in a mixture of HNO_3 and H_2O_2, 150 °C	Stock standard solutions prepared from pure metals or metal salts (Alfa Aesar, Merck); matrix matching with Ti and B	ICP OES
	B_2O_3	2 g	According to the conventional method M1	H_3BO_3	ICP OES
	C			WC; W granules + Fe chips as additive	Comb-IR
	N			Si_3N_4; in Ni capsule with pure Fe chips as additive	CGHE-TC
	O			CuO; W granules + Fe chips as additive	CGHE-IR

* elements not requested in the characterisation study

6.2 Statistical evaluation of ILC results

Individual results of the participants grouped per element are compiled in Tables C.1 to C.20 of Annex C. These tables show the single results of each laboratory, the corresponding laboratories' mean values together with the intra-laboratory standard deviation (s_i). All results which were excluded from the evaluation for technical or statistical reasons are marked grey.
The graphical presentation of the results as bar graphs include the mean and standard deviation of each lab's results (accepted data sets), the certified or informative value (mean of lab means) and the corresponding expanded uncertainty (Figures C.1 – C.18).

Statistical tests and data evaluation were performed using the software program SoftCRM 1.2.2. [6].

The following tests at significance levels of 0.05 and 0.01 were carried out:

- Grubbs test for identification of outlying means
- Dixon and Nalimov test for verification of possible outlier indications
- Cochran test for identification of outlying variances
- Kolmogorov-Smirnov-Lillifors test for normality of laboratories' means distribution
- Skewness and kurtosis test for normality of laboratories' means distribution
- Snedecor F-test for equality of two standard deviations
- Bartlett test for homogeneity of variances

The results of these tests are summarised in Tables D.1 to D.18 in Annex D (with indication of the respective level of significance, α = 0.05 or α = 0.01).

An individual data set was excluded from further data processing only in case that it had been identified as Grubbs test (α = 0.05) or paired Grubbs test (α = 0.01) outlier.

Most datasets showed some outlying variances. The set of variances is often not homogeneous which is due to the fact that different methods are used each having a different repeatability and reproducibility. Furthermore, the majority of the Cochran test outliers fulfilled the criterion that the standard error of the mean ($s_i/\sqrt{n_i}$) of the dataset not exceeded the standard deviation of the distribution of all laboratory means. Therefore, no flagged outlying variances were removed.

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. After a discussion with the laboratories concerned and further examination of the methods applied, some contributions were withdrawn or excluded from the evaluation. No values were excluded from the evaluation for statistical reasons alone, data were only excluded if a sound technical reason was given. At the sessions, it was also decided to take a parameter as certified or informative value.

All accepted laboratory mean values of the characterisation study together with the mean of the laboratory means and the standard deviation of the laboratory means are listed in Tables 6 and 7.

Table 6: Means of excepted data sets, certified values

Line no.	**Ti** [%]	**B** [%]	**B_2O_3** [%]	**Al** [mg/kg]	**Ca** [mg/kg]	**Cr** [mg/kg]	**Fe** [mg/kg]	**Mg** [mg/kg]	**Mn** [mg/kg]	**Mo** [mg/kg]	**Ni** [mg/kg]	**V** [mg/kg]	**Zr** [mg/kg]
1	67.87	30.48	0.324	< 10	35.4	88.9	---	0.95	---	9.9	---	8.7	---
2	67.93	30.61	0.356	10.3	35.9	89.1	559	1.05	3.25	< 10	21.5	9.4	105
3	68.02	30.65	0.356	10.9	39.2	92.0	564	1.27	3.37	10.4	22.1	9.7	115
4	68.20	30.71	0.366	11.4	40.0	92.6	597	1.56	3.43	11.0	22.2	< 10	121
5	68.27	30.76	0.393	11.9	41.5	95.6	601	1.75	3.44	11.3	22.2	10.0	120
6	68.53	30.78		12.5	43.0	96.2	627	1.87	3.61	11.6	23.3	10.1	121
7	68.55	30.97		13.4	43.6	97.4	643	2.00	3.77	11.6	23.6	10.3	121
8	68.86	---		13.5	44.2	97.8	646	2.24	3.78	11.8	23.7	10.4	122
9				---	45.6	98.2	652	< 6	3.79	12.0	23.8	11.0	123
10				< 30	48.2	98.8	657	< 10	4.33	12.1	23.8	12.2	125
11					49.9	100.1	667		4.47	12.1	23.8	---	125
12					52.7	101.5	662		4.62	12.3	24.1		126
13					54.0	101.5	680		< 10	12.8	24.6		126
14						107.7	690			12.9	27.0		131
15						---	764						---
M :	**68.28**	**30.71**	**0.359**	**12.0**	**44.1**	**97.0**	**643**	**1.59**	**3.81**	**11.7**	**23.5**	**10.2**	**121**
s_M :	0.35	0.15	0.025	1.2	5.9	5.1	53	0.46	0.47	0.9	1.4	1.0	6

"---": indication for the omission of outlying values

Table 7: Means of excepted data sets, informative values

Line no.	***C*** *[%]*	***N*** *[%]*	***O*** *[%]*	***R_{acid}*** *[%]*	***Si*** *[mg/kg]*	***Na*** *[mg/kg]*	***Nb**** *[mg/kg]*	***S**** *[mg/kg]*	***W**** *[mg/kg]*
1	---	*0.107*	---	*0.200*	*3.5*	*0.17*	*1700*	*2*	*114*
2	---	*0.115*	---	*0.202*	*6.3*	*0.42*			
3	*0.147*	*0.115*	*0.436*	*0.202*	*9.7*	*< 1*			
4	*0.164*	*0.116*	*0.438*	*0.257*	*< 10*	*2.65*			
5	*0.168*	*0.120*	*0.475*		*10.9*	*< 5*			
6	*0.171*	*0.123*	*0.482*		*16.2*	*< 6*			
7	*0.172*	*0.127*	*0.499*		*18.3*	*< 10*			
8	*0.174*	*0.128*	*0.500*		*< 50*				
9	*0.175*	*0.133*	*0.503*						
10	*0.180*		*0.508*						
M :	*0.169*	*0.120*	*0.480*	*0.215*	*10.8*	*< 10*			
s_M :	*0.010*	*0.008*	*0.029*	*0.028*	*5.7*				

* data provided for elements not requested in the characterisation study
"---": indication for the omission of outlying values

7 Certified and informative values

7.1 Certified values and uncertainties

Certified values for all analytes are based on the unweighted mean of the means of the accepted datasets as shown in Table 6. Full uncertainty budgets following the 'Guide to the Expression of Uncertainty in Measurement' [7] were established.

The respective combined uncertainty values contain contributions from the spread resulting from the certification inter-laboratory comparison (u_{ilc}), the potential between-unit inhomogeneity (u_{bb}), of the average precision of accepted laboratory means (u_{prec}) and if significant from long-term stability (u_{lts}). The different contributions to the uncertainty are then combined using the following equation:

$$u_c = \sqrt{u_{ilc}^2 + u_{bb}^2 + u_{prec}^2 + u_{lts}^2} \qquad (3)$$

- u_{ilc} was calculated using Equation (4), where s_M is the standard deviation of the laboratories' means (see Table 4) and N is the number of accepted data sets

$$u_{ilc} = \sqrt{\frac{s_M^2}{N}} \qquad (4)$$

- u_{bb} was estimated as described in Section 4,
- u_{prec} was calculated using Equation (5), where SD_i is the standard deviation of the results of an individual participant, n is the number of replicate analyses performed by each participant and N is the number of accepted individual data sets.

$$u_{prec} = \sqrt{\sum_{i=1}^{N} SD_i^2 \Big/ n \cdot N} \qquad (5)$$

- u_{lts} was estimated as described in Section 5,

The expanded uncertainty of the certified value U_{CRM} was calculated according to GUM [4] with a coverage factor of k = 2, representing a level of confidence of approximately 95%, as

$$U_{CRM} = 2 \cdot u_c \qquad (6)$$

The certified mass fractions and the results from the calculation of the combined uncertainty and their associated expanded uncertainties are summarised in Table 8.
Finally, a summary of the certified mass fractions with their respective expanded uncertainties after rounding according to DIN 1333 [8] is given on Page 3 of this report.

Table 8: Certified values and their uncertainties (before rounding)

Parameter	u_{ilc}	u_{bb}	u_{prec}	u_{lts}	u_c	Certified value	U_{CRM}	Unit
Ti	0.1226	0.3556	0.0761	0	0.3837	68.28	0.7675	%
B	0.0578	0.0145	0.0379	0	0.0706	30.71	0.1412	%
B_2O_3	0.0111	0.0008	0.0037	0	0.0117	0.359	0.0234	%
Al	0.458	0.210	0.327	0	0.601	11.99	1.202	mg/kg
Ca	1.636	0.358	0.950	0	1.925	44.09	3.850	mg/kg
Cr	1.375	0.372	0.752	0	1.611	96.96	3.221	mg/kg
Fe	14.25	2.67	6.10	0	15.73	643.5	31.46	mg/kg
Mg	0.163	0.016	0.108	0	0.196	1.586	0.393	mg/kg
Mn	0.141	0.014	0.099	0	0.173	3.805	0.346	mg/kg
Mo	0.239	0.045	0.196	0	0.312	11.65	0.624	mg/kg
Ni	0.391	0.059	0.333	0	0.517	23.50	1.033	mg/kg
V	0.336	0.052	0.164	0	0.377	10.20	0.755	mg/kg
Zr	1.747	0.514	0.695	0	1.949	121.5	3.898	mg/kg

7.2 Informative values and uncertainties

After discussion at sessions of the GDMB Working Group "Special Materials" it was decided to take the values of the non-metals C, N and O as informative values because a major part of the laboratories based their calibrations on the use of matrix materials instead of pure substances having a definite stoichiometry.

The data obtained for the parameters R_{acid}, Si, Na, Nb, S and W did not allow a certification.

For these elements, insufficient data sets are available, or they scatter more than the elements listed above (Table 6). Moreover, except for R_{acid} homogeneity data are lacking. No uncertainty evaluation was carried out for Na, Nb, S, Ta, and W.

The informative values and the results from the calculation of the combined uncertainty and their associated expanded uncertainties are summarised in Table 9.

Finally, a summary of the informative mass fractions with their respective expanded uncertainties after rounding according to DIN 1333 [8] is given on Page 4 of this report.

Table 9: Informative values and their uncertainties

Parameter	u_{ilc}	u_{bb}	u_{prec}	u_{lts}	u_c	Informative value	U_{CRM}	Unit
C	0.00352	0.00059	0.00136	0	0.00382	0.169	0.00764	%
N	0.00275	0.00107	0.00159	0	0.00335	0.120	0.00670	%
O	0.0102	0.0123	0.0053	0.0316	0.0358	0.480	0.0715	%
R_{acid}	0.0139	0.0013	0.0055	0	0.0150	0.215	0.0299	%
Si	2.312	0	0.560	0	2.379	10.82	4.758	mg/kg

7.3 Metrological traceability

The values are traceable to the SI (Système International d'Unités) via calibration using standard solutions prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

8 Instructions for use

8.1 Area of application

The reference material is intended to be used for the calibration of analytical instruments and for the validation or verification of analytical methods suitable for the analysis of titanium diboride materials.

8.2 Handling

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. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different parameters: Ti (100 mg); B (150 mg); Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr (500 mg); C (200 mg); N, O (50 mg); B_2O_3 (5 g); R_{acid} (2.5 g). 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. The sample must be dried at (110 ± 5) °C for one hour to achieve defined starting conditions for subsequent analysis. Storage in a desiccator with appropriate absorbing reagents is strongly recommended after drying until the beginning of the analytical procedure.

8.3 Transport and storage

The material should be stored in a dry and clean environment at room temperature. Transport under normal ambient conditions.

8.4 Safety guidelines

The usual laboratory safety precautions must be applied. This material is not classified as hazardous according to Regulation (EC) No. 1272/2008 [9]. No hazardous effect is to be expected if the material is used under conditions usually adopted in analytical laboratories when handling finely dispersed powder materials. For detailed information on the safe handling of the material, please see the Material Safety Data Sheet distributed by the producer of the material (available on request).

9 Information on and purchase of the CRM

Certified reference material BAM-S012 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 „Inorganic Reference Materials“
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 – 8104 72061
E-mail: sales.crm@bam.de

Each bottle of BAM-S012 will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM:
https://www.bam.de.
Tel. +49 30 8104 1111.

10 References

[1] ISO 17034: 2016, General requirements for the competence of reference material producers.

[2] ISO Guide 31:2015, Reference materials - Contents of certificates, labels and accompanying documentation.

[3] ISO Guide 35: 2017, Reference materials - Guidance for characterization and assessment of homogeneity and stability.

[4] DIN 54387-2:2016-12, Testing of ceramic raw and basic materials - Chemical analysis of boron carbide, boron nitride, metal borides and elemental boron - Part 2: Determination of total boron, soluble boron compounds, HNO_3-soluble boron in B_4C, H_2O_2 soluble and insoluble fractions in amorphous boron and HF/HNO_3 insoluble fractions in titanium boride.

[5] A. Lamberty, H. Schimmel, J. Pauwels, The study of the stability of reference materials by isochronus measurements. Fres. J. Anal. Chem. 360 (1998) 359 -361.

[6] G. Bonas, M. Zervou, T. Papaeoannou, M. Lees, “SoftCRM”: a new software for the certification of reference materials, Accred. Qual. Assur. 8 (2003) 101-107.

[7] ISO/IEC Guide 98-3:2008, Uncertainty in measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM:1995).

[8] DIN 1333:1992-02 Zahlenangaben (Presentation of numerical data).

[9] REGULATION (EC) No 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

11 Annexes

Annex A: Data from homogeneity study

Annex B: Stability study

Annex C: Results obtained in the characterisation study

Annex D: Outcome of statistical tests on results from the ILC

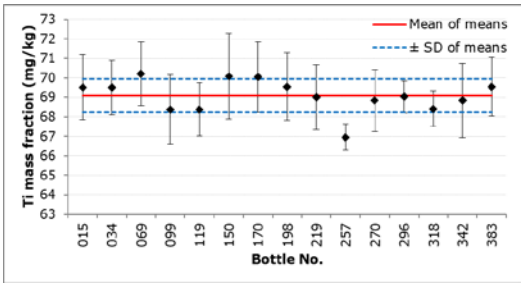
Annex E: Method M1

Annex F: Method M2

Annex A: Data from homogeneity study

A.1: Ti

Bottle No.	Ti mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	71.87	68.94	67.90	69.36	69.52	1.68	2.42
034	67.62	69.24	70.64	70.49	69.50	1.40	2.01
069	69.18	70.09	72.54	68.99	70.20	1.63	2.32
099	69.96	66.28	69.79	67.45	68.37	1.80	2.64
119	68.24	68.90	66.58	69.81	68.38	1.36	2.00
150	71.98	71.64	69.54	67.21	70.09	2.20	3.14
170	67.57	71.12	69.83	71.62	70.04	1.81	2.58
198	69.20	70.53	71.21	67.26	69.55	1.74	2.51
219	67.85	67.40	70.86	69.91	69.01	1.65	2.39
257	66.79	67.85	66.94	66.24	66.96	0.67	1.00
270	69.11	69.32	66.61	70.34	68.84	1.58	2.30
296	69.36	69.70	69.22	67.81	69.02	0.83	1.21
318	69.13	69.29	67.65	67.59	68.42	0.92	1.34
342	69.82	68.34	70.76	66.40	68.83	1.90	2.76
383	68.66	69.56	68.28	71.67	69.54	1.52	2.18
					Mean of means:		69.08
					SD of means:		0.848

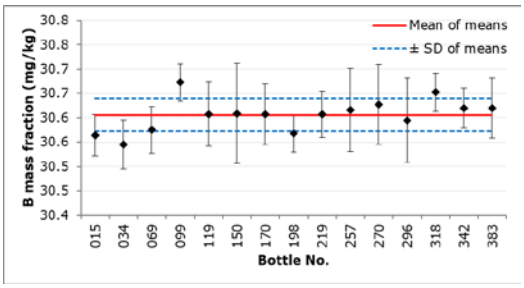


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	278.073025	69.5182563	2.82964911		
034	4	277.985563	69.4963906	1.95690552		
069	4	280.796663	70.1991656	2.66219243		
099	4	273.4758	68.36895	3.25482287		
119	4	273.53085	68.3827125	1.86252846		
150	4	280.376188	70.0940469	4.84765948		
170	4	280.145975	70.0364938	3.26258362		
198	4	278.2013	69.550325	3.03693462		
219	4	276.026913	69.0067281	2.72371021		
257	4	267.820388	66.9550969	0.4447474		
270	4	275.375625	68.8439063	2.50700114		
296	4	276.099688	69.0249219	0.69387535		
318	4	273.660563	68.4151406	0.84247963		
342	4	275.320813	68.8302031	3.61693708		
383	4	278.163113	69.5407781	2.29597727		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	40.2800144	14	2.8771439	1.1715	0.3287	1.9182
Within Groups	110.514013	45	2.4558669			
Total	150.794027	59				
n	4			status:	homogeneous	
s_{bb}	0.3245293			$s_{bb,r}$ (%)	0.47	
$s_{bb\,min}$	0.3597715			$u^*_{bb,r}$ (%)	0.52	
u_{bb}	0.3597715					
$u_{bb,r}$ (%)	0.52					

A.2: B

Bottle No.	B mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	30.57	30.62	30.55	30.52	30.56	0.043	0.14
034	30.52	30.52	30.62	30.52	30.55	0.050	0.16
069	30.65	30.55	30.57	30.54	30.58	0.048	0.16
099	30.70	30.70	30.67	30.62	30.67	0.038	0.12
119	30.70	30.62	30.57	30.55	30.61	0.066	0.22
150	30.52	30.52	30.70	30.70	30.61	0.103	0.33
170	30.67	30.52	30.62	30.62	30.61	0.063	0.21
198	30.54	30.54	30.62	30.57	30.57	0.038	0.12
219	30.62	30.67	30.57	30.57	30.61	0.048	0.16
257	30.57	30.68	30.52	30.70	30.62	0.085	0.28
270	30.70	30.70	30.55	30.57	30.63	0.081	0.27
296	30.67	30.67	30.52	30.52	30.60	0.087	0.28
318	30.62	30.70	30.67	30.62	30.65	0.039	0.13
342	30.57	30.67	30.62	30.62	30.62	0.041	0.13
383	30.70	30.62	30.62	30.55	30.62	0.061	0.20

Mean of means: 30.61
SD of means: 0.033

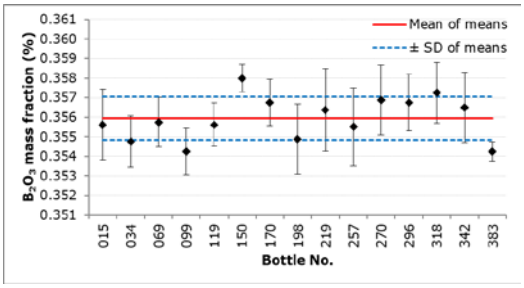


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	122.255	30.56375	0.00182292		
034	4	122.18	30.545	0.0025		
069	4	122.3	30.575	0.00235		
099	4	122.69	30.6725	0.001425		
119	4	122.43	30.6075	0.004375		
150	4	122.435	30.60875	0.01050625		
170	4	122.43	30.6075	0.00395833		
198	4	122.27	30.5675	0.001425		
219	4	122.43	30.6075	0.00229167		
257	4	122.465	30.61625	0.00728958		
270	4	122.51	30.6275	0.00664167		
296	4	122.38	30.595	0.0075		
318	4	122.61	30.6525	0.00155833		
342	4	122.48	30.62	0.00166667		
383	4	122.48	30.62	0.00375		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.06251	14	0.0044650	1.1340	0.3568	1.9182
Within Groups	0.17718125	45	0.0039374			
Total	0.23969125	59				
n	4			status:	homogeneous	
s_{bb}	0.0114852			$s_{bb,r}$ (%)	0.04	
$s_{bb\,min}$	0.0144055			$u^*_{bb,r}$ (%)	0.05	
u_{bb}	0.0144055					
$u_{bb,r}$ (%)	0.05					

A.3: B_2O_3

Bottle No.	B_2O_3 mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	0.354	0.355	0.356	0.358	0.356	0.0018	0.51
034	0.354	0.354	0.357	0.355	0.355	0.0013	0.37
069	0.355	0.358	0.356	0.356	0.356	0.0013	0.35
099	0.356	0.354	0.354	0.354	0.354	0.0012	0.34
119	0.355	0.355	0.357	0.356	0.356	0.0011	0.31
150	0.358	0.357	0.359	0.359	0.358	0.0007	0.20
170	0.358	0.356	0.356	0.358	0.357	0.0012	0.33
198	0.355	0.358	0.354	0.354	0.355	0.0018	0.51
219	0.357	0.357	0.354	0.359	0.356	0.0021	0.59
257	0.355	0.355	0.359	0.355	0.356	0.0020	0.56
270	0.358	0.359	0.355	0.357	0.357	0.0018	0.50
296	0.357	0.355	0.359	0.357	0.357	0.0014	0.40
318	0.355	0.358	0.359	0.358	0.357	0.0016	0.44
342	0.359	0.358	0.355	0.355	0.357	0.0018	0.50
383	0.355	0.355	0.355	0.354	0.354	0.0005	0.14

Mean of means: 0.356
SD of means: 0.0011

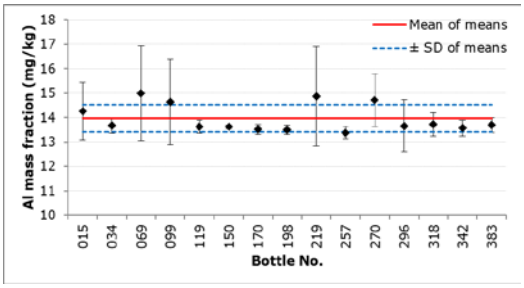


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	1.4225	0.355625	3.2292E-06		
034	4	1.419	0.35475	0.00000175		
069	4	1.423	0.35575	1.5833E-06		
099	4	1.417	0.35425	1.4167E-06		
119	4	1.4225	0.355625	1.2292E-06		
150	4	1.432	0.358	5E-07		
170	4	1.427	0.35675	1.4167E-06		
198	4	1.4195	0.354875	3.2292E-06		
219	4	1.4255	0.356375	4.3958E-06		
257	4	1.422	0.3555	4E-06		
270	4	1.4275	0.356875	3.2292E-06		
296	4	1.427	0.35675	2.0833E-06		
318	4	1.429	0.35725	2.4167E-06		
342	4	1.426	0.3565	3.1667E-06		
383	4	1.417	0.35425	0.00000025		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.9358E-05	14	4.9542E-06	2.1924	0.0237	1.9182
Within Groups	0.00010169	45	2.2597E-06			
Total	0.00017105	59				
n	4			status:	inhomogeneous	
s_{bb}	0.0008207			$s_{bb,r}$ (%)	0.23	
$s_{bb\,min}$	0.0003451			$u^*_{bb,r}$ (%)	0.10	
u_{bb}	0.0008207					
$u_{bb,r}$ (%)	0.23					

