



# Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Boron Carbide<sup>1</sup>

This standard is issued under the fixed designation C791; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover procedures for the chemical, mass spectrometric, and spectrochemical analysis of nuclear-grade boron carbide powder and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Total Carbon by Combustion in an Inductive Furnace and Infrared Measurement	7 – 16
Total Boron by Titrimetry and ICP OES	17 – 27
Isotopic Composition by Mass Spectrometry	28 – 32
Pyrohydrolysis	33 – 40
Chloride by Constant-Current Coulometry	41 – 49
Chloride and Fluoride by Ion-Selective Electrode	50 – 58
Water by Constant-Voltage Coulometry and Weight Loss on Drying	59 – 62
Metallic Impurities	63 and 64
Soluble Boron by Titrimetry and ICP OES	65 – 79
Free Carbon by a Coulometric Method	80 – 89

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

C750 Specification for Nuclear-Grade Boron Carbide Powder

C751 Specification for Nuclear-Grade Boron Carbide Pellets

D1193 Specification for Reagent Water

## 3. Significance and Use

3.1 Boron carbide is used as a control material in nuclear reactors. In order to be suitable for this purpose, the material must meet certain criteria for assay, isotopic composition, and impurity content. These methods are designed to show whether or not a given material meets the specifications for these items as described in Specifications C750 and C751.

3.1.1 An assay is performed to determine whether the material has the specified boron content.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.03 on Neutron Absorber Materials Specifications.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.2 Determination of the isotopic content of the boron is made to establish whether the content is in compliance with the purchaser's specifications.

3.1.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded.

## 4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</sup> Other grades may 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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

## 5. Safety Precautions

5.1 Many laboratories have established safety regulations governing the use of hazardous chemicals and equipment. The users of these methods should be familiar with such safety practices.

## 6. Sampling

6.1 Criteria for sampling this material are given in Specifications C750 and C751.

### TOTAL CARBON BY COMBUSTION IN AN INDUCTIVE FURNACE AND INFRARED MEASUREMENT

## 7. Scope

7.1 This method covers the determination of total carbon in nuclear-grade boron carbide in either powder or pellet form.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 8. Summary of Test Method

8.1 The sample and added combustion accelerators (mostly tungsten-and iron-granules) are heated in an inductive furnace under oxygen atmosphere. The high-frequency field of the furnace couples with electrically conductive components of sample and combustion accelerators. The sample is heated to temperatures not lower than 1400°C and the total carbon content of the sample is released as carbon dioxide and, partially, as carbon monoxide. The reaction gas is passed through a gas-treatment train to ensure that any carbon monoxide formed is converted to carbon dioxide and to remove dust and moisture. The reaction gas is then transferred to the infrared absorption cell of the analyzer. The molecular absorption of carbon dioxide is measured by using a narrow-band optical filter which is translucent for the wavelength of the characteristic infrared absorption of carbon dioxide. The mass fraction of carbon dioxide in the reaction gas is proportional to peak-area of the transient absorption signal. The mass fraction of carbon in the sample is calculated by using a calibration function established by suitable calibration standards measured under comparable conditions.

## 9. Interferences

9.1 At the specification limits usually established for nuclear-grade boron carbide, interferences are insignificant.

## 10. Apparatus

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

10.1.1 *Carbon analyzer*, with induction furnace and infrared absorption cell, suitable to correctly determine the mass fraction of carbon within the concentration range given by boron carbide.

NOTE 1—The correctness of the analysis result can be proved by using matrix analogous reference materials or by comparing with an independent alternative test method.

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

10.1.3 *Ceramic crucible*, for example, mullite or alumina.

10.1.4 *Crucible lid with hole*, for example, mullite or alumina.

## 11. Reagents

11.1 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.

11.1.1 *Tungsten granules*

NOTE 2—Depending on the particle size of the material the decomposition of the sample in the furnace may be improved by partially replacing tungsten granules by tin granules. Tungsten/tin-mixtures are commercially available.

11.1.2 *Iron granules*

11.1.3 *Calibration samples*, with defined carbon content, preferably certified reference materials with composition and carbon content similar to the analyzed material. Also suitable are primary substances preferably carbonates.

11.1.4 *Oxygen*, purity  $\geq 99.998\%$  v/v.

11.1.5 *Pneumatic gas*, for example, nitrogen, purity  $\geq 99.9\%$  v/v.

## 12. Sampling and Sample Preparation

12.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried at  $(110 \pm 5)^\circ\text{C}$  to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 3—Drying for 2 h is normally sufficient.

12.2 The sample material must have a particle size of  $\leq 150\ \mu\text{m}$  (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

## 13. Calibration

13.1 The calibration has to be performed daily according to the manufacturer's instructions. It has to be ensured that the mass of carbon in the calibration sample and test sample are within the same order of magnitude.

NOTE 4—This is achieved by choosing a suitable calibration substance and adapted weights.

13.2 The calibration has to be done according to Section 14.

## 14. Procedure

14.1 *Preparation of Analysis*—Ceramic crucibles (10.1.3) and crucible lids (10.1.4) have to be cleaned prior to use by firing in a muffle furnace at  $1200^\circ\text{C}$  for 1 h. After that, they have to be stored in a desiccator.

14.2 *Determination of Blank Value (Method Blank)*—The same procedure according to 14.4 has to be applied, however without addition of boron carbide. At least three blanks should be determined at least once in each 8-h shift in which total carbon analyses are made.

14.3 *Conditioning of Carbon Analyzer*—Prior to making the initial analysis, condition the carbon analyzer by performing at least two analysis runs. The same procedure according to section 14.4 has to be applied, however only adding a small amount of boron carbide (that is, a spatula-tip of boron carbide).

14.4 *Determination of Carbon Content*—A sub-sample of 20 to 30 mg of boron carbide powder prepared in accordance to Section 6 is weighed to the nearest 0.01mg into the ceramic crucibles (10.1.3) cleaned according to section 14.1.

NOTE 5—Using modern carbon analysis devices with an automated calculation of the mass fraction of carbon in the sub sample the sample mass has to be entered using the internal or external keyboard. Using carbon analysis devices which measure the absolute mass of carbon of the sample the sample mass has to be noted for later calculations.

The sample in the crucible is covered with approximately 0.9 g and 1.8 g of iron and tungsten granules (11.1.1 and 11.1.2), respectively. For mixing, the crucible has to be shaken

carefully. Afterwards, the crucible is closed with the lid (10.1.4), placed into the induction furnace and the combustion cycle is started. Using modern carbon analysis devices the carbon content is calculated and displayed on the internal or external screen or printed out.

NOTE 6—For the measurement of carbon as main component ( $B_4C$  approximately 20 %) carbon analysis devices which collect the formed carbon dioxide in a trap are recommended. By heating the trap the collected carbon dioxide is released and passed to the infrared absorption cell. This leads to a uniform and reproducible release of carbon dioxide and, thus, to an improved repeatability.

Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Section 14. If necessary, the sample has to be homogenized according to Section 12.

## 15. Calculation

15.1 The carbon content  $w(C_{total})$  of the sample has to be calculated under consideration of sample mass and blank values. The carbon content as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of carbon as follows:

$$w(C_{total}) = \frac{(m_c - m_{blank}) \times 100}{m_s} \quad (1)$$

where:

$m_c$  = absolute mass of carbon in the sample, mg,  
 $m_{blank}$  = absolute mass of carbon in the blank sample, mg,  
 and  
 $m_s$  = sample mass, mg

NOTE 7—Most state of the art analyzers automatically calculate the mass fraction of carbon for each measurement after input of blank values and sample masses.

## 16. Precision and Bias (1) <sup>4</sup>

NOTE 8—Please see Ref (2) for all precision and bias statements, except those denoted by Ref (3).

16.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102,<sup>5</sup> the following precision and bias data were obtained applying the described total carbon method. (See table below.)

<sup>4</sup> The boldface numbers in parentheses refer to the list of references appended to these methods.

<sup>5</sup> ERM-ED102 is a trade name of products supplied by BAM Federal Institute for Materials Research and Testing, Berlin, Germany. This information is given for the convenience of users of this ASTM Standard and does not constitute an endorsement by ASTM of the products named. Equivalent products may be used if they can be shown to lead to the same results.

Element	Mean, %	Total Carbon Method Repeatability $S_r$ , %	Reproducibility $S_R$ , %	ERM-ED102, certified value	Uncertainty, %	Bias of mean of total carbon method to certified value, % (relative)
C	21.06	0.07	0.25	21.01	0.28	+0.24

## TOTAL BORON BY TITRIMETRY AND ICP OES

### 17. Scope

17.1 This method covers the determination of total boron in samples of boron carbide powder and pellets by titrimetry and ICP OES. The recommended amount of boron for each titration is  $100 \pm 10$  mg.

### 18. Summary of Method

18.1 Powdered boron carbide is mixed with alkaline reagents and this mixture is fused to decompose the boron carbide. The melt is dissolved in diluted hydrochloric acid and heated or purged with nitrogen to remove carbon dioxide. The boron as boric acid is titrated with standardized sodium hydroxide solution, using the mannitoboric acid procedure (3), (4), and (5). Alternatively, the boron in the samples solution is measured using ICP OES.

NOTE 9—Sodium carbonate or a mixture of sodium carbonate and potassium carbonate (1:1) is normally used as alkaline reagent to decompose the boron carbide.

### 19. Interferences

19.1 *Titrimetry*—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 %,  $Ti < 1$  %. Interferences by dissolved  $CO_2$  shall be removed by heating the sample solution or by purging the sample solution with nitrogen.

19.2 *ICP OES*—Interference effects depend primarily upon the resolving power of the spectrometer and the selection of the analytical lines. In practice, line interferences (spectral interferences) and non spectral interferences are critical. Non-spectral interferences are caused primarily by different chemical composition of calibration solution and sample solution, resulting in an alteration of nebulization and excitation properties. Also, memory-effects can play a role. The best way to minimize non-spectral interferences is the use of calibration samples with the same composition of matrix, ideally certified reference materials.

### 20. Apparatus

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

20.1.1 *Balance*, analytical, capable of reading to the nearest 0.01 mg.

20.1.2 *Burner*, bunsen type.

20.1.3 *Hand torch*, with gas-cartridge.

20.1.4 *Filter Paper*, open-textured, very rapid filtering, for coarse and gelatinous precipitates.

20.1.5 *Muffle Furnace*, with temperature programmer and controllable to  $\pm 20^\circ C$  between  $700^\circ C$  and  $900^\circ C$ .

### 20.1.6 pH Meter.

20.1.7 *Platinum Crucible*, 30-mL, standard form with close-fitting cover.

20.1.8 *Titration system*, consisting of:

- (1) pH-electrode
- (2) dosage apparatus for liquids with a resolution of 10  $\mu$ l
- (3) stirrer
- (4) unit for recording the titration curve

20.1.9 *Sequential or Simultaneous Optical Emission Spectrometer with Inductively Coupled Plasma*, suited to measure in a wavelength region of 180 nm to 400 nm, preferably with freely definable background measuring points.

## 21. Reagents

21.1 Water complying Grade II of Specification **D1193** 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. Store reagents in plastic containers.

21.1.1 *Barium Carbonate*,  $\text{BaCO}_3$ .

21.1.2 *Hydrochloric Acid*, HCl, concentrated (sp gr 1.19),  $c(\text{HCl})$  approximately 10 mol/L.

21.1.3 *Hydrochloric Acid*, HCl, 1:1,  $c(\text{HCl})$  approximately 5 mol/L.

21.1.4 *Mannitol or Mannitol Solution*,  $\text{C}_6\text{H}_{14}\text{O}_6$ , with a concentration of 100 g/L.

21.1.5 *pH Buffer Solutions*, for example, with a pH of 4.0, 7.0, 9.0.

21.1.6 *Primary Substances for Determination of Molarity of NaOH Solution*, for example, potassiumhydrogenphthalate or boric acid (NBS SRM 951 or its replacement).

21.1.7 *Potassium Nitrate*,  $\text{KNO}_3$ .

21.1.8 *Sodium Carbonate*,  $\text{Na}_2\text{CO}_3$ , dried at 200°C for 1 h.

21.1.9 *Sodium/Potassium Carbonate Mixture*,  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  1:1 m/m, dried at 200°C for 1 h.

21.1.10 *Sodium Hydroxide Solution*, NaOH,  $c(\text{NaOH}) = 0.1$  mol/L. This solution must be carbonate-free.

21.1.11 *Sodium Hydroxide Solution*, NaOH, with a concentration of 200 g/L.

21.1.12 *Nitrogen*, purity  $\geq 99.99\%$  v/v.

## 22. Precautions

22.1 Consideration should be given to boron contamination that can come from reagents, glassware, and perhaps from other sources. If care is used in procuring reagents and if low-boron glassware is used, boron contamination should be negligible. The periodic determination of a blank to check for boron contamination is advisable, particularly whenever a new bottle of any reagent is used.

## 23. Sampling and Sample Preparation

23.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried at  $(110 \pm 5)^\circ\text{C}$  to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 10—Drying for 2 h is normally sufficient.

The sample material must have a particle size of  $\leq 50\ \mu\text{m}$  (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

## 24. Procedure

24.1 *Preparation of Analysis*—A sub-sample of 100 mg of boron carbide powder prepared in accordance to Section **23** is weighed to the nearest 0.01 mg into the platinum crucible and mixed with approximately 3 g  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  using a microspatula. The mixture is covered with approximately 2 g  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  and the platinum lid is placed on the crucible. Continue with fusion procedures **24.2** or **24.3**.

NOTE 11—Instead of sodium/potassium carbonate mixture, sodium carbonate can also be used for boron carbide decomposition.

