



Designation: C791 – 19

Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Boron Carbide¹

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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 values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 The analytical procedures appear in the following order:

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1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ 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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2. Referenced Documents

2.1 *ASTM Standards*:²

C750 Specification for Nuclear-Grade Boron Carbide Powder

C751 Specification for Nuclear-Grade Boron Carbide Pellets

C859 Terminology Relating to Nuclear Materials

C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials

D1193 Specification for Reagent Water

E969 Specification for Glass Volumetric (Transfer) Pipets

3. Terminology

3.1 *Definitions*—For definitions of terms relating to nuclear materials, refer to Terminology C859.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *analyte*—the constituent determined by a chemical measurement process.

3.2.2 *analytical or emission line*—the particular wavelength of electromagnetic radiation used in determining the presence or concentration of an element.

3.2.3 *background*—spectral intensity that would be measured at the wavelength of the emission line if the emission and overlapping lines were not present.

3.2.4 *calibration*—the act, process, or result of establishing the relationship between the response of an instrument and the amount of analyte present.

3.2.5 *calibration function*—the graphical or mathematical representation of the relationship between the response of an instrument and the concentration or mass of the analyte.

3.2.6 *calibration samples or solutions*—samples or solutions with known analyte contents or analyte concentrations, respectively, to establish the relationship between the response of an instrument and the amount of analyte.

² 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.

3.2.7 *certified reference material (CRM)*—a reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

3.2.8 *DCArc OES*—optical emission spectrometry (OES) with direct current arc (DCArc) as excitation source.

3.2.9 *drift correction*—the process of adjusting for a shift of an instrument calibration.

3.2.10 *ICP MS*—mass spectrometry (MS) with inductively coupled plasma (ICP) as ionization source.

3.2.11 *ICP OES*—optical emission spectrometry (OES) with inductively coupled plasma (ICP) as excitation source.

3.2.12 *interlaboratory study (ILS)*—a study undertaken to demonstrate the precision and bias of a test method.

3.2.13 *internal standard*—a material present in or added to test samples that serves as an intensity reference for spectral measurements.

3.2.14 *matrix*—all components of a material except the analyte.

3.2.15 *matrix matching*—adjustment of the composition of calibration samples or solutions to match the composition of the matrix.

3.2.16 *method*—instructions used to produce a numerical result, which are detailed in a document referred to as “the method.”

3.2.17 *nebulizer*—a device for converting a sample solution into a gas-liquid aerosol for ICP OES.

3.2.18 *optical emission spectrometry (OES)*—pertaining to emission spectrometry in the ultraviolet, visible, or infrared wavelength regions of the electromagnetic spectrum.

3.2.19 *repeatability, S_r* —the standard deviation of results collected using the same method on the same material in the same laboratory on different days.

3.2.20 *reproducibility, S_R* —the standard deviation of results obtained on the same material using the same method in different laboratories.

3.2.21 *sample*—a portion of a material selected and processed to render its composition representative of the composition of the whole.

3.2.22 *sensitivity*—the change of instrument response with change in analyte concentration.

3.2.23 *standardization*—the experimental establishment of the concentration of a reagent solution.

3.2.24 *TIMS*—thermal ionization mass spectrometry.

4. Significance and Use

4.1 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**.

4.1.1 An assay is performed to determine whether the material has the specified boron and carbon content.

4.1.2 Determination of the isotopic content of the boron and the free carbon content is made to establish whether the content is in compliance with the purchaser’s specifications.

4.1.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurities (chloride, fluoride, water, metallic impurities, soluble boron) is not exceeded.

5. Reagents

5.1 *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.³ 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.

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

6. Safety Precautions

6.1 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.

7. Sampling

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

TOTAL CARBON BY COMBUSTION IN AN INDUCTIVE FURNACE AND INFRARED MEASUREMENT

8. Scope

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

9. Summary of Test Method

9.1 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

³ *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.

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 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.

10. Interferences

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

11. Apparatus

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

11.1.1 *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.

