

**BAM**in cooperation with the WG 'Special Materials'  
of the Committee of Chemists of GDMB

European Reference Materials

# CERTIFICATE OF ANALYSIS

**ERM<sup>®</sup>-ED103**

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

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

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

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

Accepted as an ERM<sup>®</sup>, Berlin, January 2012BAM Berlin  
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<b>Indicative Values</b>		
	Mass Fraction	
	Indicative value <sup>1) 3)</sup>	Uncertainty <sup>2)</sup>
Carbon	0.018 %	0.002 %
Cobalt	< 0.1 mg/kg	
Water	< 0.1 %	

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

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

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

<b>Additional Material Information</b>		
Particle size <sup>1)</sup>	$d_{10}$	4.22 $\mu\text{m}$
	$d_{50}$	11.28 $\mu\text{m}$
	$d_{90}$	29.74 $\mu\text{m}$
Specific surface area <sup>2)</sup>		5.02 $\text{m}^2/\text{g}$

1) The particle size distribution (volume) was determined by laser light diffraction method.

2) The specific surface area was determined as multi point BET according to DIN ISO 9277.

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

## NOTE

European Reference Material ERM<sup>®</sup>-ED103 was certified under the responsibility of BAM Federal Institute for Materials Research and Testing in cooperation with the Committee of Chemists of the GDMB Society for Mining, Metallurgy, Resource and Environmental Technology according to the principles laid down in the technical guidelines of the European Reference Material ERM<sup>®</sup> cooperation agreement between BAM-LGC-IRMM. Information on these guidelines is available in the Internet (<http://www.erm-crm.org>).

## DESCRIPTION OF THE SAMPLE

The certified reference material ERM<sup>®</sup>-ED103 consists of a boron nitride powder. The material is supplied in glass bottles containing 50 g each.

## MEANS OF ACCEPTED DATA SETS

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

The “ - “ indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion in GDMB meetings.

Values given in *italic type* are indicative values only.

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

Mean: Arithmetic mean of the laboratory means

s<sub>Mean</sub>: Standard deviation of the laboratory means

\*) Boron oxide was determined as an adherent parameter.

## ANALYTICAL METHOD USED FOR CERTIFICATION

### List of abbreviations

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

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

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

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

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## **SAFETY INFORMATION**

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

## **INTENDED USE**

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

## **INSTRUCTIONS FOR USE**

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. Each sub-sample has to be taken separately. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different analytes (in parenthesis /mg): Al, Ca, Cr, Fe, Mg, Na and Ti (500), Si (15), C (150), O and N (30), B<sub>total</sub> (200), adherent B<sub>2</sub>O<sub>3</sub> (5000). The opening time of the bottle should be kept as short as possible. The samples were closed in the bottles under Ar-stream. The lid of the bottle equipped with a special sealing gasket should be locked tightly immediately after usage. It is not required to dehydrate the sample before starting the measurements. For the determination of metallic analytes, the required pressure digestion has to be tested concerning the loss of analytes.

## STORAGE

The sample should be stored in a dust-free and dry environment at room temperature (20 °C).

However, BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

## EXPIRATION OF CERTIFICATION

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

## LEGAL NOTICE

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## NOTE

A detailed technical report describing the production, characterisation as well as the analytical procedures applied and the treatment of the analytical data used to certify ERM<sup>®</sup>-ED103 is available on request from BAM.

### Supply of Reference Materials by: **BAM Bundesanstalt für Materialforschung und -prüfung**

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## Appendix 1 of Certificate of Analysis ERM<sup>®</sup>-ED103

### Recommended Method M1: Determination of Total Boron ( $B_{\text{total}}$ ) in Boron Nitride (BN) by a Titrimetric Method

#### Scope:

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

#### Summary of Method:

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

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

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

#### Apparatus:

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

- Potentiometric titration system.
- Burner, Bunsen type.
- Muffle Furnace, capable of maintaining a temperature of  $680\text{ °C} \pm 10\text{ °C}$  or  $730\text{ °C} \pm 10\text{ °C}$ .
- Platinum crucible with close-fitting cover.
- Analytical balance, capable of measuring to the nearest 0.01 mg.

#### Reagents:

All reagents must be of known analytical grade and it should be ascertained that the reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination.



The water used shall be distilled water or water which has been fully demineralized by ion exchange (deionized water). Unless otherwise specified solutions are aqueous solutions.

