Bundesanstalt für Materialforschung und -prüfung (BAM)

in co-operation with the

Committee of Chemists of GDMB
Gesellschaft der Metallurgen und Bergleute e.V.

The certification of mass fractions of C and O in niobium carbide

BAM-S013

Certification report

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Abstract

This report describes the preparation and certification of reference material BAM-S013, a niobium carbide powder, carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additional determined data are listed below.

Certified Values

Element	Mass fraction 1) in %	Uncertainty 2) in %
C	10.66	0.07
O	0.307	0.013

1) Unweighted mean value of the means of accepted sets of data (consisting of 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 approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

Informative Values

Element	Mass fraction 1) in %	Uncertainty 2) in %
C_{free}	0.10	0.04
N	0.0031	0.0009
S	0.0017	0.0005
H	0.0076	0.0007

1) Unweighted mean value of the means of accepted sets of data (consisting of at least 2 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 approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

Property	Property value 1)	Uncertainty 2)
Specific surface area (BET)	1.04 m^2 / g	0.03 m^2 / g
Particle size:		
d_{10}	1.10 µm	0.23 µm
d_{50}	3.57 µm	0.18 µm
d_{90}	6.7 µm	0.4 µm

1) Values were not certified, but given for information, because there was no homogeneity and stability investigation.

2) Estimated expanded uncertainty *U* with a coverage factor of *k* = 3, corresponding to a level of confidence of approx. 99 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

Contents

List of abbreviations
(if not explained elsewhere)

TSSP	Tetra sodium phyrophosphate
M	mean of the laboratories' means
u_c	combined uncertainty of certified mass fraction
s_M	standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification
n	number of accepted laboratory mean values of interlaboratory comparison for certification

1 Introduction

Niobium carbide (NbC) is attracting increasing attention as a substitute for tungsten carbide to reduce dependence on tungsten imports from China. The People's Republic of China obtains about 80% of the world's supply and began restricting exports around 2004 to keep more value added at home, causing tungsten prices to multiply on the world market, in part due to China's sharp increase in domestic consumption. Niobium, like tungsten, is a refractory metal. As a monocarbide, niobium carbide with a melting point of 3,520°C opens up a potential for partial or complete substitution of tungsten carbide with a melting point of 2,870°C [1].
Surprisingly, up to now there are no testing standards for C, N and O analysis in the carbide industry. Based on this experience, the Divisions 1.6 and 6.3 of BAM conducted an interlaboratory test in 2018 to determine precision data. Based on the results of this interlaboratory test the idea to produce a NbC-CRM was born.
Beside the non-metals C (C_{total} and C_{free}), O, N, S and H the properties specific surface area according to Brunauer, Emmet and Teller (BET) and particle size distribution (d_{10}, d_{50} and d_{90}) were determined.

Certification of reference material BAM-S013 was carried out in close cooperation with the working group „Special Materials" of the Committee of Chemists of the Society of Metallurgists und Miners (GDMB). All the laboratories participating in this certification project have already participated in the above mentioned interlaboratory test and showed their experience with NbC analysis.
Certification of the CRM BAM-S013 NbC was performed on the basis of ISO 17034 [2] and the relevant ISO-Guides [3, 4].

2 Companies/laboratories involved

Manufacturing and preparation of the material:

- The material was produced by Treibacher Industrie AG, Treibach-Althofen, Austria
- The material was mixed and bottled by Bundesanstalt für Materialforschung und -prüfung (BAM)

Homogeneity testing

- The analytical investigations and all statistical evaluations for the homogeneity testing were carried out by BAM.

Statistical evaluation of the data:

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

Participants in the certification inter-laboratory comparison:

Fifteen laboratories participated in the interlaboratory comparison for certification:
- Bruker AXS GmbH, Karlsruhe (Germany)
- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin (Germany)*
- ChemiLytics GmbH& Co. KG, Goslar (Germany)*
- Dorfner Analysenzentrum und Anlagenplanungsgesellschaft mbH (ANZAPLAN)*, Hirschau (Germany)
- Elementar Analysensysteme GmbH, Langenselbold (Germany)
- Forschungsinstitut für Anorganische Werkstoffe -Glas/Keramik- GmbH, Höhr-Grenzhausen (Germany)*
- Fraunhofer-Institut für Keramische Technologien und Systeme IKTS, Hermsdorf (Germany)*
- Horn & Co. Analytics GmbH, Wenden-Hünsborn, (Germany)*
- Karlsruher Institut für Technologie, Eggenstein-Leopoldshafen (Germany)
- Leibniz-Institut für Festkörper- und Werkstoffforschung (IFW), Dresden (Germany)
- LECO Europe Application and Technology Center, Berlin (Germany)

- Plansee SE, Reutte (Austria)*
- revierlabor, Essen (Germany)*
- Treibacher Industrie AG, Treibach-Althofen (Austria)
- voestalpine Böhler Welding Germany GmbH, Hamm (Germany)*

*accredited to ISO IEC 17025

3 Candidate material

25 kg of niobium carbide powder (Treibacher Industrie AG, Treibach-Althofen, Austria) were taken as candidate material. The material was mixed in a drum hoop mixer for 8 h. After the mixing step 15 test portions were taken from the whole batch to test for homogeneity. The reference material is filled into 60 ml glass bottles (400 units of 60 g).

