



Designation: C791 – 04

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 analytical procedures appear in the following order:

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Total Carbon by Combustion and Gravimetry	7-17
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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

D1193 Specification for Reagent Water

E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis³

E116 Practice for Photographic Photometry in Spectrochemical Analysis³

E130 Practice for Designation of Shapes and Sizes of Graphite Electrodes

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 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³ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

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.

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.⁴ 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.

⁴ *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.

6. Sampling

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

TOTAL CARBON BY COMBUSTION AND GRAVIMETRY

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**).⁵

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 ± 0.1 mg.
 10.2 *Crucible*, zircon ceramic.⁶
 10.3 *Crucible Covers*, porous, ceramic.⁷
 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)*⁸—**Caution:** Contact with the high-frequency induction coil will produce severe electrical shock and may cause burns.
 10.5.2 *Combustion Tube (B)*,⁹ fused silica.
 10.5.3 *Dust Trap (C)*.¹⁰
 10.5.4 *Catalyst Furnace (D)*.¹¹
 10.5.5 *Drying Tubes*¹²—The first tube (E_1) is filled with magnesium perchlorate and the second tube (E_2) is filled with anhydrous calcium sulfate.¹³ These tubes prevent water released from the sample from entering the absorption bulb.
 10.5.6 *Sulfur Trap (F)*.¹⁴
 10.6 *Gravimetric System*—The letters in parentheses refer to components shown in **Fig. 2**.
 10.6.1 *Nesbitt Absorption Bulb (A)*,¹⁵ may be modified with 12/5 socket joints on both the entrance and exit port. The bulb is filled as shown in **Fig. 2**.

⁵ The boldface numbers in parentheses refer to the list of references appended to these methods.

⁶ Leco No. 528–035 or equivalent.

⁷ Leco No. 528–042 or equivalent.

⁸ Leco No. 521–000 or equivalent.

⁹ Leco No. 550–122 or equivalent.

¹⁰ Leco No. 501–010 or equivalent.

¹¹ Leco No. 507–000 or equivalent.

¹² Kimble No. 46010 or equivalent.

¹³ Drierite has been found satisfactory for this purpose.

¹⁴ Leco No. 503–033 or equivalent.

¹⁵ Kimble No. 16010 or equivalent.

10.6.2 *Drying Tube (B)*,¹³ filled with magnesium perchlorate, anhydrous calcium sulfate, and sodium hydrate-asbestos¹⁶ to prevent any back-diffusion of water and carbon dioxide into the absorption bulb.

10.6.3 *Flowmeter (C)*¹⁷—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*¹²—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)*.¹⁸

10.7.4 *Flowmeter (D)*.¹⁷

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

11. Reagents

- 11.1 *Calcium Sulfate, Anhydrous*,¹³ indicating.
 11.2 *Copper*, granules, 30 mesh.
 11.3 *Copper*, rings.¹⁹
 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.²⁰
 11.6 *Magnesium Perchlorate*, anhydrous.
 11.7 *Manganese Dioxide*.²¹
 11.8 *Oxygen*, ultra high purity grade or equivalent.²²
 11.9 *Sodium Hydrate-Asbestos*,¹⁶ 8 to 20 mesh.
 11.10 *Tin*, Granular.²³

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.

NOTE 1—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.

¹⁶ Ascarite has been found satisfactory for this purpose.

¹⁷ Manostat No. 1044B or equivalent.

¹⁸ Matheson No. 32 or equivalent.

¹⁹ Leco No. 550–184 or equivalent.

²⁰ Leco No. 501–077 or equivalent.

²¹ Leco No. 501–060 or equivalent.

²² *Matheson Gas Data Book*, The Matheson Co. Inc., East Rutherford, N. J., Fourth Edition, 1966.

²³ Leco No. 501-076 or equivalent.

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 ± 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.

NOTE 2—To determine a blank, perform 15.1-15.15, omitting 15.2 and 15.3.

NOTE 3—Prefiring of the crucibles is recommended to minimize blanks.

NOTE 4—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 ± 0.1 mg.

15.3 Add 200 mg of sample in powder form to the weighed crucible and reweigh to ± 0.1 mg.

NOTE 5—If a sample is in pellet form, crush to a powder using the procedure given in Section 13.

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.

NOTE 6—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.

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.

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 ± 0.1 mg.