- Sodium hydroxide solution, NaOH, 0.1N, CO<sub>2</sub>-free, preferably in an airtight plastic container with an airtight connection to the titration system.
- Sodium carbonate (NaCO<sub>3</sub>), powdered or a 1:1 mixture of sodium/potassium carbonate (Na<sub>2</sub>CO<sub>3</sub> / K<sub>2</sub>CO<sub>3</sub>), powdered.
- Hydrochloric acid, 32% by volume, diluted 1:1 with water.
- Sodium hydroxide solution, NaOH, 20 % by weight.
- Sodium nitrate, NaNO<sub>3</sub>.
- Mannitol, solid or as solution 10 % by weight.
- Nitrogen, 99.998% v/v.

### **Sample preparation:**

For analysis grain sizes of less than 0.15 mm are required. For samples with grain sizes greater than 0.15 mm or sintered bodies crush the sample in a suitable crushing device to pass a 0.150 mm sieve.

If the moisture content of the sample is not known, dry the sample at 120 °C ± 5 °C for a minimum of 2 h. After cooling, the sample has to be stored in a desiccator.

If the homogeneity of the sample is not guaranteed, a representative quantity of sample has to be homogenized before analysis.

### **Procedure:**

About 150 mg of boron nitride is weighed to the nearest ± 0.01 mg and thoroughly mixed in a platinum crucible with 5 g Na<sub>2</sub>CO<sub>3</sub> or 6 g K<sub>2</sub>CO<sub>3</sub> / Na<sub>2</sub>CO<sub>3</sub> .

NOTE 3: Boron contamination that can come from reagents and glassware has to be considered.

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

#### Decomposition by melt-fusion using a Bunsen burner:

Place a lid on the platinum crucible and heat with the low flame of a Bunsen burner for 15 min. Continue heating while increasing the temperature (hot flame) until the mixture is completely molten. Maintain the temperature until the whole sample has been decomposed. Allow the melt to cool down to room temperature.

NOTE 4: When heating with the hot flame of the Bunsen burner a clear melt is readily obtained. However, this does not necessarily indicate complete sample decomposition. During further heating and increasing the temperature the formation of gas bubbles in the melt can often be observed. In this case, keep the high temperature until gas formation has ceased.

Add a spatula-tip of  $\text{NaNO}_3$  (20 to 30 mg) to the cold molten mass and heat up again in the flame of a Bunsen burner to decompose residues of boron nitride mostly located near the rim of the platinum crucible. Finally, swirl the platinum crucible outside the flame using crucible tongs until the liquid melt begins to solidify and covers the crucible wall. Return the platinum crucible to the flame, liquefy the melt again and heat with hot flame until crucible and lid are glowing. Simultaneously heat the upper part of the platinum crucible and the lid by means of a second burner. After this, the decomposition procedure is finished.

NOTE 5: A hand torch with a gas cartridge is very useful as a second burner.

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

Decomposition by melt-fusion using a combination of muffle furnace and Bunsen burner:

Place a lid on the platinum crucible and place it into the muffle furnace at ambient temperature. The platinum crucible should be placed into a ceramic crucible support. If using  $\text{Na}_2\text{CO}_3$ , heat up the muffle furnace to  $730\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$  in 45 min. If using a  $\text{K}_2\text{CO}_3$  /  $\text{Na}_2\text{CO}_3$  mixture, heat up the muffle furnace to  $680\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$  in 60 min. Keep the crucible at this temperature for at least 4 h. Allow cooling down and take out the crucible from the muffle furnace.

Place the platinum crucible on the hot flame of a Bunsen burner until the sintered mixture is completely molten. Maintain the temperature for about 5 to 10 min, until the whole sample has been decomposed, then allow the melt to cool down to room temperature.

Add a spatula-tip of  $\text{NaNO}_3$  (20 to 30 mg) to the cold molten mass and heat up again in the flame of a Bunsen burner to decompose residues of boron nitride mostly located near the rim of the platinum crucible. Finally, swirl the platinum crucible outside the flame using crucible tongs until the liquid melt begins to solidify and covers the crucible wall. Return the platinum crucible to the flame, liquefy the melt again and heat with hot flame until crucible and lid are glowing. Simultaneously heat the upper part of the platinum crucible and the lid by means of a second burner. After this, the decomposition procedure is finished.

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

NOTE 7: The temperature should not exceed  $40\text{ }^\circ\text{C}$  to avoid losses of boric acid.

