



Designation: ~~C791-04~~ Designation: C791 - 11

# 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 and Gravimetry	7-17
Total Carbon by Combustion in an Inductive Furnace and Infrared Measurement	7-16
Total Boron by Titrimetry	18-28
Total Boron by Titrimetry and ICP OES	17-27
Isotopic Composition by Mass Spectrometry	29-38
Isotopic Composition by Mass Spectrometry	28-32
Chloride and Fluoride Separation by Pyrohydrolysis	39-45
Pyrohydrolysis	33-40
Chloride by Constant Current Coulometry	46-54
Chloride by Constant Current Coulometry	41-49
Fluoride by Ion-Selective Electrode	55-63
Chloride and Fluoride by Ion-Selective Electrode	50-58
Water by Constant Voltage Coulometry	64-72
	Water by Constant Voltage Coulometry and Weight Loss on Drying
	73-81
	Metallic Impurities
Impurities by Spectrochemical Analysis	82-95
Soluble Boron by Titrimetry	65-79
Soluble Boron by Titrimetry and ICP OES	96-105
Soluble Carbon by a Manometric Measurement	96-105
Free Carbon by a Coulometric Method	96-105
Metallic Impurities by a Direct Reader Spectrometric Method	106-114
Metallic Impurities by a Direct Reader Spectrometric Method	106-114
	106-114

## 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](#)

E115 [Practice for Photographic Processing in Optical Emission Spectrographic Analysis](#)

E116 [Practice for Photographic Photometry in Spectrochemical Analysis](#)

E130 [Practice for Designation of Shapes and Sizes of Graphite Electrodes](#) - [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.

Current edition approved July 1, 2004; 2011. Published July 2004; December 2011. Originally approved in 1975. Last previous edition approved in 2000; 2004 as C791-83(2000); C791-04. DOI: 10.1520/C0791-04.10.1520/C0791-11.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at 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 AND GRAVIMETRY~~

#### 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.

#### 8. Summary of Test Method

8.1 ~~The sample mixed with a flux material is burned in an oxygen atmosphere at a temperature not lower than 1400°C. The carbon dioxide product is passed through a gas-treatment train to ensure that any carbon monoxide formed is converted to carbon dioxide and to remove dust, sulfur dioxide, and moisture. The carbon dioxide is absorbed and weighed (1,2).~~

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 *Analytical Balance*, capable of weighing to  $\pm 0.1$  mg.

10.2 *Crucible*, zircon ceramic.

10.3 *Crucible Covers*, porous, ceramic.

10.4 *Mortar*, diamond (Plattner), or boron carbide mortar.

10.5 *Combustion System*—The letters in parentheses refer to the components shown in Fig. 1.

10.5.1 *Induction Furnace (A)*—**Caution:** Contact with the high-frequency induction coil will produce severe electrical shock and may cause burns.

10.5.2 *Combustion Tube (B)*, fused silica.

10.5.3 *Dust Trap (C)*.

<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.

10.5.4 *Catalyst Furnace (D)*.

10.5.5 *Drying Tubes*—The first tube ( $E_1$ ) is filled with magnesium perchlorate and the second tube ( $E_2$ ) is filled with anhydrous calcium sulfate. These tubes prevent water released from the sample from entering the absorption bulb.

10.5.6 *Sulfur Trap (F)*.

10.6 *Gravimetric System*—The letters in parentheses refer to components shown in Fig. 2.

10.6.1 *Nesbitt Absorption Bulb (A)*, may be modified with 12/5 socket joints on both the entrance and exit port. The bulb is filled as shown in Fig. 2.

10.6.2 *Drying Tube (B)*,<sup>12</sup> filled with magnesium perchlorate, anhydrous calcium sulfate, and sodium hydrate-asbestos to prevent any back-diffusion of water and carbon dioxide into the absorption bulb.

10.6.3 *Flowmeter (C)*—The total system has two flowmeters, one located before the furnace (Fig. 3) and one after the absorption bulb (Fig. 2). This arrangement helps to detect leaks in the system.

10.7 *Oxygen Purification System*—The letters in parentheses refer to the components shown in Fig. 3.

10.7.1 *Gas Regulator (A)*, for oxygen.