A.4: Al

Bottle No.	Al mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	16.02	13.83	13.40	13.81	14.26	1.19	8.32
034	13.76	13.35	13.49	14.08	13.67	0.32	2.37
069	13.55	14.82	17.79	13.84	15.00	1.94	12.91
099	14.50	13.57	13.30	17.15	14.63	1.76	12.00
119	13.89	13.78	13.60	13.28	13.64	0.27	1.94
150	13.53	13.71	13.61	13.62	13.62	0.08	0.56
170	13.49	13.59	13.74	13.24	13.51	0.21	1.53
198	13.37	13.47	13.76	13.39	13.50	0.18	1.35
219	13.52	17.80	14.66	13.49	14.87	2.03	13.65
257	13.39	13.70	13.09	13.34	13.38	0.25	1.86
270	13.45	14.18	15.71	15.50	14.71	1.08	7.34
296	13.08	15.25	13.10	13.22	13.66	1.06	7.78
318	14.08	13.38	14.16	13.24	13.72	0.48	3.47
342	13.78	13.47	13.16	13.85	13.57	0.32	2.36
383	14.14	13.44	13.66	13.55	13.70	0.31	2.23

Mean of means: 13.96
SD of means: 0.563

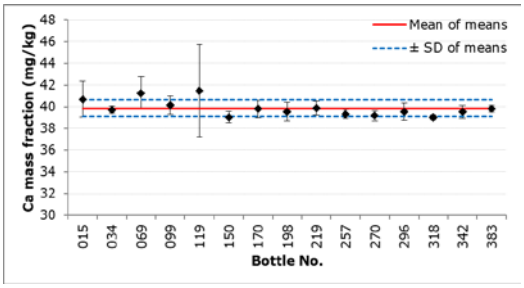


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	57.0562087	14.2640522	1.40777391		
034	4	54.6896042	13.6724011	0.10469251		
069	4	59.9894416	14.9973604	3.74715829		
099	4	58.5225685	14.6306421	3.08333159		
119	4	54.5443661	13.6360915	0.07023555		
150	4	54.4722807	13.6180702	0.0059007		
170	4	54.0539461	13.5134865	0.04285406		
198	4	53.982969	13.4957422	0.03323874		
219	4	59.4724007	14.8681002	4.12160827		
257	4	53.5302352	13.3825588	0.0619952		
270	4	58.833517	14.7083792	1.16396657		
296	4	54.6465432	13.6616358	1.12943036		
318	4	54.8656153	13.7164038	0.22631059		
342	4	54.2604125	13.5651031	0.10215055		
383	4	54.7844636	13.6961159	0.09361707		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17.7193176	14	1.2656655	1.2333	0.2862	1.9182
Within Groups	46.1827918	45	1.0262843			
Total	63.9021094	59				
n	4			status:	homogeneous	
s_{bb}	0.244633			$s_{bb,r}$ (%)	1.75	
$s_{bb\,min}$	0.2325724			$u^*_{bb,r}$ (%)	1.67	
u_{bb}	0.244633					
$u_{bb,r}$ (%)	1.75					

A.5: Ca

Bottle No.	Ca mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	43.01	40.77	39.42	39.54	40.68	1.67	4.10
034	40.17	39.55	39.38	39.74	39.71	0.34	0.86
069	39.65	41.91	42.96	40.53	41.26	1.46	3.55
099	39.07	40.75	39.87	40.90	40.15	0.85	2.11
119	40.11	47.79	39.48	38.55	41.48	4.25	10.26
150	38.89	39.21	38.44	39.61	39.04	0.49	1.26
170	39.22	40.02	40.81	39.14	39.80	0.78	1.97
198	38.77	38.90	40.41	40.14	39.55	0.84	2.12
219	40.80	39.43	39.83	39.46	39.88	0.64	1.61
257	39.32	39.57	38.73	39.65	39.32	0.41	1.05
270	39.47	38.87	38.68	39.63	39.16	0.46	1.17
296	38.55	39.86	39.37	40.42	39.55	0.80	2.01
318	39.26	38.78	39.02	39.07	39.03	0.20	0.50
342	40.04	40.05	39.14	38.94	39.54	0.59	1.48
383	39.65	39.50	40.23	39.84	39.80	0.32	0.80

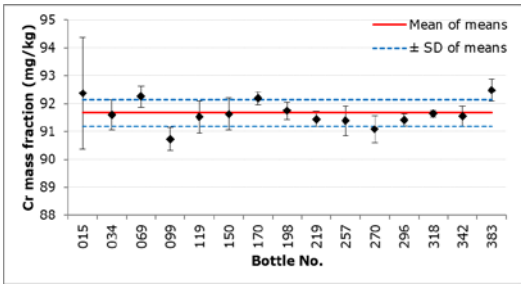
Mean of means: 39.86
SD of means: 0.75



Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	162.738633	40.6846584	2.77619488		
034	4	158.83745	39.7093624	0.11666902		
069	4	165.052289	41.2630722	2.141797		
099	4	160.592225	40.1480563	0.71930895		
119	4	165.934138	41.4835345	18.1034257		
150	4	156.143948	39.0359869	0.2436726		
170	4	159.195964	39.7989909	0.61590671		
198	4	158.215412	39.553853	0.70310729		
219	4	159.52195	39.8804875	0.4107773		
257	4	157.276869	39.3192173	0.17170016		
270	4	156.643989	39.1609972	0.21074536		
296	4	158.190282	39.5475705	0.63338374		
318	4	156.118976	39.0297441	0.03860362		
342	4	158.161627	39.5404069	0.34298081		
383	4	159.216971	39.8042429	0.10050518		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	31.360263	14	2.2400188	1.2295	0.2887	1.9182
Within Groups	81.9863348	45	1.8219186			
Total	113.346598	59				
n	4			status:	homogeneous	
s_{bb}	0.3233034			$s_{bb,r}$ (%)	0.81	
$s_{bb\,min}$	0.3098767			$u^*_{bb,r}$ (%)	0.78	
u_{bb}	0.3233034					
$u_{bb,r}$ (%)	0.81					

A.6: Cr

Bottle No.	Cr mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	94.88	93.10	90.96	90.55	92.37	2.01	2.18
034	92.26	91.71	90.92	91.49	91.59	0.55	0.60
069	92.29	92.67	91.76	92.31	92.26	0.38	0.41
099	90.13	90.99	90.80	90.99	90.73	0.41	0.45
119	91.62	92.22	91.42	90.81	91.52	0.58	0.63
150	92.44	91.61	91.30	91.15	91.63	0.58	0.63
170	92.11	92.28	91.93	92.46	92.20	0.22	0.24
198	91.35	91.69	91.84	92.08	91.74	0.31	0.33
219	91.25	91.72	91.16	91.65	91.44	0.28	0.31
257	90.92	91.68	90.95	91.99	91.39	0.53	0.58
270	90.94	90.48	91.39	91.55	91.09	0.48	0.53
296	91.28	91.43	91.71	91.25	91.42	0.21	0.23
318	91.57	91.54	91.59	91.81	91.63	0.12	0.13
342	91.96	91.46	91.66	91.08	91.54	0.37	0.40
383	92.78	92.19	92.09	92.83	92.47	0.39	0.42
				Mean of means:	91.67		
				SD of means:	0.48		

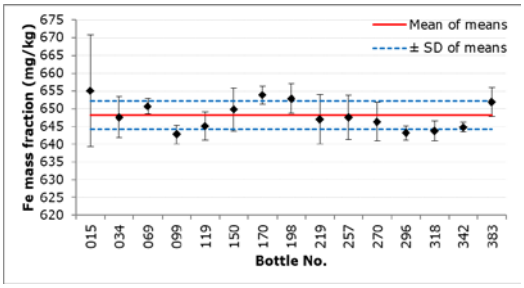


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	369.495007	92.3737518	4.0579041		
034	4	366.37898	91.5947449	0.30385172		
069	4	369.024105	92.2560263	0.14128061		
099	4	362.9094	90.72735	0.16944649		
119	4	366.069452	91.517363	0.33596571		
150	4	366.501457	91.6253643	0.33587203		
170	4	368.78358	92.1958951	0.05045954		
198	4	366.957143	91.7392857	0.0934989		
219	4	365.771474	91.4428684	0.07974798		
257	4	365.543438	91.3858594	0.28558061		
270	4	364.362975	91.0907437	0.23175748		
296	4	365.673015	91.4182537	0.04476465		
318	4	366.511499	91.6278748	0.01439504		
342	4	366.162151	91.5405377	0.13744309		
383	4	369.894827	92.4737068	0.15001028		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12.940848	14	0.9243463	2.1557	0.0262	1.9182
Within Groups	19.2959347	45	0.4287985			
Total	32.2367826	59				
n	4			status:	inhomogeneous	
s_{bb}	0.3519758			$s_{bb,r}$ (%)	0.38	
$s_{bb\,min}$	0.1503319			$u^*_{bb,r}$ (%)	0.16	
u_{bb}	0.3519758					
$u_{bb,r}$ (%)	0.38					

A.7: Fe

Bottle No.	Fe mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	676.1	657.7	645.8	640.4	655.0	15.80	2.41
034	653.9	640.5	646.0	650.0	647.6	5.77	0.89
069	647.9	653.0	651.0	650.8	650.7	2.13	0.33
099	641.0	643.9	640.2	645.9	642.8	2.62	0.41
119	647.0	649.4	643.8	640.3	645.1	3.96	0.61
150	656.2	651.6	649.5	641.6	649.7	6.08	0.94
170	654.6	656.1	650.3	654.2	653.8	2.50	0.38
198	648.1	654.4	657.8	651.1	652.8	4.16	0.64
219	642.0	650.7	640.5	654.7	647.0	6.84	1.06
257	639.4	653.2	646.4	651.4	647.6	6.19	0.96
270	648.9	638.5	648.1	650.1	646.4	5.33	0.83
296	642.8	642.7	646.0	641.3	643.2	2.00	0.31
318	640.4	644.2	643.3	647.3	643.8	2.84	0.44
342	643.5	643.8	645.9	646.1	644.8	1.34	0.21
383	654.3	645.9	652.7	654.9	651.9	4.12	0.63

Mean of means: 648.2
SD of means: 3.98

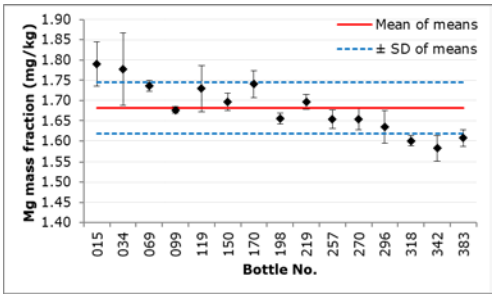


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	2619.96463	654.991157	249.482909		
034	4	2590.36629	647.591572	33.2717285		
069	4	2602.709	650.67725	4.53929737		
099	4	2571.06098	642.765244	6.88356813		
119	4	2580.54059	645.135147	15.6698351		
150	4	2598.90041	649.725101	36.9277177		
170	4	2615.23286	653.808214	6.27308363		
198	4	2611.38154	652.845385	17.3450326		
219	4	2588.00062	647.000156	46.8368173		
257	4	2590.38357	647.595893	38.2790701		
270	4	2585.57624	646.394059	28.4580016		
296	4	2572.89725	643.224313	3.98688616		
318	4	2575.10129	643.775321	8.09269544		
342	4	2579.31046	644.827614	1.78436926		
383	4	2607.76823	651.942059	16.975296		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	886.6347	14	63.331050	1.8453	0.0609	1.9182
Within Groups	1544.41892	45	34.320421			
Total	2431.05362	59				
n	4			status:	homogeneous	
s_{bb}	2.6930758			$s_{bb,r}$ (%)	0.42	
$s_{bb\,min}$	1.3449331			$u^*_{bb,r}$ (%)	0.21	
u_{bb}	2.6930758					
$u_{bb,r}$ (%)	0.42					

A.8: Mg

Bottle No.	Mg mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	1.871	1.773	1.749	1.768	1.790	0.055	3.05
034	1.886	1.711	1.697	1.815	1.777	0.089	5.04
069	1.726	1.740	1.753	1.726	1.736	0.013	0.74
099	1.676	1.686	1.667	1.678	1.677	0.008	0.48
119	1.752	1.799	1.692	1.675	1.729	0.057	3.29
150	1.699	1.687	1.676	1.726	1.697	0.022	1.27
170	1.716	1.757	1.780	1.709	1.740	0.034	1.94
198	1.672	1.656	1.655	1.639	1.655	0.013	0.80
219	1.721	1.678	1.695	1.690	1.696	0.018	1.09
257	1.650	1.661	1.626	1.681	1.654	0.023	1.39
270	1.668	1.625	1.639	1.685	1.654	0.027	1.65
296	1.613	1.694	1.606	1.628	1.635	0.040	2.45
318	1.618	1.591	1.593	1.601	1.601	0.012	0.76
342	1.581	1.626	1.559	1.563	1.582	0.030	1.92
383	1.637	1.603	1.602	1.587	1.607	0.021	1.31

Mean of means: 1.682
SD of means: 0.063

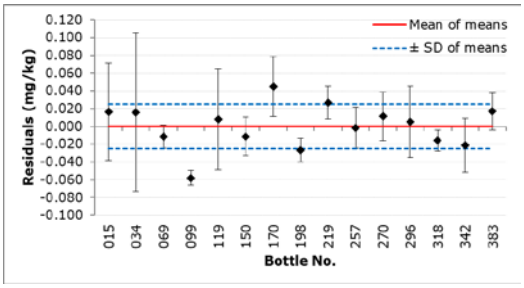


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	7.16075	1.7901875	0.00298835		
034	4	7.1075	1.776875	0.0080049		
069	4	6.944	1.736	0.00016604		
099	4	6.707	1.67675	6.5708E-05		
119	4	6.91725	1.7293125	0.00323656		
150	4	6.7885	1.697125	0.00046335		
170	4	6.96175	1.7404375	0.00113631		
198	4	6.62175	1.6554375	0.00017656		
219	4	6.784	1.696	0.00033879		
257	4	6.61775	1.6544375	0.00052714		
270	4	6.6165	1.654125	0.00074119		
296	4	6.5405	1.635125	0.00160127		
318	4	6.4025	1.600625	0.0001466		
342	4	6.32925	1.5823125	0.00092052		
383	4	6.4285	1.607125	0.00044594		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.22533041	14	0.01609503	11.5188184	1.3802E-10	1.91824856
Within Groups	0.06287766	45	0.00139728			
Total	0.28820806	59				
n	4			status:	inhomogeneous	
s_{bb}	0.0606171			$s_{bb,r}$ (%)	3.60	
$s_{bb\,min}$	0.0085816			$u^*_{bb,r}$ (%)	0.51	
u_{bb}	0.0606171					
$u_{bb,r}$	3.60					

A.8a: Mg, trend-corrected data

Bottle No.	Residuals (mg/kg)					
	#1	#2	#3	#4	Mean	SD_i
015	0.09244	-0.00313	-0.02250	-0.00182	0.01625	0.05167
034	0.12030	-0.05201	-0.06214	0.05805	0.01605	0.08828
069	-0.02583	-0.01039	0.00723	-0.01783	-0.01171	0.01411
099	-0.06271	-0.05053	-0.06590	-0.05222	-0.05784	0.00761
119	0.02640	0.07484	-0.02729	-0.04260	0.00784	0.05358
150	-0.01373	-0.02354	-0.02992	0.02226	-0.01123	0.02330
170	0.01664	0.05957	0.08669	0.01788	0.04520	0.03411
198	-0.01475	-0.02806	-0.02544	-0.03850	-0.02669	0.00976
219	0.04787	0.00631	0.02843	0.02536	0.02699	0.01701
257	-0.01026	0.00317	-0.02796	0.02923	-0.00145	0.02410
270	0.02060	-0.01996	-0.00184	0.04660	0.01135	0.02877
296	-0.02128	0.06165	-0.02147	0.00296	0.00547	0.03918
318	-0.00342	-0.02773	-0.02161	-0.01092	-0.01592	0.01085
342	-0.02655	0.01989	-0.04199	-0.03580	-0.02111	0.02806
383	0.04232	0.01000	0.01363	0.00131	0.01681	0.01777

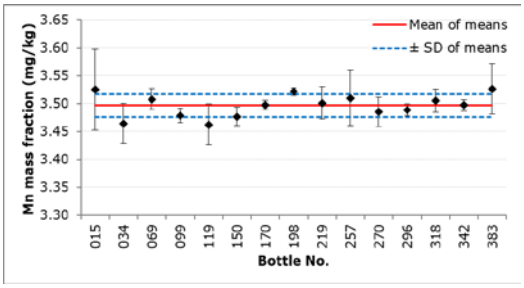
Mean of means: 0.00000
SD of means: 0.02510



Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	0.06499233	0.01624808	0.00266945		
034	4	0.06420771	0.01605193	0.00779275		
069	4	-0.04682691	-0.01170673	0.0001991		
099	4	-0.23136153	-0.05784038	5.7956E-05		
119	4	0.03135385	0.00783846	0.00287066		
150	4	-0.04493076	-0.01123269	0.00054304		
170	4	0.18078462	0.04519615	0.00116353		
198	4	-0.10675	-0.0266875	9.5207E-05		
219	4	0.10796538	0.02699135	0.0002895		
257	4	-0.00581924	-0.00145481	0.00058096		
270	4	0.04539615	0.01134904	0.00082744		
296	4	0.02186153	0.00546538	0.00153486		
318	4	-0.06367309	-0.01591827	0.00011772		
342	4	-0.08445771	-0.02111443	0.00078743		
383	4	0.06725767	0.01681442	0.00031577		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.03527203	14	0.00251943	1.90429735	0.05192156	1.91824856
Within Groups	0.05953607	45	0.00132302			
Total	0.0948081	59				
n	4			status:	homogeneous	
s_{bb}	0.0172946			$s_{bb,r}$ (%)	1.03	
$s_{bb\,min}$	0.0083504			$u^*_{bb,r}$ (%)	0.50	
u_{bb}	0.0172946					
$u_{bb,r}$ (%)	1.03					
Corrected ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.03527203	14	0.0025194	1.9043	0.0519	1.9182
Within Groups	0.05953607	44	0.0013531			
Total	0.0948081	58				
n	4			status:	homogeneous	
s_{bb}	0.0170758			$s_{bb,r}$ (%)	1.02	
$s_{bb\,min}$	0.0084924			$u^*_{bb,r}$ (%)	0.50	
u_{bb}	0.0170758					
$u_{bb,r}$ (%)	1.02					

A.9: Mn

Bottle No.	Mn mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	3.618	3.548	3.474	3.460	3.525	0.073	2.07
034	3.512	3.427	3.456	3.464	3.465	0.036	1.03
069	3.490	3.530	3.494	3.516	3.508	0.019	0.54
099	3.481	3.482	3.461	3.491	3.479	0.013	0.37
119	3.475	3.507	3.442	3.425	3.462	0.037	1.06
150	3.482	3.497	3.472	3.456	3.477	0.017	0.49
170	3.490	3.507	3.492	3.504	3.498	0.008	0.24
198	3.527	3.515	3.527	3.516	3.521	0.007	0.19
219	3.483	3.528	3.471	3.523	3.501	0.029	0.82
257	3.438	3.543	3.515	3.544	3.510	0.050	1.42
270	3.505	3.448	3.486	3.501	3.485	0.026	0.74
296	3.495	3.493	3.494	3.473	3.489	0.010	0.30
318	3.481	3.504	3.505	3.532	3.505	0.021	0.60
342	3.482	3.501	3.504	3.501	3.497	0.010	0.29
383	3.524	3.479	3.514	3.587	3.526	0.045	1.27
				Mean of means:	3.497		
				SD of means:	0.020		

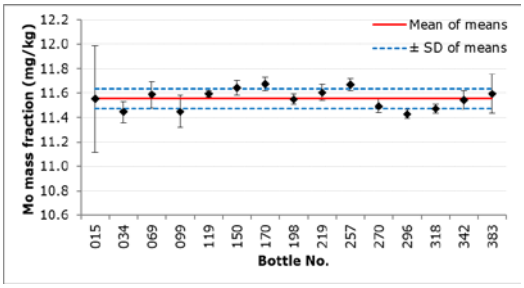


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	14.1005903	3.52514758	0.00534428		
034	4	13.8582242	3.46455605	0.00126853		
069	4	14.0305402	3.50763505	0.00035986		
099	4	13.9150044	3.4787511	0.00016535		
119	4	13.8488734	3.46221835	0.00133959		
150	4	13.9069302	3.47673255	0.00028528		
170	4	13.9919571	3.49798927	6.8565E-05		
198	4	14.0859924	3.52149811	4.6028E-05		
219	4	14.0048224	3.50120561	0.00081426		
257	4	14.0399185	3.50997962	0.00249803		
270	4	13.9410009	3.48525021	0.0006732		
296	4	13.9560444	3.48901109	0.00010843		
318	4	14.021132	3.50528301	0.00044094		
342	4	13.9888523	3.49721307	0.00010126		
383	4	14.1039601	3.52599003	0.00200499		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.02322782	14	0.0016591	1.6037	0.1152	1.9182
Within Groups	0.04655574	45	0.0010346			
Total	0.06978356	59				
n	4			status:	homogeneous	
s_{bb}	0.0124956			$s_{bb,r}$ (%)	0.36	
$s_{bb\,min}$	0.0073842			$u^*_{bb,r}$ (%)	0.21	
u_{bb}	0.0124956					
$u_{bb,r}$ (%)	0.36					

A.10: Mo

Bottle No.	Mo mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	12.14	11.61	11.24	11.21	11.55	0.437	3.78
034	11.55	11.34	11.44	11.45	11.44	0.086	0.75
069	11.48	11.56	11.58	11.73	11.59	0.105	0.91
099	11.28	11.52	11.42	11.57	11.45	0.131	1.15
119	11.56	11.63	11.60	11.59	11.59	0.027	0.23
150	11.73	11.65	11.59	11.60	11.64	0.062	0.54
170	11.66	11.73	11.61	11.70	11.67	0.053	0.46
198	11.53	11.53	11.53	11.61	11.55	0.040	0.35
219	11.51	11.64	11.64	11.64	11.60	0.066	0.57
257	11.62	11.74	11.68	11.65	11.67	0.048	0.41
270	11.55	11.47	11.53	11.43	11.49	0.054	0.47
296	11.39	11.46	11.45	11.41	11.43	0.034	0.30
318	11.45	11.47	11.52	11.44	11.47	0.036	0.31
342	11.61	11.57	11.57	11.43	11.55	0.076	0.66
383	11.74	11.52	11.71	11.41	11.59	0.158	1.36

Mean of means: 11.55
SD of means: 0.081

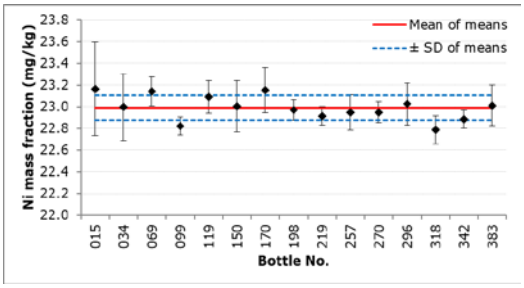


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	46.2036619	11.5509155	0.19059494		
034	4	45.7790982	11.4447745	0.00732327		
069	4	46.3485947	11.5871487	0.01108413		
099	4	45.7924753	11.4481188	0.01723299		
119	4	46.3794058	11.5948515	0.00074037		
150	4	46.5710169	11.6427542	0.00388672		
170	4	46.6983871	11.6745968	0.00284874		
198	4	46.1953102	11.5488276	0.00161088		
219	4	46.4188892	11.6047223	0.00433893		
257	4	46.6851931	11.6712983	0.00232527		
270	4	45.9782378	11.4945595	0.00290197		
296	4	45.7134207	11.4283552	0.00118781		
318	4	45.8898523	11.4724631	0.00128386		
342	4	46.1814382	11.5453596	0.00573522		
383	4	46.3780353	11.5945088	0.02491541		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.36951263	14	0.0263938	1.4241	0.1816	1.9182
Within Groups	0.83403152	45	0.0185340			
Total	1.20354415	59				
n	4			status:	homogeneous	
s_{bb}	0.0443275			$s_{bb,r}$ (%)	0.38	
$s_{bb\,min}$	0.0312543			$u^*_{bb,r}$ (%)	0.27	
u_{bb}	0.0443275					
$u_{bb,r}$ (%)	0.38					