24.2 Muffle furnace/Bunsen burner fusion procedure:

24.2.1 *Using  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$* —Put the crucible in the muffle furnace. Heat the furnace to 750°C in 2 h and hold this temperature for 4 h. Remove the crucible and let it cool to room temperature.

24.2.2 *Using  $\text{Na}_2\text{CO}_3$* —Put the crucible in the muffle furnace. Heat the furnace to 600°C in 1 h and then to 750°C in 1 h and then to 900°C in 1.5 h. Hold this temperature for 0.5 h. Remove the crucible and let it cool to room temperature.

24.2.3 Add 20 mg to 30 mg of  $\text{KNO}_3$  and heat the closed crucible with a full Bunsen flame until a clear melt is obtained (approximately 2 min). Simultaneously heat the upper part of crucible and lid with the full flame of a hand torch. Allow the melt to cool down to room temperature. If a clear melt is not obtained, repeat procedure **24.2.3**. Continue with **24.4**.

24.3 *Bunsen Burner Fusion Procedure*—If this fusion technique is used,  $\text{KNO}_3$  is not needed. Place a lid on the crucible and heat with a low flame of a Bunsen burner for 15 min. Continue heating for another 75 min while gradually increasing the temperature of the flame until the mixture is completely molten. Continue heating with a full Bunsen flame until decomposition of the boron carbide is completed. Most samples require heating with a full Bunsen flame for about 20 min for complete decomposition. Simultaneously heat the upper part of crucible and lid with the full flame of a hand torch. Allow the melt to cool to room temperature. Continue with **24.4**.

NOTE 12—Procedure **24.3** works with both  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ .

If fusion procedures **24.2** and **24.3** are applied to very fine grained (sub-micron) boron carbide powders lower results for total boron may be obtained. If this is the case, instead of procedures **24.2** and **24.3** the following modified Bunsen burner procedure has to be applied:

Use  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  for sample decomposition. Heat the mixture in the platinum crucible carefully with a low flame just above the melting point of  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  and hold this temperature until, after a few minutes, a clear melt is obtained. Continue with section **24.4**.



**24.4 Dissolution Procedure**—Place crucible and lid in a beaker. Add 50 ml of hydrochloric acid (21.1.3). Swirl the beaker carefully to ensure that the whole surface of crucible and lid is wetted. To accelerate the leaching procedure the solution may be gently heated. To avoid losses of boric acid, the beaker must be covered with a watch-glass. After the melt is completely dissolved, rinse the watch-glass with water into the beaker. Remove crucible and lid from the beaker; rinse both carefully with water, adding the rinses to the beaker. Transfer the solution in the beaker to a 250 ml volumetric flask and rinse the beaker thoroughly with water into the volumetric flask. After this, the volumetric flask is filled up to volume with water. This solution is either used for titrimetric (Section 25) or ICP OES (Section 26) determination of boron or, if required, for barium carbonate precipitation (24.5).

**24.5 Barium Carbonate Separation**—Pipet a 50 ml aliquot of the sample solution obtained by procedure 24.4 into a beaker. To ensure reproducible starting conditions and to reduce the consumption of barium carbonate the solution in the beaker is neutralized with NaOH solution (21.1.11) using a pH meter. Add 1.5 ml of hydrochloric acid (21.1.2). Stir the solution and add barium carbonate until an excess of barium carbonate is visible. Cover the beaker with a watch-glass and bring to a boil for 5 min. Let the precipitate digest for 30 min at 50°C to 60°C (for example, using a sand-bath). Allow the suspension to cool down to room temperature. Rinse the watch-glass with water into the beaker. Separate the precipitate by filtration through an open-textured filter paper and collect the filtrate in a beaker. Rinse the filter paper and precipitate thoroughly four to six times with water and collect the rinses with the filtrate. Set the pH to 2.5 to 3 with hydrochloric acid (21.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO<sub>2</sub>. Continue with section 25.2.

## 25. Titrimetric Determination of Boron

### 25.1 Preparation of Analysis:

**25.1.1** Pipet a 50 ml aliquot of the sample solution obtained by procedure 24.4 into a beaker. Fill up with water to a volume of approximately 200 ml. Set the pH to 2.5 to 3 with hydrochloric acid (21.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO<sub>2</sub>.

### 25.2 Titration:

**25.2.1** Using the titration-system, the solution is titrated to the first inflection point with 0.1 mol/L NaOH (21.1.10). Then 35 ml of a mannitol-solution (21.1.4) or 4 g of solid mannitol is added and finally titrated with 0.1 mol/L NaOH to the second inflection point. The consumption of 0.1 mol/L NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron (titration example see 25.3). To avoid interferences by CO<sub>2</sub> the sample solution must be purged with nitrogen during titration.

**NOTE 13**—If the inflection point on the titration curve is distorted or if there are multiple inflections that are severe enough to prevent a clear determination of the end point, carbonate or hydrolyzable metals are probably present. The best procedure at this point is to start the analysis over with a new sample. The titrated solution can be salvaged, however, by adjusting the pH to 3.0 with dilute acid and then following the barium carbonate separation procedure (24.5). Once mannitol has been added at 25.2, the titrated solution can not be salvaged and a new sample must be started.

**25.2.2** Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Sections 24 and 25. If necessary, the sample has to be homogenized according to Section 23. The method blank has to be determined applying the same procedure as described in Sections 24 and 25 (without and with barium carbonate precipitation), however, without addition of boron carbide. If a measurable method blank is detected the single values have to be corrected by the method blank.

**25.3 Example of Boron Titration via Mannitoboric Acid:** (See Fig. 1.)

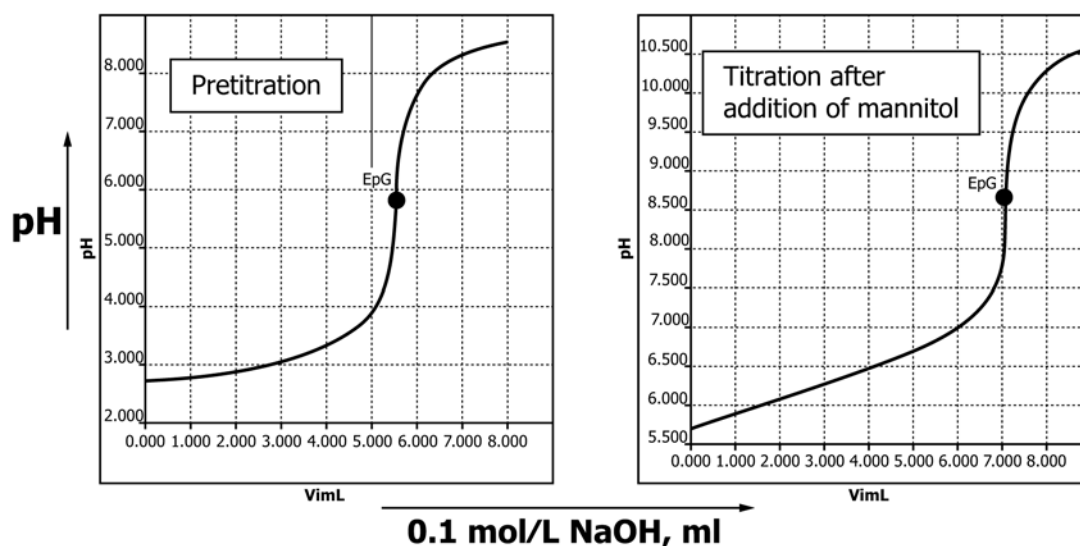


FIG. 1 Example of Boron Titration via Mannitoboric Acid

25.3.1 The titration curve on the left shows the pretitration, 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 0.1 mol/L NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron.

#### 25.4 Calibration:

25.4.1 Before a measurement series the pH calibration of the titration system has to be performed according to the manufacturer's instructions using pH buffer solutions (21.1.5). For the NaOH solution used for titration the correct molarity has to be determined. For this purpose, preferably solutions of primary substances, for example, potassiumhydrogenphthalate or boric acid (21.1.6), must be titrated with the NaOH solution. The method for total boron determination can be checked through analysis of certified boron carbide reference materials. The bias to the certified boron content can be used to derive a method correction factor which improves the accuracy of total boron determination.

NOTE 14—See Annex A1 for commercial reference materials.

#### 25.5 Calculation:

25.5.1 The total boron content  $w(B_{total})$  of the sample has to be calculated under consideration of sample mass and blank values. The boron content as mean of the corrected single values of the multiple determinations shall be expressed in

mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of boron as follows:

$$w(B_{total}) = \frac{V_{NaOH} \times F \times V_S \times q \times 100}{V_A \times m_E} \quad (2)$$

$$F = \frac{M_{meas}}{M_{nom}} \quad (3)$$

where:

- $V_{NaOH}$  = consumption of 0.1 mol/L NaOH, ml,
- $V_S$  = volume of sample solution, ml,
- $V_A$  = volume of titrated aliquot, ml,
- $F$  = titration correction factor for NaOH,
- $M_{meas}$  = measured molarity of NaOH used for titration, mol/L,
- $M_{nom}$  = nominal molarity of NaOH used for titration, mol/L,
- $q$  = titrimetric factor (see Note 15), and
- $m_E$  = sample mass, mg

NOTE 15— $q = 1.0811$  mg boron per ml 0.1 mol/L NaOH solution, for a natural  $^{10}\text{B}/^{11}\text{B}$  isotopic ratio.

25.6 *Precision and Bias*—Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data were obtained applying the described titrimetric total boron method. (See table below.)

Element	Titrimetric total Boron Method			ERM-ED102, certified value		Bias of mean of titrimetric total boron method to certified value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
B	78.42	0.13	0.34	78.47	0.31	-0.06

## 26. ICP OES

26.1 *General Comments*—The sample solution obtained in 24.4 is analyzed for boron using ICP OES. The analysis of sample solutions by ICP OES is well known and comprehensively described in numerous standard test methods. Therefore, a detailed description of the procedure for the analysis of the sample solution by ICP OES is not part of this standard test method. Only information specific to the determination of total boron is given. A precise determination of main components with ICP OES is challenging but possible. However, in routine analysis a lower precision compared to the titrimetric method can be expected.

26.2 *Preparation of Sample Solution*—Assuming a total boron content of 78 % m/m the sample solution obtained in 24.4 has a boron concentration of approximately 310 mg/L. In addition, it has a quite high salt concentration of 20 g/L  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ , respectively. It is therefore recommended to dilute the sample solution, preferably by a factor of ten. Pipet 10 ml of the solution obtained in 24.4 in a 100 ml volumetric flask. Fill up to volume with water. This solution is then analyzed by ICP OES.

26.3 *Recommended Wavelength*—Recommended boron emission lines are: 182.591 nm, 208.959 nm, 249.677 nm, 249.773 nm.

26.4 *Matrix Solution*—For preparation of calibration and control solutions, the following matrix solution must be used: Weigh 5 g of  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  (depending on the matrix of solution 24.4) into a 250 ml volumetric flask. Add approximately 100 ml of water and 50 ml of hydrochloric acid (21.1.3) and wait until the carbonate has dissolved. Degas the solution in an ultrasonic bath and fill up to volume with water.

26.5 *Calibration*—Calibration of the ICP OES has to be performed before a measurement series according to the manufacturer's instructions. To achieve a high precision of the measurement a 2-point calibration without zero-point has to be applied. Normally, the boron concentrations of the calibration solutions are selected in a manner that one is above, but nearby, and the second one is below the expected boron concentration of the sample solution. To control the calibration a control solution with a boron concentration between both standard solutions is required. The control solution is also used to detect measurement drift during a measurement series.

NOTE 16—Calibration with more than two points is also possible. Known from experience this, however, leads only to a minor improvement of accuracy. For multi-point calibrations the zero-point should also not be included in the calibration function.

Calibration and control solutions shall be prepared using boron stock standard solutions (for example, 1000 mg/L), boric acid or by decomposition of boron carbide certified reference materials. If boron solution or boric acid is used matrix-matching with the solution described in 26.4 is required.

NOTE 17—Assuming a total boron content around 78 % m/m, preparation of the sample solution according to 26.2 and the use of a 1000 mg/L boron standard solution it is recommended to prepare the following calibration and control solutions:

Calibration solution – low: pipet 10 ml of solution 26.4 and 1.0 ml of boron standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 10 mg/L.

Calibration solution – high: pipet 10 ml of solution 26.4 and 3.5 ml of stock standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 35 mg/L.

Control solution: pipet 10 ml of solution 26.4 and 3 ml of stock standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 30 mg/L.

26.6 Procedure—The sample solution obtained in 26.2 is used for measurement. To detect a measurement drift the control solution has to be measured within and at the end of the measurement series. To improve the precision each sample solution has to be measured repeatedly.

NOTE 18—For example: each sample solution of the measurement series is measured with three replicates and the measurement series is repeated three times.

NOTE 19—The precision can be improved if the measurement is carried out using an internal standard.

Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given

degree, depending on the repeatability of the method, then the analysis has to be repeated according to Sections 24 and 26. If necessary, the sample has to be homogenized according to Section 23. The method blank has to be determined applying the same procedures as described in Sections 24 and 26, however, without addition of boron carbide. If a measurable method blank is detected, the single values have to be corrected by the method blank.

26.7 Calculation—The total boron content  $w(B_{total})$  of the sample has to be calculated under consideration of sample mass, dilution factor and blank values. The boron content as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of boron as follows:

$$w(B_{total}) = \frac{C_M \times f \times V_S}{10 \times m_E} \quad (4)$$

where:

$C_M$  = measured boron concentration in sample solution (26.2), corrected by blank value, mg/L,  
 $V_S$  = volume of solution after sample decomposition (24.4), ml,  
 $f$  = dilution factor (see 26.2), and  
 $m_E$  = sample mass, mg

## 27. Precision and Bias

27.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data were obtained applying the described ICP OES total boron Method. (See table below.)