4 Homogeneity investigation of the material

15 bottles of the candidate material were taken to investigate the homogeneity of the material. For C, H, and O three determinations, for N two determinations per bottle were carried out.
The estimates of inhomogeneity contributions u_{bb} potentially hidden by the measurement uncertainty and to be included into the total uncertainty budget were estimated according to ISO Guide 35 [4] as the maximum of the values obtained from Eq. (1) and (2).

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

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

where:

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

s_{bb} signifies the between-bottle standard deviation, whereas u^{*}_{bb} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). 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_{among}, which was true for carbon.
The results of the homogeneity testing measurements as well as the ANOVA calculations can be found in the annex.

5 Stability of the material

Due to its chemical composition Niobium carbide is very stable. An aged NbC material was used as a candidate material for BAM-S013 to be sure that no oxidation will take place during the lifetime of the CRM. Therefore, no specific stability test was performed for BAM-S013. This may not be true for the hydrogen content. Since there is no stability data for hydrogen in niobium carbide, the mass fraction of hydrogen in BAM-S013 is given for information only. The oxygen content of the CRM will be checked regularly.

6 Characterisation study

6.1 Analytical methods used for certification

15 laboratories participated in the certification interlaboratory comparison. The laboratories were asked to analyse six subsamples. They were free to choose any suitable method for analysis. Table 1 shows the analytical methods used by the participating laboratories.
All participating laboratories were instructed to use only calibrants prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 1: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment/Calibration	Analytical method
1*	H	250 mg	Sn-capsules Instrument: Bruker Galileo G8	
	BET		Degassing: 250 °C (45 min, N_2)	DIN ISO 9277
2	C	200 mg	Additives: W/Sn, Fe Instrument: Bruker G4 Ikarus	AR307 WC
	S	1 g	Additives: W/Sn, Fe Instrument: Bruker G4Icarus	ECRM 088-2
	N	100 mg	Additives: Ni-capsule + graphite Instrument: Bruker G8Galileo	Gas calibration N_2
	O	100 mg	Additives: Ni-capsule + graphite Instrument: Bruker G8Galileo	JK47A
3*	C	100 mg	Leco CS230, Lecocell II (W/Sn) and Fe-Chips as additive	Leco-Std. Calcite (12% C)
	S	100 mg	Leco CS230, Lecocell II (W/Sn) and Fe-Chips as additive	Leco-Std. 502-948 (0.016% S)
	BET	7.5 g	Degassing: 250 °C (60 min, N_2) NOVA 2200 (Quantachrome)	
5*	C	50 mg	Additives: 1.2 g W, 0.6 g Fe Instrument: Eltra CS 800	Eltra Stahl Standard 92000-26
	N	45 mg	Ni-capsule + 0,4 g Ni-flux Instrument: Leco TC 600	ECRM 077-2, 179-2
	O	45 mg	Sn-capsule + Ni-basket Sn-tablet Instrument: Leco TC 600	ERM-BD103 (BN)
	S	205 mg	1, Additives: 1.2 g W, 0.6 g Fe Instrument: Eltra CS 800	Eltra Stahl Standard 92000-31
	BET		Degassing: 250 °C (45 min, N2) Instrument: Tristar 3030	
	Particle size		USB Water Instrument: Mastersizer 3000 Model: Fraunhofer	
7*	C	100 mg	Additives: W/Sn, Fe Instrument: Leco CS200	CRM (BAM, Leco, LGC, CGL)
	Particle size		Instrument: Helos	
8	C	50 mg	Additives: W18Fe5 in Sn Instrument: EMIA 820V (Horiba)	$CaCO_3$ (BAM)
	S	100 mg	Additives: W18Fe5 in Sn Instrument: EMIA 820V (Horiba)	K_2SO_4

Table 1: Analytical procedures used by the participating laboratories (cont.)