A.11: Ni

Bottle No.	Ni mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	23.78	23.11	22.80	22.97	23.17	0.430	1.86
034	23.45	22.89	22.91	22.75	23.00	0.308	1.34
069	23.25	23.09	22.97	23.25	23.14	0.133	0.57
099	22.90	22.84	22.71	22.84	22.82	0.081	0.36
119	23.10	23.29	22.93	23.04	23.09	0.151	0.65
150	23.33	22.95	22.98	22.76	23.00	0.237	1.03
170	23.24	23.04	22.93	23.40	23.15	0.208	0.90
198	22.89	23.10	22.98	22.92	22.97	0.095	0.41
219	22.85	22.87	22.90	23.04	22.91	0.084	0.37
257	22.80	22.92	22.89	23.18	22.95	0.163	0.71
270	22.91	22.83	23.06	22.99	22.95	0.098	0.43
296	22.82	23.25	23.11	22.91	23.02	0.192	0.84
318	22.69	22.67	22.91	22.89	22.79	0.129	0.57
342	22.94	22.87	22.96	22.77	22.88	0.082	0.36
383	23.02	22.84	22.91	23.27	23.01	0.190	0.82

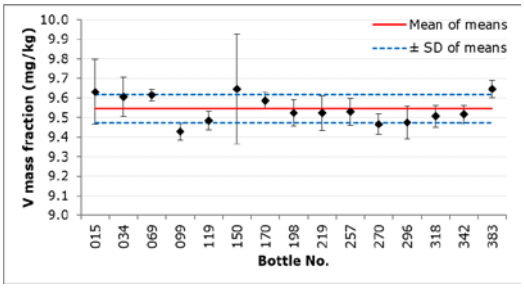
Mean of means: 22.99
SD of means: 0.113



Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	92.6625419	23.1656355	0.18471418		
034	4	91.9861998	22.99655	0.0946052		
069	4	92.5654893	23.1413723	0.01764648		
099	4	91.2914462	22.8228615	0.00658115		
119	4	92.3555178	23.0888794	0.0227703		
150	4	92.0163394	23.0040848	0.05621512		
170	4	92.6002882	23.150072	0.04344149		
198	4	91.883366	22.9708415	0.0090314		
219	4	91.6585896	22.9146474	0.00708805		
257	4	91.7846374	22.9461593	0.02661299		
270	4	91.7986262	22.9496566	0.00956764		
296	4	92.0966109	23.0241527	0.03700373		
318	4	91.1564585	22.7891146	0.016751		
342	4	91.5372479	22.884312	0.00680141		
383	4	92.0456966	23.0114242	0.035944		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.72030698	14	0.0514505	1.3427	0.2214	1.9182
Within Groups	1.72432242	45	0.0383183			
Total	2.4446294	59				
n	4			status:	homogeneous	
s_{bb}	0.057298			$s_{bb,r}$ (%)	0.25	
$s_{bb\,min}$	0.0449394			$u^*_{bb,r}$ (%)	0.20	
u_{bb}	0.057298					
$u_{bb,r}$ (%)	0.25					

A.12: V

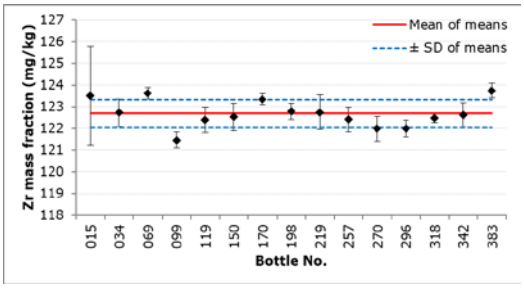
Bottle No.	V mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	9.848	9.671	9.499	9.507	9.631	0.165	1.71
034	9.735	9.552	9.506	9.632	9.606	0.100	1.04
069	9.653	9.592	9.587	9.628	9.615	0.031	0.32
099	9.386	9.482	9.442	9.404	9.429	0.043	0.45
119	9.464	9.546	9.495	9.435	9.485	0.047	0.50
150	10.07	9.511	9.494	9.513	9.647	0.282	2.92
170	9.580	9.552	9.567	9.647	9.586	0.042	0.44
198	9.427	9.536	9.565	9.567	9.524	0.066	0.69
219	9.439	9.649	9.502	9.498	9.522	0.089	0.94
257	9.461	9.590	9.479	9.585	9.529	0.068	0.72
270	9.476	9.397	9.527	9.465	9.466	0.053	0.56
296	9.376	9.560	9.438	9.525	9.475	0.083	0.88
318	9.586	9.469	9.462	9.506	9.506	0.057	0.60
342	9.564	9.514	9.535	9.453	9.517	0.047	0.50
383	9.619	9.601	9.668	9.697	9.646	0.044	0.46
				Mean of means:	9.546		
				SD of means:	0.071		



Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	38.5241165	9.63102912	0.02712921		
034	4	38.4256965	9.60642412	0.0100231		
069	4	38.4602495	9.61506237	0.00097169		
099	4	37.7149251	9.42873126	0.00182417		
119	4	37.9392713	9.48481781	0.00224914		
150	4	38.5865837	9.64664594	0.07931727		
170	4	38.3459322	9.58648305	0.0017707		
198	4	38.0955104	9.5238776	0.00434564		
219	4	38.0873067	9.52182668	0.00798979		
257	4	38.1155948	9.5288987	0.00465292		
270	4	37.8650433	9.46626082	0.00284452		
296	4	37.9002384	9.47505959	0.00692599		
318	4	38.0229802	9.50574504	0.00321077		
342	4	38.0664811	9.51662027	0.00222256		
383	4	38.5848149	9.64620372	0.00196204		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.2807727	14	0.0200552	1.9108	0.0510	1.9182
Within Groups	0.47231847	45	0.0104960			
Total	0.75309117	59				
n	4			status:	homogeneous	
s_{bb}	0.0488856			$s_{bb,r}$ (%)	0.51	
$s_{bb\,min}$	0.0235199			$u^*_{bb,r}$ (%)	0.25	
u_{bb}	0.0488856					
$u_{bb,r}$ (%)	0.51					

A.13: Zr

Bottle No.	Zr mass fraction (mg/kg)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	126.3	124.3	121.8	121.5	123.5	2.27	1.84
034	122.9	122.1	122.4	123.5	122.7	0.62	0.51
069	123.9	123.7	123.6	123.3	123.6	0.27	0.22
099	121.1	121.9	121.4	121.4	121.5	0.36	0.30
119	122.8	122.9	122.3	121.6	122.4	0.58	0.48
150	123.3	122.8	122.0	122.0	122.5	0.64	0.52
170	123.5	123.5	123.0	123.4	123.3	0.26	0.21
198	122.3	122.7	123.1	123.0	122.8	0.37	0.30
219	122.0	123.8	122.4	122.8	122.7	0.79	0.64
257	121.8	122.9	122.1	122.8	122.4	0.56	0.46
270	122.0	121.2	122.5	122.3	122.0	0.58	0.48
296	121.5	122.4	122.0	122.2	122.0	0.38	0.31
318	122.5	122.6	122.2	122.7	122.5	0.22	0.18
342	123.3	122.5	122.7	121.9	122.6	0.55	0.45
383	124.2	123.5	123.8	123.5	123.7	0.33	0.27
				Mean of means:	122.7		
				SD of means:	0.64		

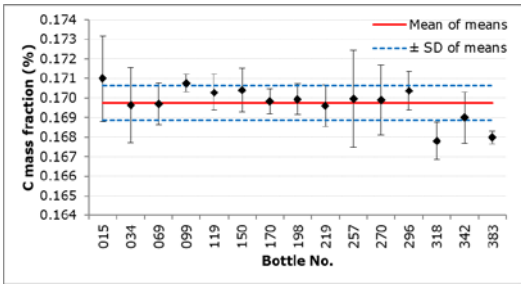


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	493.965462	123.491365	5.14092967		
034	4	490.897884	122.724471	0.3906225		
069	4	494.478395	123.619599	0.07176984		
099	4	485.848897	121.462224	0.13038432		
119	4	489.58028	122.39507	0.3414176		
150	4	490.094966	122.523741	0.40518954		
170	4	493.360627	123.340157	0.06670026		
198	4	491.13307	122.783267	0.13849693		
219	4	490.992145	122.748036	0.62444195		
257	4	489.647234	122.411809	0.3175023		
270	4	487.922272	121.980568	0.33680044		
296	4	487.974921	121.99373	0.1409977		
318	4	489.969713	122.492428	0.05060211		
342	4	490.494875	122.623719	0.3075434		
383	4	494.967	123.74175	0.11179586		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	23.1176716	14	1.6512623	2.8884	0.0035	1.9182
Within Groups	25.7255833	45	0.5716796			
Total	48.8432549	59				
n	4			status:	inhomogeneous	
s_{bb}	0.5195148			$s_{bb,r}$ (%)	0.42	
$s_{bb\,min}$	0.1735804			$u^*_{bb,r}$ (%)	0.14	
u_{bb}	0.5195148					
$u_{bb,r}$ (%)	0.42					

A.14: C

Bottle No.	C mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	0.1731	0.1724	0.1683	0.1703	0.1710	0.0022	1.28
034	0.1697	0.1675	0.1722	0.1691	0.1696	0.0019	1.13
069	0.1691	0.1687	0.1699	0.1711	0.1697	0.0011	0.63
099	0.1706	0.1703	0.1708	0.1713	0.1708	0.0004	0.26
119	0.1705	0.1693	0.1714	0.1699	0.1703	0.0009	0.54
150	0.1700	0.1716	0.1710	0.1690	0.1704	0.0011	0.66
170	0.1708	0.1696	0.1696	0.1693	0.1698	0.0007	0.39
198	0.1697	0.1709	0.1700	0.1691	0.1699	0.0008	0.46
219	0.1708	0.1688	0.1686	0.1702	0.1696	0.0011	0.63
257	0.1675	0.1728	0.1713	0.1683	0.1700	0.0025	1.47
270	0.1694	0.1688	0.1725	0.1688	0.1699	0.0018	1.05
296	0.1698	0.1718	0.1696	0.1703	0.1704	0.0010	0.58
318	0.1668	0.1689	0.1683	0.1673	0.1678	0.0010	0.57
342	0.1681	0.1709	0.1682	0.1688	0.1690	0.0013	0.77
383	0.1679	0.1679	0.1684	0.1677	0.1680	0.0003	0.19

Mean of means: 0.1697
SD of means: 0.0009

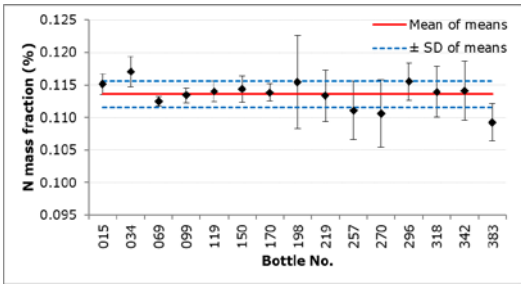


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	0.6839881	0.17099703	4.8E-06		
034	4	0.67856573	0.16964143	3.7061E-06		
069	4	0.67881936	0.16970484	1.127E-06		
099	4	0.68305115	0.17076279	1.9248E-07		
119	4	0.68114865	0.17028716	8.4194E-07		
150	4	0.6815799	0.17039498	1.2823E-06		
170	4	0.67932912	0.16983228	4.3833E-07		
198	4	0.67975609	0.16993902	6.092E-07		
219	4	0.67847968	0.16961992	1.1369E-06		
257	4	0.67982827	0.16995707	6.2094E-06		
270	4	0.67954482	0.16988621	3.1868E-06		
296	4	0.68147206	0.17036802	9.8448E-07		
318	4	0.67127769	0.16781942	9.0606E-07		
342	4	0.67598882	0.16899721	1.7107E-06		
383	4	0.6719504	0.1679876	9.9856E-08		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.4807E-05	14	3.2005E-06	1.7629	0.0759	1.9182
Within Groups	8.1694E-05	45	1.8154E-06			
Total	0.0001265	59				
n	4			status:	homogeneous	
s_{bb}	0.0005884			$s_{bb,r}$ (%)	0.35	
$s_{bb\,min}$	0.0003093			$u^*_{bb,r}$ (%)	0.18	
u_{bb}	0.0005884					
$u_{bb,r}$ (%)	0.35					

A.15: N

Bottle No.	N mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	0.1147	0.1153	0.1172	0.1133	0.1151	0.0016	1.40
034	0.1170	0.1162	0.1203	0.1148	0.1170	0.0023	1.99
069	0.1121	0.1134	0.1119	0.1126	0.1125	0.0007	0.61
099	0.1125	0.1123	0.1146	0.1142	0.1134	0.0012	1.03
119	0.1140	0.1135	0.1123	0.1161	0.1140	0.0016	1.36
150	0.1148	0.1142	0.1118	0.1167	0.1144	0.0020	1.76
170	0.1151	0.1142	0.1142	0.1120	0.1139	0.0013	1.17
198	0.1136	0.1133	0.1258	0.1090	0.1154	0.0072	6.24
219	0.1193	0.1111	0.1117	0.1115	0.1134	0.0039	3.47
257	0.1122	0.1112	0.1159	0.1051	0.1111	0.0045	4.02
270	0.1067	0.1170	0.1126	0.1061	0.1106	0.0052	4.71
296	0.1195	0.1144	0.1128	0.1154	0.1155	0.0028	2.47
318	0.1110	0.1114	0.1138	0.1195	0.1139	0.0039	3.43
342	0.1124	0.1097	0.1139	0.1203	0.1141	0.0045	3.96
383	0.1075	0.1063	0.1125	0.1108	0.1093	0.0028	2.60

Mean of means: 0.1136
SD of means: 0.0020

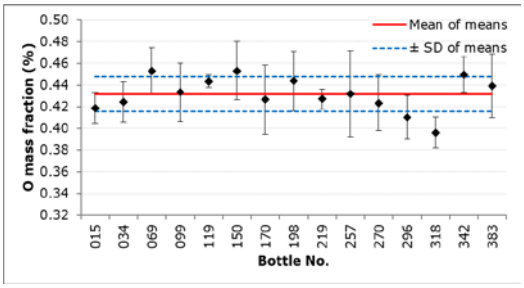


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	0.46053376	0.11513344	2.5838E-06		
034	4	0.46815977	0.11703994	5.4291E-06		
069	4	0.44992597	0.11248149	4.6372E-07		
099	4	0.4536271	0.11340678	1.3595E-06		
119	4	0.45598126	0.11399532	2.4056E-06		
150	4	0.4575081	0.11437702	4.0419E-06		
170	4	0.45547906	0.11386977	1.765E-06		
198	4	0.46172991	0.11543248	5.196E-05		
219	4	0.45354217	0.11338554	1.5473E-05		
257	4	0.44441574	0.11110393	1.9975E-05		
270	4	0.44246084	0.11061521	2.7089E-05		
296	4	0.46197902	0.11549475	8.1203E-06		
318	4	0.45577773	0.11394443	1.5231E-05		
342	4	0.45631382	0.11407845	2.0366E-05		
383	4	0.43713009	0.10928252	8.0496E-06		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00022968	14	1.6405E-05	1.3351	0.2255	1.9182
Within Groups	0.00055293	45	1.2287E-05			
Total	0.00078261	59				
n	4			status:	homogeneous	
s_{bb}	0.0010146			$s_{bb,r}$ (%)	0.89	
$s_{bb\,min}$	0.0008047			$u^*_{bb,r}$ (%)	0.71	
u_{bb}	0.0010146					
$u_{bb,r}$ (%)	0.89					

A.16: O

Bottle No.	O mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	0.4275	0.4133	0.4017	0.4324	0.4187	0.0139	3.33
034	0.4059	0.4472	0.4306	0.4141	0.4244	0.0183	4.32
069	0.4834	0.4356	0.4495	0.4441	0.4531	0.0210	4.63
099	0.4013	0.4666	0.4345	0.4307	0.4333	0.0267	6.16
119	0.4422	0.4362	0.4473	0.4484	0.4435	0.0056	1.25
150	0.4593	0.4690	0.4134	0.4708	0.4531	0.0270	5.95
170	0.3912	0.4655	0.4363	0.4127	0.4264	0.0319	7.49
198	0.4319	0.4606	0.4709	0.4111	0.4436	0.0272	6.14
219	0.4316	0.4170	0.4375	0.4220	0.4270	0.0092	2.16
257	0.4431	0.4808	0.4156	0.3879	0.4318	0.0397	9.18
270	0.4499	0.4413	0.4015	0.4011	0.4235	0.0258	6.10
296	0.3924	0.4028	0.4391	0.4071	0.4104	0.0201	4.90
318	0.4102	0.3865	0.4065	0.3813	0.3961	0.0144	3.63
342	0.4498	0.4268	0.4679	0.4536	0.4495	0.0170	3.79
383	0.4408	0.4378	0.4036	0.4754	0.4394	0.0293	6.67

Mean of means: 0.4316
SD of means: 0.0161

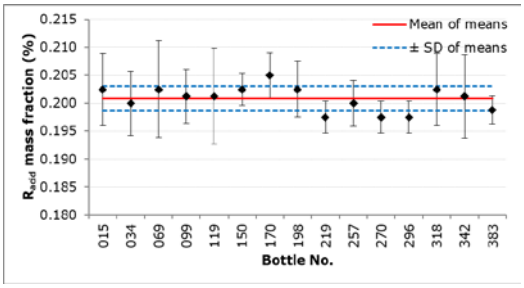


Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	1.67487871	0.41871968	0.00019451		
034	4	1.69778	0.424445	0.00033642		
069	4	1.81250307	0.45312577	0.00043925		
099	4	1.73314838	0.4332871	0.00071329		
119	4	1.77401589	0.44350397	3.0918E-05		
150	4	1.81248572	0.45312143	0.00072672		
170	4	1.7057174	0.42642935	0.00101967		
198	4	1.77441913	0.44360478	0.00074166		
219	4	1.7081095	0.42702738	8.5254E-05		
257	4	1.72734121	0.4318353	0.00157223		
270	4	1.69386917	0.42346729	0.00066665		
296	4	1.64143977	0.41035994	0.00040413		
318	4	1.58449779	0.39612445	0.00020632		
342	4	1.79811546	0.44952887	0.00029009		
383	4	1.75768663	0.43942166	0.00085969		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.01455364	14	0.0010395	1.8817	0.0552	1.9182
Within Groups	0.02486041	45	0.0005525			
Total	0.03941405	59				
n	4			status:	homogeneous	
s_{bb}	0.0110351			$s_{bb,r}$ (%)	2.56	
$s_{bb\,min}$	0.005396			$u^*_{bb,r}$ (%)	1.25	
u_{bb}	0.0110351					
$u_{bb,r}$ (%)	2.56					

A.17: R_{acid}

Bottle No.	R_{acid} mass fraction (%)						RSD (%)
	#1	#2	#3	#4	Mean	SD_i	
015	0.205	0.200	0.210	0.195	0.203	0.0065	3.19
034	0.205	0.195	0.195	0.205	0.200	0.0058	2.89
069	0.210	0.205	0.190	0.205	0.203	0.0087	4.28
099	0.200	0.195	0.205	0.205	0.201	0.0048	2.38
119	0.190	0.200	0.210	0.205	0.201	0.0085	4.24
150	0.200	0.205	0.200	0.205	0.203	0.0029	1.43
170	0.200	0.205	0.210	0.205	0.205	0.0041	1.99
198	0.195	0.205	0.205	0.205	0.203	0.0050	2.47
219	0.200	0.200	0.195	0.195	0.198	0.0029	1.46
257	0.195	0.200	0.200	0.205	0.200	0.0041	2.04
270	0.200	0.195	0.200	0.195	0.198	0.0029	1.46
296	0.195	0.195	0.200	0.200	0.198	0.0029	1.46
318	0.210	0.200	0.195	0.205	0.203	0.0065	3.19
342	0.205	0.205	0.205	0.190	0.201	0.0075	3.73
383	0.200	0.200	0.195	0.200	0.199	0.0025	1.26

Mean of means: 0.201
SD of means: 0.0022



Anova: Single Factor						
SUMMARY						
Bottle No.	*Count*	*Sum*	*Average*	*Variance*		
015	4	0.81	0.2025	4.1667E-05		
034	4	0.8	0.2	3.3333E-05		
069	4	0.81	0.2025	0.000075		
099	4	0.805	0.20125	2.2917E-05		
119	4	0.805	0.20125	7.2917E-05		
150	4	0.81	0.2025	8.3333E-06		
170	4	0.82	0.205	1.6667E-05		
198	4	0.81	0.2025	0.000025		
219	4	0.79	0.1975	8.3333E-06		
257	4	0.8	0.2	1.6667E-05		
270	4	0.79	0.1975	8.3333E-06		
296	4	0.79	0.1975	8.3333E-06		
318	4	0.81	0.2025	4.1667E-05		
342	4	0.805	0.20125	5.625E-05		
383	4	0.795	0.19875	6.25E-06		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00028333	14	2.0238E-05	0.6873	0.7742	1.9182
Within Groups	0.001325	45	2.9444E-05			
Total	0.00160833	59				
n	4			status:	homogeneous	
s_{bb}	0			$s_{bb,r}$ (%)	0.00	
$s_{bb\,min}$	0.0012457			$u^*_{bb,r}$ (%)	0.62	
u_{bb}	0.0012457					
$u_{bb,r}$ (%)	0.62					

Annex B: Stability study

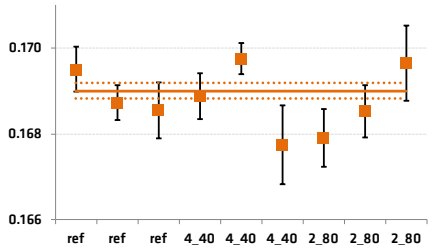
B.1: Stress test

Chi square test calculates $\sum_{k=0}^{n} \frac{(x_k - \bar{x})^2}{s_k^2}$ and compares it with the critical value of the chi-square distribution (displaying the significance)

analyte: **carbon**
values: in mass%

sample	stress level	replicates				mean per sampl	sd of the mean	average	lower	upper	chi-square	1/sd_k^2
S_388	ref	0.1693	0.1702	0.1704	0.1681	0.1695	0.000524404	0.169003422	0.168822892	0.169183952	0.896689941	3636363.636
S_389	ref	0.1686	0.1699	0.1684	0.168	0.168725	0.000411045	0.169003422	0.168822892	0.169183952	0.458804223	5918618.989
S_390	ref	0.1672	0.1702	0.1689	0.1679	0.16855	0.000651281	0.169003422	0.168822892	0.169183952	0.484695061	2357563.851
S_001	4_40	0.1675	0.1695	0.1699	0.1686	0.168875	0.000532877	0.169003422	0.168822892	0.169183952	0.058079662	3521643.434
S_002	4_40	0.1699	0.1701	0.1703	0.1687	0.16975	0.000359398	0.169003422	0.168822892	0.169183952	4.315190289	7741935.484
S_003	4_40	0.1669	0.1662	0.1675	0.1704	0.16775	0.000922406	0.169003422	0.168822892	0.169183952	1.846503409	1175318.315
S_006	2_80	0.1679	0.1675	0.1697	0.1665	0.1679	0.000668331	0.169003422	0.168822892	0.169183952	2.72583595	2238805.97
S_007	2_80	0.1687	0.1698	0.1687	0.1669	0.168525	0.000600521	0.169003422	0.168822892	0.169183952	0.634696949	2772963.605
S_008	2_80	0.1704	0.1671	0.171	0.1701	0.16965	0.000870345	0.169003422	0.168822892	0.169183952	0.551898536	1320132.013