15.16.5 Repeat 15.16.1-15.16.4 until constant weight (± 0.1 mg) is obtained.

16. Calculation

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

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

where:

W_2 = weight of absorption bulb after combustion (15.15),

W_1 = weight of absorption bulb before combustion (15.8),

$(W_2 - W_1)_s$ = weight of CO₂ from sample, g, and

$(W_2 - W_1)_b$ = blank measurement.

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

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

where:

C = amount of carbon weighed from the sample, g,

S_2 = weight of crucible plus sample (15.3), g, and

S_1 = weight of crucible (15.2), g.

17. Precision and Bias (3)

NOTE 15—Please see Ref (4) for all precision and bias statements, except those denoted by Ref (5).

17.1 *Precision*—The standard deviation is 0.14 mass %.

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

TOTAL BORON BY TITRIMETRY

18. Scope

18.1 This method covers the determination of total boron in samples of boron carbide powder and pellets. The recommended amount of boron for each titration is 100 ± 10 mg.

19. Summary of Method

19.1 Powdered boron carbide is mixed with sodium carbonate and this mixture is fused to decompose the boron carbide. The melt is dissolved in water, filtered to remove the insoluble residue, acidified, and heated to remove carbon dioxide. The boron as boric acid is titrated with standardized sodium hydroxide solution, using the mannitoboric acid procedure (5,6,7).

20. Interferences

20.1 Metals that form hydrous oxides may distort the end point of the titration.

21. Apparatus

21.1 *Balance*, analytical, with a sensitivity of at least 0.05 mg.

21.2 *Beakers*, 400 and 600-mL, low-boron glass.

21.3 *Burners*, bunsen and Meker (alternative to muffle furnace).

21.4 *Combination Electrode*, glass-calomel.

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

21.6 *Muffle Furnace*, capable of maintaining a temperature of at least 1000°C .

21.7 *pH Meter*.

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

21.9 *Polyethylene Funnel*.

21.10 *Recording Titrator*, capable of a precision of titration of 100 ng of boron of at least 0.15 %.

21.11 *Temperature Programmer*, used with muffle furnace (optional).

22. Reagents

22.1 Avoid purchasing reagents contained in glass to eliminate a possible source of boron contamination. Store reagents in plastic containers.

22.2 *Barium Carbonate*, powdered.

22.3 *Boric Acid*, NBS SRM 951 or its replacement.

22.4 *Hydrochloric Acid*, concentrated (sp gr 1.19).

22.5 *Methyl Red Solution*. Dissolve 0.1 g in 100 mL of 60 % ethyl alcohol and dilute to 250 mL with 60 % alcohol.

22.6 *Nitric Acid*, concentrated (sp gr 1.42).

22.7 *Nitric Acid (1 M)*—Add 32 mL of concentrated HNO_3 to 400 mL of water and dilute to 500 mL.

22.8 *Nitric Acid (0.1 M)*—Pipet 50 mL of 1 N HNO_3 into a 500-mL flask and dilute to volume with water.

22.9 *Potassium Nitrate*, crystals.

22.10 *Sodium Carbonate*, powder.

22.11 *Sodium Hydroxide Solution (0.25 N)*, standardized against NBS SRM 951. This solution should be carbonate-free.

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 lowboron glassware is used, boron contamination should be negligible.

23.2 The periodic determination of a blank to check for boron contamination is advisable, particularly whenever a new bottle of any reagent is used. Titrating reagents alone does not give a true blank, however (5). A given amount of boric acid should be titrated with and without reagents; the difference, if any, represents the true blank.

24. Standardization of Titrant

24.1 Standardize the 0.25 N NaOH solution by dissolving 560 to 700 mg of boric acid standard weighed to ± 0.1 mg in 100 mL of cooled, freshly boiled water. Adjust the pH to 3 with 1 M HNO_3 and titrate with the 0.25 N NaOH solution, beginning at 26.2.1.

24.2 Calculate the normality of the NaOH solution as described in 27.6.1.

25. Blank

25.1 Add 2 g of sodium carbonate to a 30-mL platinum crucible.

25.2 Take this crucible through the analysis, starting at 26.2 and omitting 26.4 and 26.5.

25.3 Calculate the reagent blank as described in 27.4.

26. Procedure

26.1 *Sample Preparation*:

26.1.1 Add 2 g of sodium carbonate to a 30-mL platinum crucible. Allow it to equilibrate with room atmosphere until constant weight is obtained.