10.7.2 *Drying Tubes*<sup>11</sup>—The three tubes are filled as follows: the first ( $B_1$ ) with magnesium perchlorate to dry the oxygen; the second ( $B_2$ ) with anhydrous calcium sulfate to indicate when trap  $B_1$  is spent; the third tube ( $B_3$ ) with sodium hydrate-asbestos to remove carbon dioxide.

10.7.3 *Gas Flow-Regulating Valve (C)*.

10.7.4 *Flowmeter (D)*.<sup>16</sup>

10.8 *Sieve*, No. 100 (150- $\mu$ m), U.S. Standard Sieve Series, 3-in. diameter, brass or stainless steel.

## 11. Reagents

11.1 *Calcium Sulfate, Anhydrous*,<sup>12</sup> indicating.

11.2 *Copper*, granules, 30 mesh.

11.3 *Copper*, rings.

11.4 *Cupric Oxide*, reagent grade, used in the catalyst furnace (Fig. 1) to assure that any carbon monoxide formed during combustion is converted to carbon dioxide.

11.5 *Iron*, chips.

11.6 *Magnesium Perchlorate*, anhydrous.

11.7 *Manganese Dioxide*.

11.8

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*, ultra-high purity grade or equivalent.

11.9 *Sodium Hydrate-Asbestos*,<sup>15</sup> 8 to 20 mesh.

11.10 *Tin, Granular*, purity  $\geq 99.998\%$  v/v.

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

## 12. Precautions

12.1 Care should be taken to avoid carbon contamination of reagents and laboratory equipment. Prior to making the initial analysis, condition the furnace tube and absorption bulb by taking a sample from 15.1-15.13 without making any measurements (omit 15.2, for example).

### 13. Sample Preparation

13.1 Crush a pellet with a mortar. *Important:* when using the diamond (Plattner) mortar, crush with a few, light hammer blows. 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.

NOTE1—Do not crush and grind the boron carbide extensively in the diamond mortar because significant iron contamination can occur, which will require an iron correction in the analysis.

13.2 Pass the crushed sample through a metal No. 100 sieve.

13.3 Repeat 13.1 and 13.2 until the whole pellet has passed through the sieve.

13.4 Thoroughly mix the sieved sample.

### 14. Blank

14.1 A blank should be determined at least once in each 8-h shift in which total carbon analyses are made. The long-term average blank less than 1.5% of the long-term average amount of carbon dioxide weighed in the analyses. If any individual blank varies from the long-term average by more than  $\pm 20\%$ , investigate and correct the cause before continuing the analysis of samples. Use the long-term average blank in calculating the concentration of carbon in samples.

### 15. Procedure

15.1 Add 2 g of tin, 3 copper rings (m1.8 g), and 1.2 g of copper granules (30 mesh) to a crucible. 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.

NOTE2—To determine a blank, perform 15.1-15.15, omitting 15.2 and 15.3 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. Note3—Prefiring of the crucibles is recommended to minimize blanks.

NOTE4—These quantities of flux and coupler, including the 3 g of iron chips added in 15.4, have been found satisfactory. Since furnaces may have different power outputs and coupling characteristics, the quantities of flux and coupler and iron chips required may differ among furnaces.

15.2 Weigh the crucible and its contents to  $\pm 0.1 \text{ mg}$ .

15.3 Add 200 mg of sample in powder form to the weighed crucible and reweigh to  $\pm 0.1 \text{ mg}$ .

NOTE5—If a sample is in pellet form, crush to a powder using the procedure given in Section 13

### 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.

15.4 Cover the sample with 3 g of iron chips.

15.5 Cover the crucible with a porous ceramic cover.

15.6 Load the crucible into the induction furnace.

15.7 Purge the crucible and its contents with oxygen for 2 min.

NOTE6—The flow rate of the gas should be about 0.5/min.

15.8 Weigh the closed absorption bulb, using the weighing technique given in 15.16. 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 7—Before taking the initial weight of the absorption bulb, condition it by purging with oxygen for 1 h at 0.5/min.

NOTE 8—*Important*—After obtaining the initial weight of the absorption bulb, do not touch it with the hands until all analyses have been completed. Lintless nylon gloves or their equivalent should be used to handle the absorption bulb.