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

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

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

12. Reagents

12.1 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.

12.1.1 *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.

12.1.2 *Iron granules*.

12.1.3 *Calibration and control 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 (for example, calcium carbonate, CaCO_3). When certified reference materials are not available, consider Guide C1128 for preparation of working reference materials.

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

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

13. Sampling and Sample Preparation

13.1 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.

13.2 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.

14. Calibration

14.1 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 (12.1.3) and test sample are within the same order of magnitude.

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

14.2 The calibration has to be done according to Section 15.

15. Procedure

15.1 *Preparation of Analysis*—Ceramic crucibles (11.1.3) and crucible lids (11.1.4) have to be cleaned prior to use by firing in a muffle furnace at 1200°C for 1 h. After that, they have to be stored in a desiccator.

15.2 *Determination of Blank Value (Method Blank)*—The same procedure according to 15.4 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.

15.3 *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 15.4 has to be applied, however only adding a small amount of boron carbide (that is, a spatula-tip of boron carbide).

15.4 *Determination of Carbon Content*—A sub-sample of 20 to 30 mg of boron carbide powder prepared in accordance to Section 12 is weighed to the nearest 0.01 mg into the ceramic crucibles (11.1.3) cleaned according to section 15.1.

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 (12.1.1 and 12.1.2), respectively. For mixing, the crucible has to be shaken carefully. Afterwards, the crucible is closed with the lid (11.1.4), 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.

To ensure correctness of results and to detect measurement drift a control sample (12.1.3) shall be measured within and at the end of the measurement series.

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 15. If necessary, the sample has to be homogenized according to Section 13.

16. Calculation

16.1 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 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 6—Most state of the art analyzers automatically calculate the mass fraction of carbon for each measurement after input of blank values and sample masses.

17. Precision and Bias (1)⁴

NOTE 7—Please see Ref (2) for all precision and bias statements, except those denoted by Ref (3).

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

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

⁵ 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	Total Carbon Method		ERM-ED102, certified value	ERM-ED102, certified value		Bias of mean of total carbon method to certified value, % (relative)
	Mean, %	Repeatability S_r , %		Mean, %	Uncertainty, %	
C	21.06	0.07	21.01	0.28	+0.24	

TOTAL BORON BY TITRIMETRY AND ICP OES

18. Scope

18.1 This method covers the determination of total boron in samples of boron carbide powder and pellets by titrimetry and ICP OES.

19. Summary of Method

19.1 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 8—Sodium carbonate or a mixture of sodium carbonate and potassium carbonate (1:1) is normally used as alkaline reagent to decompose the boron carbide.

20. Interferences

20.1 *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 CO₂ shall be removed by heating the sample solution or by purging the sample solution with nitrogen.

20.2 *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 inter-

ferences) 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.

21. Apparatus

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

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

21.1.2 *Burner*, Bunsen type.

21.1.3 *Hand torch*, with gas-cartridge.

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

21.1.5 *Muffle Furnace*, with temperature programmer and controllable to ±20°C between 700°C and 900°C.

21.1.6 *pH Meter*.

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

21.1.8 *Glass volumetric pipet*, 50 mL, Class A, according to Specification E969.

21.1.9 *Titration system*, consisting of:

(1) pH-electrode

(2) dosage apparatus for liquids with a resolution of 10 µL

(3) stirrer

(4) unit for recording the titration curve

21.1.10 *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.

22. Reagents

22.1 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.

22.1.1 *Barium Carbonate*, BaCO₃.

22.1.2 *Hydrochloric Acid*, HCl, concentrated (sp gr 1.19), *c*(HCl) approximately 10 mol/L.

22.1.3 *Hydrochloric Acid*, HCl, 1:1, *c*(HCl) approximately 5 mol/L.

22.1.4 *Mannitol*, C₆H₁₄O₆, or *Mannitol Solution*, with a concentration of 100 g/L.