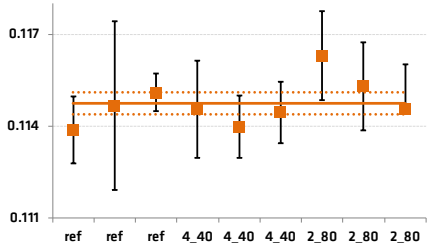
average:	0.169003422
u(average):	0.00018053
chi-square sum:	11.97239402
# of sampling points:	9
significance:	0.152439851
assessment:	**compliant**



analyte: **nitrogen**
values: in mass%

sample	stress level	replicates				mean per sampl	sd of the mean	average	lower	upper	chi-square	1/sd_k^2
S_388	ref	0.1108	0.1142	0.1145	0.116	0.113875	0.00109801	0.114744061	0.11437659	0.115111532	0.626452278	829445.3084
S_389	ref	0.1159	0.1187	0.1175	0.1066	0.114675	0.002752083	0.114744061	0.11437659	0.115111532	0.000629708	132031.3574
S_390	ref	0.1133	0.1155	0.1161	0.1155	0.1151	0.000616441	0.114744061	0.11437659	0.115111532	0.333402038	2631578.947
S_001	4_40	0.1099	0.1158	0.1155	0.117	0.11455	0.001583509	0.114744061	0.11437659	0.115111532	0.015018768	398803.5892
S_002	4_40	0.1141	0.1111	0.115	0.1157	0.113975	0.001012731	0.114744061	0.11437659	0.115111532	0.576677035	975015.2346
S_003	4_40	0.1163	0.1135	0.1159	0.1121	0.11445	0.000997914	0.114744061	0.11437659	0.115111532	0.086833511	1004184.1
S_006	2_80	0.1168	0.1201	0.115	0.1133	0.1163	0.001454304	0.114744061	0.11437659	0.115111532	1.144655819	472813.2388
S_007	2_80	0.1126	0.1191	0.1137	0.1158	0.1153	0.001430035	0.114744061	0.11437659	0.115111532	0.151133735	488997.555
S_008	2_80	0.1148	0.1106	0.1152	0.1176	0.11455	0.00145459	0.114744061	0.11437659	0.115111532	0.017798926	472627.0185

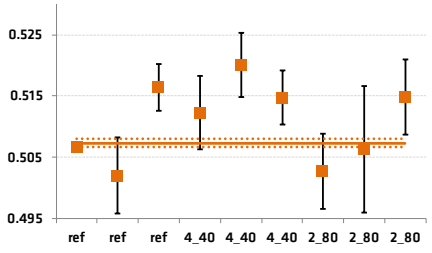
average:	0.114744061
u(average):	0.00036747
chi-square sum:	2.952601817
# of sampling points:	9
significance:	0.937296698
assessment:	**fully compliant**



analyte: **oxygen**
values: in mass%

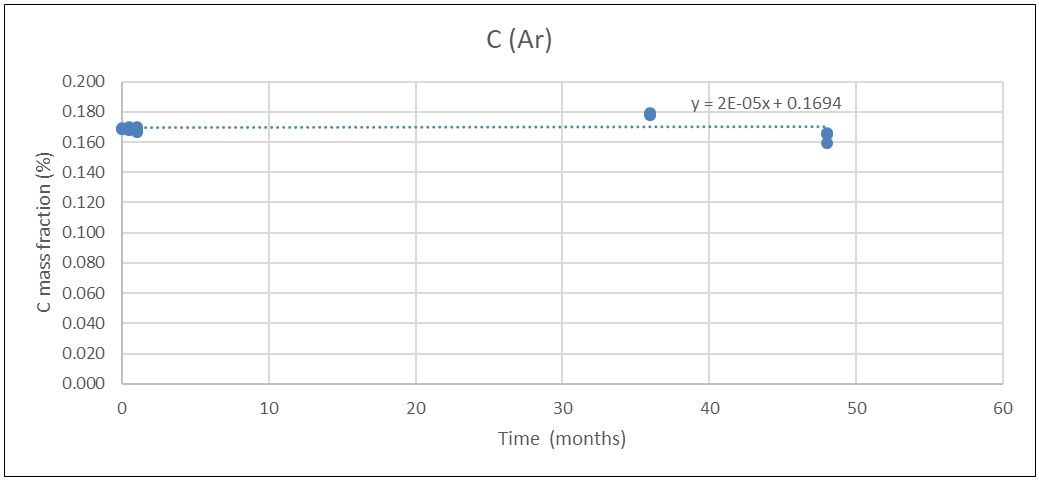
sample	stress level	replicates				mean per sampl	sd of the mean	average	lower	upper	chi-square	1/sd_k^2
S_388	ref	0.5056	0.5086	0.5058	0.5065	0.506625	0.000686021	0.507335138	0.506688928	0.507981348	1.071545253	2124833.997
S_389	ref	0.4911	0.5001	0.4972	0.5197	0.502025	0.006182957	0.507335138	0.506688928	0.507981348	0.737597017	26158.1807
S_390	ref	0.5228	0.5079	0.5232	0.5118	0.516425	0.003879514	0.507335138	0.506688928	0.507981348	5.489844515	66442.42349
S_001	4_40	0.5153	0.5121	0.5252	0.4965	0.512275	0.005951803	0.507335138	0.506688928	0.507981348	0.688862501	28229.48217
S_002	4_40	0.5132	0.5342	0.511	0.522	0.5201	0.005266561	0.507335138	0.506688928	0.507981348	5.874595665	36053.35897
S_003	4_40	0.5259	0.517	0.505	0.5111	0.51475	0.004451311	0.507335138	0.506688928	0.507981348	2.774791357	50468.94057
S_006	2_80	0.5099	0.4854	0.5027	0.5129	0.502725	0.006158784	0.507335138	0.506688928	0.507981348	0.560322231	26363.92097
S_007	2_80	0.4818	0.5129	0.5305	0.5	0.5063	0.010284049	0.507335138	0.506688928	0.507981348	0.010131371	9455.221646
S_008	2_80	0.5247	0.521	0.4972	0.5166	0.514875	0.006119828	0.507335138	0.506688928	0.507981348	1.517918301	26700.63581

average:	0.507335138
u(average):	0.00064621
chi-square sum:	18.72560821
# of sampling points:	9
significance:	0.016398014
assessment:	**slightly non-compliant**



B.2: Long-term stability C (Ar)

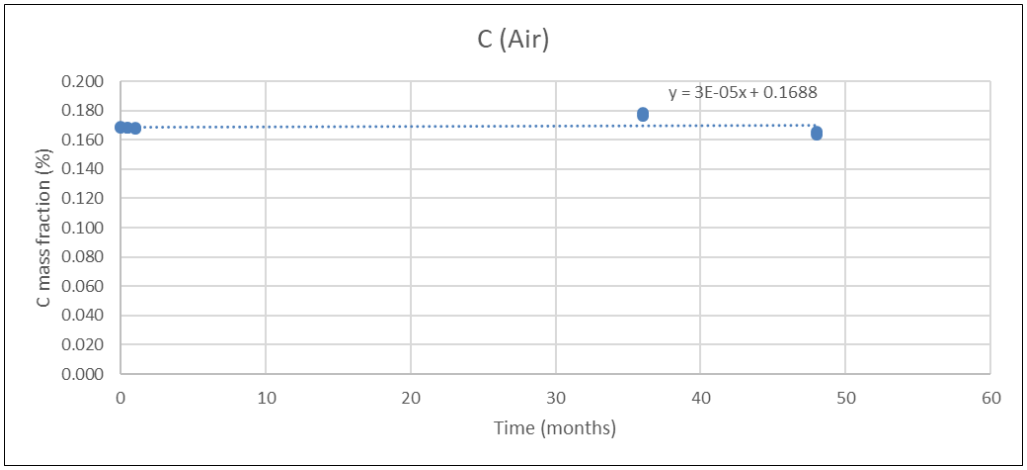
Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_388	0	0.1693	0.1702	0.1704	0.1681	**0.1695**	0.0010
2014S_389	0	0.1686	0.1699	0.1684	0.1680	**0.1687**	0.0008
2014S_390	0	0.1672	0.1702	0.1689	0.1679	**0.1686**	0.0013
2014S_006	0.5	0.1679	0.1675	0.1697	0.1665	**0.1679**	0.0013
2014S_007	0.5	0.1687	0.1698	0.1687	0.1669	**0.1685**	0.0012
2014S_008	0.5	0.1704	0.1671	0.1710	0.1701	**0.1697**	0.0017
2014S_001	1	0.1679	0.1683	0.1689	0.1696	**0.1687**	0.0008
2014S_002	1	0.1694	0.1692	0.1698	0.1701	**0.1696**	0.0004
2014S_003	1	0.1630	0.1662	0.1675	0.1704	**0.1668**	0.0031
2017_187	36	0.1796	0.1802	0.1778	0.1802	**0.1795**	0.0011
2017_287	36	0.1797	0.1777	0.1795	0.1770	**0.1785**	0.0013
2017_387	36	0.1786	0.1790	0.1802	0.1747	**0.1781**	0.0024
2018_109	48	0.1652	0.1596	0.1688	0.1677	**0.1653**	0.0041
2018_223	48	0.1695	0.1638	0.1669	0.1635	**0.1659**	0.0028
2018_354	48	0.1597	0.1606	0.1530	0.1650	**0.1596**	0.0049



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.057325742				
R Square	0.003286241				
Adjusted R Squar	-0.013898479				
Standarderror	0.005585564				
Observations	60				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	5.96611E-06	5.96611E-06	0.191230387	
Residual	58	0.001809515	3.11985E-05		
Total	59	0.001815481			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.169395438	0.000935605	181.0545123	1.52381E-81	
X Variable 1	1.52451E-05	3.48619E-05	0.437298967	0.66351854	
Very insignificant change over time. Stable.					

B.3: Long-term stability C (Air)

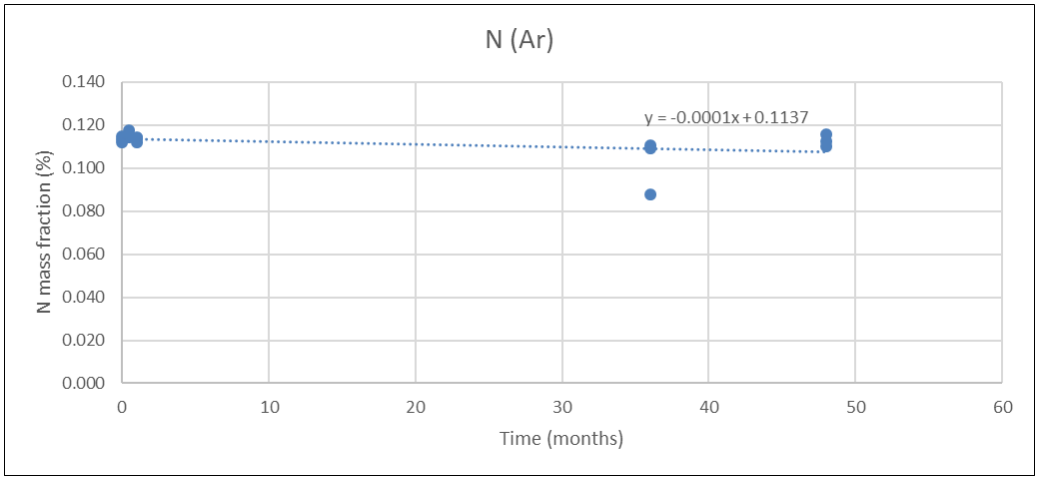
Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_401	0	0.1692	0.1679	0.1684	0.1694	**0.1688**	0.0007
2014S_402	0	0.1688	0.1691	0.1692	0.1663	**0.1683**	0.0014
2014S_009	0.5	0.1691	0.1682	0.1677	0.1688	**0.1685**	0.0006
2014S_010	0.5	0.1706	0.1686	0.1682	0.1659	**0.1683**	0.0020
2014S_004	1	0.1663	0.1680	0.1677	0.1680	**0.1675**	0.0008
2014S_005	1	0.1662	0.1690	0.1690	0.1680	**0.1680**	0.0013
2017_401	36	0.1776	0.1790	0.1785	0.1779	**0.1782**	0.0006
2017_402	36	0.1763	0.1782	0.1746	0.1765	**0.1764**	0.0015
2018_401	48	0.1595	0.1743	0.1599	0.1610	**0.1637**	0.0071
2018_402	48	0.1698	0.1585	0.1670	0.1682	**0.1659**	0.0051



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.126148106				
R Square	0.015913345				
Adjusted R Squar	-0.009983673				
Standarderror	0.005062187				
Observations	40				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	1.57466E-05	1.57466E-05	0.614485618	
Residual	38	0.000973778	2.56257E-05		
Total	39	0.000989525			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.168841584	0.001038506	162.5811932	1.23837E-55	
X Variable 1	3.03336E-05	3.86961E-05	0.78389133	0.43796298	
Very insignificant change over time.					
Slightly less insignifanct than under Ar, however stable.					

B.4: Long-term stability N (Ar)

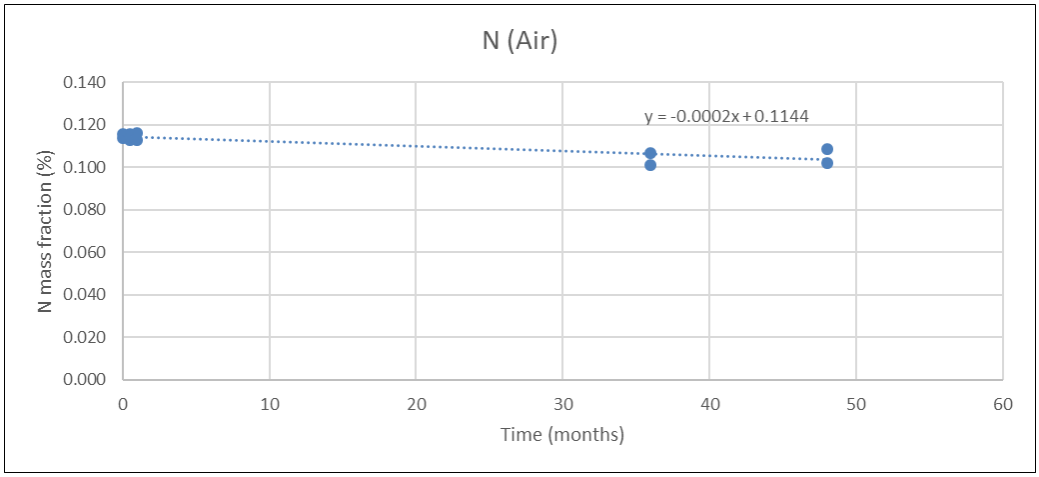
Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_388	0	0.1108	0.1064	0.1145	0.1160	**0.1119**	0.0043
2014S_389	0	0.1159	0.1187	0.1175	0.1066	**0.1147**	0.0055
2014S_390	0	0.1133	0.1155	0.1161	0.1096	**0.1136**	0.0029
2014S_006	0.5	0.1168	0.1201	0.1204	0.1133	**0.1176**	0.0033
2014S_007	0.5	0.1126	0.1191	0.1137	0.1158	**0.1153**	0.0028
2014S_008	0.5	0.1148	0.1106	0.1152	0.1176	**0.1145**	0.0029
2014S_001	1	0.1099	0.1158	0.1155	0.1170	**0.1146**	0.0032
2014S_002	1	0.1141	0.1111	0.1150	0.1157	**0.1140**	0.0020
2014S_003	1	0.1163	0.1135	0.1059	0.1121	**0.1119**	0.0044
2017_187	36	0.1132	0.1242	0.1119	0.0927	**0.1105**	0.0131
2017_287	36	0.1199	0.1169	0.0887	0.1115	**0.1092**	0.0141
2017_387	36	0.1018	0.1007	0.0640	0.0851	**0.0879**	0.0176
2018_109	48	0.1112	0.1089	0.1176	0.1116	**0.1123**	0.0037
2018_223	48	0.1203	0.0939	0.1110	0.1159	**0.1103**	0.0116
2018_354	48	0.1125	0.1178	0.1196	0.1136	**0.1159**	0.0034



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.265408818				
R Square	0.07044184				
Adjusted R Squar	0.054414976				
Standarderror	0.009457953				
Observations	60				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	0.000393166	0.000393166	4.395235201	
Residual	58	0.005188267	8.94529E-05		
Total	59	0.005581433			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.113731737	0.001584245	71.78921459	2.33202E-58	
X Variable 1	-0.000123758	5.90311E-05	-2.096481624	**0.040411572**	
Slightly significant change towards lower N values.					

B.5: Long-term stability N (Air)

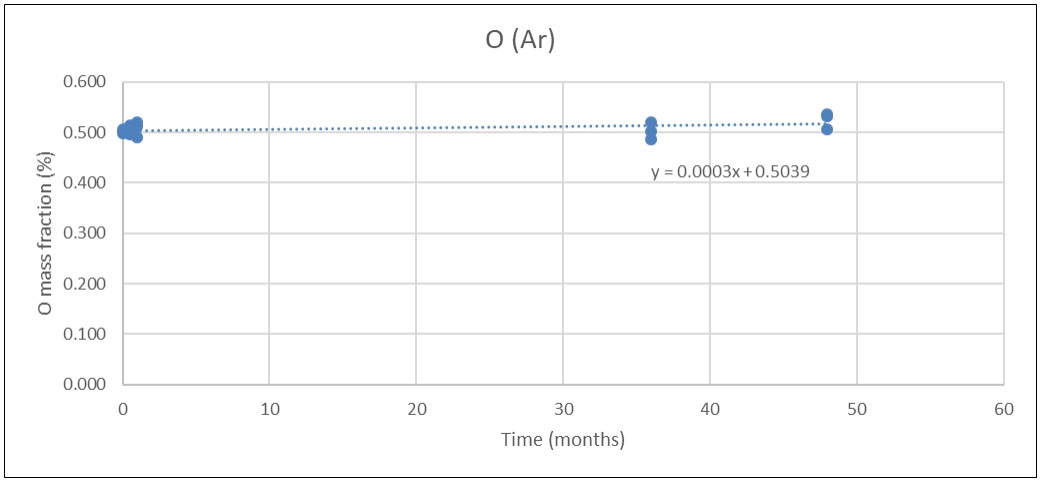
Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_401	0	0.1120	0.1182	0.1189	0.1137	**0.1157**	0.0034
2014S_402	0	0.1152	0.1134	0.1127	0.1136	**0.1137**	0.0010
2014S_009	0.5	0.1166	0.1123	0.1126	0.1219	**0.1158**	0.0045
2014S_010	0.5	0.1089	0.1162	0.1105	0.1149	**0.1126**	0.0035
2014S_004	1	0.1145	0.1150	0.1113	0.1109	**0.1129**	0.0021
2014S_005	1	0.1181	0.1166	0.1157	0.1130	**0.1159**	0.0021
2017_401	36	0.1064	0.0990	0.0817	0.1167	**0.1010**	0.0147
2017_402	36	0.1105	0.0989	0.1068	0.1114	**0.1069**	0.0057
2018_401	48	0.1073	0.0965	0.1201	0.1110	**0.1087**	0.0098
2018_402	48	0.0973	0.1141	0.0892	0.1067	**0.1018**	0.0109



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.567006525				
R Square	0.321496399				
Adjusted R Squar	0.303641041				
Standarderror	0.006943959				
Observations	40				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	0.000868204	0.000868204	18.00559814	
Residual	38	0.001832306	4.82186E-05		
Total	39	0.00270051			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.114362591	0.001424551	80.27972546	5.04381E-44	
X Variable 1	-0.000225237	5.30807E-05	-4.243300382	**0.000136307**	
Significant over time, with a negative coefficient.					

B.6: Long-term stability O (Ar)

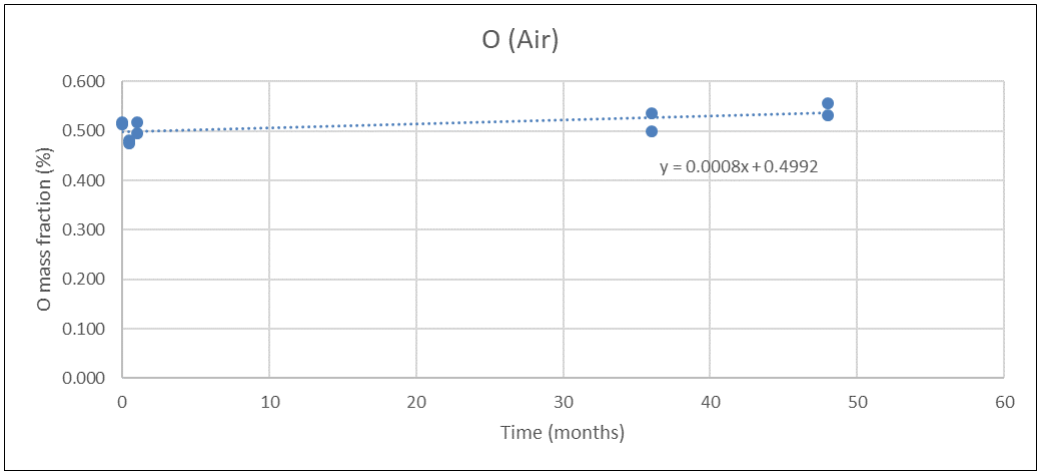
Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_388	0	0.5056	0.5086	0.5058	0.5065	**0.5066**	0.0014
2014S_389	0	0.4911	0.5001	0.4972	0.5197	**0.5020**	0.0124
2014S_390	0	0.5228	0.5079	0.5232	0.4406	**0.4986**	0.0393
2014S_006	0.5	0.5099	0.4854	0.5027	0.5129	**0.5027**	0.0123
2014S_007	0.5	0.4431	0.5129	0.5305	0.5000	**0.4966**	0.0378
2014S_008	0.5	0.5247	0.5210	0.4972	0.5166	**0.5149**	0.0122
2014S_001	1	0.5153	0.5121	0.5252	0.4965	**0.5123**	0.0119
2014S_002	1	0.5132	0.5342	0.5110	0.5220	**0.5201**	0.0105
2014S_003	1	0.5259	0.5170	0.4093	0.5111	**0.4908**	0.0547
2017_187	36	0.5295	0.4017	0.5388	0.4722	**0.4856**	0.0632
2017_287	36	0.5264	0.5424	0.5102	0.5009	**0.5200**	0.0183
2017_387	36	0.5206	0.4829	0.4845	0.5197	**0.5019**	0.0210
2018_109	48	0.5299	0.5401	0.5233	0.5370	**0.5326**	0.0075
2018_223	48	0.5702	0.4149	0.5081	0.5316	**0.5062**	0.0660
2018_354	48	0.5437	0.5159	0.5447	0.5414	**0.5364**	0.0137



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.176864705				
R Square	0.031281124				
Adjusted R Squar	0.014579074				
Standarderror	0.031571347				
Observations	60				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	0.001866804	0.001866804	1.872891339	
Residual	58	0.057811497	0.00099675		
Total	59	0.059678301			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.50387806	0.005288328	95.28115742	1.97919E-65	
X Variable 1	0.00026967	0.00019705	1.368536203	0.176422089	
Insignificant change over time, but a positive (increasing) coefficient is obvious.					
There might be some little take-up of oxygen.					