8	N	200 mg	Additives: Graphit + NiSn Instrument: Leco ON 836	KNO_3
	O	200 mg	Additives: Graphit + NiSn Instrument: Leco ON 836	CO_2 gas
	BET	0.5 g	Degassing: 110 °C (Vacuum, 20 h) Quantachrome Quadrasorb SI version 5.04	
	Particle size		USB water (20 min) Instrument: Microtrac S3500 Particle Size Analyzer Model: modified Mie model	BCR066
9	C	10 – 20 mg	Additives: Lecocell II HP Instrument: LECO TC600	WC
	N	50 – 100 mg	Ni-capsules Additives: Ni Instrument: Bruker Galileo G8	KED 1025 Alpha Lot: 1212C
	O	100 – 400 mg	Sn-capsules Additives: Graphit + Ni Instrument: LECO TC600	KED 1025 Alpha Lot: 1212C
	H	50 mg	Sn-capsules Instrument: Bruker Galileo G8	Helium
11	C, S		LECO CS744	
	O, N, H		LECO ONH836	
	Particle size		Malvern Mastersizer 2000 Water	
12*	C	250 mg	W and Fe (Eltra) Instrument: Bruker G4 Icarus	ERM-ED 102 B_4C
	N, O	100 mg	Ni-Körbchen (HRT) Sn-Kapsel (HRT) Instrument: LECO TCH-600	Ti-standards (LECO)
	H		1) Eltra ONH2000 2) LECO TCH 600	Steel-standard Ti-Standard
14	C, S	3 mg (C) 500 mg (S)	1.3 g W (Eltra 90220) 0.7 g Fe (Eltra 90260) Sn-Kapsel Instrument: ELTRA CS-800	$BaCO_3$ $BaSO_4$
	N	250 mg (N) 50 mg (O)	Ni-Körbchen (Leco 502-344) Sn-Kapsel Instrument: LECO TCH-600	KNO_3 Fe_2O_3
	Particle size	350 mg	Mastersizer 3000, TSPP without ultrasound during measurement	
15	C	130 mg	Additives: 1.5 g W, 3 g Cu Instrument: Leco WC600	
	C(free)	1 g	Instrument: Eltra CS 580	
	N, O	100 mg	Sn-capsule + 0.1 g graphite Instrument: Leco TCH 600	
	S	0.5 g	1.5g W; 1g Fe; 1g NbO_2 Instrument: Leco CS-744	
	BET		Degassing: 250°C (60 min, N2) Instrument: Tristar 3030	
	Particle size		USB Water + Daxad 11 Instrument: Mastersizer 3000 Model: Fraunhofer	

Table 1: Analytical procedures used by the participating laboratories (cont.)

16	C	0.25 g	Additives: W, Cu Instrument: Leco WC600	Leco Standard WC 501-123
	BET		Degassing: 250 °C (Vacuum)	Acc. to DIN ISO 9277
	Particle size		USB 0.05% TSPP-solution Instrument: Mastersizer 2000 Model: Fraunhofer	Acc. to ISO/DIS 13320
17	C, S	200 mg	LECO CS-200, W and Fe	
	O, N	150 mg	LECO CS-400, Ni-baskets, Sn-capsules	
	Particle size		1) Cilas 1064, Na-hexametaphosphate with ultrasound 2) Cilas 1190, without ultrasound during measurement 3) Microtrac S3500, TSPP without ultrasound during measurement USB water (20 min) Instrument: Microtrac S3500 Particle Size Analyzer Model: modified Mie model	
18*	C	250 mg	Bruker G4 Icarus W and Fe	ERM-ED102 B_4C (CRM BCS 352)
	O, N	100 mg	Leco TCH 600 Ni-baskets Sn-capsules	Leco Ti-standards (CRM ERM-ED102 B_4C)
	H		1) Eltra ONH2000 2) Leco TCH 600	1) Steel-CRM 2) Ti-standard
19	H	200 mg	Instrument: Bruker Galileo G8, mass spectrometry Sn-capsules	

*accredited acc. to ISO IEC 17025

6.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are shown in Figures 1 to 10. These figures show the mean value of each laboratory with the inner-laboratory standard deviation, the mean of the laboratories' mean values (continuous line), and the standard deviation of laboratory means (dotted line).

