



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

This standard is issued under the fixed designation C 791; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

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

1.2 The analytical procedures appear in the following order:

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## 2. Referenced Documents

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

C 750 Specification for Nuclear-Grade Boron Carbide Powder

C 751 Specification for Nuclear-Grade Boron Carbide Pellets

D 1193 Specification for Reagent Water

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis

E 116 Practice for Photographic Photometry in Spectrochemical Analysis

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes

## 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 C 750 and C 751.

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.<sup>3</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

## 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.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.03 on Neutron Absorber Materials Specifications.

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

<sup>3</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

## 6. Sampling

6.1 Criteria for sampling this material are given in Specifications C 750 and C 751.

### 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).<sup>4</sup>

## 9. Interferences

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

## 10. Apparatus

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

10.2 *Crucible*, zircon ceramic.<sup>5</sup>

10.3 *Crucible Covers*, porous, ceramic.<sup>6</sup>

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)*<sup>7</sup>—**Caution:** Contact with the high-frequency induction coil will produce severe electrical shock and may cause burns.

10.5.2 *Combustion Tube (B)*,<sup>8</sup> fused silica.

10.5.3 *Dust Trap (C)*.<sup>9</sup>

10.5.4 *Catalyst Furnace (D)*.<sup>10</sup>

10.5.5 *Drying Tubes*<sup>11</sup>—The first tube ( $E_1$ ) is filled with magnesium perchlorate and the second tube ( $E_2$ ) is filled with anhydrous calcium sulfate.<sup>12</sup> These tubes prevent water released from the sample from entering the absorption bulb.

10.5.6 *Sulfur Trap (F)*.<sup>13</sup>

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

10.6.1 *Nesbitt Absorption Bulb (A)*,<sup>14</sup> may be modified with 12/5 socket joints on both the entrance and exit port. The bulb is filled as shown in Fig. 2.

10.6.2 *Drying Tube (B)*,<sup>12</sup> filled with magnesium perchlorate, anhydrous calcium sulfate, and sodium hydrate-asbestos<sup>15</sup> to prevent any back-diffusion of water and carbon dioxide into the absorption bulb.

10.6.3 *Flowmeter (C)*<sup>16</sup>—The total system has two flowmeters, one located before the furnace (Fig. 3) and one after the absorption bulb (Fig. 2). This arrangement helps to detect leaks in the system.

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

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

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

10.7.3 *Gas Flow-Regulating Valve (C)*.<sup>17</sup>

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

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

## 11. Reagents

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

11.2 *Copper*, granules, 30 mesh.

11.3 *Copper*, rings.<sup>18</sup>

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.<sup>19</sup>

11.6 *Magnesium Perchlorate*, anhydrous.

11.7 *Manganese Dioxide*.<sup>20</sup>

11.8 *Oxygen*, ultra high purity grade or equivalent.<sup>21</sup>

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

11.10 *Tin*, Granular.<sup>22</sup>

## 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.

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

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

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

<sup>7</sup> Leco No. 521-000 or equivalent.

<sup>8</sup> Leco No. 550-122 or equivalent.

<sup>9</sup> Leco No. 501-010 or equivalent.

<sup>10</sup> Leco No. 507-000 or equivalent.

<sup>11</sup> Kimble No. 46010 or equivalent.

<sup>12</sup> Drierite has been found satisfactory for this purpose.

<sup>13</sup> Leco No. 503-033 or equivalent.

<sup>14</sup> Kimble No. 16010 or equivalent.

<sup>15</sup> Ascarite has been found satisfactory for this purpose.

<sup>16</sup> Manostat No. 1044B or equivalent.

<sup>17</sup> Matheson No. 32 or equivalent.

<sup>18</sup> Leco No. 550-184 or equivalent.

<sup>19</sup> Leco No. 501-077 or equivalent.

<sup>20</sup> Leco No. 501-060 or equivalent.

<sup>21</sup> *Matheson Gas Data Book*, The Matheson Co. Inc., East Rutherford, N. J., Fourth Edition, 1966.

<sup>22</sup> 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  $\pm 20\%$ , investigate and correct the cause before continuing the analysis of samples. Use the long-term average blank in calculating the concentration of carbon in samples.

#### 15. Procedure

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

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  $\pm 0.1$  mg.

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

15.16.5 Repeat 15.16.1-15.16.4 until constant weight ( $\pm 0.1$  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 CO<sub>2</sub> 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  $100 \pm 10$  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  $\text{HNO}_3$  to 400 mL of water and dilute to 500 mL.

22.8 *Nitric Acid (0.1 M)*—Pipet 50 mL of 1 N  $\text{HNO}_3$  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  $\pm 0.1$  mg in 100 mL of cooled, freshly boiled water. Adjust the pH to 3 with 1 M  $\text{HNO}_3$  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  $100 \pm 10$  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°C/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  $\text{Na}_2\text{BO}_2^+$  ion. When mixing the boron carbide and sodium hydroxide or sodium carbonate, a Na to B ratio of 1:1 is maintained, which gives a stable ion emission within a few minutes after operational vacuum is attained. There is no apparent bias caused by selective volatilization of  $^{10}\text{B}$  (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  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5 % of its height. Abundance sensitivity

is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ .

32.1.3 *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*.<sup>23</sup>

32.4 *Plastic Pipet*, 5- $\mu$ l, with a changeable plastic barrel.<sup>24</sup> 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* ( $\text{Na}_2\text{CO}_3$ ) *Solution*, 0.14 *M*.