B.7: Long-term stability O (Air)

Sample ID	Storage time (months)	Mass fraction (%)					
		#1	#2	#3	#4	**Mean**	SD
2014S_401	0	0.5129	0.5203	0.5262	0.5124	**0.5179**	0.0066
2014S_402	0	0.4853	0.5151	0.5272	0.5265	**0.5135**	0.0196
2014S_009	0.5	0.4830	0.4851	0.4769	0.4804	**0.4814**	0.0035
2014S_010	0.5	0.4711	0.4645	0.4803	0.4857	**0.4754**	0.0094
2014S_004	1	0.5127	0.5128	0.5056	0.4521	**0.4958**	0.0293
2014S_005	1	0.5145	0.5107	0.5225	0.5246	**0.5181**	0.0066
2017_401	36	0.5123	0.5513	0.5243	0.5558	**0.5359**	0.0210
2017_402	36	0.5220	0.5259	0.5185	0.4291	**0.4989**	0.0466
2018_401	48	0.4897	0.5526	0.5659	0.5161	**0.5311**	0.0347
2018_402	48	0.5695	0.5508	0.5488	0.5577	**0.5567**	0.0094



SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.515691088				
R Square	0.265937298				
Adjusted R Squar	0.246619858				
Standarderror	0.02741264				
Observations	40				
ANOVA					
	df	*SS*	*MS*	*Significance F*	
Regression	1	0.010345022	0.010345022	13.76669498	
Residual	38	0.028555208	0.000751453		
Total	39	0.03890023			
	Coefficients	*Standard Error*	*t-Stat*	*P-Value*	
Intercept	0.499172585	0.005623696	88.76237512	1.13154E-45	
X Variable 1	0.00077749	0.000209546	3.710349711	0.000660037	
Significant change over time, with a positive coefficient.					
A take-up of oxygen might be suspected.					

Annex C: Results obtained in the characterisation study

Table C.1: Individual results for Ti (values in %)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	10	Photometry	67.96	67.74	67.82	67.84	67.81	68.04	**67.87**	0.11
L2	14	ICP OES	67.7	67.7	68.4	67.5	68.2	68.1	**67.93**	0.35
L3	16	ICP OES	68.2	67.7	67.7	68.2	68.1	68.2	**68.02**	0.25
L4	8	XRF	68.17	68.15	68.31	68.50	68.11	67.97	**68.20**	0.18
L5	15	XRF	68.29	68.37	68.12	68.39	68.25	68.19	**68.27**	0.10
L6	5	Photometry	68.6	68.6	68.4	68.4	68.5	68.7	**68.53**	0.12
L7	17	ICP OES	68.42	68.69	68.60	68.67	68.45	68.48	**68.55**	0.12
L8	12	Photometry	68.81	68.80	68.88	68.99	68.95	68.74	**68.86**	0.10

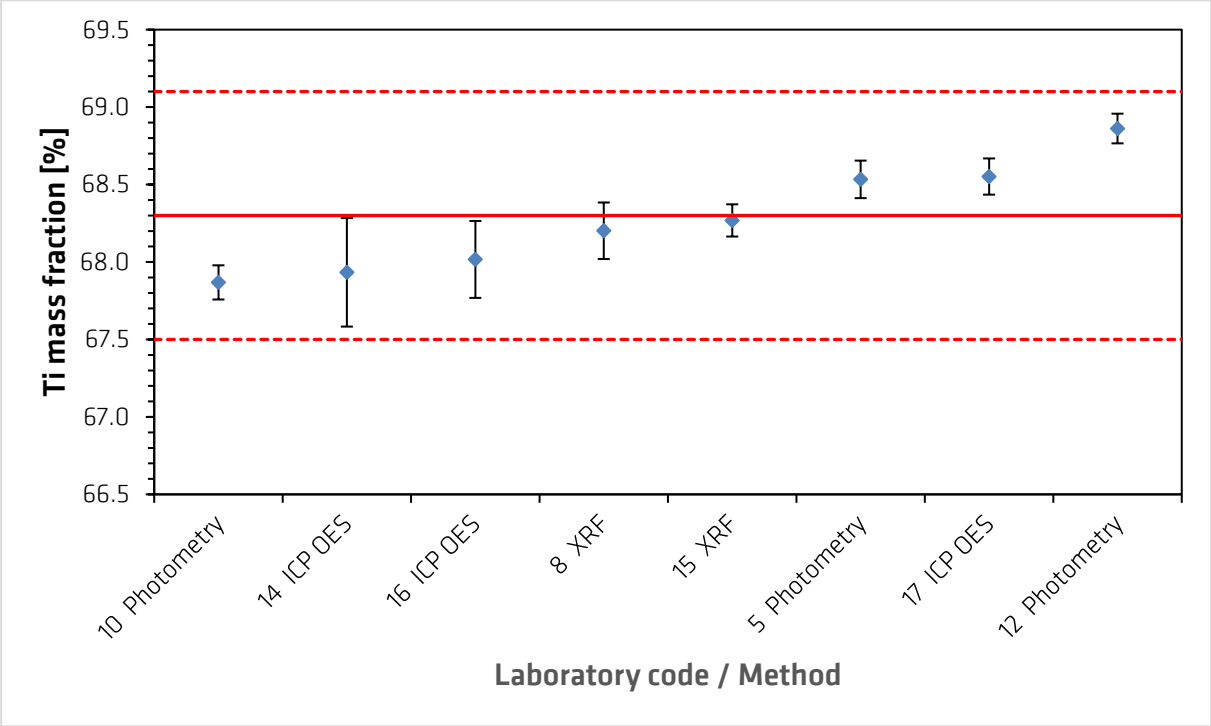


Figure C.1: Accepted laboratory means for Ti. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.2 Individual results for B (values in %)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	12	Titrimetry	30.45	30.50	30.45	30.46	30.50	30.50	**30.477**	0.026
L2	5	Titrimetry	30.50	30.67	30.54	30.65	30.75	30.57	**30.613**	0.093
L3	11	ICP OES	30.7	30.7	30.7	30.6	30.6	30.6	**30.650**	0.055
L4	15	ICP OES	30.61	30.78	30.68	30.69	30.72	30.75	**30.705**	0.060
L5	17	ICP OES	30.68	30.71	30.69	30.80	30.96	30.72	**30.760**	0.107
L6	10	Titrimetry	30.71	30.77	30.85	30.77	30.76	30.81	**30.778**	0.048
L7	16	ICP OES	30.9	31.0	31.3	30.8	30.9	30.9	**30.967**	0.175
L8 [1)]	14	ICP OES	31.7	31.6	31.7	32.0	32.2	31.8	**31.833**	0.225

[1)] Outlier, dataset rejected

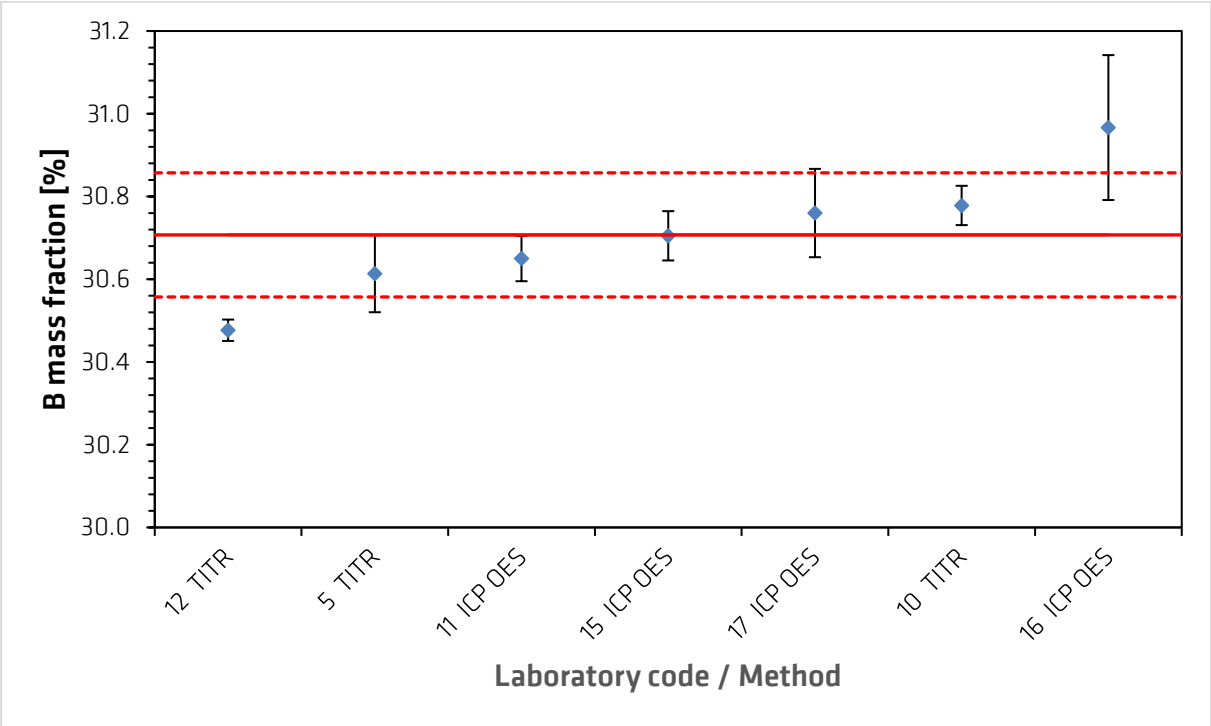


Figure C.2: Accepted laboratory means for B. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.3: Individual results for B_2O_3 (values in %)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	17	ICP OES	0.3245	0.3286	0.3246	0.3209	0.3218	0.3254	**0.3243**	0.0027
L2	10	Titrimetry	0.360	0.358	0.354	0.357	0.353	0.354	**0.3560**	0.0028
L3	5	Titrimetry	0.353	0.360	0.353	0.352	0.361	0.354	**0.3555**	0.0039
L4	11	Titrimetry	0.362	0.371	0.368	0.369	0.372	0.355	**0.3662**	0.0065
L5	12	Titrimetry	0.41	0.39	0.42	0.37	0.38	0.39	**0.3933**	0.0186

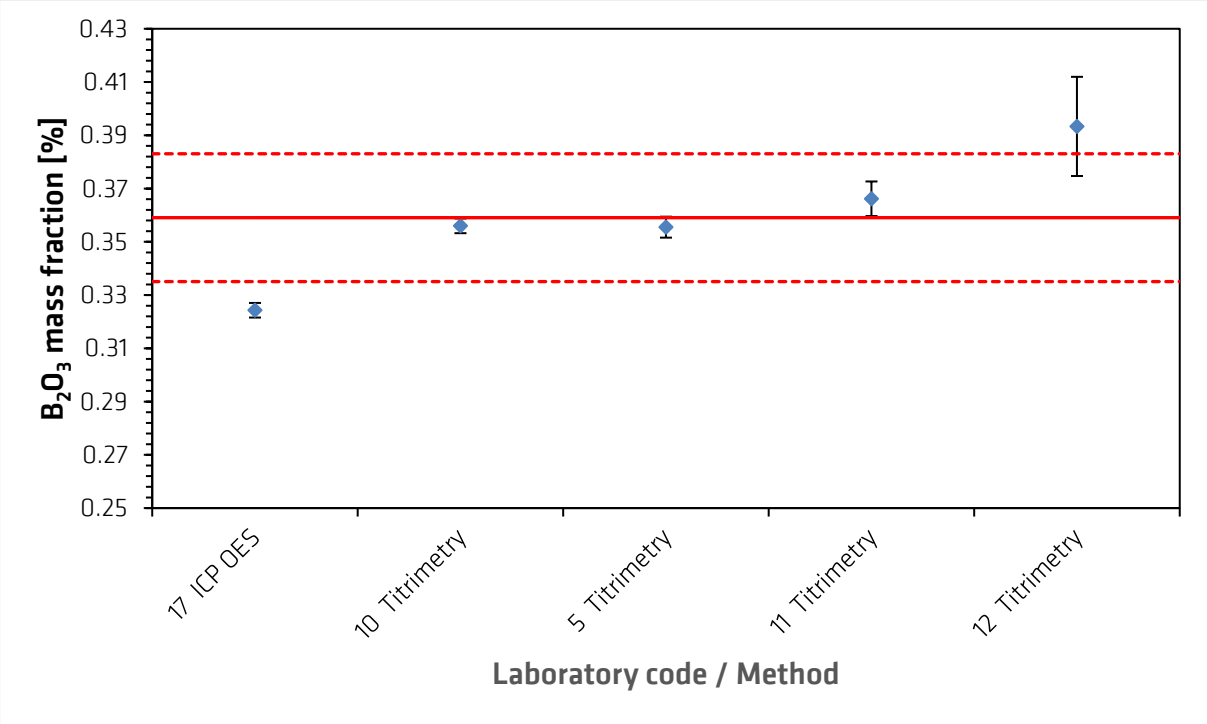


Figure C.3: Accepted laboratory means for B_2O_3. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value value.

Table C.4: Individual results for Al (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1 [1)]	11	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	
L2	17	ICP OES	10.9	9.8	10.3	10.8	10.3	9.7	**10.30**	0.49
L3	7	ICP OES	10.7	10.8	10.8	10.7	11.1	11.4	**10.92**	0.28
L4	5	ICP OES	10.2	10.1	10.9	12.6	13.3	11.5	**11.43**	1.30
L5	2	ICP OES	11.3	12.4	13.2	11.8	11.4	11.2	**11.88**	0.78
L6	10	ICP OES	13.1	12.6	13.1	12.8	11.1	12.3	**12.50**	0.75
L7	14	ICP OES	13.6	14.2	12.7	14.8	12.1	12.9	**13.38**	1.01
L8	9a	ICP OES	13	14	14	14	13	13	**13.50**	0.55
L9 [2)]	12	ICP OES	18.29	17.88	19.30	18.35	17.99	17.59	**18.23**	0.59
L10 [1)]	8	ICP OES	< 30	< 30	< 30	< 30	< 30	< 30	**< 30**	

[1)] Data given as below limit of quantification
[2)] Outlier, dataset rejected

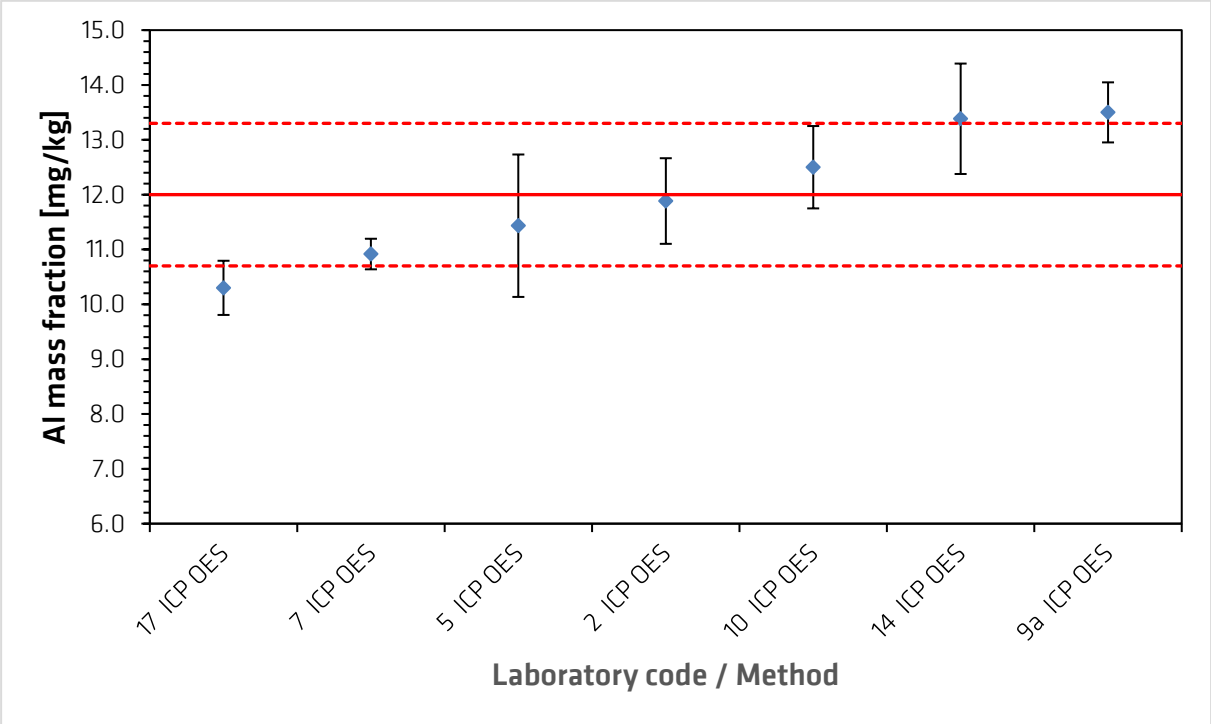


Figure C.4: Accepted laboratory means for Al. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.5: Individual results for Ca (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	16	ICP OES	68 [1)]	33	38	33	35	38	**35.40**	2.51
L2	12	F AAS	35.5	34.5	35.5	38.0	36.5	35.5	**35.92**	1.20
L3	2	ICP OES	45.0	37.5	42.7	37.4	37.2	35.2	**39.17**	3.80
L4	8	ICP OES	40.4	40.2	39.6	39.6	40.0	39.9	**39.95**	0.32
L5	14	ICP OES	39.1	39.5	39.9	45.2	43.8	41.6	**41.52**	2.50
L6	5	ICP OES	41.6	45.2	41.1	44.3	43.8	42.1	**43.02**	1.65
L7	10	ICP OES	43.4	44.1	43.8	43.0	43.9	43.3	**43.58**	0.42
L8	7	ICP OES	44.6	43.9	44.0	44.9	43.1	44.5	**44.17**	0.64
L9	4	ICP OES	46.6	47.8	46.7	43.8	45.3	43.5	**45.62**	1.72
L10	17	ICP OES	44.7	50.8	44.9	53.7	46.1	49.2	**48.23**	3.62
L11	1	ICP-MS	51.4	48.2	47.0	51.0	49.1	52.4	**49.85**	2.08
L12	11	ICP OES	50.1	48.9	49.7	55.2	57.1	55.4	**52.73**	3.55
L13	9a	ICP OES	51	57	52	53	56	55	**54.00**	2.37

[1)] Data not accepted on technical grounds

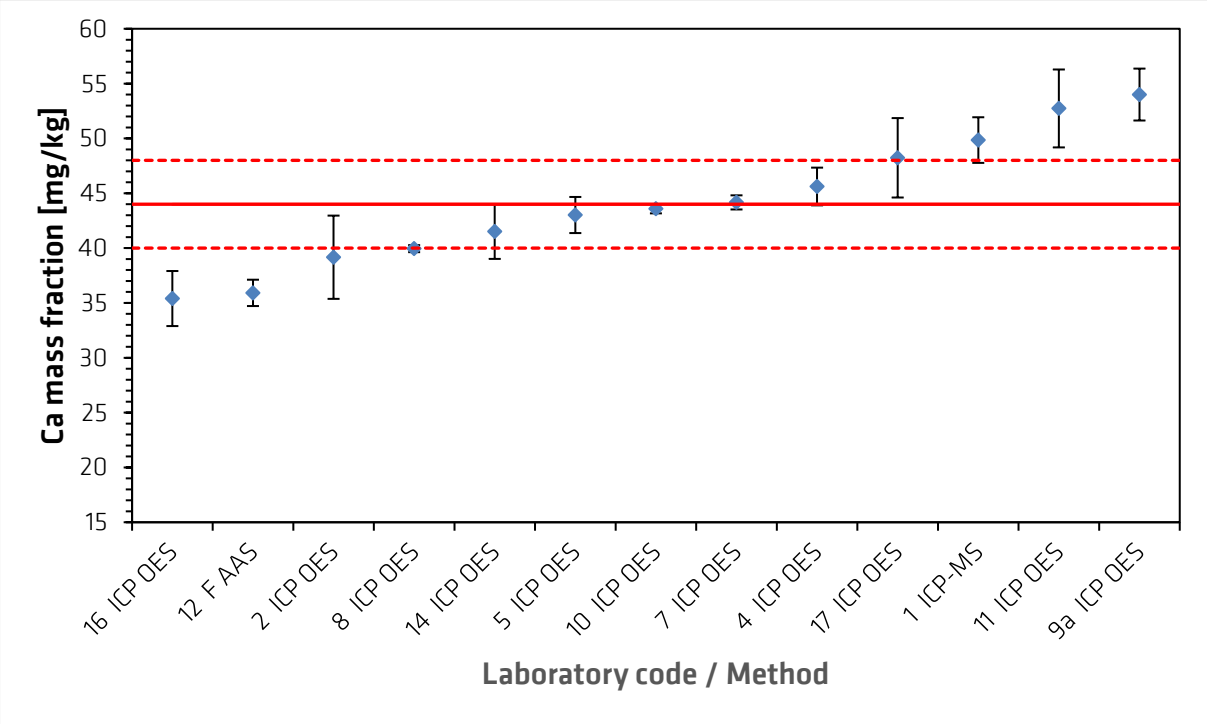


Figure C.5: Accepted laboratory means for Ca. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.6: Individual results for Cr (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	10	ICP OES	85.3	90.9	90.0	89.3	89.8	88.3	**88.93**	1.97
L2	7	ICP OES	89.2	90.4	88.4	89.3	88.4	89.0	**89.12**	0.74
L3	9	ICP OES	91	90	91	94	93	93	**92.00**	1.55
L4	9a	ICP-MS	91.6	92.7	92.7	92.9	92.4	93.1	**92.57**	0.53
L5	2	ICP OES	97.2	97.6	95.5	95.4	93.9	94.1	**95.62**	1.53
L6	17	ICP OES	98.0	95.2	96.6	95.4	96.0	95.7	**96.15**	1.03
L7	5	ICP OES	96.2	99.5	98.3	96.3	97.2	97.0	**97.42**	1.27
L8	14	ICP OES	96.5	99.8	97.7	98.9	98.1	95.8	**97.80**	1.48
L9	11	ICP OES	100.0	99.1	97.2	94.8	98.7	99.6	**98.23**	1.94
L10	15	ICP OES	99.0	98.8	98.7	99.3	98.6	98.3	**98.78**	0.34
L11	1	ICP-MS	101.0	99.4	98.8	103.0	100.0	98.4	**100.10**	1.69
L12	16	ICP OES	99	98	101	99	102	110	**101.50**	4.42
L13	8	ICP OES	101	100	103	100	102	103	**101.50**	1.38
L14	4	ICP OES	110	106	105	106	109	110	**107.67**	2.25
L15 [1)]	12	ICP OES	117.2	114.4	116.0	121.7	116.4	117.5	**117.20**	2.46