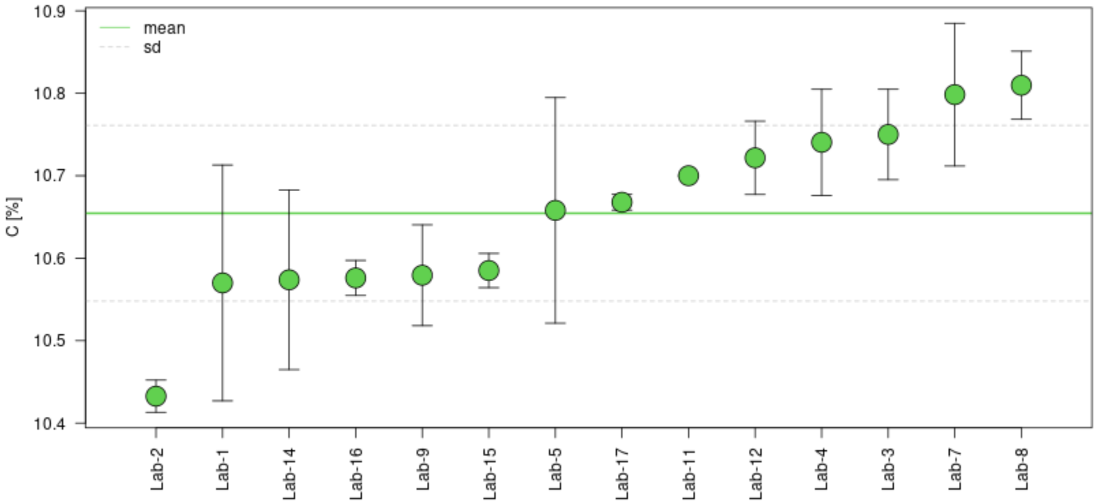

Figure 1: results for C

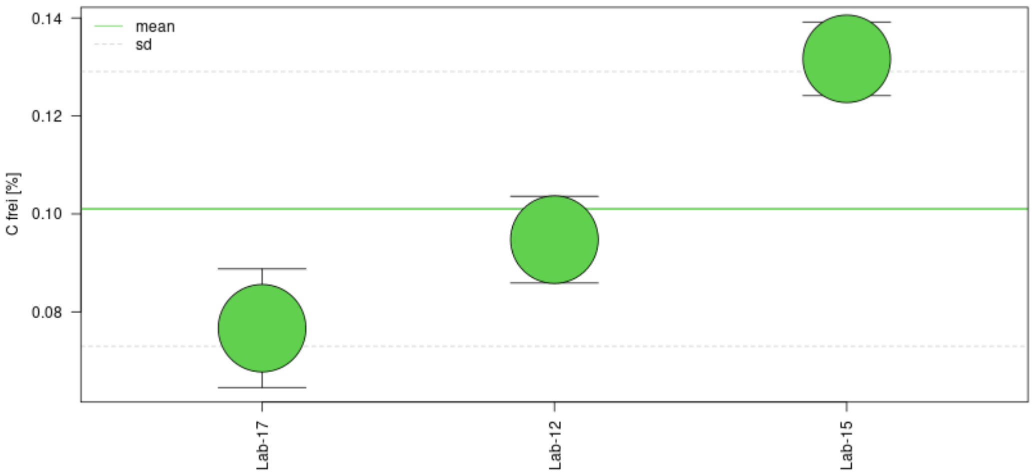

Figure 2: results for C(free)