15.9 Place the absorption bulb into position in the apparatus.

NOTE 9—Use dry (no grease) ball and socket joints. Greased joints add to the problem of reproducing weighings.

15.10 Open the absorption bulb to the system and readjust the oxygen flow to 0.5/min, if necessary.

15.11 Turn on the induction furnace.

NOTE 10—The induction furnace should be preset at its highest grid current setting so that the maximum temperature can be obtained. Follow the manufacturer's recommended procedure for operating the furnace.

15.12 Burn the sample.

NOTE 11—If the combustion is incomplete after 8 min by visual inspection, investigate the flux and coupler conditions to determine conditions that will give complete combustion.

15.13 Turn off the furnace and wait an additional 22 min, allowing the oxygen to continue flowing through the entire system.

15.14 Close the absorption bulb and remove it from the apparatus.

15.15 Weigh the bulb using *exactly* the same technique used in 15.16.6—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.

15.16 *Weighing Absorption Bulb:*

15.16.1 Wipe the *closed* absorption bulb thoroughly and evenly with a moist chamois, being careful not to touch the bulb with the hands.

NOTE 12—Wiping the absorption bulb with a moist chamois minimizes the adverse effects on weighing produced by static charges.

15.16.2 Place the bulb on the balance pan with the balance door open.

NOTE 13—If a single-pan balance with two doors is used, open both doors.

15.16.3 Wait 3 min and close the door.

NOTE 14—Leaving the balance door open decreases the amount of time required for the absorption bulb to come to equilibrium after it has been wiped with the moist chamois. The length of time required to reach equilibrium depends upon the relative humidity in the laboratory.

15.16.4 Weigh the bulb to  $\pm 0.1$  mg.

15.16.5 Repeat 15.16.1-15.16.4 until constant weight ( $\pm 0.1$  mg) is obtained.

## 16.

### 15. Calculation

16.1 Calculate the grams of carbon,  $C$ , weighed as follows:

$$(1) \quad C = [(W_2 - W_1)_s - (W_2 - W_1)_b](0.2729)$$

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:

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

$m_c$

where:  $W_2$

=weight of

$W_1$  = weight of absorption bulb before combustion (15.8);  
 $(W_2 - W_1)/m_c$  = weight of  $\text{CO}_2$  from sample, g, and absolute mass of carbon in the sample, mg;

$W_1$ ;  $m_c$   
 $(W_2 - W_1)/m_{blank}$  = blank measurement.

16.2 Calculate the weight percent of carbon,  $C_a$ , in the sample as follows:

$$(2) \quad C_a = [(S_2 - S_1) \times 100]$$

where: absolute mass of carbon in the blank sample, mg, and  
 $m$  = 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, the following precision and bias data was obtained applying the described total carbon method. (See table below.)

Element	Total Carbon Method			ERM-ED102; certified value		Bias of mean of total carbon method to certified value, % (relative)
	Mean, %	Repeatability $S_r$ , %	Reproducibility $S_{RT}$ , %	Mean, %	Uncertainty, %	
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  $\text{CO}_2$  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.

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

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

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  $10\ \mu\text{l}$

(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 2 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  $200^\circ\text{C}$  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  $200^\circ\text{C}$  for 1 h.

21.1.10 *Sodium Hydroxide Solution*, NaOH,  $c(\text{NaOH}) = 0.1\ \text{mol/L}$ . 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  $750^\circ\text{C}$  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  $600^\circ\text{C}$  in 1 h and then to  $750^\circ\text{C}$  in 1 h and then to  $900^\circ\text{C}$  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  $50^\circ\text{C}$  to  $60^\circ\text{C}$  (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  $\text{CO}_2$ . 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  $\text{CO}_2$ .

### 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  $\text{CO}_2$  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.)

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

where:

$A$  = pH change preceding largest pH change,

$B$  = largest pH change,

$C$  = pH change following largest pH change,

$D$  = increment of titrant used, and

$E$  = millilitres of titrant added at the beginning of the largest pH change.