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

22.1.6 *Primary Substances for Determination of Molarity of NaOH Solution*, for example, potassiumhydrogenphthalate, C₈H₅KO₄, or boric acid, H₃BO₃, (NBS SRM 951 or its replacement).

22.1.7 *Potassium Nitrate*, KNO₃.

22.1.8 *Sodium Carbonate*, Na₂CO₃, dried at 200°C for 1 h.

22.1.9 *Sodium/Potassium Carbonate Mixture*, Na₂CO₃/K₂CO₃ 1:1 m/m, dried at 200°C for 1 h.

22.1.10 *Sodium Hydroxide Solution*, NaOH, *c*(NaOH) = 0.1 mol/L. This solution must be carbonate-free.

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

22.1.12 *Nitrogen*, purity ≥ 99.99 % v/v.

23. Precautions

23.1 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.

24. Sampling and Sample Preparation

24.1 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 ± 5)°C to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 9—Drying for 2 h is normally sufficient.

The sample material must have a particle size of ≤150 μm (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.

25. Procedure

25.1 *Preparation of Analysis*—A sub-sample of 100 mg of boron carbide powder prepared in accordance to Section 24 is weighed to the nearest 0.01 mg into the platinum crucible and mixed with approximately 3 g Na₂CO₃/K₂CO₃ using a microspatula. The mixture is covered with approximately 2 g Na₂CO₃/K₂CO₃ and the platinum lid is placed on the crucible. Continue with fusion procedures 25.2 or 25.3.

NOTE 10—Instead of sodium/potassium carbonate mixture, sodium carbonate can also be used for boron carbide decomposition.

25.2 Muffle furnace/Bunsen burner fusion procedure:

25.2.1 *Using Na₂CO₃/K₂CO₃*—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.

25.2.2 *Using Na₂CO₃*—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.

25.2.3 Add 20 mg to 30 mg of KNO₃ 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 25.2.3. Continue with 25.4.

25.3 *Bunsen Burner Fusion Procedure*—If this fusion technique is used, KNO₃ 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 25.4.

NOTE 11—Procedure 25.3 works with both Na₂CO₃/K₂CO₃ and Na₂CO₃.

If fusion procedures 25.2 and 25.3 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 25.2 and 25.3 the following modified Bunsen burner procedure has to be applied:

Use Na₂CO₃/K₂CO₃ for sample decomposition. Heat the mixture in the platinum crucible carefully with a low flame just above the melting point of Na₂CO₃/K₂CO₃ and hold this temperature until, after a few minutes, a clear melt is obtained. Continue with section 25.4.

25.4 *Dissolution Procedure*—Place crucible and lid in a beaker. Add 50 mL of hydrochloric acid (22.1.3). 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 used for titrimetric (Section 26) determination of boron or, if metallic impurities in high concentrations are present in the solution (Section 20), for barium carbonate precipitation (25.5). The solution can directly be used for ICP OES determination of boron (Section 27).

25.5 Barium Carbonate Separation—Pipet a 50 mL aliquot (21.1.8) of the sample solution obtained by procedure 25.4 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 (22.1.11) using a pH meter. Add 1.5 mL of hydrochloric acid (22.1.2). 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 (22.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO₂. Continue with section 26.2.

26. Titrimetric Determination of Boron

26.1 Preparation of Analysis:

26.1.1 Pipet a 50 mL aliquot (21.1.8) of the sample solution obtained by procedure 25.4 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 (22.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO₂.

26.2 Titration:

26.2.1 Using the titration-system, the solution is titrated to the first inflection point with 0.1 mol/L NaOH (22.1.10). Then 35 mL of a mannitol-solution (22.1.4) 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 26.3). To avoid interferences by CO₂ the sample solution must be purged with nitrogen during titration.

NOTE 12—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 (25.5). Once mannitol has been added at 26.2, the titrated solution can not be salvaged and a new sample must be started.

26.2.2 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 25 and 26. If necessary, the sample has to be homogenized according to Section 24. The method blank has to be determined applying the same procedure as described in Sections 25 and 26 (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.