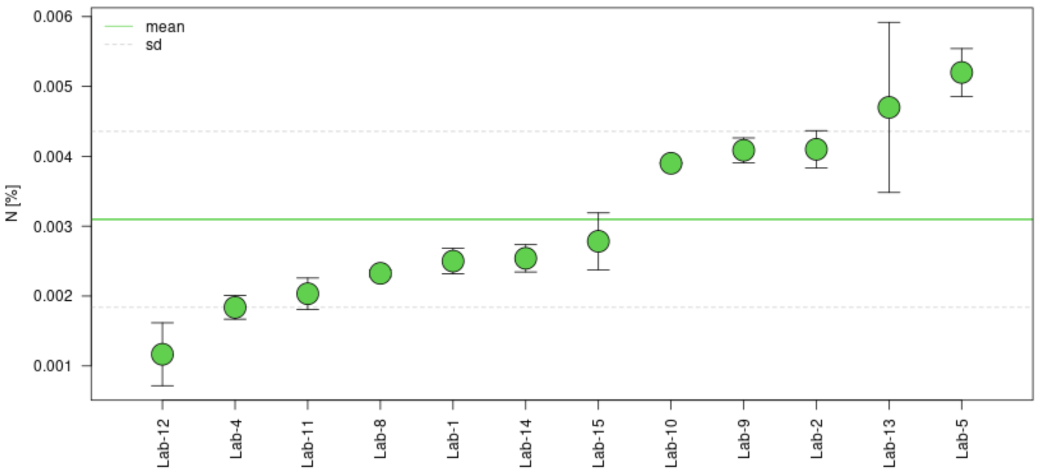

Figure 3: results for N

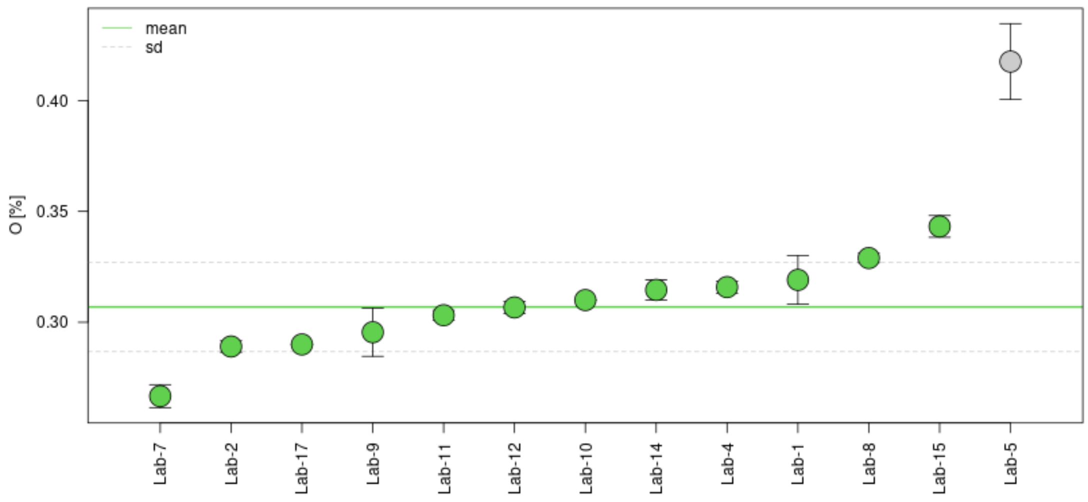

Figure 4: results for O

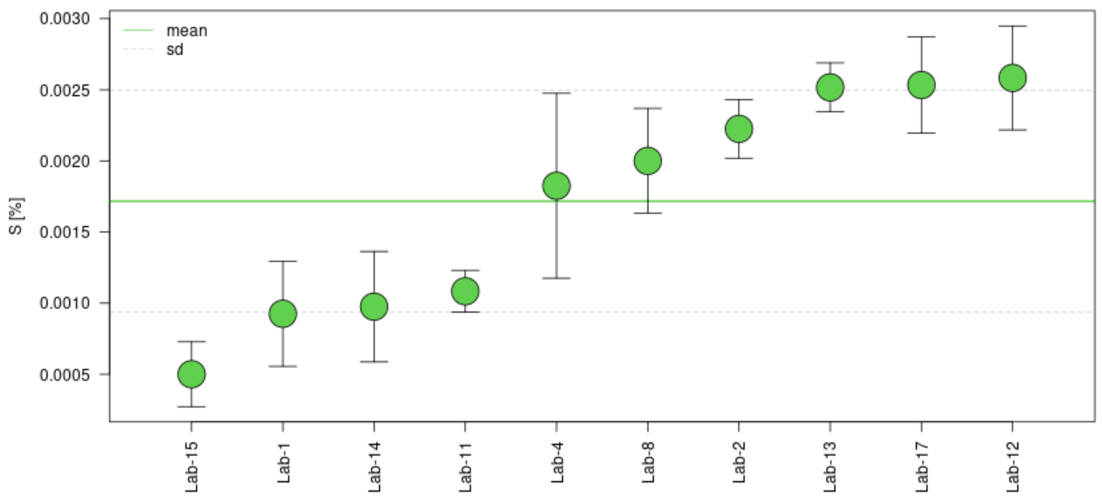

Figure 5: results for S

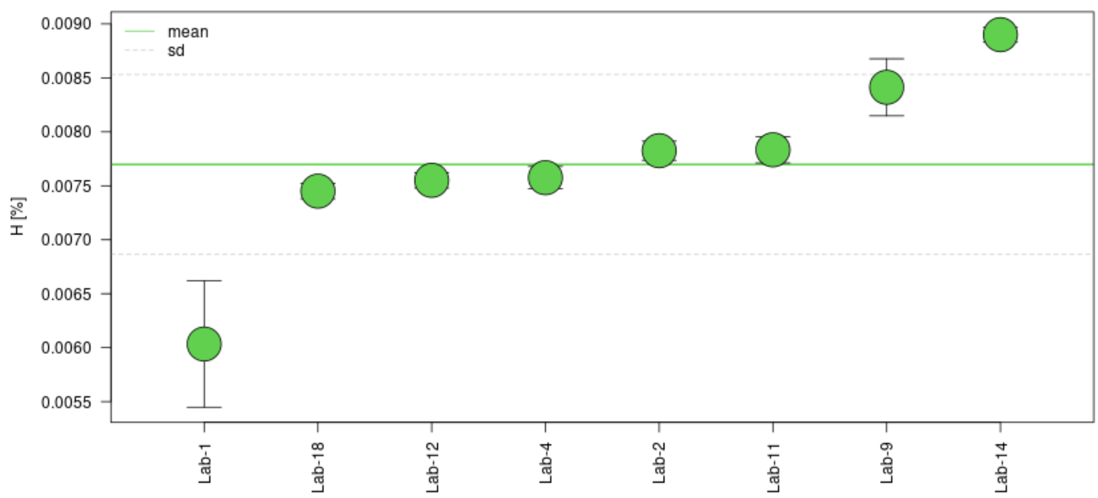

Figure 6: results for H

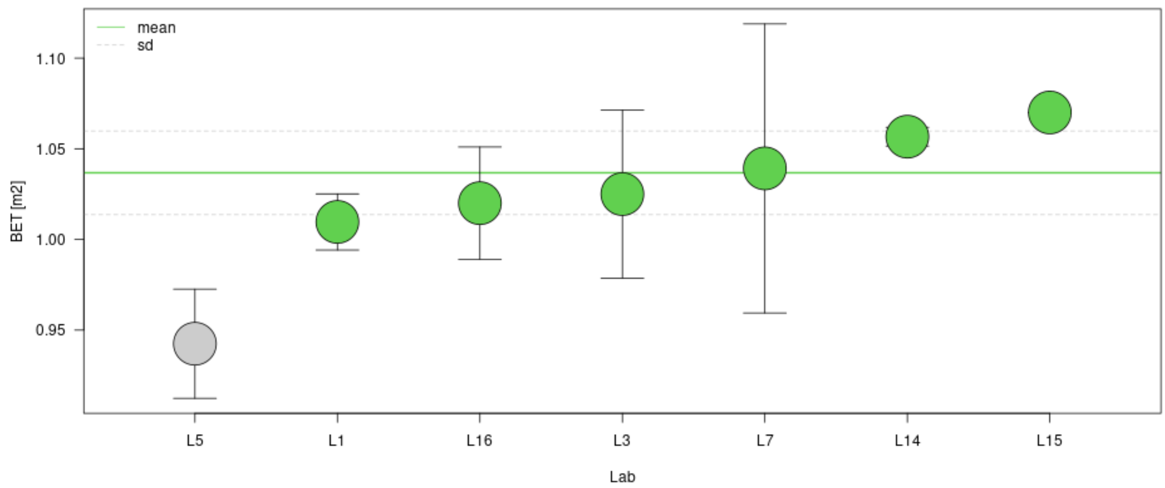

Figure 7: results for pore volume (BET)