26.1.2 Weigh into the crucible from 0.13 to 0.15 g of sample in powder form, weighed to the nearest 0.05 mg.

NOTE 16—See Section 11 for instructions on crushing pellets into powder.

26.1.3 Weigh into the crucible 100 ± 10 mg of potassium nitrate.

NOTE 17—Omit this step if the sample is to be fused using a burner (26.3).

26.1.4 Thoroughly mix the materials in the crucible with a small-diameter plastic rod or a short length of wire.

26.1.5 Add an additional 2 g of sodium carbonate to the crucible, covering the mixture completely.

NOTE 18—The sample is ready for fusion by using either a muffle furnace (26.2) or burner (26.3).

26.2 *Fusion by Muffle Furnace*:

26.2.1 Place a lid on the crucible and put it in the muffle furnace.

26.2.2 Do one of the following steps if a programmable furnace is used:

26.2.2.1 Use a $150^{\circ}\text{C}/\text{h}$ heating rate until 900°C is reached; hold 900°C for 2 h and remove the crucible immediately, letting it cool to room temperature.

26.2.2.2 Increase the temperature to 1000°C using the 150°C/h heating rate and hold at 1000°C for 20 min; remove the crucible immediately and let it cool to room temperature.

26.2.3 Do the following steps if a manually controlled (nonprogrammable electronic control) furnace is used:

26.2.3.1 Preheat the furnace to 300°C before putting in the crucible.

26.2.3.2 Reset the temperature controller to 600°C and let the temperature reach 600°C.

26.2.3.3 Increase the temperature 50°C every 20 min until 1000°C is reached and keep the crucible at this temperature for 20 min.

26.2.3.4 Remove the crucible immediately and let it cool to room temperature.

26.2.4 Proceed to 26.4.1.

26.3 *Fusion by Burner:*

26.3.1 If this fusion technique is used, potassium nitrate is not needed and 26.1.3 can be omitted.

26.3.2 Place a lid on the crucible and heat with a low flame of a bunsen burner for 15 min.

26.3.3 Continue heating for another 75 min while gradually increasing the temperature for the flame until the mixture is completely molten.

26.3.4 Replace the bunsen flame with a full Meker flame and continue heating until decomposition of the boron carbide is completed. Most samples require about 20 min for dissolution.

26.3.5 Allow the melt to cool to room temperature.

26.4 *Titration of Boron:*

26.4.1 This subsection includes a precipitation of hydrolyzable metals from a basic solution containing sodium carbonate. This separation is adequate for boron carbides having metallic impurity contents no greater than those found in most nuclear-grade materials. For “dirtier” boron carbide, precipitation using barium carbonate provides a better separation (26.5). For the sodium carbonate separation, proceed as follows:

26.4.2 Place the crucible and lid into a 400-mL, low-boron glass beaker and add enough water to cover the crucible and lid.

26.4.3 Allow the melt to dissolve. Use heat and stirring to reduce the time required for dissolution.

NOTE 19—An alternative approach is to let the melt dissolve overnight while the beaker sits in a warm location. If this is done, go from 26.4.4-26.4.6, omitting 26.4.5.

26.4.4 Remove the crucible and lid from the beaker; rinse both carefully with water, adding the rinse to the beaker.

26.4.5 Stir the solution and allow it to stand for at least 2 h.

NOTE 20—The solution can be warmed and then allowed to stand for several hours to improve the filtering characteristics of the precipitate. After the precipitate settles, the supernate should be colorless.

26.4.6 Separate the precipitate by filtration through an open-textured, very rapid, filter paper using a polyethylene funnel and collect the filtrate in a 600-mL low-boron glass beaker.

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

26.4.8 Acidify the filtrate with nitric acid to a pH of 3.0 ± 0.1.

26.4.9 Cover the beaker and boil the solution gently for 15 min to remove dissolved carbon dioxide.

26.4.10 Allow the solution to cool. If a blank is being determined, proceed to 26.4.11; otherwise, continue at 26.4.12.

26.4.11 Determine the blank as follows:

26.4.11.1 Add 560 to 700 mg of the NBS SRM 951 standard weighed to the nearest 0.1 mg to the beaker containing the blank and stir the solution to dissolve the boric acid; add a second similarly weighed portion of the standard to another beaker containing 100 mL of cooled, freshly boiled water to which nitric acid has been added to give a pH of 3.