Element	ICP OES total Boron Method			ERM-ED102, certified value		Bias of mean of ICP OES total boron method to certified value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
B	78.70	0.61	0.63	78.47	0.31	+0.29

## ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

### 28. Scope

28.1 This method covers the determination of the isotopic composition of boron in nuclear-grade boron carbide, in powder and pellet form, containing natural to highly enriched boron.

### 29. Summary of Method

29.1 Boron isotopic ratios are measured in boron carbide by thermal ionization mass spectrometry (TIMS) without prior chemical separation of boron. Boron is converted to sodium borate by fusion of the boron carbide with sodium hydroxide or sodium carbonate directly on the tantalum filament of the mass spectrometer. The loaded filament is transferred to the mass spectrometer where boron isotopic ratios are measured using the  $\text{Na}_2\text{BO}_2^+$  ion. When mixing the boron carbide and sodium hydroxide or sodium carbonate, a Na to B ratio of 1:1 is maintained, which gives a stable ion emission within a few

minutes after operational vacuum is attained. There is no apparent bias caused by selective volatilization of  $^{10}\text{B}$  (6), (7), (8), (9), (10), (11).

As an alternative method, the boron isotopic ratios are measured in boron carbide by ICP-MS.

### 30. Interferences

30.1 Impurity elements, at the specification limits usually established for nuclear-grade boron carbide, do not interfere. Strontium is a potential interference and it is an impurity element in the tantalum filament material. At the temperature used to ionize sodium borate, however, the strontium impurity in the filament does not volatilize to cause a high bias at mass 88. This potential interference does not occur in ICP-MS.

### 31. Isotopic Composition by TIMS

#### 31.1 Apparatus:

31.1.1 Mass Spectrometer—Commercial instruments are available that meet or exceed the following requirements:

31.1.1.1 *Source*, thermal ionization using single filaments. A vacuum lock is recommended to maintain source vacuum, which increases sample throughput.

31.1.1.2 *Analyzer*, with a vacuum system capable of producing a resolving power of at least 400 and an abundance sensitivity at mass 100 of at least 20 000. Resolving power is defined as  $M/\Delta M$ , where  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5 % of its height. Abundance sensitivity is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ .

31.1.1.3 *Detector; Faraday Cup, Electron Multiplier, or Scintillatory Photomultiplier*—Data acquisition can be accomplished by a potentiometric recorder or a pulse counting system.

31.1.2 *Mass Spectrometer Accessories*—The following items are required:

31.1.2.1 *Filaments*, tantalum ribbon, nominally 0.001 in. thick, 0.030 in. wide, with optional V-groove. Filaments should be prepared and stored in a manner to minimize contamination, and they should be cleaned before use.

31.1.2.2 *Forming Jig*, used to form filaments into the configuration required by the mass spectrometer used and to hold the filaments in place for welding.

31.1.2.3 *Spot Welder*, used to weld the filament ribbons to the support posts. Welds should be made carefully to ensure good electrical contact, which is necessary for beam stability.

31.1.2.4 *Sample-Loading Unit*, used to heat filaments to at least 800°C. A system permitting an electrical current to pass through the filament is required.

31.1.3 *Mixer Mill*.<sup>6</sup>

31.1.4 *Plastic Pipet*, 5- $\mu$ L, with a changeable plastic barrel.<sup>7</sup> Use a pipet only once and then discard it.

31.1.5 *Plastic Vial and Ball*—12.7-mm (0.5-in.) outside diameter by 25.4-mm (1-in.) long vial and 9.52-mm (0.375-in.) diameter ball.

31.2 *Reagents*:

31.2.1 *Acetone*.

31.2.2 *Distilled Water*.

31.2.3 *Isopropyl Alcohol*.

31.2.4 *Sodium Carbonate* ( $\text{Na}_2\text{CO}_3$ ) *Solution*, 0.14 *M*.

31.2.5 *Sodium Hydroxide* ( $\text{NaOH}$ )—Pulverize in stainless steel containers with stainless steel balls in a mixer mill and store in a desiccator.

31.2.6 *Toluene*.

31.3 *Precautions*—Consideration should be given to boron contamination from reagents and other sources. Sources of natural boron contamination can be checked by using NBS<sup>10</sup> B-enriched boric acid (SRM 952) as an internal standard (8).

31.4 *Calibration*—Periodic attention should be given to bias and linearity and to counting dead time when an ion-counting technique is used. These factors should be determined when the mass spectrometer is first used and they should be checked whenever a calibration result is obtained that significantly

deviates from the accepted value. These factors should also be checked at intervals of not greater than three months.

31.5 *Procedure*:

31.5.1 *Filament Cleaning*—Filament assemblies are made in accordance with a procedure that is appropriate for the mass spectrometer used.

31.5.1.1 Clean the filament assembly by sequentially dipping it in toluene, isopropyl alcohol, and distilled water.

31.5.1.2 Rinse the assembly twice with acetone.

31.5.1.3 Dry the assembly under a heat lamp.

31.5.2 *Filament Loading*—Steps 31.5.2.1 – 31.5.2.5 are instructions for fusing the sample with  $\text{NaOH}$  and 31.5.2.6 – 31.5.2.9 are instructions for an alternative fusion with  $\text{Na}_2\text{CO}_3$ .

31.5.2.1 Weigh  $25 \pm 2$  mg of sample in powder form and transfer it to a plastic vial.

NOTE 20—For pellet samples, crush to a powder using the procedure in Section 12. Sample materials prepared for other analyses can be used if care is taken to prevent cross contamination between samples, particularly between samples of differing boron isotopic compositions.

NOTE 21—To obtain a representative sample if the original sample is in powdered form, thoroughly blend the bulk sample before taking the 25-mg aliquot.

NOTE 22—A quantitative transfer is not required because isotopic ratios only are being determined.

31.5.2.2 Add  $72 \pm 2$  mg of pulverized  $\text{NaOH}$  from the desiccator to the vial containing the sample.

31.5.2.3 Add a plastic ball and immediately close the vial.

NOTE 23—Avoid atmospheric moisture pickup; moisture interferes with good mixing.

31.5.2.4 Mix for 1 min on the mixer mill.

31.5.2.5 Transfer about 0.1 mg of the mixture to a filament. Proceed to 31.5.2.10 for the fusion.

31.5.2.6 Weigh  $5 \pm 0.2$  mg of sample in powder form and transfer it to a plastic vial (Note 20).

31.5.2.7 Add 1.25 mL of 0.14 *M*  $\text{Na}_2\text{CO}_3$  solution to the vial containing the sample.

31.5.2.8 Slurry the mixture with the tip of a plastic pipet until a uniform suspension is obtained.

31.5.2.9 Transfer about 5  $\mu$ L of the slurry to a filament. Proceed to 31.5.2.10 for the fusion.

31.5.2.10 Heat the filament gradually just to the point where the filament glows brightly.

NOTE 24—The bright glow is caused by the exothermic reaction of tantalum with  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$ . The fusion produces sodium borate and the melt tightly adheres to the filament.

31.5.3 *Mass Spectrometric Measurement*:

31.5.3.1 Insert the filament assembly into the mass spectrometer.

31.5.3.2 Evacuate the system to about 66  $\mu$ Pa ( $5 \times 10^{-7}$  torr).

31.5.3.3 Heat the sample by passing an electrical current through the filament until a stable beam of  $\text{Na}_2\text{BO}_2^+$  ions is obtained.

31.5.3.4 Scan the spectrum repeatedly in both directions over the mass range desired until at least nine spectra have been obtained.

<sup>6</sup> A Spex Industries mixer mill, Model 5100, has been used for this method.

<sup>7</sup> A Kimble automatic pipet, No. 56300, with disposable polypropylene tips has been used for this method.



31.6 *Calculation*—Determine the boron isotopic composition from the mass spectra recorded. Calculate the 89 to 88 peak height ratio from the average peak heights. Subtract 0.00078 to correct for  $^{17}\text{O}$ . Then correct the ratio for mass bias.

31.7 *Precision and Accuracy*:

31.7.1 *Precision*—For the B-10 isotope, the relative standard deviation is 0.22 atom % at a concentration in the boron of 20 atom percent.

31.7.2 *Bias*—The average percent recovery obtained from the analysis of boron carbide control standards over a two-year period was 100.1 %. Those standards were prepared and certified by LASL (2).

## 32. Isotopic Composition by ICP MS

32.1 *General Comments*—The determination of isotopic ratios by ICP-MS is nowadays a well known state-of-the-art technique and widely applied to various matrices. Therefore, a detailed description of the procedure for the determination of boron isotopic ratio by ICP-MS is not part of this standard test method. Only information specific to the determination of boron isotopic ratio is given.

32.2 *Summary of Method*—In a first step the boron carbide powder sample is decomposed by pyrohydrolysis to boric acid.

A sub-sample of the boric acid obtained according to Section 39 is dissolved in water, acidified and measured by ICP-MS.

32.3 The following has to be considered:

(a) the solution measured by ICP-MS should have a boron and nitric acid concentration of approximately 0.5 mg/L and 1 %, respectively.

(b) check thoroughly for boron contamination originating from glassware, nebulizer and tubing.

(c) a certified boric acid reference material (for example, NBS 951) is used as standard to determine the mass-bias per amu. This apparatus-specific factor is used for correction of the isotopic ratio measurements of the sample solutions. To improve the accuracy standard and sample solutions shall be measured alternately. For each standard the mass-bias/amu has to be determined and used for correction of the following sample solution.

32.4 *Precision and Bias*—Within the frame of the certification of the boron carbide powder European reference material ERM-ED102 the following precision and bias data were obtained applying the described ICP MS method for isotopic composition. (See table below.)

Element	Isotopic composition by ICP MS			ERM-ED102, certified value		Bias of mean of isotopic composition by ICP MS to certified value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
$^{10}\text{B}$	19.910	0.027	0.031	19.907	0.014	+ 0.016

## PYROHYDROLYSIS

### 33. Scope

33.1 This method covers the separation of up to 100  $\mu\text{g}$  of halides per gram of boron carbide. The separated halides are measured using other methods found in this standard. It also covers the sample preparation for the determination of isotopic composition by ICP MS.

### 34. Summary of Method

34.1 A stream of moist gas is passed over a mixture of powdered sample and  $\text{U}_3\text{O}_8$  accelerator heated at 1000 to

1100°C. Alternatively, a stream of moist oxygen is passed over the powdered sample at 1100°C, which requires no accelerators. The pyrohydrolytic reaction releases chloride and fluoride as hydrochloric and hydrofluoric acids, which volatilize and collect in the condensate (12), (13), and (14).

### 35. Interferences

35.1 Interferences are not expected. The conditions given in this method for pyrohydrolysis must be controlled to ensure complete recovery of the halides.

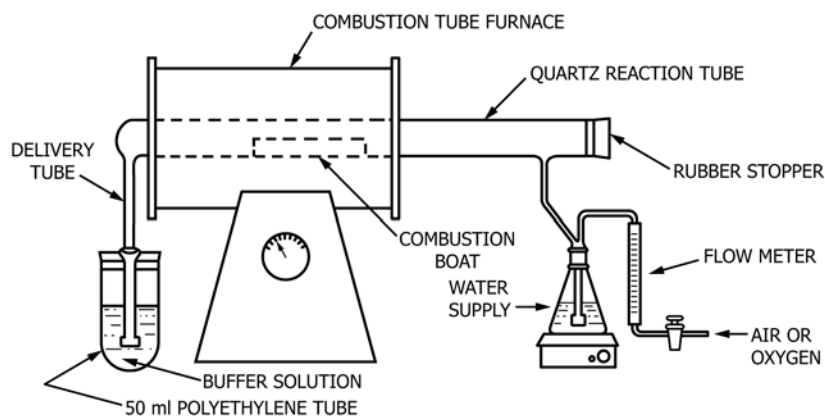


FIG. 2 Pyrohydrolysis Apparatus

## 36. Apparatus

(See Fig. 2.)

36.1 *Flowmeter*, capable of measuring a gas flow of up to 250 mL/min.

36.2 *Water Heating Flask*, in which water is boiled by either a hot plate or immersion heater.

36.3 *Tube Furnace*, capable of maintaining a temperature of 1100°C, having 178 to 305-mm (7 to 12-in.) long by about 32-mm (1.25-in.) diameter heating chamber having the heating element extending to near the furnace ends.

36.4 *Pyrohydrolytic Tube*, fused silica or nickel, 30-mm diameter by about 350 mm long with a 29/42 standard taper (inner) joint on one end. To the opposite end is sealed a hang-down tube with a condenser. The condenser is attached to the hang-down tube 10 mm from the top. The hang-down tube is 6 mm outside diameter and the condenser is 152 mm (6 in.) long, 25-mm outside diameter. The distance that the pyrohydrolytic tube extends outside of the furnace to the hang-down tube is 10 mm. This distance is critical in preventing the formation of a boric acid plug in the top end of the hang-down tube.

36.5 *Sample Boat*, fused silica or nickel with a capacity to hold at least 6 g of  $U_3O_8$  and 2 g of sample.

36.6 *Collection Vessel*, a graduated cylinder or graduated centrifuge tube with a volume of about 25 mL.

36.7 *Mixer Mill*.

## 37. Reagents

37.1 *Accelerator*,  $U_3O_8$  or sodium tungstate with tungsten trioxide:

37.1.1  $U_3O_8$ , powdered, <1  $\mu\text{g}$  Cl and F. Prepare by air calcining  $UO_2$  at 400°C or by oxidizing uranium metal in the following manner: Slowly air-oxidize the metal starting at 300°C and raising the temperature gradually to 800°C over several days. Then ignite the oxide for 20 min at 1000°C in moist argon (conditions for pyrohydrolysis). These two preparations provide  $U_3O_8$  with satisfactory accelerator characteristics, which are thought to be dependent upon the surface area of the oxide.