[1)] Outlier, dataset rejected

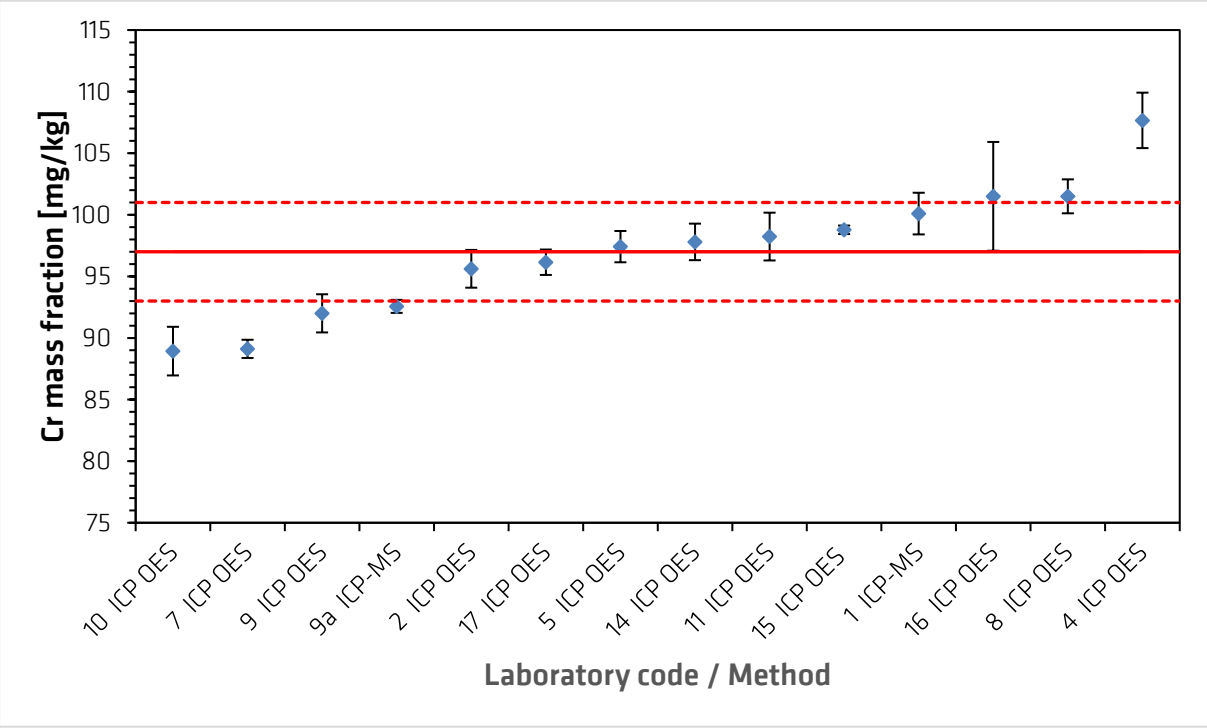


Figure C.6: Accepted laboratory means for Cr. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.7: Individual results for Fe (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1[1)]	16a	ICP OES	450	439	445	473	462	466	**455.83**	13.20
L2	16b	F AAS	525	512	541	537	622	618	**559.17**	48.21
L3	15	ICP OES	563	560	563	564	567	564	**563.50**	2.26
L4	10	ICP OES	582.7	615.9	600.0	595.7	595.7	594.7	**597.45**	10.75
L5	7	ICP OES	605	602	597	603	598	598	**600.50**	3.27
L6	4	ICP OES	627	626	624	626	630	630	**627.17**	2.40
L7	17	ICP OES	634.0	643.1	642.9	645.2	649.3	645.5	**643.33**	5.12
L8	8	ICP OES	646	649	647	642	645	644	**645.50**	2.43
L9	5	ICP OES	645.3	656.4	667.1	664.2	657.0	648.9	**656.48**	8.43
L10	2	ICP OES	658.9	666.0	653.7	647.6	643.9	639.5	**651.60**	9.87
L11	1	ICP-MS	675	656	659	677	669	667	**667.17**	8.40
L12	14	ICP OES	669	664	665	650	663	661	**662.00**	6.45
L13	12	F AAS	675	684	691	681	671	680	**680.33**	6.98
L14	11	ICP OES	682	688	684	696	705	685	**690.00**	8.83
L15	9a	ICP OES	751	785	765	751	754	779	**764.17**	14.86

[1)] Outlier, dataset rejected

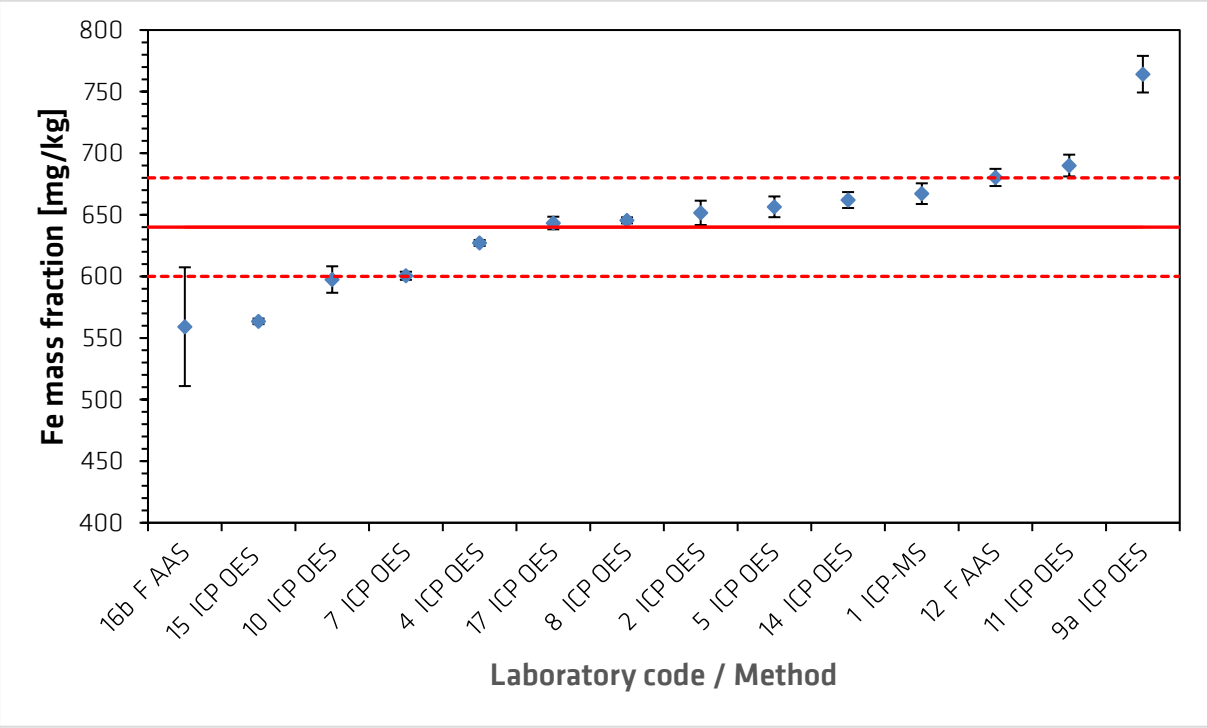


Figure C.7: Accepted laboratory means for Fe. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.8: Individual results for Mg (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	5	ICP OES	0.73	1.21	1.22	0.74	0.71	1.09	**0.950**	0.249
L2	7	ICP OES	1.0	1.1	1.0	1.2	1.0	1.0	**1.050**	0.084
L3	2	ICP OES	1.29	1.06	1.94	1.05	1.07	1.22	**1.272**	0.342
L4	17	ICP OES	1.54	1.54	1.51	1.65	1.63	1.50	**1.562**	0.063
L5	12	F AAS	1.5	1.5	2.0	1.5	1.5	2.5	**1.750**	0.418
L6	10	ICP OES	1.9	1.9	1.8	1.9	1.9	1.8	**1.867**	0.052
L7	9	ICP OES	2.0	2.2	2.0	1.8	1.9	2.1	**2.000**	0.141
L8	14	ICP OES	2.33	2.21	2.89	2.22	1.58	2.18	**2.235**	0.417
L9 [1)]	11	ICP-MS	< 6	< 6	< 6	< 6	< 6	< 6	**< 6**	
L10 [1)]	1	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	

[1)] Data given as below limit of quantification

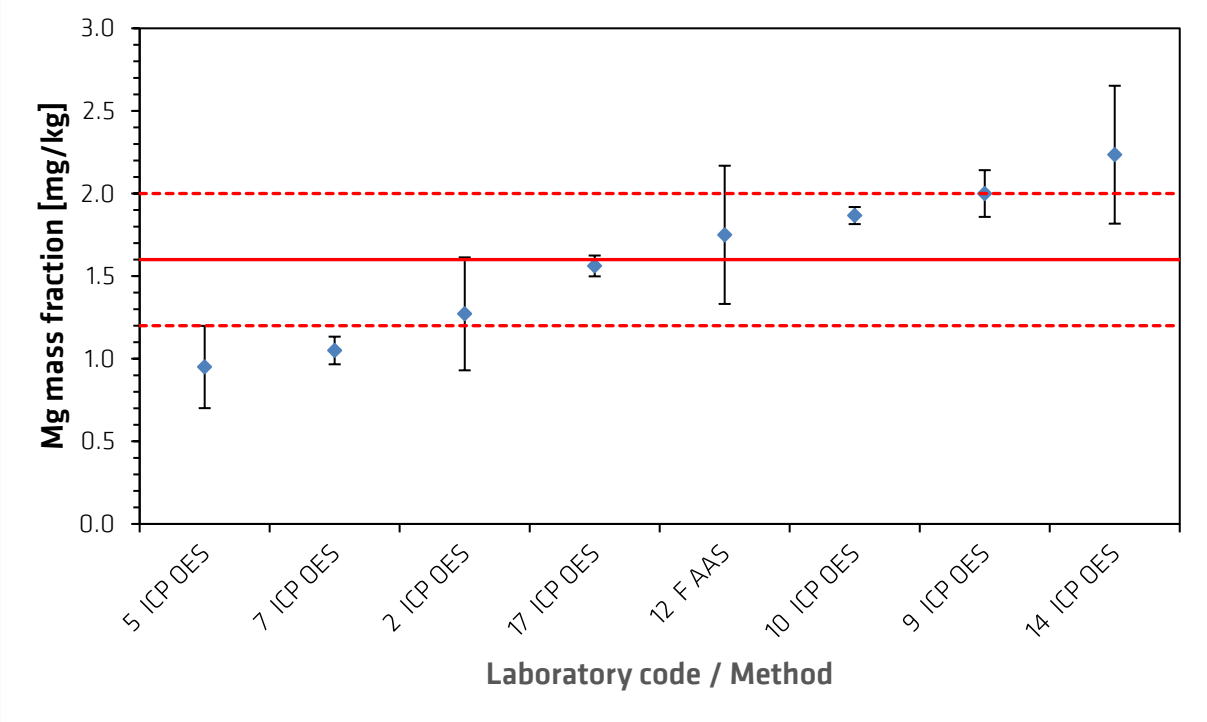


Figure C.8: Accepted laboratory means for Mg. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.9: Individual results for Mn (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1 [1)]	10	ICP OES	1.9	2.0	2.0	2.2	2.1	2.2	**2.067**	0.121
L2	15	ICP OES	3.2	3.2	3.3	3.3	3.2	3.3	**3.250**	0.055
L3	2	ICP OES	3.40	3.43	3.37	3.35	3.36	3.32	**3.372**	0.039
L4	17	ICP OES	3.46	3.36	3.48	3.40	3.41	3.44	**3.425**	0.044
L5	5	ICP OES	3.24	3.30	3.38	3.63	3.53	3.54	**3.437**	0.153
L6	9b	ICP-MS	3.60	3.62	3.63	3.61	3.57	3.65	**3.613**	0.027
L7	1	ICP-MS	3.79	3.71	3.76	3.80	3.78	3.78	**3.770**	0.032
L8	14	ICP OES	3.61	3.84	3.60	3.86	3.76	4.02	**3.782**	0.161
L9	8	ICP OES	3.81	3.71	3.93	3.70	3.79	3.82	**3.793**	0.084
L10	12	F AAS	3.0	4.0	4.5	5.0	4.5	5.0	**4.333**	0.753
L11	9a	ICP OES	4.4	4.6	4.5	4.4	4.3	4.6	**4.467**	0.121
L12	7	ICP OES	4.7	4.6	4.5	4.7	4.6	4.6	**4.617**	0.075
L13 [2)]	11	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	

[1)] Outlier, dataset rejected
[2)] Data given as below limit of quantification

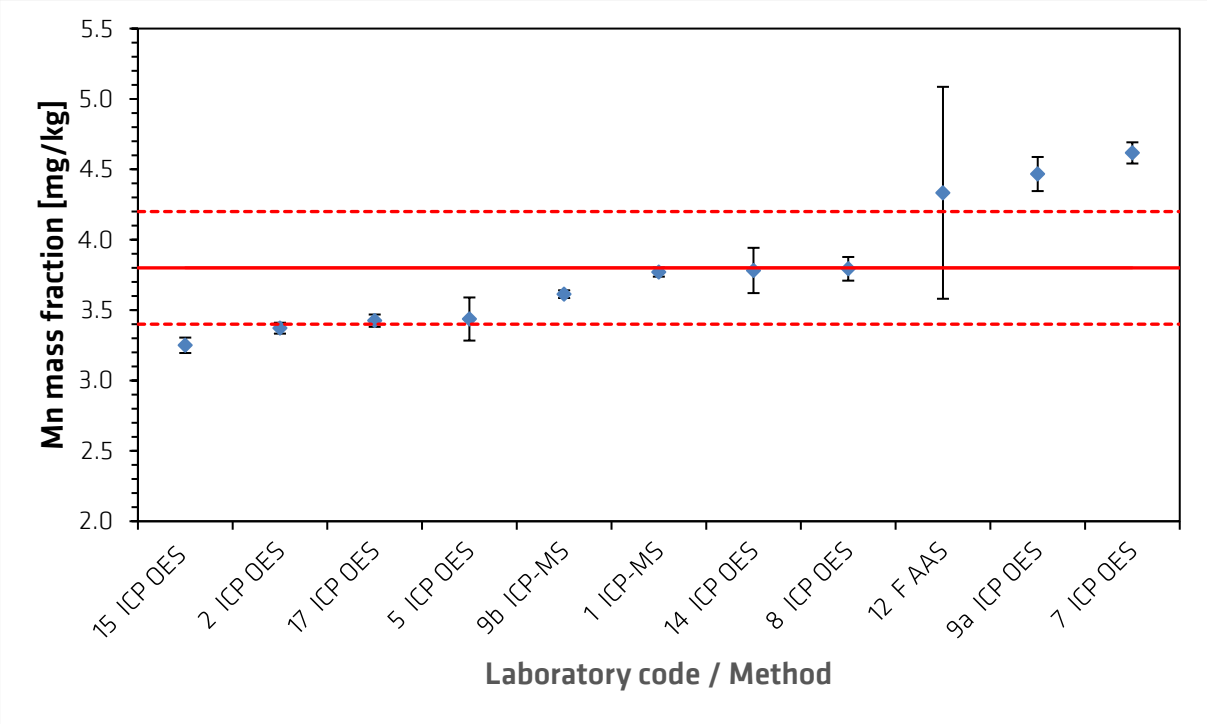


Figure C.9: Accepted laboratory means for Mn. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.10: Individual results for Mo (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	7	ICP OES	10.0	9.9	9.9	9.7	9.9	9.9	**9.883**	0.098
L2 [1)]	11	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	
L3	15	ICP OES	10.5	10.3	10.4	10.6	10.3	10.3	**10.400**	0.126
L4	2	ICP OES	11.2	11.2	10.9	10.9	10.6	11.0	**10.967**	0.225
L5	4	ICP OES	12.1	12.3	10.6	10.1	10.2	12.4	**11.283**	1.094
L6	9a	ICP OES	11.8	11.9	12.0	11.4	11.0	11.3	**11.567**	0.393
L7	10	ICP OES	13.1	11.7	11.4	11.0	10.9	11.4	**11.583**	0.799
L8	9b	ICP-MS	11.8	11.7	11.7	11.8	11.8	11.7	**11.750**	0.055
L9	5	ICP OES	12.5	11.9	11.7	11.7	11.8	12.6	**12.033**	0.408
L10	12	ICP OES	11.75	12.6	12.29	11.21	12.02	12.48	**12.058**	0.518
L11	14	ICP OES	12.4	12.2	12.9	11.6	12.0	11.3	**12.067**	0.572
L12	1	ICP-MS	12.3	12.2	12.2	12.1	12.2	12.5	**12.250**	0.138
L13	17	ICP OES	12.7	12.5	12.9	12.6	12.9	12.9	**12.750**	0.176
L14	8	ICP OES	12.8	13.1	12.9	13.0	12.3	13.2	**12.883**	0.319

[1)] Data given as below limit of quantification

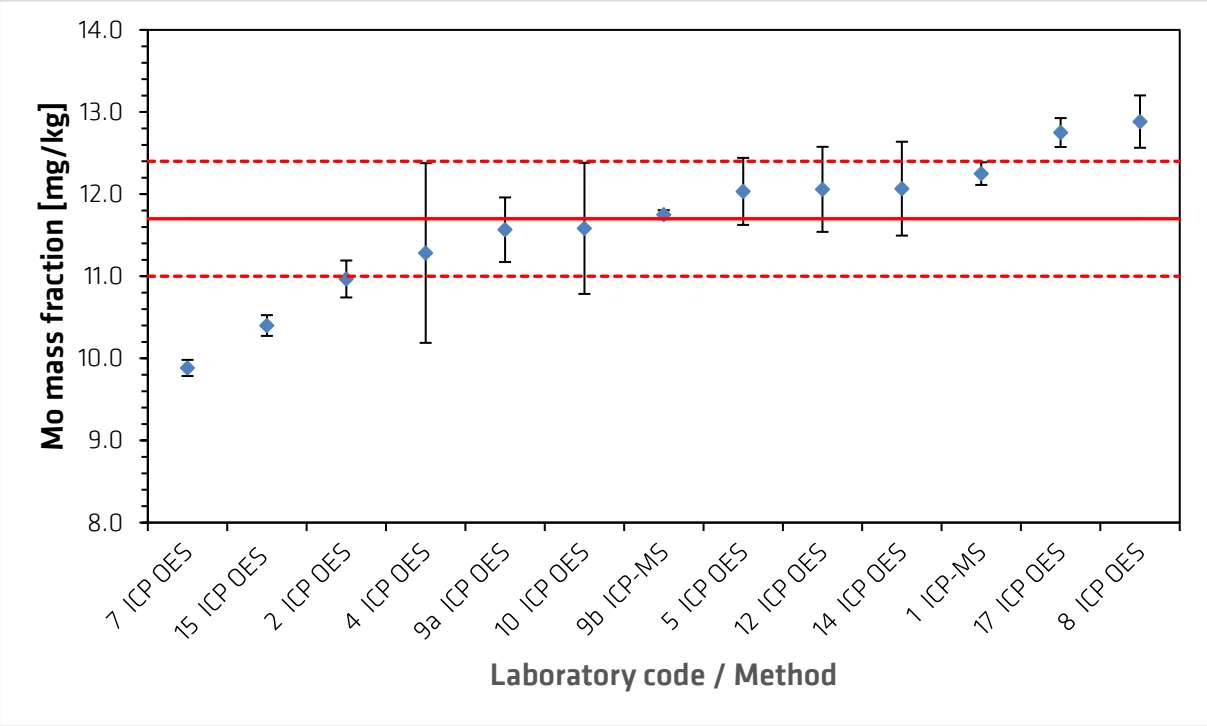


Figure C.10: Accepted laboratory means for Mo. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.11: Individual results for Ni (values in mg/kg)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1[1)]	11	ICP OES	15	16	15	16	15	15	**15.33**	0.52
L2	10	ICP OES	20.1	22.2	21.4	20.4	23.1	21.6	**21.47**	1.12
L3	15	ICP OES	22.0	22.0	22.2	22.2	21.9	22.2	**22.08**	0.13
L4	7	ICP OES	22.1	22.1	22.3	21.8	22.5	22.2	**22.17**	0.23
L5	12	F AAS	22.0	23.2	21.5	25.2	21.2	20.0	**22.18**	1.81
L6	9b	ICP-MS	22.9	23.3	23.2	23.5	23.2	23.5	**23.27**	0.23
L7	14	ICP OES	24.0	24.2	24.1	23.8	23.6	22.1	**23.63**	0.78
L8	9a	ICP OES	23.5	23.5	23.8	23.9	23.6	23.6	**23.65**	0.16
L9	17	ICP OES	23.6	23.7	23.6	23.6	24.0	24.0	**23.75**	0.20
L10	2	ICP OES	24.3	24.5	23.9	23.7	23.4	23.1	**23.82**	0.53
L11	4	ICP OES	23.6	22.8	23.7	24.1	25.2	23.5	**23.82**	0.80
L12	8	ICP OES	23.9	23.7	25.0	24.2	23.9	23.8	**24.08**	0.48
L13	1	ICP-MS	25.5	24.0	23.7	25.0	24.9	24.5	**24.60**	0.67
L14	5	ICP OES	27.8	27.9	28.2	27.4	25.1	25.6	**27.00**	1.31

[1)] Outlier, dataset rejected

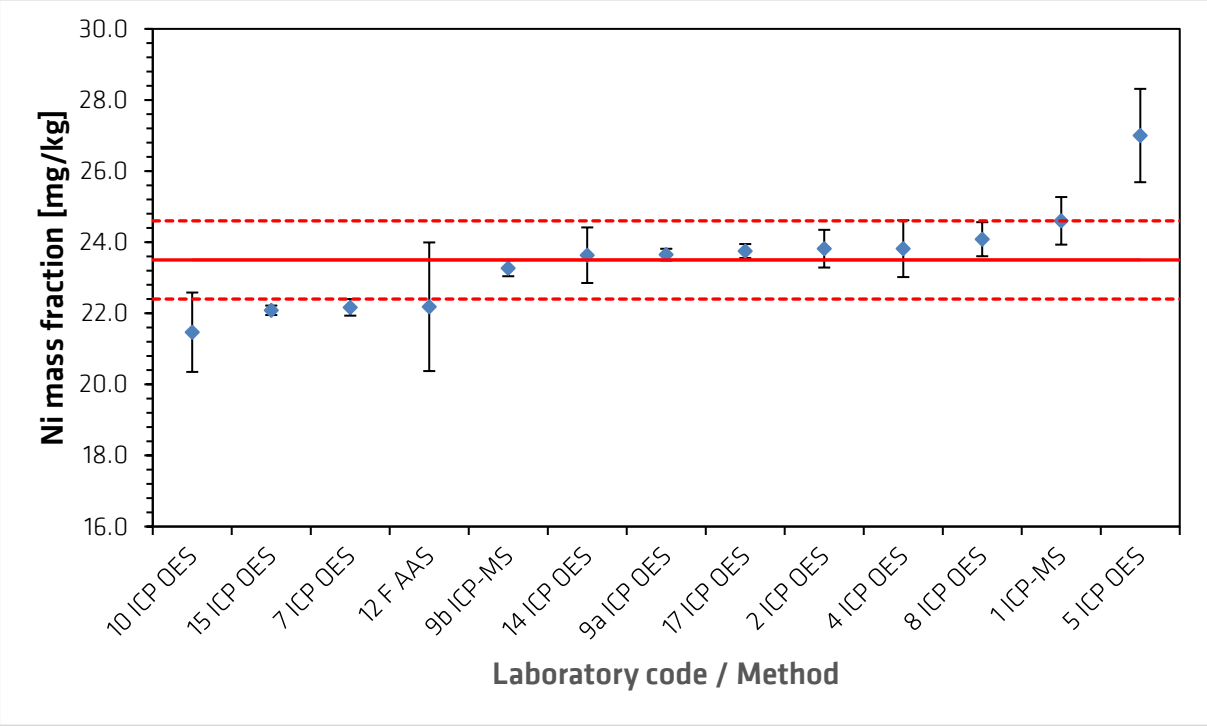


Figure C.11: Accepted laboratory means for Ni. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.12: Individual results for V (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	8	ICP OES	8.25	9.12	9.43	8.33	8.42	8.53	**8.68**	0.48
L2	9a	ICP OES	9.1	9.4	9.4	9.5	9.4	9.6	**9.40**	0.17
L3	2	ICP OES	9.57	9.77	9.61	9.76	9.56	9.66	**9.66**	0.09
L4 [1)]	11	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	
L5	10	ICP OES	10.0	10.5	9.5	10.6	9.3	10.1	**10.00**	0.52
L6	1	ICP-MS	10.30	9.80	10.80	10.10	10.10	9.79	**10.15**	0.37
L7	17	ICP OES	10.2	10.4	10.3	10.1	10.1	10.4	**10.25**	0.14
L8	7	ICP OES	10.4	10.2	10.5	10.6	10.5	10.4	**10.43**	0.14
L9	5	ICP OES	10.3	11.4	11.1	11.3	11.3	10.5	**10.98**	0.47
L10	12	ICP OES	12.33	10.82	12.61	12.72	12.65	12.31	**12.24**	0.72
L11	14	ICP OES	15.2	14.7	15.5	14.4	13.4	14.1	**14.55**	0.76