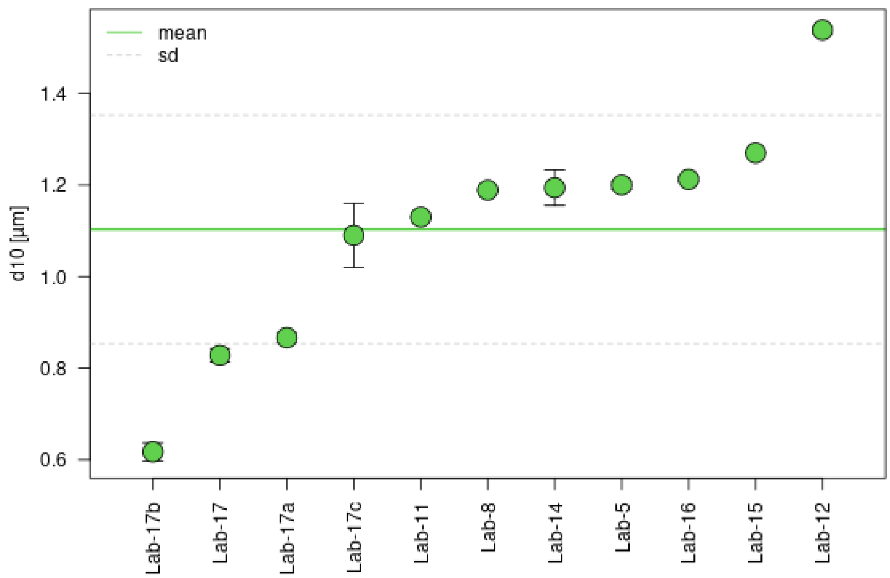

Figure 8: results for particle size d_{10}

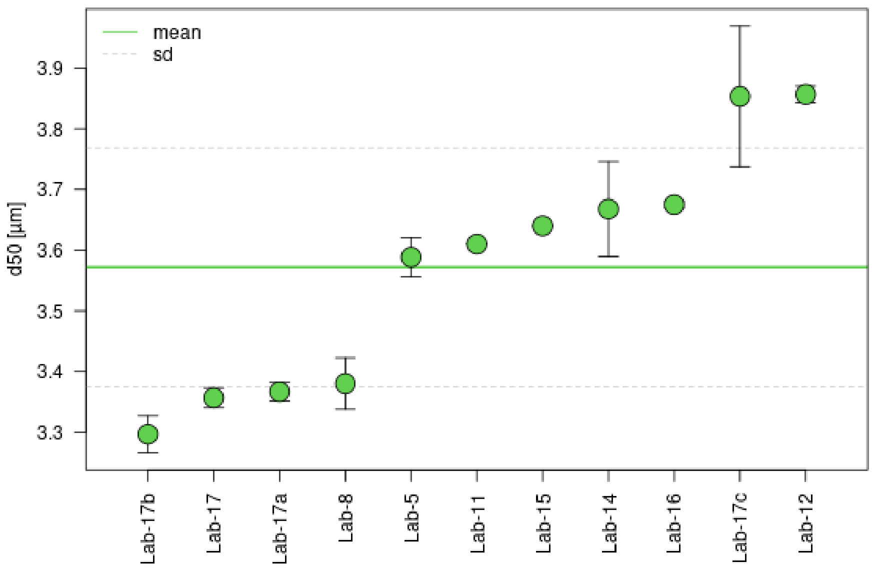

Figure 9: results for particle size d_{50}

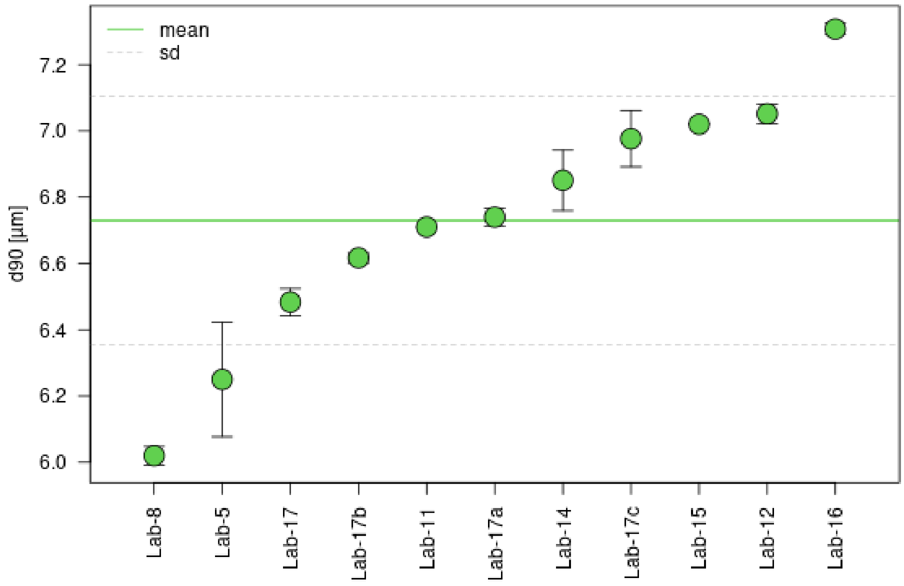

Figure 10: results for particle size d_{90}

The statistical evaluation of the data was performed using the software program eCerto [5]. The following results were obtained from outlier tests:

Tab. 2: Outcome of statistical tests on the results obtained for C and N

	C	N
Number of data sets	14	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Laboratory 2	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Laboratory 14	Laboratory 13
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying results were not removed.

Tab. 3: Outcome of statistical tests on the results obtained for O

	1st run	2nd run
Number of data sets	13	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Laboratory 5	---
Dixon (α = 0.01)	Laboratory 5	---
Nalimov (α = 0.05)	Laboratory 5	---
Nalimov (α = 0.01)	Laboratory 5	---
Grubbs (α = 0.05)	Laboratory 5	---
Grubbs (α = 0.01)	Laboratory 5	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Laboratory 5	Laboratory 1
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (Lab. 5) was removed.

Tab. 4: Outcome of statistical tests on the results obtained for S and H

	S	H
Number of data sets	10	8
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	Laboratory 1
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	Laboratory 1
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	Laboratory 1
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (Lab. 1) was not removed.

Tab. 5: Outcome of statistical tests on the results obtained for C(free)

	1st run
Number of data sets	3
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

Tab. 6: Outcome of statistical tests on the results obtained for BET

	1st run	2nd run
Number of data sets	7	6
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	Laboratory 5	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Laboratory 5	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	Laboratory 5	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Laboratory 8	Laboratory 8
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (Lab. 5) was removed.

Tab. 7: Outcome of statistical tests on the results obtained for d_{10}

	1st run
Number of data sets	11
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	Laboratory 17b
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	Laboratory 17c