37.1.2 *Sodium Tungstate ( $Na_2WO_4$ ) with Tungsten Trioxide ( $WO_3$ )* may be used. Dehydrate 165 g of  $Na_2WO_4$  in a large platinum dish. Transfer the dried material to a mortar, add 116 g of  $WO_3$ , and grind the mixture to ensure good mixing. Transfer the mixture into a platinum dish and heat with a burner for 2 h. Cool the melt, transfer the flux to a mortar and grind to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each portion of sample to be pyrohydrolyzed.

37.2 *Argon*, purity  $\geq 99.99\%$  v/v.

37.3 *Boric Acid*, powder and a saturated solution in distilled water.

37.4 *Distilled Water*, chloride- and fluoride-free, <0.1  $\mu\text{g/g}$ .

37.5 *Oxygen*, purity  $\geq 99.99\%$  v/v.

## 38. Precautions

38.1 Care must be taken to avoid chloride and fluoride contamination of reagents and laboratory equipment.

## 39. Procedure

39.1 Prepare a sample and reagent blank as follows:

39.1.1 Crush pellet samples to a powder using the procedure in Section 12. If the pyrohydrolysis is done with oxygen, continue with 39.1.6.

39.1.2 Line two sample boats with 3 g of  $U_3O_8$ .

39.1.3 Weigh 1 to 2 g of powdered sample to  $\pm 0.01$  g and mix thoroughly with 3 g of  $U_3O_8$  accelerator in a mixer mill.

39.1.4 Quantitatively transfer this mixture to one of the sample boats and spread it uniformly along the length of the boat.

39.1.5 Add 3 g of  $U_3O_8$  accelerator to the second sample boat and spread it uniformly along the length of the boat. Continue with 39.2.

NOTE 25—This second boat, which is used for the measurement of the reagent blank, is taken through 39.2 – 39.14.

39.1.6 Take two sample boats. Weigh 1 to 2 g of powdered sample to the nearest 0.01 g into one sample boat (Note 25).

39.2 Prepare the pyrohydrolysis apparatus for use as follows:

39.2.1 Turn on the tube furnace and allow it to reach 1000 to 1100°C.

NOTE 26—The furnace can be turned on early to avoid delaying analyses.

NOTE 27—Whatever temperature is used within the above range, the same temperature within  $\pm 10^\circ\text{C}$  must be used for both samples and standards.

39.2.2 Turn on the cooling water to the condenser on the pyrohydrolytic tube.

39.2.3 Add distilled water to the water heater and turn on the heater to boil the water.

NOTE 28—Start this step early to avoid delaying analyses.

39.2.4 If an accelerator is used, turn on the argon and adjust its flow to about 190 mL/min. Otherwise, turn on the oxygen and adjust its flow to about 190 mL/min.

39.2.5 Adjust the gas flow and water temperature such that  $15 \pm 2$  mL of condensate is produced in about 20 min of operation.

39.3 Open the pyrohydrolytic tube. For determination of chloride by constant-current coulometry, continue with 39.4 and end with 39.9. For determination of chloride and fluoride by ion-selective electrode, continue with 39.10 and end with 39.14.

39.4 Place a collection vessel containing 2 mL of the saturated boric acid solution and 1.5 g of boric acid into position.

NOTE 29—The tip of the hang-down tube should be at least 10 mm below the surface of the boric acid solution.

39.5 Insert a sample boat into the pyrohydrolytic tube and immediately close the tube.

NOTE 30—The sample boat shall be placed in the center of the hot zone of the furnace.

39.6 Collect  $15 \pm 2$  mL of condensate in about 20 min.

39.7 Remove the collection vessel.

39.8 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

39.9 Dilute the condensate to 20.0 mL with distilled water and mix thoroughly.

NOTE 31—This solution is used for the determination of chloride by constant-current coulometry.

39.10 Place a collection vessel (50 ml volumetric flask) containing 20 mL of water into position.

NOTE 32—The tip of the hang-down tube should be at least 10 mm below the surface of the water level.

39.11 Insert a sample boat into the pyrohydrolytic tube and immediately close the tube.

NOTE 33—The sample boat shall be placed in the center of the hot zone of the furnace.

39.12 Collect approximately 20 mL of condensate in about 20 min.

39.13 Remove the collection vessel.

NOTE 34—This solution is used for the determination of chloride and fluoride by ion-selective electrode.

39.14 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

#### 40. Pyrohydrolysis as Sample Preparation Procedure for Isotopic Composition by ICP MS

40.1 Use oxygen as carrier gas.

40.2 Crush pellet samples to a powder using the procedure in Section 12.

40.3 Weigh approximately 2 g of powdered sample into a sample boat.

40.4 Prepare the pyrohydrolysis apparatus according to 39.2.1 – 39.2.3.

40.5 Turn on the oxygen and adjust the heating of water heater and flow-rate of oxygen in a way that approximately 200 ml of condensate is collected in approximately 1.5 h.

40.6 Open the pyrolytic tube.

40.7 Place a 250 ml beaker as collecting vessel into position. The tip of the hang-down tube should be near the bottom of the beaker.

40.8 Insert the sample boat into the pyrohydrolytic tube and immediately close the tube.

40.9 Collect approximately 200 ml of condensate in approximately 1.5 h.

40.10 Remove the beaker and switch off the pyrohydrolysis apparatus.

40.11 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

40.12 Place the beaker in a drying cabinet and evaporate at  $110^{\circ}\text{C}$  to dryness.

40.13 Scratch out the crystalline residue of boric acid with a plastic spatula and use it for determination of isotopic composition by ICP MS.

### CHLORIDE BY CONSTANT-CURRENT COULOMETRY

#### 41. Scope

41.1 This method covers the measurement of chloride after separation from boron carbide by pyrohydrolysis. The lower limit of the method is about 2  $\mu\text{g}$  of chloride per titration.

#### 42. Summary of Method

42.1 The condensate is analyzed for chloride with an automatic chloride titrator that coulometrically generates silver ion to form insoluble silver chloride. The end point is sensed amperometrically and the generating current is stopped automatically at a preset increment of indicator current. Since the rate of generating silver ion is constant, the titration time is proportional to the amount of chloride precipitated (12), (15).

#### 43. Interferences

43.1 At the specification limits for impurities usually established for nuclear-grade boron carbide, interference effects are insignificant. Bromide and iodide, if present, would be measured as chloride. Care should be taken at all times to prevent contamination from extraneous chloride.

#### 44. Apparatus

44.1 *Automatic Chloride Titrator*.<sup>8</sup>

#### 45. Reagents

45.1 *Boric Acid*, saturated solution.

45.2 *Gelatin Solution* (see the operations manual for the chloride titrator).

45.3 *Nitric-Acetic Acid Solution*, 1 M  $\text{HNO}_3$ , 4 M acetic acid containing 20 to 30  $\mu\text{g}$  Cl/mL of solution.

45.4 *Silver Cleaning Paste* (see the operations manual for the chloride titrator).

45.5 *Chloride Standard*, about 1 mg Cl/mL. Prepare a solution with an accurately known concentration using sodium chloride, previously dried at  $110^{\circ}\text{C}$ , and distilled water.

#### 46. Calibration of Titrator

46.1 Clean the silver electrodes with silver cleaning paste if their surfaces are not bright.

46.2 Rinse the electrodes with distilled water and blot them with absorbent tissue.

46.3 Pipet 5.0 mL of the saturated boric acid solution into a clean, dry, 10-mL titration cell.

<sup>8</sup> An Aminco-Cotlove, AMINCO, chloride titrator has been found satisfactory for this method.

46.4 Pipet 1.00 mL of the nitric-acetic acid solution containing chloride into the cell.

NOTE 35—Since this chloride constitutes a significant blank, the amount of acid solution added shall be accurately pipetted. Chloride is added to the nitric-acetic acid solution to improve the sensitivity of the titration by adding sufficient chloride to exceed the solubility product of silver chloride. Otherwise, a significant error occurs when titrating a few micrograms of chloride.

46.5 Pipet 50.0 µL of the 1 mg Cl/mL chloride standard into the cell.

46.6 Add 2 drops of the gelatin solution.

46.7 Place the titration cell into position on the chloride titrator.

46.8 Begin stirring by turning the titrate switch to the *I* position.

46.9 Set the timer counter to zero.

46.10 Begin the titration by turning the titrate switch to the 2 position.

46.11 Record the time when the counter stops.

46.12 Repeat 46.2 – 46.4 and 46.6 – 46.11 to determine a blank.

46.13 Calculate the calibration factor, *F*, as follows:

$$F = \frac{Cl}{T_{st} - T_{cb}} \quad (5)$$

where:

Cl = chloride added from the chloride standard, µg,

$T_{st}$  = titration time of standard, and

$T_{cb}$  = titration time of blank.

## 47. Procedure

47.1 Pipet 5.00 mL of the diluted condensate from 39.9 into a clean, dry 10-mL titration cell.

47.2 Pipet 1.00 mL of the nitric-acetic acid solution into the cell.

47.3 Perform 46.6 – 46.11, rinsing the electrode assembly between each titration.

## 48. Calculation

48.1 Calculate the micrograms of chloride, Cl, µg, titrated as follows:

$$Cl, \mu g = \frac{V \times F \times (T_s - T_{rb})}{A} \quad (6)$$

where:

*V* = volume of diluted condensate, normally 20.0 mL (39.9),

*F* = calibration factor (46.13),

$T_s$  = titration time of sample,

$T_{rb}$  = titration time of reagent blank (pyrohydrolysis), and

*A* = sample aliquot from diluted condensate, normally 5.00 mL (47.1).

48.2 Calculate the concentration in µg/g (ppm) of chloride, Cl, in a boron carbide sample as follows:

$$Cl = \frac{Cl, \mu g}{W} \quad (7)$$

where:

*Cl*, µg = chloride from 48.1, µg, and

*W* = sample weight, g.

## 49. Precision and Accuracy

49.1 *Precision*—The relative standard deviation is 17 % at concentration levels between 10 and 100 µg/g.

49.2 *Accuracy*—The average percent recovery obtained from the analysis of LASL control standards over a 2-year period was 94 %.

## CHLORIDE AND FLUORIDE BY ION-SELECTIVE ELECTRODE

## 50. Scope

50.1 This method covers the measurement of chloride and fluoride after separation from boron carbide by pyrohydrolysis. The limit of detection for chloride and fluoride in the boron carbide sample is 3 mg/kg and 2 mg/kg, respectively.

## 51. Summary of Method

51.1 The condensate from the pyrohydrolysis step is analyzed for chloride and fluoride with ion-selective electrodes.

## 52. Interferences

52.1 At the specification limits for impurities usually established for nuclear-grade boron carbide, interference effects are insignificant.

## 53. Apparatus

53.1 *Fluoride-Selective Electrode*.

53.2 *Chloride-Selective Electrode with Reference Electrode*.

53.3 *pH/Ion-Meter*.

53.4 *Magnetic Stirrer*.

## 54. Reagents

54.1 Water complying Grade II of Specification D1193 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.

54.2 *Fluoride Standard Solution*, 100 mg/L, prepared by dilution of commercially available stock standard solutions or sodium fluoride.

54.3 *Chloride Standard Solution*, 1000 mg/L, commercially available stock standard solution or sodium chloride.

54.4 *TISAB*, total ionic strength adjustment buffer.

NOTE 36—Ready to use TISAB solutions are commercially available.

54.5 *Nitric Acid*, HNO<sub>3</sub>, c(HNO<sub>3</sub>) = 65 %.



## 55. Calibration of Electrode

55.1 Before each measurement series the slope of the electrodes must be determined according to the instruction manuals of the ion-selective electrodes.

## 56. Procedure

56.1 The collection vessel (50 ml volumetric flask) with the condensate obtained by pyrohydrolysis of the boron carbide sample (see 39.13) is filled up to volume with water. This solution is used for measurement of chloride and fluoride concentration by ion-selective electrode.

### 56.2 Fluoride

56.2.1 Pipet 10 ml of the sample solution in a small beaker.

56.2.2 Add 10 ml of TISAB solution.

56.2.3 Put the fluoride-selective electrode into the solution and switch the magnetic stirrer on.

56.2.4 After stabilization of the voltage indicated at the ion-meter, add 25  $\mu$ l of fluoride standard. The addition of 25  $\mu$ l of fluoride standard has to be done four times. After each standard addition, the voltage change must be recorded. Continue with Section 56.4.

### 56.3 Chloride

56.3.1 Pipet 10 ml of the sample solution in a small beaker.

56.3.2 Add 25  $\mu$ l of nitric acid.

56.3.3 Put the chloride-selective electrode and the reference electrode into the solution and switch on the magnetic stirrer.

56.3.4 After stabilization of the voltage indicated at the ion-meter, add 25  $\mu$ l of chloride standard. The addition of 25  $\mu$ l of chloride standard has to be done four times. After each standard addition, the voltage change must be recorded. Continue with Section 56.4.

56.4 Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Section 56. The method blank has to be determined applying the same procedure but using the blank solutions from the pyrohydrolysis. If a measurable method blank is detected the single values have to be corrected by the method blank.

## 57. Calculation

57.1 The calculation of the concentration of chloride and fluoride in the sample solution has to be done graphically according to the instruction manuals of the ion-selective electrodes. In this diagram the number of standard addition steps (y-axis) is plotted vs. the decadic logarithm of  $\Delta E / S$  (x-axis, where:  $\Delta E$  = voltage change after standard addition,  $S$  = slope of the electrode). The intercept of the linear regression with the y-axis for  $x = 0$  multiplied with the concentration change after standard addition (for chloride and fluoride 1.25 mg/L and 0.125 mg/L, respectively) gives the concentration of the sample solution.