26.4.11.2 Analyze each solution as described in 26.4.12 and 26.4.13.

26.4.12 Titrate slightly beyond the first potentiometric end point with the standardized 0.25 N NaOH solution.

NOTE 21—If the end-point inflection on the titration curve is distorted or if there are multiple inflections that are severe enough to prevent a clear determination of the 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 (26.5). Once mannitol has been added at 26.4.13, the titrated solution can not be salvaged and a new sample must be started.

26.4.13 Add 20 g of mannitol and continue the titration past the second end point.

26.4.14 Refer to Section 27 for calculation of results.

26.5 *Barium Carbonate Separation:*

26.5.1 Place the crucible and lid into a 400-mL, low-boron glass beaker and add enough water to cover the crucible and lid.

26.5.2 Add 6.5 mL of 12 M hydrochloric acid and 3 drops of methyl red.

NOTE 22—If the sodium carbonate from 26.1 and the 12 M hydrochloric acid were measured carefully, the solution will be slightly acidic when the melt has dissolved. If not acidic, add 12 M hydrochloric acid until acidic and add 4 drops excess.

26.5.3 Remove the crucible and lid from the beaker; rinse both carefully with water, adding the rinses to the beaker.

NOTE 23—If the melt has not dissolved completely, gently heat the solution.

26.5.4 Add 1.3 g of barium carbonate to the solution.

NOTE 24—The 1.3 g of barium carbonate can be added only if the sodium carbonate and hydrochloric acid were carefully measured (see 26.5.2). Otherwise, the barium carbonate is added until the solution is basic and then an excess of 1 g is added.

26.5.5 Cover the beaker with a watch glass and bring the solution to a boil.

NOTE 25—Let the precipitate digest for 30 min at a temperature just below the boiling point of the solution.

26.5.6 Continue with 26.4.5.

27. Calculations

27.1 Calculate the weight percent of boron in the samples and control standards, determine the reagent blank, calculate the normality of the sodium hydroxide, and calculate the

percent recovery of the calibration standard using the appropriate equations as follows:

27.2 End Points—Calculate the end points from the two potentiometric breaks using the second derivative technique by noting the pH changes for equal increments of titrant near the end point. Subtract the pH change preceding the largest pH change from the largest. Subtract the pH change following the largest from the largest. Divide the first of these second derivatives by their sum. Multiply the quotient obtained by the increment of titrant. This fraction of an increment is then added to the millilitres of titrant noted at the beginning of the largest pH change to determine the end point as given as follows:

$$\text{Titrant at end point, mL} = \left[\frac{B - A}{(B - A) + (B - C)} \times D \right] + E \quad (3)$$

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:

$$T = S - F \quad (4)$$

where:

- T = millilitres of NaOH solution used,
- S = millilitres of NaOH solution used at the second end point, and
- F = millilitres of NaOH solution used at the first end point.

27.4 Reagent Blank—Calculate the reagent blank as follows:

$$R = T_a - T_c \left(\frac{W_a}{W_c} \right) \quad (5)$$

where:

- R = millilitres of sodium hydroxide reagent blank,
- T_a = millilitres of NaOH solution used in the titration of the standard *with* reagents,
- W_a = grams of the standard titrated *with* reagents,
- T_c = millilitres of NaOH solution used in the titration of the standard *without* reagents, and
- W_c = grams of the standard titrated *without* reagents.

27.5 Concentration of Boron in the Sample—Calculate the concentration of boron in the sample as follows:

$$\text{Boron, weight \%} = \frac{(T_s - R)NA}{W_s} \times 100 \quad (6)$$

where:

- T_s = millilitres of NaOH solution used in the titration of the sample,
- R = reagent blank,
- N = normality of the NaOH solution,
- A = atomic weight of the boron computed for the sample based upon the measured isotopic composition, and
- W_s = sample weight, mg.

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

$$N = \frac{W_x}{T_x M} \quad (7)$$

where:

- N = normality of the NaOH solution,
- W_x = milligrams of the NBS standard titrated,
- T_x = millilitres of NaOH solution used in the titration of the standard, and
- M = molecular weight of the boric acid.

28. 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

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 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 **(8,9,10,11,12,13).**

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.