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying results were not removed.

Tab. 8: Outcome of statistical tests on the results obtained for d_{50} and d_{90}

	d_{50}	d_{90}
Number of data sets	11	11
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Laboratory 17c	Laboratory 5
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying results were not removed.

The certified mass fractions of all elements were calculated as mean of the accepted data sets. These values are given in Table 9.
The resp. combined uncertainties were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity (u_{bb}) of the material using Equation 4.

$$u_c = \sqrt{u_{ilc}^2 + u_{bb}^2} \qquad (4)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$: uncertainty contribution resulting from inter-laboratory comparison

n : number of data sets used for calculating the certified mass fraction of each element

Table 9: Uncertainty calculation

	uncertainty contribution from										
	M	n	s_M	u_{ilc}	u_{bb}	$u_{combined}$	U		u_{bb} (rel)		
	%		%	%	%	%	%				
C	10.66	14	0.1066	0.0285	0.0096	0.0301	0.0602		0.0904		
C_{free}	0.10	3	0.0281	0.0162		0.0162	0.0324				
N	0.0031	12	0.0013	0.0004	0.0002	0.0004	0.0009		7.2441		
O	0.3070	12	0.0202	0.0058	0.0022	0.0062	0.0125		0.7193		
S	0.0017	10	0.0008	0.0003	0.0000	0.0003	0.0005		1.2000	*	
H	0.0076	8	0.0009	0.0003	0.0001	0.0003	0.0007		1.2096		
	**calculated from u_{bb}(rel):			$u_{bb} = \frac{M \cdot u_{bb}(rel)}{100}$			*estimated from homogeneity test for H				
d10	1.1033	11	0.2495	0.0752		0.0752	0.2257				
d50	3.5719	11	0.1969	0.0594		0.0594	0.1781				
d90	6.7297	11	0.3749	0.1130		0.1130	0.3391				
BET	1.0367	6	0.0231	0.0094		0.0094	0.0283				

The expanded uncertainties U are calculated by multiplication of u_c with a coverage factor of k = 2 (physical properties: k = 3) using Equation 5.

$$U = k \cdot u_c \qquad (5)$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 2 of this report. Rounding was done according to DIN 1333 [6].

7 Instructions for use

7.1 Area of application

The main area of application is to check the trueness of results when one or more of the certified parameters in niobium carbide are determined by a laboratory. Based on own results and on certified values the uncertainty of own measurements can be calculated.

7.2 Recommendations for correct sampling and sample preparation

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. Each sub-sample has to be taken separately.