57.2 The chloride and fluoride content,  $w(Cl)$  or  $w(F)$ , of the sample has to be calculated under consideration of sample mass and blank values. The chloride and fluoride content as mean of the corrected single values of the multiple determina-

tions shall be expressed in mass fractions in mg/kg and rounded off in accordance to the uncertainty of measurement.

57.3 Calculate the mass fraction of chloride and fluoride as follows:

$$w(Cl) = \frac{C_M \times V}{m_E} \quad (8)$$

$$w(F) = \frac{2 \times C_M \times V}{m_E} \quad (9)$$

where:

$C_M$  = measured concentration of chloride or fluoride, mg/L,

$V$  = volume of collection vessel of pyrohydrolysis, ml, and

$m_E$  = sample mass, g

## 58. Precision and Accuracy

58.1 *Precision*—The relative standard deviation for chloride and fluoride is 7.5 % and 10 %, respectively, at concentration levels between 10 and 100 mg/kg.

58.2 *Bias*—For boron carbide, no bias data is available.

## WATER BY CONSTANT-VOLTAGE COULOMETRY AND WEIGHT LOSS ON DRYING

## 59. Preface

59.1 Coulometric water analyzers as stand-alone laboratory apparatus are currently not commercially available any more. However, old analyzers are still in use for water determination. The limited availability of these analyzers is the reason why in Section 62 an alternative test method is given. The described “Weight Loss on Drying” method is commonly applied for boron carbide and accepted in the specifications between buyer and seller. Besides water, the “Weight Loss on Drying” method, however, detects other volatile substances in the boron carbide sample (mainly boric acid). For this reason, the “Weight Loss on Drying” method will deliver for a given temperature higher values than the coulometric method. It depends on the contract between buyer and seller which test method has to be applied.

## 60. Scope

60.1 This method covers the determination of water in boron carbide in either powder or pellet form. The lower limit of the water by constant-voltage coulometry method is 5  $\mu$ g of water. The lower limit of the weight loss on drying method is 20 mg/kg for a sample mass of 5 g.

## 61. Water by Constant-Voltage Coulometry

61.1 *Summary of Method*—Water is removed from the sample by heating at 400°C. A carrier gas sweeps the water into an electrolytic cell containing phosphorus pentoxide to absorb the water. A potential applied across the cell causes the absorbed water to be electrolyzed. The total current is integrated and displayed digitally as micrograms of water (16), (17).

61.2 *Interferences*—Hydrogen, alcohols, and amines will give a high bias. Other materials can coat the inside of the cell, making it inactive.

### 61.3 Apparatus:

61.3.1 *Analytical Balance*, capable of weighing to  $\pm 0.01$  mg.

61.3.2 *Gas Dryer*.

61.3.3 *Gas Flowmeter*.

61.3.4 *Platinum Boat*,  $10 \times 30 \times 5$  mm.

61.3.5 *Water Analyzer*.<sup>9</sup>

### 61.4 Reagents:

61.4.1 *Magnesium Perchlorate*, anhydrous, for gas dryer.

61.4.2 *Nitrogen*, prepurified grade or equivalent.

61.4.3 *Sodium Tartrate Dihydrate*, crystals, weighing from one to several milligrams. This compound contains 15.6 weight percent water and it is used as a standard.

### 61.5 Calibration of Analyzer:

61.5.1 The analyzer is precalibrated electronically by the manufacturer; however, recalibration is recommended at least twice each year. Follow the manufacturer's recommended procedure for calibration.

61.5.2 A control standard, which can be sodium tartrate dihydrate, should be analyzed at least once in each 8-h shift in which samples are analyzed.<sup>10</sup>

61.5.3 Analyze sodium tartrate dihydrate as follows to serve as a control standard:

61.5.3.1 Weigh accurately, using either a semimicro or micro balance, from 1 to 2 mg of sodium tartrate dihydrate.

NOTE 37—Use only very clear crystals to avoid low results that occur when using cloudy crystals.

61.5.3.2 Analyze the weighed sodium tartrate dihydrate in accordance with Section 61.6 with the following exception: use  $125 \pm 5^\circ\text{C}$  instead of the stated temperature in 61.6.2, 61.6.4, 61.6.9, and 61.6.15.

NOTE 38—Do not heat above  $150^\circ\text{C}$  because sodium tartrate dihydrate decomposes to give high results.

61.5.3.3 Calculate the percent water in the control standard in accordance with 61.7.2. The control limits are 14.8 to 16.4 %. If the result is outside, investigate and correct the problem before analyzing samples.

### 61.6 Procedure:<sup>11</sup>

61.6.1 Adjust the nitrogen flow rate to 100 mL/min at 34.5 kPa (5 psi) gage.

NOTE 39—The flow rate adjustment is not critical. Because the cell current is integrated as a function of time, the total water present is independent of carrier-gas flow rate. However, a flow rate less than 150 mL/min is recommended.

61.6.2 Set the temperature controller at  $400^\circ\text{C}$ .

NOTE 40—This temperature was chosen because  $400^\circ\text{C}$  is considered to be high enough to release all water from the sample and yet low enough to minimize the reaction of hydrogen to form water if the sample contains absorbed hydrogen.

<sup>9</sup> Du Pont Instrument Inc. CEC water analyzer, Model 26-321 AMA, has been found satisfactory for this method.

<sup>10</sup> A method of calibration using an injection of measured amounts of hydrogen that is converted to water has been used (see LA-4622, Los Alamos Scientific Laboratory, Los Alamos, N. M., March 1971). Another technique that is used is to add a measured amount of water to the analyzer by way of a capillary tube.

<sup>11</sup> If a water analyzer other than the CEC Model 26-321 AMA is used, consult the manufacturer's operation manual for the method of calibration and operation.

61.6.3 Place an empty platinum boat in the oven.

NOTE 41—Platinum is preferred over nickel for boats because nickel may have an oxide-film coating that is a source of oxygen to react with hydrogen.

61.6.4 Start the timer and heat at  $400^\circ\text{C}$  until the count rate of the integrator decreases to a constant rate over a 10-min period.

NOTE 42—The system must be dried sufficiently at this step to permit setting the zero of the analyzer at 68.5. The count rate that indicates sufficient drying is determined by experience.

61.6.5 Zero the instrument at a count rate of 0.6  $\mu\text{g}/\text{min}$ .

NOTE 43—Consult the manufacturer's operation manual for instructions on how to zero the analyzer.

61.6.6 Turn off the timer and set the integrator to zero.

61.6.7 Remove the boat when the oven reaches room temperature.

61.6.8 Replace the boat in the oven after about 10 s and turn on the timer.

NOTE 44—The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

61.6.9 Heat at  $400^\circ\text{C}$  until the count rate of the integrator decreases to a constant rate of 0.6  $\mu\text{g}/\text{min}$ .

61.6.10 Record the reading ( $R_b$ ) on the integrator and the time ( $T_b$ ) required to complete 61.6.9.

NOTE 45—If the analyzer is not used in a controlled environment, the blank will vary from day to day, particularly if the humidity varies. Therefore, with samples containing less than 30  $\mu\text{g}$  of water, it is recommended that a blank be determined between each sample analysis.

61.6.11 Stop the timer and reset the integrator to zero.

61.6.12 Remove the boat when the oven reaches room temperature.

NOTE 46—The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

61.6.13 Add a sample weighed to  $\pm 1$  mg ( $W_s$ ) to the boat.

61.6.14 Replace the boat in the oven.

61.6.15 Heat at  $400^\circ\text{C}$  until the count rate of the integrator decreases to a constant rate of 0.6  $\mu\text{g}/\text{min}$ .

61.6.16 Record the reading ( $R_s$ ) on the integrator and the time ( $T_s$ ) required to complete 61.6.15.

NOTE 47—The reading and time are  $R_c$  and  $T_c$  respectively when a control standard is analyzed.

61.6.17 Stop the timer and reset the integrator to zero.

61.6.18 Repeat 61.6.12 – 61.6.17 for subsequent sample analyses.

### 61.7 Calculation:

61.7.1 Calculate the micrograms of water,  $W_H$ , per gram of sample as follows:

$$W_H = \frac{(R_s - B \times T_s)}{W_s} \quad (10)$$

where:

$R_s$  = water from sample measurement,  $\mu\text{g}$ ,

$B$  =  $R_b/T_b$  (see 61.6.10),

$T_s$  = min required for sample measurement, and

$W_s$  = sample weight, g.

61.7.2 Calculate the weight percent of water,  $W_p$ , in the control standard as follows:

$$W_p = \frac{(R_c - B \times T_c)}{W_c \times 10^4} \quad (11)$$

where:

- $R_c$  = water from control standard measurement, mg,
- $B$  =  $R_b/T_b$  (see 61.6.10),
- $T_c$  = min required for control standard measurement, and
- $W_c$  = control standard weight, g.

#### 61.8 Precision and Accuracy:

61.8.1 *Precision*—The relative standard deviation is about 20 % for 20 to 40 µg of water and 2 to 5 % for >100 µg.

61.8.2 *Accuracy*—Over a 2-month period, 17 sodium tartrate standards containing 300 to 1000 µg of water were analyzed and the recovery varied from 95 to 101 %.

## 62. Weight Loss on Drying Method

### 62.1 Scope:

62.1.1 This method covers the determination of water and other volatile substances in boron carbide powder by a gravimetric method.

### 62.2 Summary of Method:

62.2.1 The boron carbide powder sample is heated in a suited heating device. The mass before and after heating is measured by weighing and the difference expressed as loss on drying (LOD) in mass %.

### 62.3 Interferences:

62.3.1 Because of possible oxidation of boron carbide the procedure must be carried out under inert gas conditions at temperatures above 150°C.

### 62.4 Apparatus:

62.4.1 *Analytical Balance*—at least capable of reading to the nearest 0.01 mg.

62.4.2 *Sample Boat*—for example, labware glass, quartz, steel, nickel, platinum, suited to carry a sample mass required for a reliable determination of LOD.

62.4.3 *Heating Device*—capable for a reproducible setting of the temperature specified for LOD measurement.

NOTE 48—Temperature and heating time for LOD measurement are usually agreed between buyer and seller. Commonly used temperatures and heating time are 110°C, 400°C, 500°C and 2 h, respectively.

NOTE 49—For temperatures below 150°C drying cabinets or commercially available moisture analyzers with halogen lamp heating are well suited. For higher temperatures a tube-furnace with inert gas flushing can be used.

### 62.5 Preparation:

62.5.1 The sample boats are dried at the temperature selected for LOD measurement, cooled down to room temperature in a desiccator and stored therein. For temperatures above 150°C metal samples boats must be used.

### 62.6 Procedure:

62.6.1 Take the weight of the empty sample boat, prepared according to 62.5.1.

62.6.2 Fill the boron carbide powder into the sample boat (usually 5 g) and take the weight again.

62.6.3 Place the sample boat in the heating device and, if required, turn inert gas flushing on.

62.6.4 Heat the sample boat to the specified temperature (for example, 110°C) and hold this temperature for the specified time (for example, 2 h).

62.6.5 Place the sample boat in a desiccator and let it cool down to room temperature.

62.6.6 Take the weight of the sample boat again.

62.6.7 Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to 62.6.

### 62.7 Calculation:

62.7.1 The LOD as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of boron as follows:

$$w(LOD) = \frac{100 \times (m_2 - m_3)}{m_2 - m_1} \quad (12)$$

Where:

- $m_1$  = mass of empty sample boat, g,
- $m_2$  = mass of sample boat with boron carbide before heat treatment, g, and
- $m_3$  = mass of sample boat with boron carbide after heat treatment, g.

### 62.8 Precision and Bias:

62.8.1 For boron carbide there is no data available.

## METALLIC IMPURITIES

## 63. DC Arc OES Method

### 63.1 Scope:

63.1.1 This method covers the determination of mass fractions of the impurities Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Si, Ti, W and Zr in boron carbide in either powder or pellet form. This method is applicable to mass fractions of the impurities mentioned above from approximately 1 mg/kg up to approximately 30 000 mg/kg depending on element, wavelength, arc parameter, and sample weight.

### 63.2 Summary of Method:

63.2.1 The optical emission spectrometry is based on generation of line spectra of excited atoms or ions, in which each spectral line can be definitely related to an element and the line intensities are proportional to the mass fractions of elements in the measured sample. Contrary to wet-chemical methods via solution the classical sample decomposition is replaced by evaporation and excitation in a DC-Arc. The combustion and evaporation of the crushed sample material takes place in the arc in an atmosphere of mixed argon and oxygen, oxygen or in air. The metallic traces in the arc plasma are excited to emission of light. The light is guided into a simultaneous emission spectrometer (for example, by coupling via fiber-optics or directly). The light is split in its spectral lines and measured by suitable detectors. The mass fractions of elements in the sample are calculated by comparison of the

intensities of the element-specific spectral line with those of a calibration sample of the identical material.

### 63.3 Interferences:

63.3.1 Interference effects depend primarily upon the resolving power of the spectrograph and the selection of the analytical lines. In practice, line interferences (spectral interferences) and interferences in volatilizing the sample and by impacting the Arc-plasma by accompanying or matrix elements (non spectral interferences) are critical.

### 63.4 Apparatus:

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

63.4.2 *Emission Spectrometer*—simultaneous, preferably with the possibility of time resolved registration of signal, and coupled to DC-Arc device.

63.4.3 *DC-Arc Device*—with Stallwood jet, controlled gas-flows for argon and oxygen (preferably with mass-flow control) and controlled setting of arc-current (preferably with the possibility of programmable current vs. time programs with freely definable ramp-and hold-steps).