32. Apparatus

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

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

32.1.2 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 $M-1$.

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

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

32.2.1 *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 *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 *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 *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 *Mixer Mill*.²⁴

32.4 *Plastic Pipet*, 5- μ l, with a changeable plastic barrel.²⁵ Use a pipet only once and then discard it.

32.5 *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 *Acetone*.

33.2 *Distilled Water*.

33.3 *Isopropyl Alcohol*.

33.4 *Sodium Carbonate (Na₂CO₃) Solution*, 0.14 *M*.

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

33.6 *Toluene*.

34. Precautions

34.1 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) as an internal standard (10).

35. Calibration

35.1 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 3 months.

36. Procedure

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

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

36.1.2 Rinse the assembly twice with acetone.

36.1.3 Dry the assembly under a heat lamp.

36.2 *Filament Loading*—Steps 36.2.1-36.2.5 are instructions for fusing the sample with NaOH and 36.2.6-36.2.9 are instructions for an alternative fusion with Na₂CO₃.

36.2.1 Weigh 25 ± 2 mg of sample in powder form and transfer it to a plastic vial.

NOTE 26—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 27—To obtain a representative sample if the original sample is in powdered form, thoroughly blend the bulk sample before taking the 25-mg aliquot.

NOTE 28—A quantitative transfer is not required because isotopic ratios only are being determined.

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

36.2.3 Add a plastic ball and immediately close the vial.

NOTE 29—Avoid atmospheric moisture pickup; moisture interferes with good mixing.

36.2.4 Mix for 1 min on the mixer mill.

36.2.5 Transfer about 0.1 mg of the mixture to a filament. Proceed to 36.2.10 for the fusion.

36.2.6 Weigh 5 ± 0.2 mg of sample in powder form and transfer it to a plastic vial (Note 25 and Note 26).

36.2.7 Add 1.25 mL of 0.14 *M* Na₂CO₃ solution to the vial containing the sample.

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

36.2.9 Transfer about 5 μ l of the slurry to a filament. Proceed to 36.2.10 for the fusion.

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

NOTE 30—The bright glow is caused by the exothermic reaction of tantalum with NaOH or Na₂CO₃. The fusion produces sodium borate and the melt tightly adheres to the filament.

36.3 *Mass Spectrometric Measurement*:

36.3.1 Insert the filament assembly into the mass spectrometer.

36.3.2 Evacuate the system to about 5×10^{-7} torr (66 μ Pa).

36.3.3 Heat the sample by passing an electrical current through the filament until a stable beam of Na₂BO₂⁺ ions is obtained.

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

37. Calculation

37.1 Determine the boron isotopic composition from the mass spectra recorded. Calculate the 89 to 88 peak height ratio

²⁴ A Spex Industries mixer mill, Model 5100, has been used for this method.

²⁵ A Kimble automatic pipet, No. 56300, with disposable polypropylene tips has been used for this method.

from the average peak heights. Subtract 0.00078 to correct for ^{17}O . Then correct the ratio for mass bias.

38. Precision and Accuracy

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

38.2 *Bias*—The average percent recovery obtained from the analysis of boron carbide control standards over a two-year period was 100.1 %. Those standards were prepared and certified by LASL (4).

CHLORIDE AND FLUORIDE SEPARATION BY PYROHYDROLYSIS

39. Scope

39.1 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.

40. Summary of Method

40.1 A stream of moist gas is passed over a mixture of powdered sample and U_3O_8 accelerator heated at 1000 to 1100°C. The pyrohydrolytic reaction releases chloride and fluoride as hydrochloric and hydrofluoric acids, which volatilize and collect in the condensate (14,15,16).

41. Interferences

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

42. Apparatus (See Fig. 4)

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

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

42.3 *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.

42.4 *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.

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

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

42.7 *Mixer Mill*.

43. Reagents

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

43.1.1 U_3O_8 , powdered, <1 μg Cl and F/g. 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.

43.1.2 *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.

43.2 *Argon*, prepurified grade or equivalent.²²

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

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

44. Precautions

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

45. Procedure

45.1 Prepare a sample and reagent blank as follows:

45.1.1 Crush pellet samples to a powder using the procedure in Section 13.

45.1.2 Line two sample boats with 3 g of U_3O_8 .

45.1.3 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.