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

26.3.1 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.

26.4 Calibration:

26.4.1 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 (22.1.5). 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 (22.1.6), 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 13—See Annex A1 for commercial reference materials.

26.5 Calculation:

26.5.1 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 blank 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 14), and
m_E	= sample mass, mg

NOTE 14— $q = 1.0811$ mg boron per mL 0.1 mol/L NaOH solution, for a natural $^{10}\text{B}/^{11}\text{B}$ isotopic ratio.

26.6 *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

27. ICP OES

27.1 *General Comments*—The sample solution obtained in 25.4 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.

27.2 *Preparation of Sample Solution*—Assuming a total boron content of 78 % m/m the sample solution obtained in 25.4 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 Na_2CO_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 25.4 in a 100 mL volumetric flask. Fill up to volume with water. This solution is then analyzed by ICP OES.

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

27.4 *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 Na_2CO_3 (depending on the matrix of solution 25.4) into a 250 mL volumetric flask. Add approximately 100 mL of water and 50 mL of hydrochloric acid (22.1.3) and wait until the carbonate has dissolved. Degass the solution in an ultrasonic bath and fill up to volume with water.

27.5 *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 (so called "bracket calibration"). 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 15—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 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 27.4 is required.

NOTE 16—Assuming a total boron content around 78 % m/m, preparation of the sample solution according to 27.2 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 27.4 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 27.4 and 3.5 mL of boron 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 27.4 and 3 mL of boron standard solution into a 100 mL volumetric flask and fill up to volume. Resulting boron concentration: 30 mg/L.

27.6 *Procedure*—The sample solution obtained in 27.2 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 17—For example: each sample solution of the measurement series is measured with three replicates and the measurement series is repeated three times.

NOTE 18—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 25 and 27. If necessary, the sample has to be homogenized according to Section 24. The method blank has to be determined applying the same procedures as described in Sections 25 and 27, however, without addition of boron carbide. If a measurable method blank is detected, the single values have to be corrected by the method blank.

27.7 *Calculation*—The total boron content $w(B_{\text{total}})$ of the sample has to be calculated under consideration of sample mass, dilution factor and blank values. The boron content as mean of the blank 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 (27.2), corrected by blank value, mg/L,

V_S = volume of solution after sample decomposition (25.4), mL,

f = dilution factor (see 27.2), and

m_E = sample mass, mg

28. Precision and Bias

28.1 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	Uncertainty, %	Bias of mean of ICP OES total boron method to certified value, % (relative)
	Mean, %	Repeatability S_r , %	Reproducibility S_R , %			
B	78.70	0.61	0.63	78.47	0.31	+0.29

ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

29. 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. 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 Na_2BO_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}B (6), (7), (8), (9), (10), (11).

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

31. Interferences

31.1 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. Isotopic Composition by TIMS

32.1 Apparatus:

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

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

32.1.1.2 *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 ΔM 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 $M-1$.

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

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

32.1.2.1 *Filaments*, tantalum ribbon, nominally 0.25 m (0.001 in.) thick, 0.75 mm (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.

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

32.1.2.3 *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.

32.1.2.4 *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.

32.1.3 *Mixer Mill*.⁶

32.1.4 *Plastic Pipet*, 5- μL , with a changeable plastic barrel.⁷ Use a pipet tip only once and then discard it.

32.1.5 *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.

32.2 Reagents:

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

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

32.2.1 *Acetone*.

32.2.2 *Water*, complying Grade II of Specification **D1193**.

32.2.3 *Isopropyl Alcohol*.

32.2.4 *Sodium Carbonate* (Na_2CO_3) *Solution*, 0.14 M.

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

32.2.6 *Toluene*.

32.3 *Precautions*—Consideration should be given to boron contamination from reagents and other sources. Sources of natural boron contamination can be checked by using NBS¹⁰ B-enriched boric acid (SRM 952 or alternate) as an internal standard (**8**).

32.4 *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.