NOTE 50—When working with air, Stallwood jet and controllers for argon and oxygen can be omitted.

63.4.4 *Tweezers*—self-locking.

63.4.5 *Microspatula*.

63.4.6 *Analytical Balance*—at least capable of reading to the nearest 0.01 mg.

63.4.7 *Drying Cabinet*—capable of maintaining a temperature of  $(110 \pm 5)^{\circ}\text{C}$ .

63.4.8 *High Resistance Carbon Electrodes or Graphite Electrodes*—spectral-grade, peak-shaped or elliptical counter electrode (cathode), cup-shaped carrier electrode (anode) with groove or taper.

### 63.5 Reagents:

63.5.1 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.

63.5.2 *Calibration Standards*—with defined mass fractions of trace-impurities, preferably certified reference materials with composition and mass fractions of trace-impurities similar to the analyzed material.

63.5.3 *Oxygen*—purity  $\geq 99.99\%$  v/v.

63.5.4 *Argon*—purity  $\geq 99.99\%$  v/v.

### 63.6 Sampling and Sample Preparation:

63.6.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material.

63.6.2 In an unknown drying state the sample has to be dried in a drying cabinet at  $(110 \pm 5)^{\circ}\text{C}$  to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 51—Drying for 2 h is normally sufficient.

63.6.3 The sample material must have a particle size of  $\leq 150\text{ }\mu\text{m}$  (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for

crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

### 63.7 Preparation of Apparatus:

63.7.1 Consult the manufacturer's instructions for operation of the emission spectrometer and DC-Arc device. Assign the appropriate operating parameters to both emission spectrometer and DC-Arc device so that the desired elements can be determined.

NOTE 52—Operation parameters have to be developed individually for the used combination of emission spectrometer and DC-Arc device. For optimization of method parameters the time resolved registration of background corrected net signal intensities of spectral lines is very helpful (18).

### 63.8 Calibration:

63.8.1 Calibration is carried out for each measuring cycle (minimum once per day) with calibration standards (63.5.2) of defined mass fractions of traces-impurities in accordance with 63.9. Calibration standards have to be measured at the beginning and at the end of the measuring cycle. Within the calibration range at least a three-point calibration has to be performed. Calibration samples (63.5.2) of identical or similar material, if possible certified reference materials or matrix matched synthetic calibration samples, have to be used. The mass fractions of trace-impurities in the calibration samples should be in the range of the sample material. The analytical functions shall be calculated using the known mass fractions of trace-impurities in the calibration samples (63.5.2) and the measured net intensities of spectral lines of the analytes. Calculation of analytical functions shall be performed by linear or quadratic regression. Within the calibrated range of mass fractions of trace-impurities the analytical functions shall have a monotonic increasing slope.

### 63.9 Procedure:

63.9.1 A sub-sample of the sample material prepared in accordance with 63.6 is weighed using a microspatula to the nearest  $\pm 0.01\text{ mg}$  into the carrier electrode in a defined narrow weighing range (for example, between 4.5 and 5.5 mg). The mass of the weighed sub-sample has to be documented. The carrier electrodes shall be touched in the clamp-region of the electrode holder using tweezers (63.4.4). Depending on dimension and shape of the carrier electrode the mass of the sub-sample can vary. The sample mass can be reduced in case of high analyte contents (for example, with mass fractions above the calibrated concentration range) to a minimum of approximately 1 mg. In this case, the weighed sub-sample has to be mixed in the electrode with a material of the same type, which does contain the respective analytes below the limit of detection. Instead of a pure material of the same type spectral-grade graphite powder can be used. The total mass of material in the electrode shall correspond to that of the calibration standards (63.5.2). Subsequently, the sub-sample has to be compacted in the cup of the carrier electrode by slightly striking it on a rigid underlay or by knocking with the microspatula at the tweezers holding the carrier electrode. The carrier electrode has to be fixed in the optical path of the optical system of the emission spectrometer (63.4.2) using the electrode holder of the DC-Arc device (63.4.3). The distance to the



upper counter electrode (cathode) has to be adjusted to the nearest  $\pm 0.1$  mm at a value of 3.5 to 4.0 mm.

NOTE 53—The distance between the electrodes can vary according to the diameter of the electrodes.

63.9.2 The position of the electrodes, and thus the arc discharge, has to be constant with respect to the optical axis of the optical system. Any change of the optical adjustment will lead to different results. Parts of the electrodes shall not be visible to the emission spectrometer. This is especially true for the upper electrode (cathode) whereas the lower electrode (anode), because of the high burn-off rate, normally remains a significantly shorter time in the optical path.

NOTE 54—Electrodes visible in the optical path result in a strong enhancement of the spectral background in some spectral ranges.

63.9.3 The arc discharge has to be started simultaneous to the data acquisition of the spectrometer. The evaporation or combustion of the sample in the DC-Arc has to be carried out preferably under shielding gas excluding any nitrogen. Argon/oxygen mixtures (preferably 70 % v/v argon and 30 % v/v oxygen) and pure oxygen can be used as shielding gas.

NOTE 55—Argon/oxygen mixtures reduce the burn-off rate of the carrier electrode and may require higher arc-currents.

63.9.4 Principally, the evaporation or combustion in air is possible resulting, however, in increased spectral interferences (for example, CN-bands). In addition, a negative influence on the reproducibility can be expected. Each sample has to be measured at least three times. If the deviation of the single values of the analyte concentrations is greater than the specified value of repeatability, the procedure has to be repeated according to section 63.9. **Warning**—It is not safe to look into the arc plasma without eye protection (UV- and IR-radiation). Reflections on reflective areas can be dangerous, too.

#### 63.10 Wavelength and Working Range:

63.10.1 It is critical that all selected analyte wavelength are free of line-interferences with respect to sample matrix and other components in the sample. Only spectral lines have to be

selected where under the chosen working conditions neither self-absorption nor self-reversal will occur. When combining Echelle optics with plane solid-state detectors (CID- or CCD-detectors) also order-interferences have to be considered. The wavelength of spectral lines and the background measuring points used for calibration and sample analysis have to be the same. The lower limit of the working range is defined by the limits of determination of the analytes. The upper limit of the working range is defined by a decrease of sensitivity (slope of calibration function) to about 80 % of its initial value. If applicable, the upper limit of the working range can be extended by using less sensitive spectral lines.

#### 63.11 Calculation and Report of Results:

63.11.1 The intensities of spectral lines measured by the emission spectrometer have to be corrected to net-intensities using the background intensities measured at the background measuring points. The analyte contents of the sample have to be calculated under consideration of net-intensities, analytical functions (see 63.8) and mass of the sub samples. The analyte contents as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in mg/kg and rounded off in accordance to the uncertainty of measurement.

NOTE 56—Additionally, the ratio of the net-intensities of the analyte lines to the net-intensity of an emission line of a reference element with constant mass fraction (for example, the matrix element B) can also be calculated. This ratio can be used as correction factor to compensate fluctuations and drifts of the analyte lines intensities during the measurement run. This so called method of internal standard can increase trueness and precession of the analysis results.

63.11.2 Table 1 lists the wavelength and concentration range for 15 elements determined by this method.

#### 63.12 Precision and Bias

63.12.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102 one laboratory participated using the described DC-Arc OES method. The following precision and bias data were obtained:

TABLE 1 Analytical Lines and Concentration Ranges

Element	Wavelength, nm	Concentration Range, µg/g
Al	308.215, 309.271, 394.401, 396.152	20 to 5000
Ca	315.887, 317.933	20 to 7000
Co	345.350	20 to 2000
Cr	267.716, 283.563, 284.984	10 to 1000
Cu	324.754, 327.396	1 to 500
Fe	239.562, 259.941, 261.187, 275.573, 294.788, 302.064	50 to 10 000
Mg	279.553, 280.270	5 to 1000
Mn	260.569, 294.921	10 to 1000
Mo	313.259	10 to 1000
Na	588.995, 589.592	5 to 500
Ni	232.003, 313.411, 341.476	5 to 2000
Si	250.690, 251.920, 252.851, 288.158	50 to 30 000
Ti	323.452, 334.941, 336.121	30 to 10 000
W	294.699	50 to 8000
Zr	267.863, 327.305, 339.198, 343.823	20 to 25 000

Element	DCArc OES			ERM-ED102, certified values		Bias of DCArc OES method to certified values, %
	Mean, mg/kg	STDev, mg/kg	RSD, %	Mean, mg/kg	STDev, mg/kg	
Al	154	5	3.2	157	5	-1.9
Ca	97	7	7.2	97	8	±0.0
Cu	1.6	0.3	18.8	2.2	0.4	-27.3
Fe	696	19	2.7	686	22	+1.5
Mn	8.1	0.4	4.9	10.4	0.5	-22.1
Ni	11	0.7	6.4	8.0	1.6	+37.5
Si	304	17	5.6	268	22	+13.4
Ti	104	5	4.8	96	5	+8.3
Zr	55	4	7.3	48.9	2.3	+12.5

## 64. Wet Chemical Methods

**64.1 General Comments**—The determination of metallic impurities in boron carbide by wet chemical methods requires a decomposition of the sample prior to analysis. For sample decomposition melt-fusion with sodium carbonate or sodium/potassium carbonate and decomposition with nitric acid at high temperature and pressure is recommended. The resulting sample solutions can be analyzed for metallic impurities using standard analytical techniques such as ICP OES, ICP MS and AAS. The determination of metallic impurities in sample solutions by ICP OES, ICP MS and AAS is well known and comprehensively described in numerous standard test methods. Therefore, a detailed description of the procedures for the analysis of samples solutions is not part of this standard test method.

**64.2 Sampling and Sample Preparation**—(See 63.6.)

**64.3 Reagents**—Water complying Grade II of Specification D1193 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.

**64.4 Sample Decomposition by Melt-Fusion**—Decompose a sub-sample of 200 to 300 mg of powdered boron carbide prepared in accordance with 64.2 in a platinum crucible by melt-fusion with sodium carbonate or sodium/potassium carbonate according to the procedure described in Section 24. After dissolving the melt in hydrochloric acid the sample solution is transferred to a 250 ml volumetric flask and filled up to volume with water. Prepare a blank sample according to the same procedure but without boron carbide powder. These solutions are then used for determination of metallic impurities. At least two decompositions for sample and blank have to be carried out.

**64.5 Acid/Pressure Decomposition:**

**64.5.1 Scope**—This method covers the complete decomposition of boron carbide with nitric acid in suitable reaction vessels at high temperature and pressure.

**64.5.2 Apparatus**—Commonly used laboratory equipment and special equipment according to the following:

**64.5.2.1 Analytical balance**—at least capable of reading to the nearest 0.1 mg.

**64.5.2.2 Decomposition system**—steel pressure vessels with hermetically sealable fluoropolymere liners (for example, PTFE, PFA).

**64.5.2.3 Drying cabinet**—capable of maintaining a temperature of  $(230 \pm 5)^{\circ}\text{C}$ .

NOTE 57—Commercially available microwave sample decomposition systems are also well suited for decomposition of boron carbide.

**64.5.3 Reagents**—See 64.3.

**64.5.3.1 Nitric acid**— $\text{HNO}_3$ ,  $c(\text{HNO}_3) = 65\%$

**64.5.4 Procedure**—**Warning**—Operation of decomposition system has to be carried out according to the manufacturers instructions. Safety advices have to be strictly obeyed.

A sub-sample of 200 to 300 mg of the sample material prepared in accordance with 64.2 is weighed to the nearest  $\pm 0.1$  mg into the fluoropolymere liner. Add 10 ml of nitric acid (64.5.3.1) and put the lid onto the liner. The sealed liner is transferred to the steel pressure vessel which is closed applying a torque recommended by the manufacturer. The steel pressure vessel is put in the drying cabinet and heated to  $(230 \pm 5)^{\circ}\text{C}$  for 14 h.

NOTE 58—When working with a microwave sample decomposition system sample mass and volume of nitric acid is the same. However, the operation parameters have to be developed individually for the apparatus used. Microwave assisted sample decomposition results in a significantly reduced decomposition time.

The steel pressure vessel is removed from the drying cabinet, cooled down to room temperature and opened according to the manufacturers instructions. The solution is transferred to a 100 ml volumetric flask. Liner and lid are thoroughly rinsed with water into the volumetric flask. After this, the volumetric flask is filled up to volume with water. Prepare a blank sample according to the same procedure but without addition of boron carbide powder. These solutions are then used for determination of metallic impurities. At least two decompositions for sample and blank have to be carried out. Before they can be used again, liner and lid have to be cleaned. For this purpose, fill the liner with 10 ml of nitric acid (64.5.3.1), put the lid on and fix it with a steel clamp. Heat the sealed liner at  $(100 \pm 5)^{\circ}\text{C}$  for 4 h.

**64.6 Determination of Metallic Impurities**—The concentration of metallic impurities in both sample and blank solutions are measured using standard ICP OES, ICP MS and AAS procedures. The content of metallic impurities in the boron carbide sample is calculated under consideration of sub-sample mass and analyte concentration of sample and blank solution. Calibration solutions shall be prepared by digestion of certified reference materials or by dilution of single element standard solutions which may be purchased or prepared from high-purity grade chemicals or metals. In case of standard solutions they have to be matched to the matrix of the sample solution.

## SOLUBLE BORON BY TITRIMETRY AND ICP OES

## 65. Scope

**65.1** This method covers the determination of soluble boron in boron carbide. Soluble boron is defined as that boron dissolved under the conditions of the test.