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

45.1.5 Add 3 g of U_3O_8 accelerator to the second sample boat and spread it uniformly along the length of the boat.

NOTE 31—This second boat, which is used for the measurement of the reagent blank, is taken through 45.2-45.9.

45.2 Prepare the pyrohydrolysis apparatus for use as follows:

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

NOTE 32—The furnace can be turned on early to avoid delaying analyses.

NOTE 33—Whatever temperature is used within the above range, the same temperature within $\pm 10^\circ\text{C}$ must be used for both samples and standards.

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

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

NOTE 34—Start this step early to avoid delaying analyses.

45.2.4 Turn on the argon and adjust its flow to about 190 mL/min.

45.2.5 Adjust the argon flow and water temperature such that 15 ± 2 mL of condensate is produced in about 20 min of operation.

45.3 Open the pyrohydrolytic tube.

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

NOTE 35—The tip of the hang-down tube should be at least 10 mm below the surface of the boric acid solution.

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

NOTE 36—The sample boat shall be placed in the center of the hot zone of the furnace.

45.6 Collect 15 ± 2 mL of condensate.

NOTE 37—The time required should be about 20 min.

45.7 Remove the collection vessel.

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

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

NOTE 38—This solution can serve for the determination of chloride and fluoride.

CHLORIDE BY CONSTANT-CURRENT COULOMETRY

46. Scope

46.1 This method covers the measurement of chloride after separation from boron carbide by pyrohydrolysis. The lower limit of the method is about 2 μ g of chloride per titration.

47. Summary of Method

47.1 The condensate is analyzed for chloride with an automatic chloride titrator that coulometrically generates silver ion to form insoluble silver chloride. The end point is sensed amperometrically and the generating current is stopped automatically at a preset increment of indicator current. Since the rate of generating silver ion is constant, the titration time is proportional to the amount of chloride precipitated (14,17).

48. Interferences

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

49. Apparatus

49.1 *Automatic Chloride Titrator*.²⁶

²⁶ An Aminco-Cotlove, AMINCO, chloride titrator has been found satisfactory for this method.

50. Reagents

50.1 *Boric Acid*, saturated solution.

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

50.3 *Nitric-Acetic Acid Solution*, 1 M HNO₃, 4 M acetic acid containing 20 to 30 μ g Cl/mL of solution.

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

50.5 *Chloride Standard*, about 1 mg Cl/mL. Prepare a solution with an accurately known concentration using sodium chloride, previously dried at 110°C, and distilled water.

51. Calibration of Titrator

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

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

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

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

NOTE 39—Since this chloride constitutes a significant blank, the amount of acid solution added shall be accurately pipetted. Chloride is added to the nitric-acetic acid solution to improve the sensitivity of the titration by adding sufficient chloride to exceed the solubility product of silver chloride. Otherwise, a significant error occurs when titrating a few micrograms of chloride.

51.5 Pipet 50.0 μ l of the 1 mg Cl/mL chloride standard into the cell.

51.6 Add 2 drops of the gelatin solution.

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

51.8 Begin stirring by turning the titrate switch to the 1 position.

51.9 Set the timer counter to zero.

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

51.11 Record the time when the counter stops.

51.12 Repeat 51.2-51.4 and 51.6-51.11 to determine a blank.

51.13 Calculate the calibration factor, F , as follows:

$$F = Cl/(T_{st} - T_{cb}) \quad (8)$$

where:

Cl = chloride added from the chloride standard, μ g,

T_{st} = titration time of standard, and

T_{cb} = titration time of blank.

52. Procedure

52.1 Pipet 5.00 mL of the diluted condensate from 45.9 into a clean, dry 10-mL titration cell.

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

52.3 Perform 51.6-51.11, rinsing the electrode assembly between each titration.

53. Calculation

53.1 Calculate the micrograms of chloride, Cl, titrated as follows:

$$\text{Cl, } \mu\text{g} = [VF(T_s - T_{rb})]/A \quad (9)$$

where:

V = volume of diluted condensate, normally 20.0 mL (45.9),

F = calibration factor (51.13),

T_s = titration time of sample,

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

A = sample aliquot from diluted condensate, normally 5.00 mL (52.1).

53.2 Calculate the micrograms of chloride, Cl, in a boron carbide sample as follows:

$$\text{Cl} = \text{Cl}_c/W \quad (10)$$

where:

Cl_c = chloride from 53.1, μg , and

W = sample weight, g.