[1)] Data given as below limit of quantification
[2)] Outlier, dataset rejected

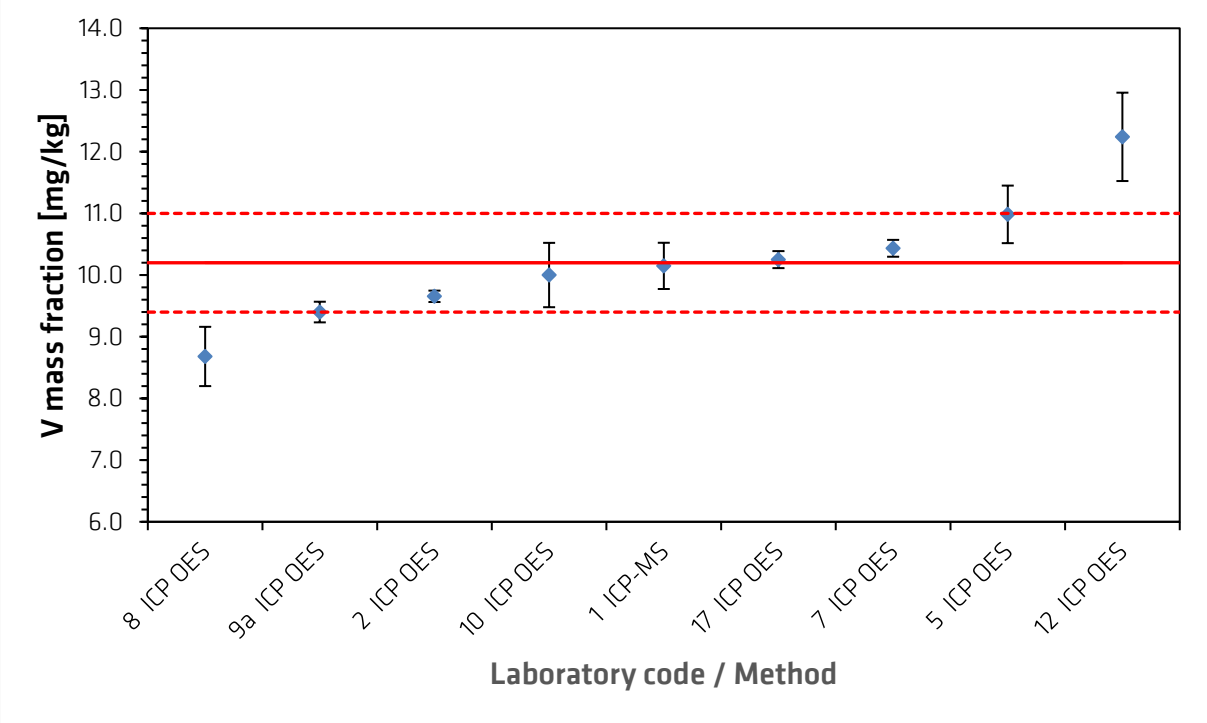


Figure C.12: Accepted laboratory means for V. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.13: Individual results for Zr (values in mg/kg)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1 [1)]	16	ICP OES	92	94	92	93	95	90	**92.67**	1.75
L2	11	ICP OES	105	105	106	105	104	103	**104.67**	1.03
L3	10	ICP OES	114.0	116.7	114.2	114.9	117.6	114.2	**115.27**	1.52
L4	8	ICP OES	120	118	123	117	119	121	**119.67**	2.16
L5	5	ICP OES	117.2	124.3	122.5	120.9	119.4	119.7	**120.67**	2.50
L6	2	ICP OES	121.0	122.4	120.2	120.9	119.4	120.4	**120.72**	1.00
L7	15	ICP OES	120.3	121.0	120.8	120.7	121.1	120.8	**120.78**	0.28
L8	14	ICP OES	120	122	127	123	118	124	**122.33**	3.14
L9	17	ICP OES	122.7	122.7	121.8	123.0	123.4	122.0	**122.60**	0.60
L10	9b	ICP-MS	126	125	125	124	124	124	**124.67**	0.82
L11	1	ICP-MS	124	124	124	126	128	125	**125.17**	1.60
L12	7	ICP OES	126	125	125	125	127	125	**125.50**	0.84
L13	4	ICP OES	124	126	124	129	128	125	**126.00**	2.10
L14	12	ICP OES	129.39	128.33	132.03	133.75	130.39	131.08	**130.83**	1.93
L15 [1)]	9a	ICP OES	147	155	152	142	141	146	**147.17**	5.49

[1)] Outlier, dataset rejected

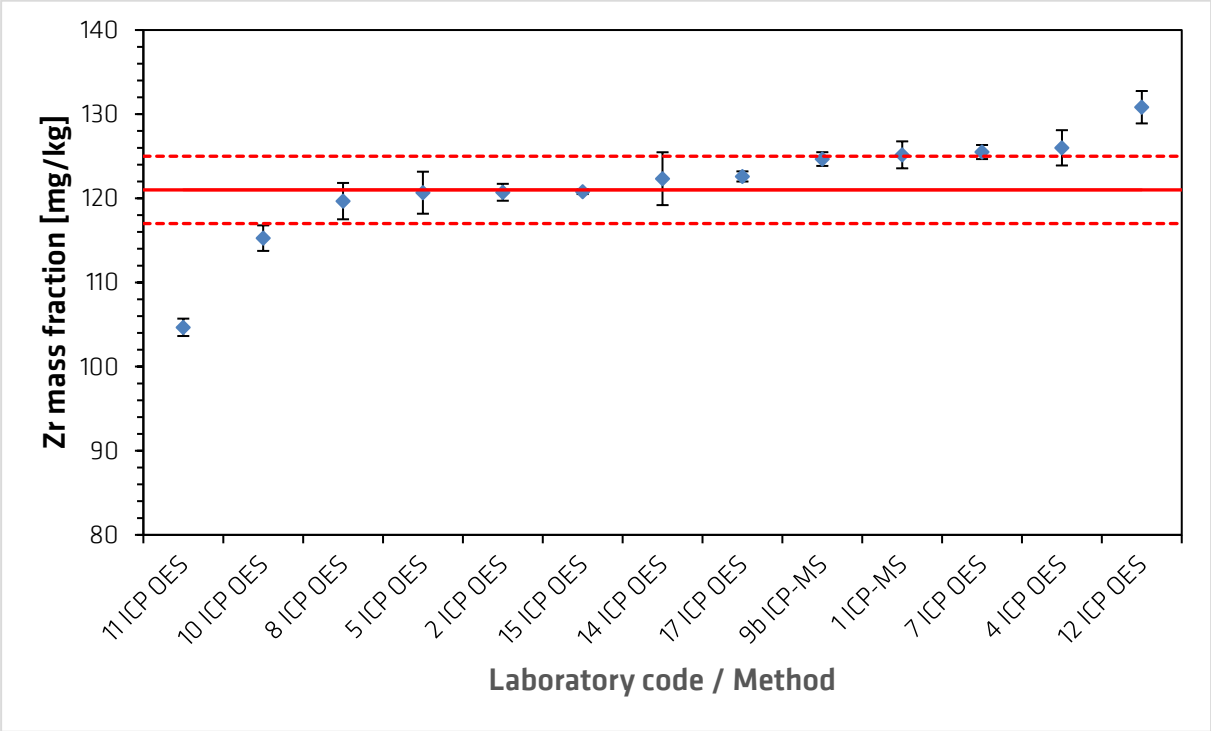


Figure C.13: Accepted laboratory means for Zr. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.14: Individual results for C (values in %)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1 [1)]	17	Comb-IR	0.1055	0.0907	0.1001	0.1004	0.1138	0.0965	**0.1012**	0.0079
L2 [1)]	11	Comb-IR	0.141	0.150	0.162	0.100	0.101	0.124	**0.1297**	0.0258
L3	5	Comb-IR	0.150	0.142	0.143	0.144	0.150	0.152	**0.1468**	0.0043
L4	12	Comb-IR	0.171	0.154	0.164	0.159	0.171	0.167	**0.1643**	0.0068
L5	8	Comb-IR	0.170	0.166	0.167	0.173	0.166	0.166	**0.1680**	0.0029
L6	10	Comb-IR	0.169	0.173	0.168	0.172	0.173	0.172	**0.1712**	0.0021
L7	2	Comb-IR	0.173	0.173	0.175	0.169	0.171	0.173	**0.1723**	0.0021
L8	7	Comb-IR	0.172	0.175	0.175	0.172	0.173	0.175	**0.1737**	0.0015
L9	16	Comb-IR	0.176	0.173	0.178	0.173	0.174	0.174	**0.1747**	0.0020
L10	6	Comb-IR	0.17993	0.17935	0.17924	0.18063	0.17853	0.17977	**0.1796**	0.0007

[1)] Outlier, dataset rejected Paired Grubbs test outlier (α = 0.01)

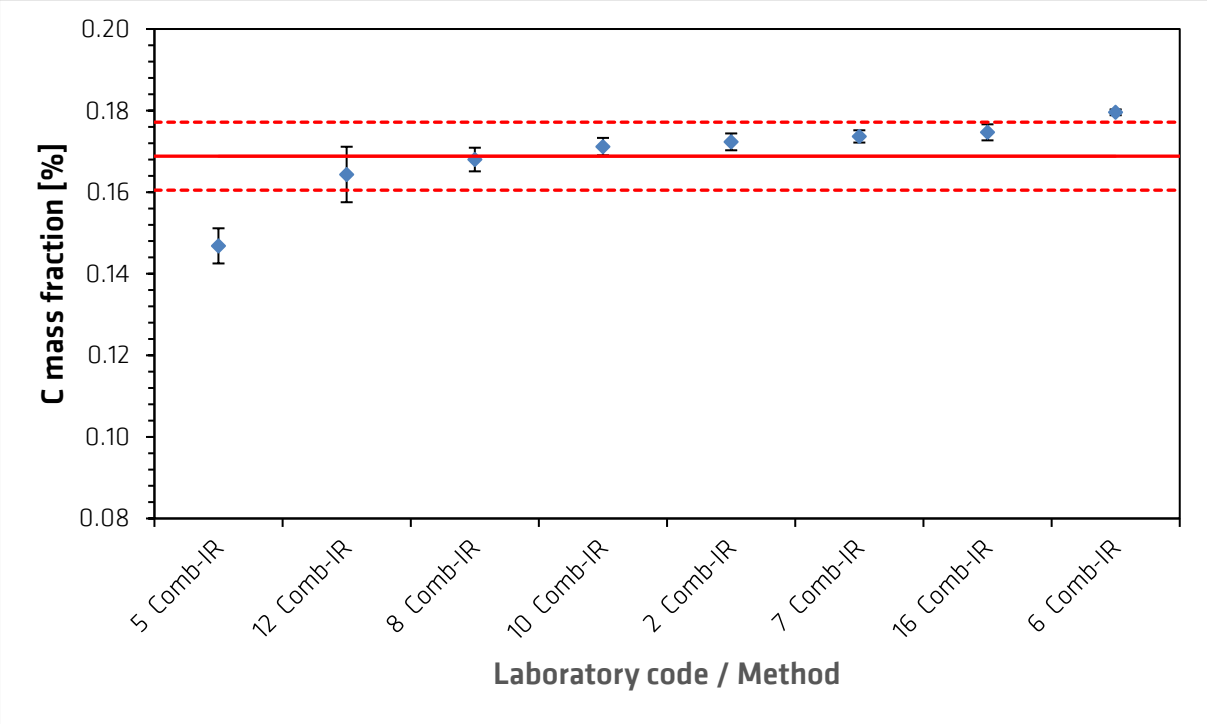


Figure C.14: Accepted laboratory means for C. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.15: Individual results for N (values in %)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	16	CGHE-TC	0.109	0.112	0.105	0.103	0.103	0.108	**0.1067**	0.0036
L2	9	CGHE-TC	0.112	0.109	0.125	0.115	0.112	0.114	**0.1145**	0.0055
L3	8	CGHE-TC	0.115	0.115	0.113	0.115	0.115	0.117	**0.1150**	0.0013
L4	2	CGHE-TC	0.1175	0.1174	0.1145	0.1190	0.1130	0.1120	**0.1156**	0.0028
L5	17	CGHE-TC	0.1219	0.1209	0.1216	0.1257	0.1207	0.1068	**0.1196**	0.0065
L6	12	CGHE-TC	0.126	0.121	0.120	0.123	0.124	0.125	**0.1232**	0.0023
L7	11	CGHE-TC	0.121	0.132	0.129	0.118	0.131	0.128	**0.1265**	0.0057
L8	5	CGHE-TC	0.128	0.127	0.126	0.130	0.127	0.129	**0.1278**	0.0015
L9	6	CGHE-TC	0.13383	0.13308	0.13315	0.13389	0.13310	0.13273	**0.1333**	0.0005

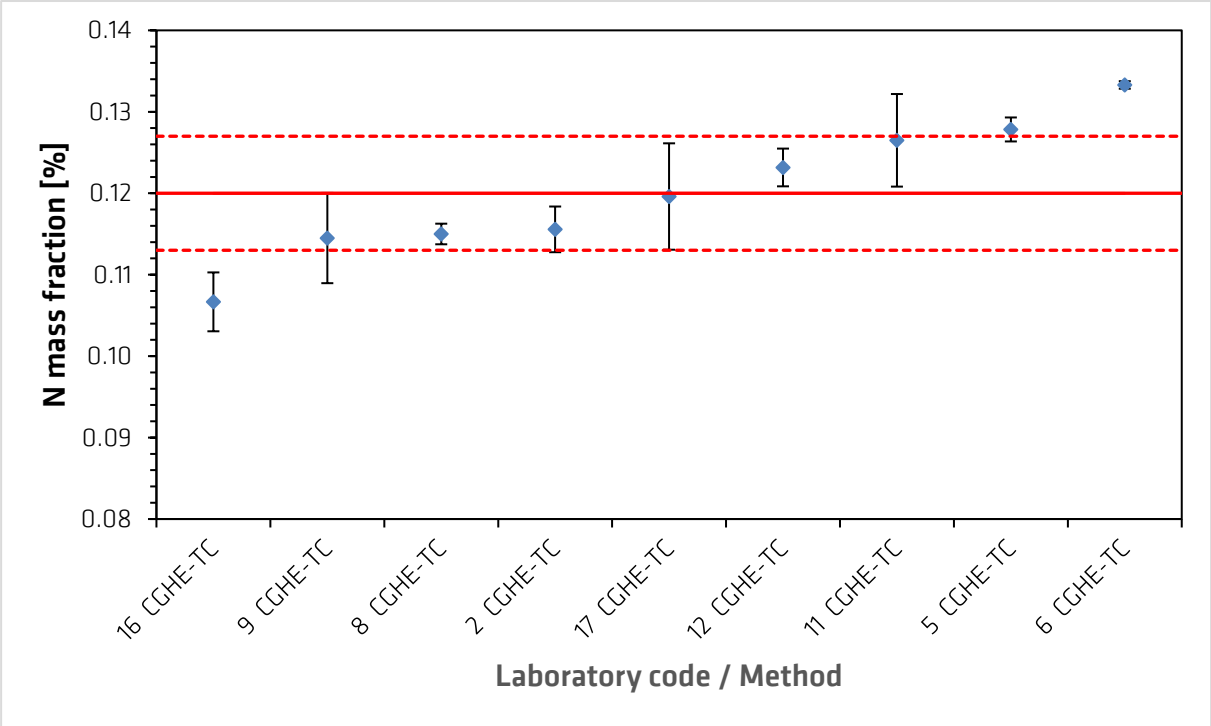


Figure C.15: Accepted laboratory means for N. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.16: Individual results for O (values in %)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1[1)]	16	CGHE-IR	0.283	0.317	0.339	0.302	0.290	0.301	**0.3053**	0.0202
L2[1)]	17	CGHE-IR	0.325	0.331	0.332	0.325	0.330	0.316	**0.3265**	0.0060
L3	11	CGHE-IR	0.433	0.451	0.439	0.428	0.432	0.431	**0.4357**	0.0083
L4	5	CGHE-IR	0.433	0.440	0.443	0.433	0.443	0.437	**0.4382**	0.0046
L5[1)]	7	CGHE-IR	0.472	0.477	0.472	0.475	0.478	0.475	**0.4748**	0.0025
L6	2	CGHE-IR	0.4275	0.4686	0.4982	0.5275	0.4740	0.4932	**0.4815**	0.0337
L7[1)]	8	CGHE-IR	0.496	0.497	0.502	0.494	0.498	0.506	**0.4988**	0.0044
L8	6	CGHE-IR	0.4998	0.4921	0.4996	0.5033	0.5069	0.5012	**0.5005**	0.0049
L9	9	CGHE-IR	0.508	0.507	0.504	0.499	0.501	0.498	**0.5028**	0.0042
L10	12	CGHE-IR	0.511	0.517	0.502	0.501	0.509	0.506	**0.5077**	0.0060

[1)] Outlier, dataset rejected Paired Grubbs test outlier (α = 0.01)

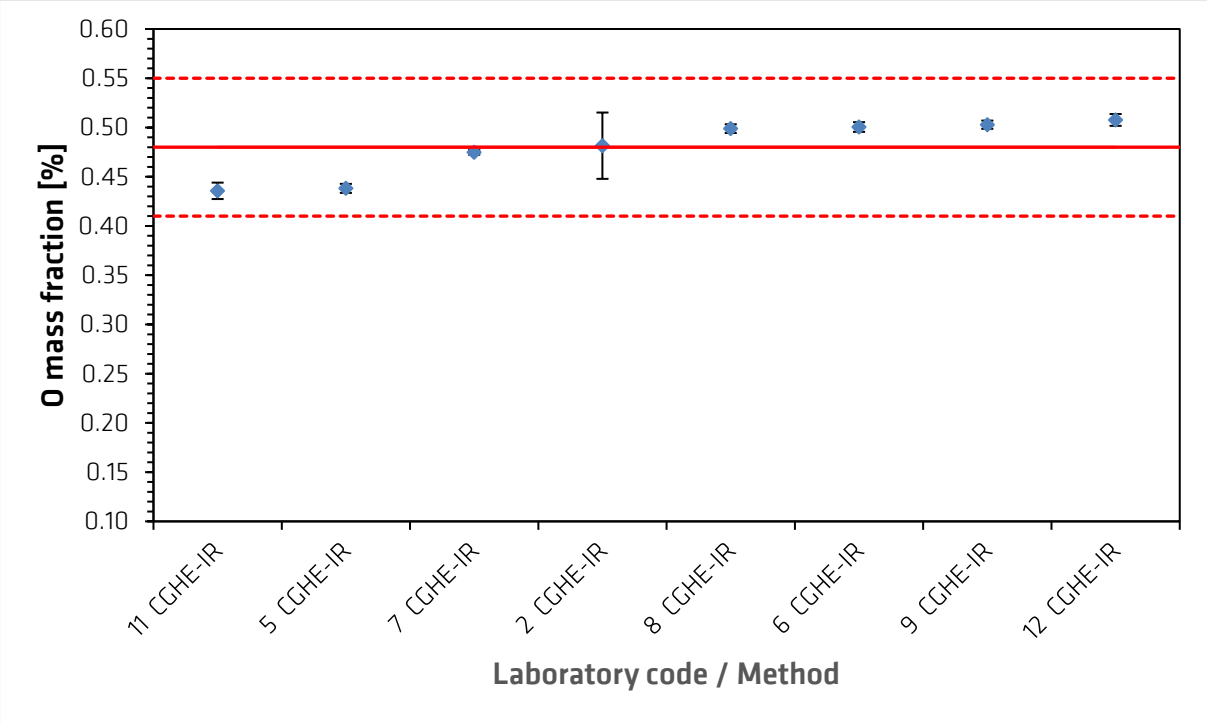


Figure C.16: Accepted laboratory means for O. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the certified value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the certified value.

Table C.17: Individual results for R_{acid} (values in %)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	5	Gravimetry	0.21	0.18	0.22	0.20	0.19	0.20	**0.2000**	0.0141
L2	11	Gravimetry	0.205	0.209	0.198	0.221	0.179	0.199	**0.2018**	0.0139
L3	10	Gravimetry	0.199	0.201	0.211	0.200	0.198	0.203	**0.2020**	0.0047
L4	12	Gravimetry	0.26	0.28	0.23	0.27	0.25	0.25	**0.2567**	0.0175

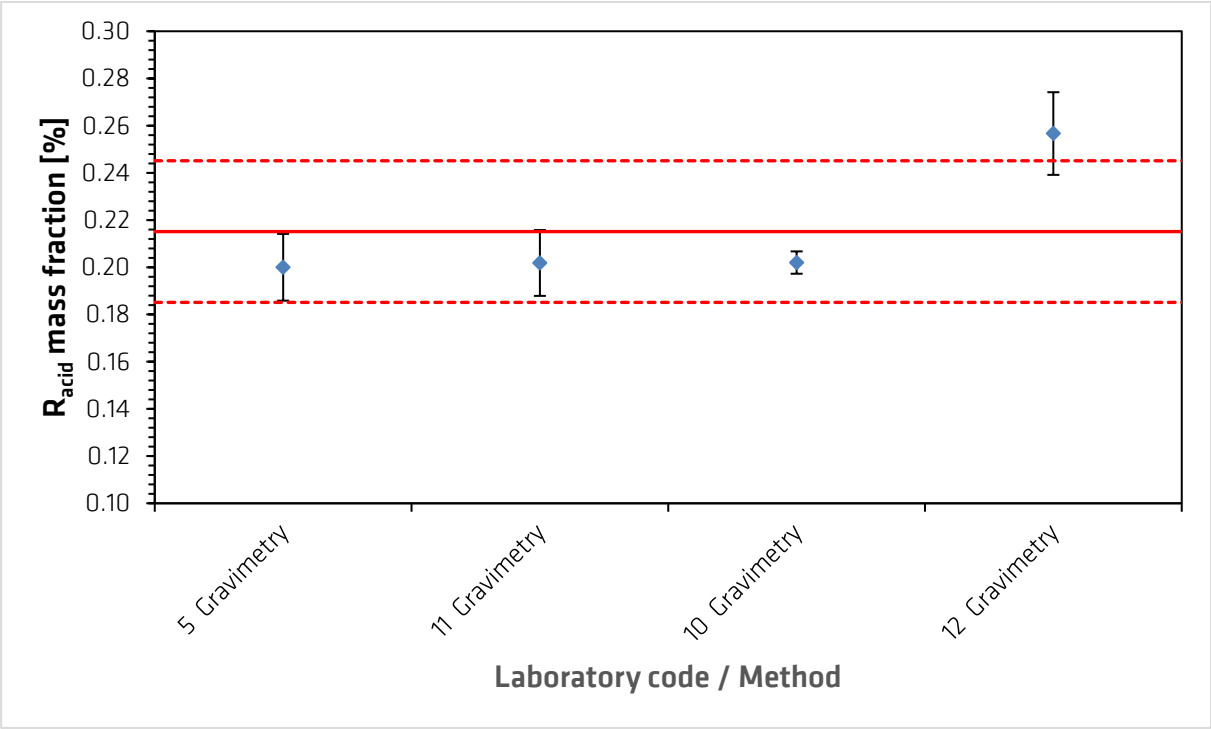


Figure C.17: Accepted laboratory means for R_{acid}. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the informative value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the informative value.