## 66. Summary of Method

**66.1** This method is empirical but has been found useful in characterizing boron carbide (3), (4), (5), (19). It is based on

the assumption that hydrochloric acid or, alternatively, water extracts only boron oxide and that nitric acid extracts both boron oxide and elemental boron. The choice of hydrochloric acid or water extract will be determined by individual need or may be specified by the purchase order. In comparison studies, it was found that the water-soluble boron test gave lower values for boron with improved precision. In case a precipitation step for hydrolyzable metals is not required the water extract procedure is shorter. The hydrochloric acid test has been used for many years and has found a wide degree of acceptance. The measurement of soluble boron is, in all cases, by titration with standardized sodium hydroxide using the mannitoboric acid procedure. Because the method is empirical, it is important that the analysis conditions be exactly as described in the test.

## 67. Interferences

67.1 Hydrochloric and nitric acid may dissolve metallic impurities whose hydrous oxides distort the end point of the strong acid titration. If this is the case, metallic impurities must be precipitated from the sample solution using sodium hydroxide or barium carbonate.

## 68. Apparatus

68.1 *Allihn Condenser*, 200-mL jacket with a 24/40 standard-taper (inner) joint at one end.

68.2 *Beaker*, 400-mL and 600-mL, low-boron glass.

68.3 *pH-electrode*.

68.4 *Erlenmeyer Flask*, 200-mL, low-boron glass, with a 24/40 standard-taper (outer) joint at the neck.

68.5 *Filter Paper*, open-textured, very rapid filtering, for coarse and gelatinous precipitates.

68.6 *pH Meter*.

68.7 *Polyethylene Funnel*.

68.8 *Recording Titrator*.<sup>12</sup>

68.9 *Hot Plate*.

## 69. Reagents

69.1 Avoid purchasing reagents contained in glass to eliminate a possible source of boron contamination. Store reagents in plastic containers for the same reason.

69.2 *Boric Acid, Standard*—NBS SRM 951 or its replacement.

69.3 *Hydrochloric Acid*, 3 mol/L and 0.1 mol/L.

69.4 *Mannitol*.

69.5 *Nitric Acid*, 3 mol/L, 1.6 mol/L, and 0.1 mol/L.

69.6 *Sodium Hydroxide Solution*, 10 mol/L.

69.7 *Sodium Hydroxide Solution*, 0.1 mol/L, standardized, carbonate-free.

<sup>12</sup> The use of a recording titrator is recommended because the presence of impurities, such as carbonate and aluminum, will be revealed by distortions in the titration curves at the end point. Such distortions may be overlooked when using manual titrations.

## 70. Precautions

(See Section 22.)

## 71. Standardization of Titrant

71.1 For the NaOH solution used for titration (69.7) the correct molarity has to be determined. For this purpose, preferably solutions of primary substances, for example, potassiumhydrogenphthalate or boric acid (69.2), must be titrated with the NaOH solution.

## 72. Blank

72.1 The method blank has to be determined applying the same procedures as described in Sections 74 (without and with precipitation) and 76, however, without addition of boron carbide. If a measurable method blank is detected the single values have to be corrected by the method blank.

## 73. Sample Preparation

73.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried in a drying cabinet at  $(110 \pm 5)^{\circ}\text{C}$  to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 59—Drying for 2 h is normally sufficient.

73.2 If not otherwise specified between buyer and seller boron carbide powders must have a particle size of  $\leq 150 \mu\text{m}$  (No. 100 sieve). Shaped or sintered bodies of boron carbide must be crushed to a particle size of  $\leq 150 \mu\text{m}$  (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

## 74. Procedure

74.1 *HCl and HNO<sub>3</sub> Soluble Boron*:

74.1.1 Weigh two separate 1-g samples in powder form to  $\pm 1 \text{ mg}$  and transfer them quantitatively to separate 200-mL flasks fitted with Allihn condensers.

74.1.2 Add 100 mL of 1.6 M HNO<sub>3</sub> to one flask and 100 mL of 0.1 M HCl to the other flask.

NOTE 60—Take both samples through the remainder of the procedure. Exceptions or special treatments required for either sample are given at the appropriate steps.

74.1.3 Boil gently under reflux for 4 h.

74.1.4 Let the solution cool to ambient temperature with the condenser attached.

74.1.5 Rinse the condenser with 10 to 20 mL of water.

NOTE 61—Modern pH-electrodes work also well in suspensions. If such an electrode is used, filtration of the sample suspension obtained in 74.1.5 is therefore not necessary. If filtration is not necessary and a precipitation is not required continue with 74.1.15. Otherwise, continue with 74.1.6.

74.1.6 Filter the solution through filter paper and collect the filtrate in a 400-mL beaker.

NOTE 62—The filtrate contains solubilized boron.

NOTE 63—A retentive filter paper is necessary to retain the undissolved sample.

74.1.7 Rinse the flask and the filter with a wash of 0.1 M HCl.

NOTE 64—The use of water as a rinse may cause the formation of colloids which pass through the filter. This has not been found to affect the results.

Normally, the level of metallic impurities does not require a precipitation step prior to titration (see also Section 67). If the end-point inflection on the titration curve is distorted or if there are multiple inflections that are severe enough to prevent a clear determination of the first end point, carbonate or hydrolyzable metals probably are present. In this case, a precipitation is required. Continue then with 74.1.8, otherwise with 74.1.15.

74.1.8 Adjust the pH of the solution while stirring to about 11 using 10 M NaOH solution and then adjust back to pH 5.3  $\pm$  0.2 using dilute acid.

74.1.9 Let the solution stand for at least 2 h.

NOTE 65—The solution can be warmed and then allowed to stand for several hours to improve the filtering characteristics of the precipitate.

NOTE 66—After the precipitate settles, the supernate should be colorless.

74.1.10 Filter the solution through filter paper and collect the filtrate in a 600-mL beaker.

74.1.11 Rinse the filter paper and precipitate thoroughly with hot water and collect the rinses with the filtrate.

74.1.12 Acidify the filtrate with dilute acid to a pH of 3.0  $\pm$  0.1.

74.1.13 Cover the beaker and boil the solution gently for 15 min.

NOTE 67—Dissolved carbon dioxide is removed by boiling. A longer boiling time or purging with an inert gas can improve the removal of carbon dioxide.

74.1.14 Let the solution cool to ambient temperature.

NOTE 68—The precipitation separation can be modified using the barium carbonate procedure described in 24.5.

74.1.15 Titrate slightly beyond the first potentiometric end point with the standardized 0.1 mol/L NaOH solution.

74.1.16 Add 10 g of mannitol and continue the titration past the second end point.

74.1.17 Boron titration via mannitoboric-acid normally shows definite inflection points in both titration-steps. However, if the concentration of boric acid in the sample solution is very low the detection of inflection points is difficult. If this is observed, the following alternative titration procedure must be used: In the first titration-step, the suspension is titrated with 0.1 mol/L NaOH to pH 7, and then 10 g of mannitol is added. Wait until the pH has stabilized (it decreases to approximately pH 5). In the second titration-step, the suspension is titrated with 0.1 n NaOH to pH 8. The consumption of NaOH in the second titration-step corresponds to the mass of boric acid in the sample solution.

## 75. Calculation

75.1 The  $\text{HNO}_3$ -soluble and HCl-soluble boron  $w(B_{\text{sol}})$  of the sample has to be calculated under consideration of sample mass and blank values. The  $\text{HNO}_3$ -soluble and HCl-soluble boron content shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of  $\text{HNO}_3$ -soluble and HCl-soluble boron as follows:

$$w(B_{\text{sol}}) = \frac{V_{\text{NaOH}} \times F \times q}{10 \times m_E} \quad (13)$$

$$F = \frac{M_{\text{meas}}}{M_{\text{nom}}} \quad (14)$$

where:

$V_{\text{NaOH}}$  = consumption of 0.1 mol/L NaOH, ml,

$F$  = titration correction factor for NaOH,

$M_{\text{meas}}$  = measured molarity of NaOH used for titration, mol/L,

$M_{\text{nom}}$  = nominal molarity of NaOH used for titration, mol/L,

$q$  = titrimetric factor (see Note 69), and

$m_E$  = sample mass, g

NOTE 69— $q = 1.0811$  mg boron per ml 0.1 mol/L NaOH solution, for a natural  $^{10}\text{B}/^{11}\text{B}$  isotopic ratio.

## 76. Procedure

### 76.1 Water-Soluble Boron:

76.1.1 Depending on the expected content of water-soluble boron weigh 1 to 6-g aliquots of sample in powder form to  $\pm 0.1$  mg in 400-mL beakers.

76.1.2 Add 200 mL of water, cover the beaker with a watch-glass and stir for 5 min using a magnetic stirrer.

76.1.3 Heat the mixture in a water-bath at  $(60 \pm 5)^\circ\text{C}$  for 1 h or bring to a boil for 1 h. If the mixture is boiled, a combination of Erlenmeyer flask and reflux condenser has to be used instead of a beaker.

76.1.4 Using vacuum, filter through filter paper and wash 2 to 3 times with hot water.

NOTE 70—Modern pH-electrodes work also well in suspensions. If such an electrode is used, filtration of the sample suspension obtained in Section 76.1.3 is therefore not necessary. In this case, omit section 76.1.4 and continue with Section 76.1.5.

76.1.5 Cool to room temperature and titrate the soluble boron by following 74.1.15, 74.1.16, and 74.1.17.

## 77. Calculation

77.1 Calculate the weight percent water soluble boron in the sample in accordance with Section 75.

NOTE 71—It is common to calculate the water-soluble boron  $w(B_{\text{sol}})$  as mass fraction of boron oxide  $w(B_2O_3)$  using the following equation:  $w(B_2O_3) = 3.22 \times w(B_{\text{sol}})$ .

## 78. Precision and Bias

### 78.1 HCl and $\text{HNO}_3$ soluble boron:

78.1.1 *Precision*—The relative standard deviation for HCl and  $\text{HNO}_3$  soluble boron is 3.4 % at concentration levels between 0.03 and 0.12 weight %.

78.1.2 *Bias*—For HCl soluble boron no bias can be established because no material traceable to a national standards base is available. For  $\text{HNO}_3$  soluble boron see 78.3.

78.2 Comparison of HCl extract method and water extract method:

78.2.1 *Scope*—Each of three laboratories analyzed six samples from each of two types of  $\text{B}_4\text{C}$  material. In every case,



the HCl extract method and the water extract method were used and the results compared.

#### 78.2.2 HCl Extract Method:

78.2.2.1 *Precision*—The standard deviation for water-soluble boron is 0.009 mass % at a mean concentration level of 0.02 mass %.

78.2.2.2 *Bias*—No bias can be established because no material traceable to a national standards base is available.

#### 78.2.3 Water Extract Method:

78.2.3.1 *Precision*—In the experiment, the percent relative standard deviations (coefficients of variation  $\times 100$ ) ranged from 1.1 to 5.4 % (1).

78.2.3.2 *Bias*—No bias can be established because no material traceable to a national standards base is available. In the experiment, however, the results for the water reflux method averaged 39.0 % lower than results from the 0.1 N HCl method. (1)

78.3 Further precision and bias data is available which was obtained within the frame of the certification of the boron carbide powder European reference material ERM-ED102. The following precision and bias data were obtained applying the described titrimetric method. (See table on following page.)

Parameter	Titrimetric Method			ERM-ED102, certified value		Bias of mean of Titrimetric Method to Certified Value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
HNO <sub>3</sub> -Soluble Boron	0.112	0.007	0.012	0.116	0.013	-3.4
Water-Soluble Boron	0.076	0.005	0.023	0.075	0.023	+1.3
Calculated as B <sub>2</sub> O <sub>3</sub>						

## 79. Determination of Soluble Boron by ICP OES

79.1 *General Comments*—The soluble boron in the samples suspensions obtained according to sections 74.1.5 and 76.1.3 can also be measured by ICP OES. This can be done analogously to the ICP OES method described in Section 26 for total boron. ICP OES is the method of choice if the content of soluble boron in the sample is below the limit of determination of the titrimetric method.

79.2 *Procedure*—The sample suspensions obtained in sections 74.1.5 and 76.1.3 are transferred to a volumetric flask (for example, 250 ml) and filled up to volume with water. After sedimentation of the boron carbide powder the clear supernate is used for measurement of boron concentration. Special care has to be taken to very fine boron carbide particles suspended

in the apparently clear supernate. The boron of these particles is also measured by ICP OES and will increase the results for soluble boron. In case of a sufficient high content of soluble boron the trueness of the ICP OES method can be validated through the titrimetric method. If this is not possible the sample solution used for ICP OES must be filtered through a membrane filter (for example, with a pore-size of 0.20  $\mu\text{m}$  or smaller).

NOTE 72—For filtration of sample solutions a combination of single-use syringes with single-use syringe-filters is highly practical.

79.3 *Precision and Bias*—Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data were obtained applying the described ICP OES method. (See table below.)

Parameter	ICP OES Method			ERM-ED102, certified value		Bias of mean of ICP OES Method to Certified Value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
HNO <sub>3</sub> -Soluble Boron	0.122	0.016	0.020	0.116	0.013	+5.2
Water-Soluble Boron	0.081	0.005	0.005	0.075	0.023	+8.0
Calculated as B <sub>2</sub> O <sub>3</sub>						

## FREE CARBON BY A COULOMETRIC METHOD

### 80. Scope

80.1 This method covers the determination of free carbon (also called soluble carbon) in boron carbide powders and shaped or sintered bodies of boron carbide after crushing. This method is applicable to mass fractions of free carbon of 0.01 % to 10 %.

### 81. Summary of Method

81.1 The free carbon of the sample is oxidized to carbon dioxide (CO<sub>2</sub>) by chromic-sulfuric-iodic-acid at 100°C. The formed CO<sub>2</sub> is transported with an inert carrier gas stream to the coulometric detection system. CO<sub>2</sub> is absorbed in an alkaline barium-perchlorate solution and measured coulometrically. The conditions selected for this method are empirical. It

is therefore important that the analysis parameters are used exactly as described in this method.