The solution is transferred to a 250 ml volumetric flask and made up to volume with water. An aliquot of 50 ml is pipetted into a 400 ml tall-form beaker and neutralized with 20 % NaOH solution using pH-indicator paper or pH-meter. The aliquot is diluted to 200 ml with water and acidified with HCl 1:1 to pH 2.5 - 3.0, covered with a watch glass and boiled for 3 minutes to remove  $\text{CO}_2$ .

NOTE 8: Alternatively  $\text{CO}_2$  can also be removed by purging the solution with  $\text{N}_2$ .

Allow the solution to cool down to room temperature and purge the solution with N<sub>2</sub> for at least 10 min before starting the titration procedure. Continue purging with nitrogen during the whole titration procedure.

#### Titration of Boron:

Using the titration-system, the solution is titrated to the first inflection point with 0.1N NaOH. Then 35 ml of a 10% mannitol-solution or 4 g of solid mannitol is added and finally titrated to the second inflection point. The consumption of 0.1N NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron (see also given example below).

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

#### **Calculation:**

The content of total boron (B<sub>total</sub>) shall be calculated as mass%, to the nearest 0.1%, using the following equation:

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

V <sub>NaOH</sub>	=	consumption of 0.1N NaOH [ml]
F	=	titrimetric factor in mg B / ml 0.1N NaOH (theoretically 1.0811)
f	=	titration correction factor of NaOH (should be near to 1.000)
a	=	aliquot of sample solution [ml]
m <sub>s</sub>	=	sample mass [mg]

#### **Precision:**

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

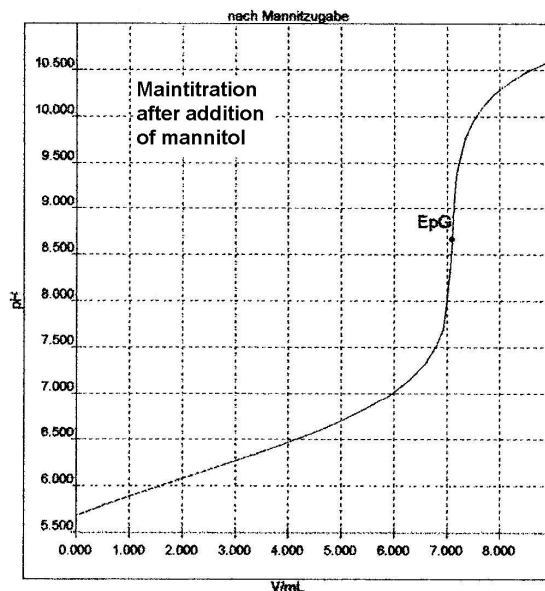
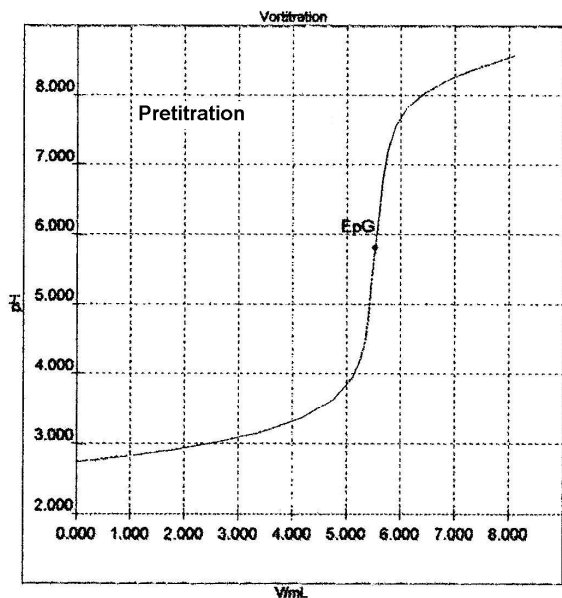
#### **Calibration:**

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

#### **Literature:**

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

Example of Boron titration via mannitoboric acid:



The titration curve on the left shows the pre-titration, starting at pH 2.75. The first inflection point is at pH 5.76. The titration is continued to pH 8.50. After that, mannitol is added.

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

The consumption of 0.1N NaOH between first inflection point and mannitol addition is 2.5741 ml and the consumption after mannitol addition and second inflection point is 7.0956 ml. This leads to a total consumption of 0.1N NaOH between first and second inflection point of 9.6697 ml.