27.3 *Volume of NaOH Solution Used*—Calculate the volume of NaOH solution as follows:

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:

$$(2) \quad w(B_{total}) = V_{NaOH} \times F \times VS \times q \times 100VA \times mE$$

C0791-11\_2

$V_{NaOH}$  = 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,

$M_{meas}$  =  $T_s$

where: *measured molarity of NaOH used for titration, mol/L,*

$F_s M_{nom}$  = millilitres of NaOH solution used in the titration of the sample, nominal molarity of NaOH used for titration, mol/L,

$Rq$  = reagent blank, titrimetric factor (see Note 15), and

$Nm_E$  = normality of the NaOH solution, sample mass, mg

NOTE 15— $q = 1.0811$  mg boron per ml 0.1 mol/L NaOH solution, for a natural  $^{10}B/^{11}B$  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 was 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, %		
AB	78.42	0.13	0.34	78.47	0.31	=	atomic weight of the boron computed for the sample based upon the measured isotopic composition, and atomic weight of the boron computed for the sample based upon the measured isotopic composition, and
B	78.42	0.13	0.34	78.47	0.31	=	
$W_s$	= sample weight, mg.						
$W_s$	= sample weight, mg.-0.06						

27.6 *Normality of NaOH Solution*—Calculate the normality of the sodium hydroxide solution as follows:

E0791-04\_7

where:

$CM$

where:

$N_{CM}$  = normality of the NaOH solution, measured boron concentration in sample solution (26.2), corrected by blank value, mg/L,

$W_s V_s$  = milligrams of the NBS standard titrated, volume of solution after sample decomposition (24.4), ml,

$F_d$  = millilitres of NaOH solution used in the titration of the standard, and dilution factor (see 26.2), and

$M_{mE}$  = molecular weight of the boric acid, sample mass, mg

28.

## 27. Precision and Bias

28.1 *Precision*—The standard deviation is 0.05 mass %

28.2 *Accuracy*—No bias can be established because no material traceable to a national standards base is available

27.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data was 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 $S_B$ , %	Mean, %	Uncertainty, %	
B	78.70	0.61	0.63	78.47	0.31	±0.29

## ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

29.

## 28. Scope

29.1 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.

## 30.29. Summary of Method

30.1 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), (11,12,13).

31.

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.

## 32.31. Apparatus Isotopic Composition by TIMS

32.1.1 *Apparatus:*

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

32.1.1

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

32.1.2

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  $M-1$ .

32.1.3

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.

32.2

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

32.2.1

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.

32.2.2

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.

32.2.3

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.

32.2.4

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.

32.3

31.1.3 Mixer Mill.

32.4<sup>5</sup>

31.1.4 Plastic Pipet, 5- $\mu$ l, with a changeable plastic barrel.<sup>6</sup> Use a pipet only once and then discard it.

32.5

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.

### 33.Reagents

33.1

31.2 Reagents:

31.2.1 Acetone.

33.2

31.2.2 Distilled Water.

33.3

31.2.3 Isopropyl Alcohol.

33.4

31.2.4 Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>) Solution, 0.14 M.

33.5

31.2.5 Sodium Hydroxide (NaOH)—Pulverize in stainless steel containers with stainless steel balls in a mixer mill and store in a desiccator.

33.6

31.2.6 Toluene. **34.Precautions**

**34.1 Consideration**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

**(108)**. 35:

31.4 Calibration

35.1 Periodic—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 3three months. 36:

31.5 Procedure:

36.1

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

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

361.5.1.2 Rinse the assembly twice with acetone.

361.5.1.3 Dry the assembly under a heat lamp.

36.2.1-36.2.5 31.5.2.1-31.5.2.5 are instructions for fusing the sample with NaOH and 36.2.6-36.2.9-31.5.2.6-31.5.2.9 are instructions for an alternative fusion with Na<sub>2</sub>CO<sub>3</sub>.

36.2.1

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

NOTE26—For 20—For pellet samples, crush to a powder using the procedure in Section 4312. 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.

NOTE27—To 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.

<sup>5</sup> Leco No. 528-035 or equivalent.

<sup>5</sup> A Spex Industries mixer mill, Model 5100, has been used for this method.

<sup>6</sup> Leco No. 528-042 or equivalent.

<sup>6</sup> A Kimble automatic pipet, No. 56300, with disposable polypropylene tips has been used for this method.