54. Precision and Accuracy

54.1 *Precision*—The relative standard deviation is 17 % at concentration levels between 10 and 100 $\mu\text{g/g}$.

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

FLUORIDE BY ION-SELECTIVE ELECTRODE

55. Scope

55.1 This method covers the measurement of fluoride after separation from boron carbide by pyrohydrolysis. The lower limit of the method is about 2 μg of fluoride per measurement.

56. Summary of Method

56.1 The condensate is analyzed for fluoride with a fluoride-selective electrode in a saturated solution of boric acid (14,18,19).

57. Interferences

57.1 At the specification limits for impurities usually established for nuclear-grade boron carbide, interference effects are insignificant. The measurements are made in saturated boric acid solutions because: (1) variations in both pH and ionic strength of solutions affect the response of the electrode to fluoride in activity, and (2) boric acid is produced during pyrohydrolysis in varying amounts and it suppresses fluoride ion activity through complex reactions.

58. Apparatus

58.1 *Fluoride-Selective Electrode*.²⁷

58.2 *pH/Specific-ion Meter*.²⁸

58.3 *Polyethylene Sample Container*—Cut a 2-oz polyethylene bottle in half and use the bottom half for the sample container.

58.4 *Reference Electrode*, saturated calomel.

²⁷ An Orion fluoride-selective electrode, Model 94-09, has been found satisfactory for this method.

²⁸ An Orion specific-ion meter, Model 401, has been found satisfactory for this method.

59. Reagents

59.1 *Boric Acid*, saturated solution.

59.2 *Distilled Water*, fluoride-free, <0.1 $\mu\text{g F/mL}$.

59.3 *Fluoride Standards*—Prepare a 1.00-mg F/mL standard using sodium fluoride, previously dried at 110°C, and distilled water. Dilute 1.00 mL of this standard to 200.0 mL with a saturated solution of boric acid (this standard contains 100 $\mu\text{g F/20 mL}$). Dilute 10.0 mL and 20.0 mL of this second standard to separate 200.0-mL volumes with a saturated solution of boric acid (these standards contain 5 and 10 $\mu\text{g F/20 mL}$, respectively). Store the above standards in polyethylene containers.

60. Calibration of Electrode

60.1 Turn the function switch of the specific-ion meter to the F position and let it stabilize for 30 min before continuing.²⁹

60.2 Rinse the electrodes (fluoride-selective electrode and saturated calomel electrode) with distilled water and dry by blotting them with absorbent tissue.

60.3 Transfer 5 to 7 mL of the 10 $\mu\text{g F/20-mL}$ standard into a clean and dry polyethylene sample container and immerse the electrodes in the solution.

NOTE 40—Make certain that no air bubbles are trapped at the bottom of the fluoride electrode.

60.4 Wait 1 to 2 min and then adjust the calibration control of the meter to read 100 on the red meter scale with the slope adjust setting at 100 % and the temperature-compensator control knob set at the temperature of the solution.

60.5 Remove the electrodes; rinse them with distilled water and dry by blotting with absorbent tissue.

NOTE 41—It is not necessary to switch the meter to OFF when removing the electrodes.

60.6 Transfer 5 to 7 mL of the 100 $\mu\text{g F/20-mL}$ standard into a clean and dry polyethylene sample container and immerse the electrodes.

NOTE 42—Make certain that no air bubbles are trapped at the bottom of the fluoride electrode.

60.7 Wait for 1 to 2 min and then adjust the temperature-compensator control so that the meter reads exactly 1000 on the red scale.

NOTE 43—This step adjusts the slope of the electrode response over the concentration range of 10 to 100 $\mu\text{g F/20-mL}$.

60.8 Rotate the slope indicator so that the temperature-compensator control again reads the same temperature as in 60.4.

NOTE 44—The slope indicator now reads in terms of the percent of theoretical Nernst slope. A reading between 90 and 105 % is expected; if not, determine the source of the problem.

60.9 Repeat 51.3 with the 5 $\mu\text{g F/20-mL}$ standard.

NOTE 45—The meter should read 50 ± 3 ; if not, repeat by starting at 60.1.

²⁹ If a meter other than the Orion Model 401 is used, consult the manufacturer's operation manual for the method of operation.