32.5 *Procedure*:

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

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

32.5.1.2 Rinse the assembly twice with acetone.

32.5.1.3 Dry the assembly under a heat lamp.

32.5.2 *Filament Loading*—Steps **32.5.2.1** – **32.5.2.5** are instructions for fusing the sample with NaOH and **32.5.2.6** – **32.5.2.9** are instructions for an alternative fusion with Na_2CO_3 .

32.5.2.1 Weigh 25 ± 2 mg of sample in powder form and transfer it to a plastic vial. To obtain a representative sample if the original sample is in powdered form, thoroughly blend the bulk sample before taking the 25-mg aliquot. For pellet samples, crush to a powder using the procedure in Section **13**. 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 19—A quantitative transfer is not required because isotopic ratios only are being determined.

32.5.2.2 Add 72 ± 2 mg of pulverized NaOH from the desiccator to the vial containing the sample.

32.5.2.3 Add a plastic ball and immediately close the vial. Avoid atmospheric moisture pickup; moisture interferes with good mixing.

32.5.2.4 Mix for 1 min on the mixer mill.

32.5.2.5 Transfer about 0.1 mg of the mixture to a filament. Proceed to **32.5.2.10** for the fusion.

32.5.2.6 Weigh 5 ± 0.2 mg of sample in powder form and transfer it to a plastic vial.

32.5.2.7 Add 1.25 mL of 0.14 M Na_2CO_3 solution to the vial containing the sample.

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

32.5.2.9 Transfer about 5 μL of the slurry to a filament. Proceed to **32.5.2.10** for the fusion.

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

NOTE 20—The bright glow is caused by the exothermic reaction of tantalum with NaOH or Na_2CO_3 . The fusion produces sodium borate and the melt tightly adheres to the filament.

32.5.3 *Mass Spectrometric Measurement*:

32.5.3.1 Insert the filament assembly into the mass spectrometer.

32.5.3.2 Evacuate the system to about 66 μPa (5×10^{-7} torr).

32.5.3.3 Heat the sample by passing an electrical current through the filament until a stable beam of Na_2BO_2^+ ions is obtained.

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

32.6 *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 ¹⁷O. Then correct the ratio for mass bias.

32.7 *Precision and Accuracy*:

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

32.7.2 *Bias*—The average percent recovery obtained from 10 analyses of boron carbide control standards over a two-year period was 100.1 %. Those standards were prepared and certified by LASL (**2**).

33. Isotopic Composition by ICP MS

33.1 *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.

33.2 *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 **40** is dissolved in water, acidified and measured by ICP-MS.

33.3 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 951a) 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.

33.4 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. If necessary, the sample has to be homogenized according to Section 13.

33.5 *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}B	19.910	0.027	0.031	19.907	0.014	+0.016

PYROHYDROLYSIS

34. Scope

34.1 This method covers the separation of up to 100 μg 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.

35. Summary of Method

35.1 A stream of moist gas is passed over a mixture of powdered sample and U_3O_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).

36. Interferences

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

37. Apparatus

(See Fig. 2.)

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

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

37.3 *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.

37.4 *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.

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

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

37.7 *Mixer Mill*.

38. Reagents

38.1 *Accelerator*, U_3O_8 or sodium tungstate with tungsten trioxide:

38.1.1 U_3O_8 , powdered, <1 μg 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.

38.1.2 *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.

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

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

38.4 *Water*, complying Grade II of Specification D1193, chloride- and fluoride-free, <0.1 $\mu\text{g/g}$.

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

39. Precautions

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

40. Procedure

40.1 Prepare a sample and reagent blank as follows:

40.1.1 Crush pellet samples to a powder using the procedure in Section 13. If the pyrohydrolysis is done with oxygen, continue with 40.1.6.

40.1.2 Line two sample boats with 3 g of U_3O_8 .

40.1.3 Weigh 1 to 2 g of powdered sample to ± 0.01 g and mix thoroughly with 3 g of U_3O_8 accelerator in a mixer mill.

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