NOTE 73—For CO<sub>2</sub> detection, conductometric or infrared absorption systems can be used, as well.

NOTE 74—By this method, organic carbon and carbonate carbon is measured, as well.

### 82. Interferences

82.1 Depending on the specific surface the boron carbide powder is oxidized in chromic-sulfuric-iodic-acid at 100°C to a more or less pronounced extent increasing the measured mass fraction of free carbon. This interference can be significantly reduced by an appropriate data evaluation method which is described in Section 88.

NOTE 75—Correction for boron carbide oxidation is limited if a sample with a defined grain size also contains a fraction of very fine

grains. The oxidation of these boron carbide fines, which increases the measured mass fraction of free carbon, can be corrected only to a limited extent by the method described in Section 88. For an estimation of this possible source of error the measurement of the particle size distribution of the sample is helpful.

### 83. Apparatus

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

83.1.1 *Device for coulometric titration*—preferably with automated registration of CO<sub>2</sub> titration curves (for example, by means of a computer and appropriate software).

83.1.2 *Reaction apparatus for wet-chemical oxidation*—see Fig. 3.

83.1.3 *Heating-block*—adapted to the dimensions of the reaction vessel and suited to heat the reaction vessel to (100 ± 3)°C.

83.1.4 *Analytical balance*—capable of reading to the nearest 0.01 mg.

83.1.5 *Drying cabinet*—capable of maintaining a temperature of (110 ± 5)°C.

### 84. Reagents

84.1 Water complying Grade II of Specification D1193 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.

84.1.1 *Drying reagent*—for example, phosphorus pentoxide, P<sub>2</sub>O<sub>5</sub>.

84.1.2 *Sodium dichromate*—Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> × 2H<sub>2</sub>O.

84.1.3 *Potassium iodate*—KIO<sub>3</sub>.

84.1.4 *Sulfuric acid*—H<sub>2</sub>SO<sub>4</sub>, ρ = 1,84 g/ml, c(H<sub>2</sub>SO<sub>4</sub>) approximately 18 mol/L.

84.1.5 *Inert carrier gas*—Argon Ar, or nitrogen N<sub>2</sub>, purity ≥ 99.99 % v/v.

84.1.6 *Chromic-sulfuric-iodic-acid solution*—prepared by the following procedure: Dissolve 22 g of sodium dichromate (84.1.2) in 300 ml H<sub>2</sub>O. Add carefully 700 ml of sulfuric acid (84.1.4). Heat the solution for 30 min to (150 ± 10)°C. Add 10 g of potassium iodate (84.1.3). After cooling to room temperature, the solution is stored in a glass bottle. **Warning**—Chromic-sulfuric-iodic-acid should be handled with care in accordance with local safety regulations.

84.1.7 *Control sample*—with defined carbon content, for example, CaCO<sub>3</sub> or preferably a certified reference material with composition and free carbon content similar to the sample to be analyzed.

84.1.8 *Aluminium capsules*—for example, diameter = 6 mm, length = 15 mm, prepared from aluminium foil with low carbon content.

### 85. Sample Preparation

85.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried in a drying cabinet at (110 ± 5)°C to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 76—Drying for 2 h is normally sufficient.

85.2 If not otherwise specified between buyer and seller boron carbide powders must have a particle size of ≤32 μm (No. 400 sieve). Shaped or sintered bodies of boron carbide must be crushed to a particle size of ≤32 μm (No. 400 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

### 86. Calibration

86.1 Coulometry is an absolute method which does not require calibration before analysis. However, to ensure the trueness of the analysis result the entire analysis system has to be checked for correct function. This has to be done before and within a measurement series using appropriate control samples (84.1.7).

### 87. Procedure

87.1 *Preparation of Analysis*—Consult the manufacturer's instructions for operation of the coulometric titration device. Set the temperature of the heating block to (100 ± 3)°C. Fill 30 ml chromic-sulfuric-iodic-acid solution into the reaction vessel, connect it to the cooler (see Fig. 3) and insert it into the preheated heating-block. Connect the outlet of the drying trap (see Fig. 3) with a suited plastic-hose to the coulometric titration device. Adjust the carrier gas stream according to the manufacturer's instructions. Coulometric titration devices where the carrier gas is sucked by a pump usually work with a surplus of carrier gas and pressure compensation via a gas-washing bottle. After equilibrating the analysis system for 30 min the analysis is started and the blank value is measured for 10 min. If the blank value does not exceed a specified limit (see manufacturer's instructions), which indicates the gas-tightness of the analysis system, sample analysis can be started.

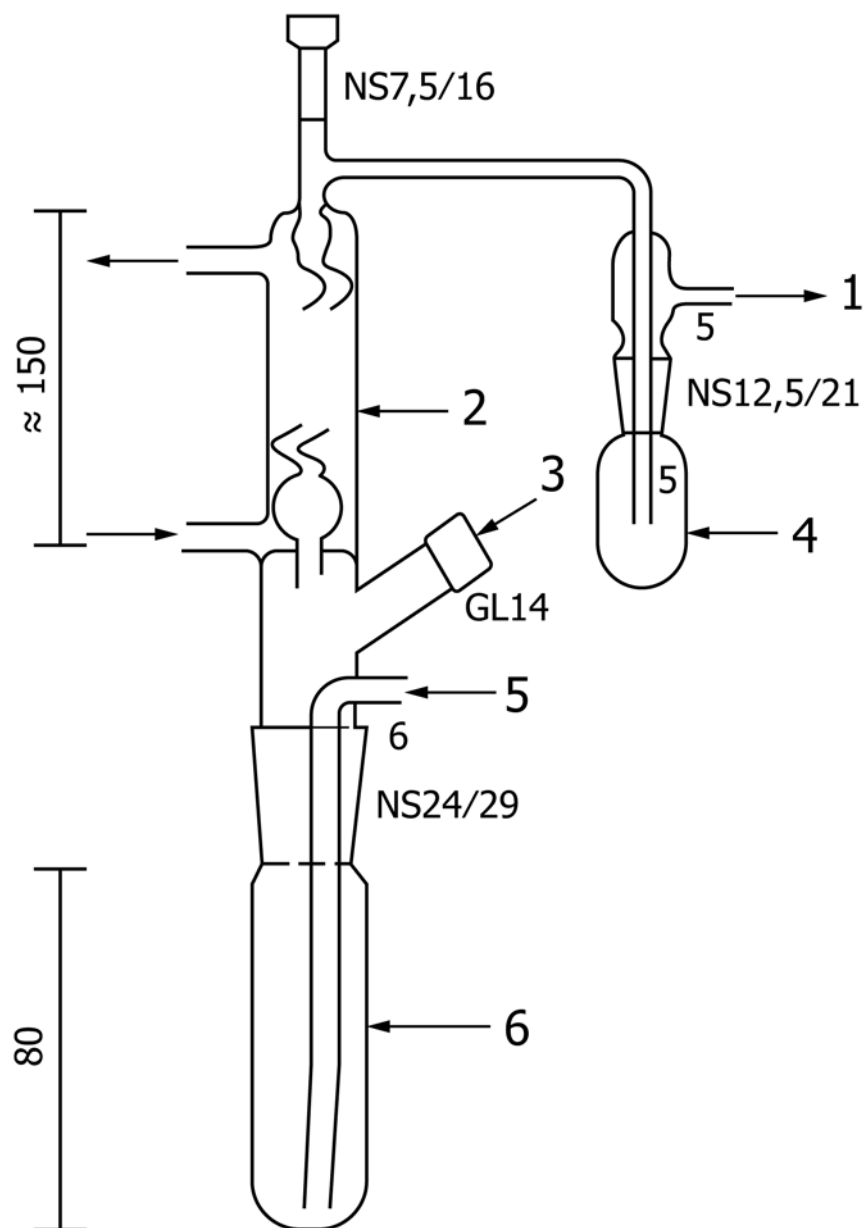
87.2 *Determination of Carbon Content*—Depending on the expected free carbon content a sub-sample of 20 to 100 mg of the sample material prepared in accordance with Section 85 is weighed to the nearest 0.01 mg into an aluminium capsule. Close the capsule using tweezers. Put it into the sample lock (see Fig. 3), drop it into the hot chromic-sulfuric-iodic-acid and start the measurement at the coulometric titration system. The CO<sub>2</sub> titration curve is recorded and used for calculation of free carbon content according to Section 88.

NOTE 77—Depending on the grain size of the boron carbide powder the measurement time varies between 90 min and 120 min.

87.3 Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Section 87. If necessary, the sample has to be homogenized according to Section 85.

### 88. Calculation of Free Carbon Content

88.1 In Fig. 4, the typical development of CO<sub>2</sub> release (presented as carbon mass, C [mg]) during wet-chemical oxidation of boron carbide is given. The slight increase



(Dimensions in mm)

**Key**

- 1 To coulometric titration system
- 2 Cooler
- 3 Sample lock
- 4 Drying trap
- 5 Carrier gas inlet
- 6 Reaction vessel

**FIG. 3 Reaction Apparatus for Wet-Chemical Oxidation of Boron Carbide**

between  $t_0$  (start of measurement) and  $t_1$  (start of reaction of free carbon) is caused by  $\text{CO}_2$  blank in the carrier gas. At  $t_2$ , all free carbon in the sample has reacted to  $\text{CO}_2$ . The mass of carbon measured between  $t_1$  and  $t_2$ , however, also contains carbon originating from carrier gas and oxidation of boron

carbide. To compensate this contribution the increase of carbon mass between  $t_2$  (end of reaction of free carbon) and  $t_3$  (end of measurement) is measured and used to calculate the so called mean drift rate  $C_{\text{Drift}}$ . Under the assumption that between  $t_1$  and  $t_3$  the contribution rate of carbon originating from carrier gas

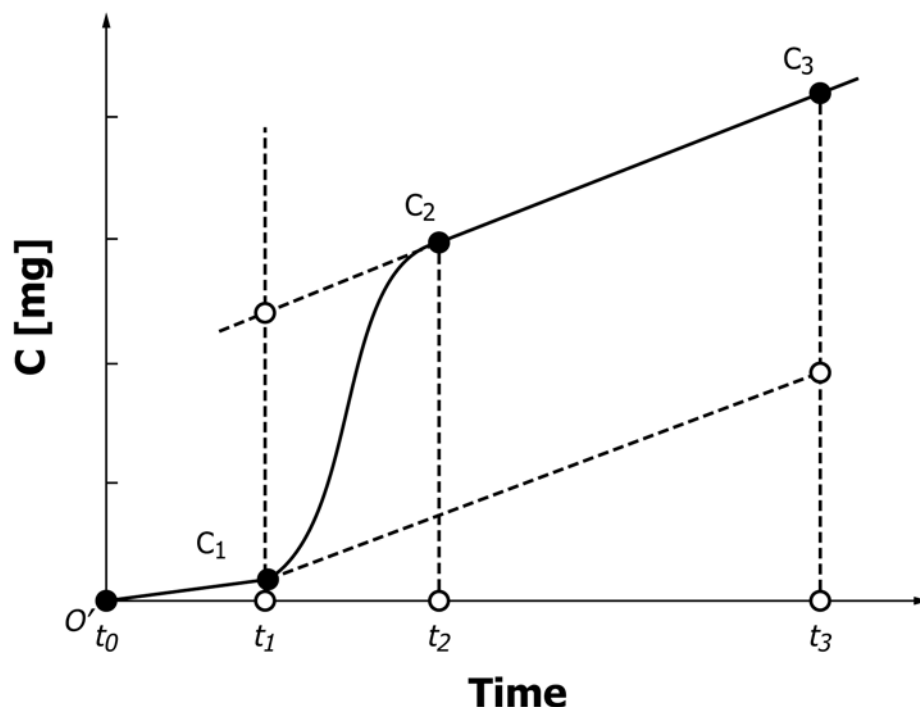


FIG. 4 Evaluation of CO<sub>2</sub> Titration Curve

and oxidation of boron carbide is constant the correct free carbon content of the boron carbide sample is calculated as follows:

$$C_{Drift} = (C_3 - C_2) / (t_3 - t_2) [mg/min] \quad (15)$$

$$m(C_{free}) = (C_2 - C_1) - C_{Drift} (t_2 - t_1) [mg]$$

The free carbon  $w(C_{free})$  of the sample has to be calculated under consideration of sample mass. The free carbon content shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

$$w(C_{free}) = \frac{100 \times m(C_{free})}{m_E} \quad (16)$$

where:

$m(C_{free})$  = drift-rate corrected mass of free carbon, mg, and  
 $m_E$  = sample mass, mg

NOTE 78—Modern coulometric titration systems allow an automated evaluation of the CO<sub>2</sub> titration curve and calculation of mass fraction of free carbon in the sample. The data evaluation of these systems is based on the same principle as described in Section 88.

## 89. Precision and Bias

89.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102 the following precision and bias data were obtained applying the described free carbon method. (See table below.)

Parameter	Free Carbon Method			ERM-ED102, Indicative Value		Bias of Mean of Free Carbon Method to Indicative Value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_R$ , %	Mean, %	Uncertainty, %	
$C_{free}$	0.48	0.04	0.08	0.51	0.12	-5.9



## ANNEX

### (Mandatory Information)

#### A1. Commercial Reference Materials

There are numerous commercial reference materials for a wide spectrum of materials. These reference materials are listed in various databases. A recommended international database is COMAR (COde d'Indexation des MATériaux de Référence).

For the reference materials used for this standard, there should exist as many data as possible for the mass concentrations of main-, minor-, and trace-components. For the following reference material, these data are available: ERM-ED102<sup>5</sup> Boron carbide powder

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