7.3 Recommendations for correct storage

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

7.4 Safety guidelines

Niobium carbide is not known to be toxic. 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.

8 Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions (see Table 1).

9 References

[1] M. Woydt, H. Mohrbacher, Niobcarbid - Ein vergessener Hartstoff für den Verschleißschutz in offenen und geschlossenen Tribosystemen, 55. Tribologie-Fachtagung - Reibung, Schmierung und Verschleiß - Forschung und praktische Anwendungen, 2014

[2] DIN EN ISO 17034, General requirements for the competence of reference material producers, 2016

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

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

[5] J. Lisec, eCerto Software, BAM 2021

[6] DIN 1333:1992-02 Zahlenangaben

10 Information on and purchase of the CRM

Certified reference material BAM-S013 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

Each unit 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.

Appendix: Homogeneity testing

Carbon

	1	2	3
Bottle 1	10.782	10.786	10.781
Bottle 2	10.785	10.753	10.778
Bottle 3	10.807	10.763	10.780
Bottle 4	10.769	10.779	10.768
Bottle 5	10.797	10.831	10.771
Bottle 6	10.835	10.726	10.906
Bottle 7	10.790	10.834	10.785
Bottle 8	10.787	10.781	10.813
Bottle 9	10.758	10.774	10.763
Bottle 10	10.777	10.790	10.756
Bottle 11	10.770	10.773	10.783
Bottle 12	10.743	10.799	10.781
Bottle 13	10.803	10.835	10.768
Bottle 14	10.770	10.868	10.793
Bottle 15	10.746	10.744	10.788

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.01401	14	0.00100	0.90534	0.56255	2.03742
Within groups	0.03317	30	0.00111			
Total	0.04718	44				
within-sd	0.03325					
effective n	3.00					
s_{bb}	0					
u^*_{bb}	0.00975					
u_{bb}	0.00975					
u_{bb}(rel.)	0.09044					

Oxygen

	1	2	3
Bottle 1	0.387	0.382	0.393
Bottle 2	0.388	0.393	0.389
Bottle 3	0.380	0.393	0.383
Bottle 4	0.386	0.389	0.385
Bottle 5	0.391	0.389	0.390
Bottle 6	0.390	0.399	0.393
Bottle 7	0.392	0.393	0.391
Bottle 8	0.393	0.398	0.391
Bottle 9	0.391	0.394	0.393
Bottle 10	0.397	0.395	0.392
Bottle 11	0.392	0.390	0.394
Bottle 12	0.405	0.395	0.396
Bottle 13	0.392	0.388	0.396
Bottle 14	0.396	0.396	0.391
Bottle 15	0.392	0.394	0.399

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00053	14	0.00004	2.69652	0.01107	2.03742
Within groups	0.00042	30	0.00001			
Total	0.00095	44				
within-sd	0.00375					
effective n	3.00					
s_{bb}	0.002819					
u^{*}_{bb}	0.00110					
u_{bb}	0.00282					
u_{bb}(rel.)	0.71931					

Nitrogen

	1	2
Bottle 1	0.00045	0.00040
Bottle 2	0.00055	0.00060
Bottle 3	0.00066	0.00045
Bottle 4	0.00065	0.00062
Bottle 5	0.00053	0.00044
Bottle 6	0.00045	0.00058
Bottle 7	0.00059	0.00057
Bottle 8	0.00081	0.00038
Bottle 9	0.00049	0.00062
Bottle 10	0.00059	0.00080
Bottle 11	0.00046	0.00067
Bottle 12	0.00079	0.00090
Bottle 13	0.00050	0.00049
Bottle 14	0.00069	0.00052
Bottle 15	0.00060	0.00049

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.00000027	14	0.00000002	1.37694	0.27286	2.42436
Within groups	0.00000021	15	0.00000001			
Total	0.00000048	29				
within-sd	0.00012					
effective n	3.00					
s_{bb}	4.18709E-05					
u^*_{bb}	0.00004					
u_{bb}	0.00004					
u_{bb}(rel.)	7.24411					

Hydrogen

	1	2	3
Bottle 1	92.83	91.91	92.34
Bottle 2	94.29	92.76	95.32
Bottle 3	90.67	89.78	88.35
Bottle 4	91.46	94.66	94.69
Bottle 5	94.17	90.66	92.98
Bottle 6	94.43	93.38	91.18
Bottle 7	89.66	90.36	90.37
Bottle 8	91.75	90.59	91.21
Bottle 9	89.80	92.67	94.30
Bottle 10	90.58	93.78	91.69
Bottle 11	90.89	91.30	89.86
Bottle 12	92.91	92.14	94.12
Bottle 13	92.50	89.09	91.57
Bottle 14	92.97	91.51	94.80
Bottle 15	90.93	90.41	89.60

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	78.80781	14	5.62913	2.93370	0.00653	2.03742
Within groups	57.56345	30	1.91878			
Total	136.37126	44				
within-sd	1.38520					
effective n	3.00					
s_{bb}	1.11210731					
u^*_{bb}	0.40638					
u_{bb}	1.11211					
u_{bb}(rel.)	1.20963					