Table C.18: Individual results for Si (values in mg/kg)
Data not used for certification is indicated by a grey background.

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	17	ICP OES	4.9	1.5	1.4	4.5	3.9	4.7	**3.48**	1.61
L2	7	ET AAS	5.8	6.2	8.7	6.6	4.8	5.8	**6.32**	1.31
L3	5	ICP OES	12.76	8.29	7.89	7.45	11.36	10.41	**9.69**	2.14
L4 [1)]	16	PHOTOM	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	
L5	10	ICP OES	12.1	10.5	10.7	10.5	11.3	10.5	**10.93**	0.65
L6	2	SS-ET AAS	15.87	15.82	15.18	16.18	16.53	17.49	**16.18**	0.78
L7	12	ICP OES	18.42	20.05	18.87	17.83	18.20	16.55	**18.32**	1.16
L8 [1)]	12	ICP OES	< 50	< 50	< 50	< 50	< 50	< 50	**< 50**	

[1)] Data given as below limit of quantification

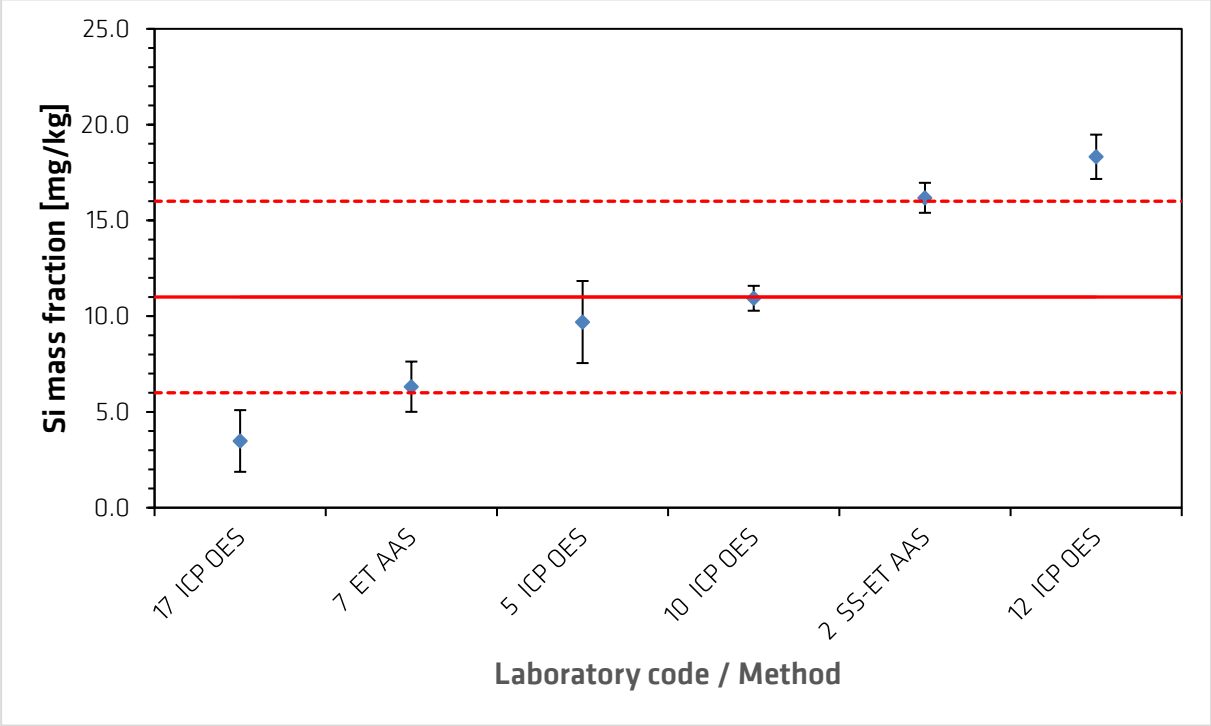


Figure C.18: Accepted laboratory means for Si. Uncertainty bars represent the standard deviation of each lab's results. The solid red line represents the informative value (the mean of laboratory means), while the broken red lines give the expanded uncertainty of the informative value.

Table C.19: Individual results for Na (values in mg/kg)

Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
L1	17	ICP OES	0.21	0.23	0.24	0.13	0.07	0.12	**0.167**	0.069
L2	2	SS-ET AAS	0.411	0.396	0.407	0.423	0.432	0.432	**0.417**	0.015
L4 [1)]	10	ICP OES	< 1	< 1	< 1	< 1	< 1	< 1	**< 1**	
L3	7	ICP OES	2.5	3.0	2.5	2.6	2.7	2.6	**2.650**	0.187
L5 [1)]	12	F AAS	< 5	< 5	< 5	< 5	< 5	< 5	**< 5**	
L6 [1)]	5	ICP OES	< 6	< 6	< 6	< 6	< 6	< 6	**< 6**	
L7 [1)]	11	ICP OES	< 10	< 10	< 10	< 10	< 10	< 10	**< 10**	

[1)] Data given as below limit of quantification

Table C.20: Individual results for Nb, S and W (values in mg/kg)

Parameter	Lab No.	Lab code	Method	Sub-sample #1	Sub-sample #2	Sub-sample #3	Sub-sample #4	Sub-sample #5	Sub-sample #6	**Mean**	s_i
Nb	L1	11	ICP OES	1700	1700	1750	1700	1680	1670	**1700**	28
S	L1	11	ICP OES	1.6	1.7	2.8	2.2	1.8	2.0	**2.02**	0.44
W	L1	11	ICP OES	115	113	112	115	112	115	**113.7**	1.5

Annex D: Outcome of statistical tests on results from the ILC

Tab. D.1: Outcome of statistical tests on results obtained for Ti

Parameter			**Ti**
Run of evaluation program			Run 1
Number of data sets			8
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 14
		$\alpha = 0.01$	Lab 14
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

Tab. D.2: Outcome of statistical tests on results obtained for B

Parameter			**B**
Run of evaluation program			Run 1
Number of data sets			8
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 14
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 14
		$\alpha = 0.01$	Lab 14
	Grubbs test outlier	$\alpha = 0.05$	Lab 14
		$\alpha = 0.01$	Lab 14
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 14, Lab 16
		$\alpha = 0.01$	Lab 14, Lab 16
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 14 removed

(continued)

Element			**B**
Run of evaluation program			Run 2 after removal of Lab 14
Number of data sets			7
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 16
		$\alpha = 0.01$	Lab 16
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.3: Outcome of statistical tests on results obtained for B_2O_3

Parameter			**B_2O_3**
Run of evaluation program			Run 1
Number of data sets			5
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	Insufficient data
		$\alpha = 0.01$	Insufficient data
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

Tab. D.4: Outcome of statistical tests on results obtained for Al

Parameter			**Al**
Run of evaluation program			Run 1
Number of data sets			8
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
	Grubbs test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 12 removed

* 2 from 10 datasets submitted were not included into the statistical evaluation (cf. Table C.4)

(continued)

Parameter			**Al**
Run of evaluation program			Run 2 after removal of Lab 12
Number of data sets			7
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.5: Outcome of statistical tests on results obtained for Ca

Element			**Ca**
Run of evaluation program			Run 1
Number of data sets			13
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

Tab. D.6: Outcome of statistical tests on results obtained for Cr

Parameter			**Cr**
Run of evaluation program			Run 1
Number of data sets			15
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
	Grubbs test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 16
		$\alpha = 0.01$	Lab 16
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 12 removed

(continued)

Parameter			**Cr**
Run of evaluation program			Run 2 after removal of Lab 12
Number of data sets			14
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 4
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 16
		$\alpha = 0.01$	Lab 16
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.7: Outcome of statistical tests on results obtained for Fe

Parameter			**Fe**
Run of evaluation program			Run 1
Number of data sets			15
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 16a, Lab 9a
		$\alpha = 0.01$	Lab 16a
	Grubbs test outlier	$\alpha = 0.05$	Lab 16a
		$\alpha = 0.01$	--
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 16b
		$\alpha = 0.01$	Lab 16b
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 16a removed

(continued)

Parameter			**Fe**
Run of evaluation program			Run 2 after removal of Lab 16a
Number of data sets			14
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 9a
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	none
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 16b, Lab 9a
		$\alpha = 0.01$	Lab 16b
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.8: Outcome of statistical tests on results obtained for Mg

Parameter			**Mg**
Run of evaluation program			Run 1
Number of data sets			8*
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

* 2 from 10 datasets submitted were not included into the statistical evaluation (cf. Table C.8)

Tab. D.9: Outcome of statistical tests on results obtained for Mn

Parameter			**Mn**
Run of evaluation program			Run 1
Number of data sets			12*
Testing for outlying Lab means	Dixon test outlier	α = 0.05	Lab 10
		α = 0.01	---
	Nalimov test outlier	α = 0.05	Lab 10
		α = 0.01	Lab 10
	Grubbs test outlier	α = 0.05	Lab 10
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12
		α = 0.01	Lab 12
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 10 removed

* 1 from 13 datasets submitted were not included into the statistical evaluation (cf. Table C.9)

(continued)

Parameter			**Mn**
Run of evaluation program			Run 2 after removal of Lab 10
Number of data sets			11
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	---
		α = 0.01	---
	Grubbs test outlier	α = 0.05	---
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12, Lab 14, Lab 5, Lab 9a
		α = 0.01	Lab 12, Lab 5
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	not normal
		α = 0.01	not normal
	Skewness & Kurtosis test	α = 0.05	not normal
		α = 0.01	not normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.10: Outcome of statistical tests on results obtained for Mo

Parameter			**Mo**
Run of evaluation program			Run 1
Number of data sets			13*
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	Lab 7
		α = 0.01	---
	Grubbs test outlier	α = 0.05	---
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 4, Lab 10, Lab 12, Lab 14
		α = 0.01	Lab 4, Lab 10,
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted, the straggler (Lab 7) was not removed

* 1 from 14 datasets submitted were not included into the statistical evaluation (cf. Table C.10)

Tab. D.11: Outcome of statistical tests on results obtained for Ni

Parameter			**Ni**
Run of evaluation program			Run 1
Number of data sets			14
Testing for outlying Lab means	Dixon test outlier	α = 0.05	Lab 11, Lab 5
		α = 0.01	Lab 11
	Nalimov test outlier	α = 0.05	Lab 11
		α = 0.01	Lab 11
	Grubbs test outlier	α = 0.05	Lab 11
		α = 0.01	Lab 11
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12, Lab 5, Lab 10
		α = 0.01	Lab 12, Lab 5, Lab 10
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	Not normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 11 removed

(continued)

Parameter			**Ni**
Run of evaluation program			Run 2 after removal of Lab 11
Number of data sets			13
Testing for outlying Lab means	Dixon test outlier	α = 0.05	Lab 5
		α = 0.01	--
	Nalimov test outlier	α = 0.05	Lab 5
		α = 0.01	Lab 5
	Grubbs test outlier	α = 0.05	Lab 5
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12, Lab 5, Lab 10
		α = 0.01	Lab 12, Lab 5, Lab 10
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	not normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted, the outlier Lab 5 was not removed

Tab. D.12: Outcome of statistical tests on results obtained for V

Parameter			**V**
Run of evaluation program			Run 1
Number of data sets			10*
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	--
	Nalimov test outlier	α = 0.05	Lab 14
		α = 0.01	Lab 14
	Grubbs test outlier	α = 0.05	Lab 14
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	---
		α = 0.01	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	not normal
		α = 0.01	not normal
	Skewness & Kurtosis test	α = 0.05	not normal
		α = 0.01	not normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 14 removed

* 1 from 11 datasets submitted were not included into the statistical evaluation (cf. Table C.12)

(continued)

Parameter			**V**
Run of evaluation program			Run 2 after removal of Lab 14
Number of data sets			9
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	Lab 12
		α = 0.01	---
	Grubbs test outlier	α = 0.05	---
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12
		α = 0.01	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted, the straggler (Lab 12) was not removed

Tab. D.13: Outcome of statistical tests on results obtained for Zr

Parameter			**Zr**
Run of evaluation program			Run 1
Number of data sets			15
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 16, Lab 9a
		$\alpha = 0.01$	Lab 16, Lab 9a
	Nalimov test outlier	$\alpha = 0.05$	Lab 16, Lab 9a
		$\alpha = 0.01$	Lab 16
	Grubbs test outlier	$\alpha = 0.05$	Lab 16
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 9a, Lab 14
		$\alpha = 0.01$	Lab 9a
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 16 removed

(continued)

Parameter			**Zr**
Run of evaluation program			Run 2 after removal of Lab 16
Number of data sets			14
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 9a, Lab 11
		$\alpha = 0.01$	Lab 9a, Lab 11
	Nalimov test outlier	$\alpha = 0.05$	Lab 9a, Lab 11
		$\alpha = 0.01$	Lab 9a
	Grubbs test outlier	$\alpha = 0.05$	Lab 9a
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 9a, Lab 14
		$\alpha = 0.01$	Lab 9a
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Outlier Lab 9a removed

(continued)

Parameter			**Zr**
Run of evaluation program			Run 3 after removal of Lab 9a
Number of data sets			13
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 11
		$\alpha = 0.01$	Lab 11
	Nalimov test outlier	$\alpha = 0.05$	Lab 11
		$\alpha = 0.01$	Lab 11
	Grubbs test outlier	$\alpha = 0.05$	Lab 11
		$\alpha = 0.01$	Lab 11
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 14
		$\alpha = 0.01$	Lab 14
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 3 accepted, the outlier (Lab 11) was not removed

Tab. D.14: Outcome of statistical tests on results obtained for C

Parameter			**C**
Run of evaluation program			Run 1
Number of data sets			10
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	Lab 17
		α = 0.01	Lab 17
	Grubbs test outlier	α = 0.05	Lab 17
		α = 0.01	---
	Paired Grubbs test outliers	α = 0.05	Lab 17, Lab 11
		α = 0.01	Lab 17, Lab 11
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 11, Lab 17, Lab 12, Lab 5
		α = 0.01	Lab 11, Lab 17, Lab 12
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	not normal
		α = 0.01	not normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Datasets of Lab 17 and 11 rejected as paired Grubbs outlier (α = 0.01)

(continued)

Parameter			**C**
Run of evaluation program			Run 2 after removal of Labs 17 and 11
Number of data sets			8
Testing for outlying Lab means	Dixon test outlier	α = 0.05	Lab 5
		α = 0.01	---
	Nalimov test outlier	α = 0.05	Lab 5
		α = 0.01	Lab 5
	Grubbs test outlier	α = 0.05	Lab 5
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	Lab 12, Lab 5
		α = 0.01	Lab 12
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	Not normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted, no outlier removed

Tab. D.15: Outcome of statistical tests on results obtained for N

Parameter			**N**
Run of evaluation program			Run 1
Number of data sets			9
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	---
		α = 0.01	---
	Grubbs test outlier	α = 0.05	---
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	---
		α = 0.01	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	normal
		α = 0.01	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

Tab. D.16: Outcome of statistical tests on results obtained for O

Parameter			**O**
Run of evaluation program			Run 1
Number of data sets			10
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	Lab 16
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Paired Grubbs test outliers	$\alpha = 0.05$	Lab 16, Lab 17
		$\alpha = 0.01$	Lab 16, Lab 17
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 2, Lab 16
		$\alpha = 0.01$	Lab 2, Lab 16
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Datasets of Lab 16 and 17 rejected as paired Grubbs outlier ($\alpha = 0.01$)

(continued)

Parameter			**O**
Run of evaluation program			Run 2 after removal of Labs 17 and 11
Number of data sets			8
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Nalimov test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
	Grubbs test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	Lab 2
		$\alpha = 0.01$	Lab 2
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
	Skewness & Kurtosis test	$\alpha = 0.05$	normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 2 accepted

Tab. D.17: Outcome of statistical tests on results obtained for R_{acid}

Parameter			**R_{acid}**
Run of evaluation program			Run 1
Number of data sets			4
Testing for outlying Lab means	Dixon test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
	Nalimov test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
	Grubbs test outlier	$\alpha = 0.05$	Lab 12
		$\alpha = 0.01$	Lab 12
Testing for outlying Lab variances	Cochran test outlier	$\alpha = 0.05$	---
		$\alpha = 0.01$	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	not normal
	Skewness & Kurtosis test	$\alpha = 0.05$	not normal
		$\alpha = 0.01$	normal
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted, no outlier removed

Tab. D.18: Outcome of statistical tests on results obtained for Si

Parameter			**Si**
Run of evaluation program			Run 1
Number of data sets			6*
Testing for outlying Lab means	Dixon test outlier	α = 0.05	---
		α = 0.01	---
	Nalimov test outlier	α = 0.05	---
		α = 0.01	---
	Grubbs test outlier	α = 0.05	---
		α = 0.01	---
Testing for outlying Lab variances	Cochran test outlier	α = 0.05	---
		α = 0.01	---
Normality of Lab means distribution:	Kolmogorov-Smirnov-Lilliefors test	α = 0.05	normal
		α = 0.01	normal
	Skewness & Kurtosis test	α = 0.05	Insufficient data
		α = 0.01	Insufficient data
Snedecor F-test and Bartlett test show that pooling is:			not allowed
Decision concluded			Run 1 accepted

* 2 from 8 datasets submitted were not included into the statistical evaluation (cf. Table C.18)

Annex E: Method M1

Extraction Method for Measurement of B_2O_3 Content of TiB_2

Summary

Soluble boron compounds are extracted from a TiB_2 sub-sample with boiling water. The concentration of dissolved boron in the extract is measured using an appropriate analysis method and calculated as mass fraction of boron oxide $w(B_2O_3)$ in the TiB_2 sub-sample.

Procedure

Depending on the analysis method a sub-sample of 1 – 5 g of TiB_2 is weighed with a precision of ± 1 mg into a 250 mL Erlenmeyer flask with joint. 100 mL of deionized water is added, a condenser is connected to the joint of the Erlenmeyer flask and the TiB_2/water suspension is gently boiled under reflux for 1 h. After extraction, the condenser is thoroughly rinsed with water into the Erlenmeyer flask, the condenser is removed, and the TiB_2/water suspension is rapidly cooled down to room temperature by placing the Erlenmeyer flask into a bath with cold water.

Measurement

For measurement of boron concentration, the extract may be directly used (e.g. using titrimetric methods) or transferred into a volumetric flask (e.g. 250 mL) and filled up to volume with water. After sedimentation of the TiB_2 powder the clear supernatant shall be used for measurement of boron concentration (e.g. using photometric or spectrometric methods). The measured boron concentration is used to calculate the mass fraction of water-soluble boron $w(B_{sol})$ in the TiB_2 sub-sample which is then expressed as mass fraction of boron oxide $w(B_2O_3)$ according to $w(B_2O_3) = 3.22 \times w(B_{sol})$.

Annex F: Method M2

Measurement of Acid Insoluble Residue of TiB_2

Summary

The acid insoluble residue is measured gravimetrically after dissolution of a TiB_2 sub-sample in a mixture of hydrofluoric acid (HF) and nitric acid (HNO_3).

NOTE: The HF/HNO_3 insoluble residue is an important parameter for process and quality control of TiB_2 production. The residue contains mainly boron carbide, boron nitride, titanium nitride, titanium dioxide and carbon.

Apparatus

Commonly used laboratory equipment and special equipment according to the following:

2.1 Membrane filter, cellulose nitrate, Ø 20 mm or 50 mm, pore size 0.45 µm.

2.2 Analytical balance, capable of reading to the nearest 0.01 mg.

2.3 Plastic beaker, 400 mL, resistant against HF and HNO_3.

2.4 Magnetic stirrer, with magnetic stir bar.

2.5 Cooling device, basin (2000 mL) with ice/water mixture or chiller with external cooling bath, suited to cool down the content of the plastic beaker to a temperature of 4 °C or below.

2.6 Filtration device, vacuum filter holder suited for membrane filters (2.1) with 2 L suction flask.

Reagents

Deionized water and reagents of known analytical grade shall be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.1 Hydrofluoric acid, HF, c(HF) = 40 % (w/w), approx. 23 mol/L.

3.2 Nitric acid, HNO_3, $c(HNO_3)$ = 65 % (w/w), approx. 14 mol/L.

3.3 Acid mixture, HF (3.1) / HNO_3 (3.2), 1:3 by volume.

Procedure

The membrane filter (2.1) is dried at 105 °C ± 5 °C for 15 min. After cooling down to ambient temperature in a desiccator the mass of the membrane filter (m_1) is determined. The cooling device (2.5) is placed on the magnetic stirrer (2.4). A sub-sample of 3.0 g ± 0.1 g of TiB_2 is weighed into the beaker (2.3), a magnetic stir bar is added, and the beaker is placed into the cooling device. 30 mL HF (3.1) is added to the sub-sample and the mixture is stirred for at least 20 min to cool down to the temperature of the cooling device. Then 30 mL of the acid mixture (3.3) is slowly dosed within 20 min into the beaker.

CAUTION: The exothermal reaction of TiB_2 with the acid mixture is vigorous and releases nitrous and hydrofluoric fumes.

NOTE: A controlled addition of the acid mixture can be achieved using a peristaltic pump with HF/HNO_3 resistant tubing.

After addition of the acid mixture the mixture is stirred for 20 min. The mixture is then diluted with water to a volume of approx. 200 mL and filtered using the filtration device (2.6) through the membrane filter (2.1). The residue on the membrane filter is washed with 500 mL water. The membrane filter is removed from the filtration device and dried at 105 °C ± 5 °C for 15 min. After cooling down to ambient temperature in a desiccator the mass of the membrane filter (m_2) is determined.

Calculation

The acid insoluble residue $w(R_{acid})$ in the TiB_2 sub-sample is calculated in mass fractions in % according to:

$$w(\mathrm{R_{acid}}) = \frac{(m_2 - m_1) \cdot 100}{m_S}$$

where:

m_1 = mass of empty membrane filter, mg
m_2 = mass of membrane filter with residue, mg
m_S = sample mass, mg