33.5 *Sodium Hydroxide* ( $\text{NaOH}$ )—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 NBS<sup>10</sup> 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  $\text{NaOH}$  and 36.2.6-36.2.9 are instructions for an alternative fusion with  $\text{Na}_2\text{CO}_3$ .

36.2.1 Weigh  $25 \pm 2$  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  $72 \pm 2$  mg of pulverized  $\text{NaOH}$  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  $5 \pm 0.2$  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*  $\text{Na}_2\text{CO}_3$  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  $\mu$ 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  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$ . 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  $5 \times 10^{-7}$  torr (66  $\mu$ Pa).

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

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

<sup>23</sup> A Spex Industries mixer mill, Model 5100, has been used for this method.

<sup>24</sup> 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  $^{17}\text{O}$ . 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 ten 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  $\mu\text{g}$  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  $\text{U}_3\text{O}_8$  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  $\text{U}_3\text{O}_8$  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*,  $\text{U}_3\text{O}_8$  or sodium tungstate with tungsten trioxide:

43.1.1  $\text{U}_3\text{O}_8$ , powdered, <1  $\mu\text{g}$  Cl and F/g. Prepare by air calcining  $\text{UO}_2$  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  $\text{U}_3\text{O}_8$  with satisfactory accelerator characteristics, which are thought to be dependent upon the surface area of the oxide.

43.1.2 *Sodium Tungstate (Na<sub>2</sub>WO<sub>4</sub>) with Tungsten Trioxide (WO<sub>3</sub>)* may be used. Dehydrate 165 g of  $\text{Na}_2\text{WO}_4$  in a large platinum dish. Transfer the dried material to a mortar, add 116 g of  $\text{WO}_3$ , 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.<sup>21</sup>

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  $\text{U}_3\text{O}_8$ .

45.1.3 Weigh 1 to 2 g of powdered sample to  $\pm 0.01$  g and mix thoroughly with 3 g of  $\text{U}_3\text{O}_8$  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  $\text{U}_3\text{O}_8$  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  $15 \pm 2$  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  $15 \pm 2$  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  $\mu\text{g}$  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*.<sup>25</sup>

<sup>25</sup> 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 HNO<sub>3</sub>, 4 M acetic acid containing 20 to 30  $\mu\text{g}$  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  $\mu\text{l}$  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 *I* 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:

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

where:

Cl = chloride added from the chloride standard,  $\mu\text{g}$ ,

$T_{st}$  = 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:

$\text{Cl}_c$  = chloride from 53.1,  $\mu\text{g}$ , 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  $\mu\text{g}$  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*.<sup>26</sup>

58.2 *pH/Specific-ion Meter*.<sup>27</sup>

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.

#### 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.<sup>28</sup>

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  $50 \pm 3$ ; if not, repeat by starting at 60.1.

<sup>28</sup> If a meter other than the Orion Model 401 is used, consult the manufacturer's operation manual for the method of operation.

<sup>26</sup> An Orion fluoride-selective electrode, Model 94-09, has been found satisfactory for this method.

<sup>27</sup> An Orion specific-ion meter, Model 401, has been found satisfactory for this method.

60.10 Multiply all readings by 0.1 before recording.

60.11 Leave the electrodes immersed in the 10 µg F/20-mL standard and leave the function switch of the meter in the *F* position in preparation for measuring fluoride during the analysis of samples.

### 61. Procedure

61.1 Rinse the electrodes with distilled water and dry by blotting them with absorbent tissue.

61.2 Transfer 5 to 7 mL of the diluted condensate from 45.9 into a dry, clean polyethylene container.

61.3 Immerse the electrodes into the dilute condensate and swirl the solution around the electrodes.

NOTE 46—Make certain that no air bubbles are trapped at the bottom of the fluoride electrode.

NOTE 47—The function switch of the meter should be in the *F* position.

61.4 Let the reading stabilize for 1 to 2 min.

61.5 Multiply the reading on the red scale by 0.1 to obtain µg F/20-mL of the diluted condensate.

61.6 Record the value obtained.

61.7 Turn the function switch to the OFF position and leave the electrodes immersed in the 10 µg F/20-mL standard.

### 62. Calculation

62.1 Subtract the micrograms of fluoride measured in the reagent blank (pyrohydrolysis) from the micrograms of fluoride measured in the sample.

62.2 Calculate the micrograms of fluoride, *F*, in a boron carbide sample as follows:

$$F = F_c/W \quad (11)$$

where:

$F_c$  = fluoride from 62.1, µg, and

$W$  = sample weight, g.

### 63. Precision and Accuracy

63.1 *Precision*—The relative standard deviation is 13 % at concentration levels between 10 and 100 µg/g.

63.2 *Accuracy*—The average percent recovery obtained from the analysis of LASL control standards over a 2-year period was 110 %.

## WATER BY CONSTANT-VOLTAGE COULOMETRY

### 64. Scope

64.1 This method covers the determination of water in boron carbide in either powder or pellet form. The lower limit of the method is 5 µg of water.

### 65. Summary of Method

65.1 Water is removed from the sample by heating at 400°C. A carrier gas sweeps the water into an electrolytic cell containing phosphorus pentoxide to absorb the water. A potential applied across the cell causes the absorbed water to be electrolyzed. The total current is integrated and displayed digitally as micrograms of water (**20,21**).

### 66. Interferences

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

### 67. Apparatus

67.1 *Analytical Balance*, capable of weighing to ±0.01 mg.

67.2 *Gas Dryer*.

67.3 *Gas Flowmeter*.

67.4 *Platinum Boat*, 10 by 30 by 5 mm.

67.5 *Water Analyzer*.<sup>29</sup>

### 68. Reagents

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

68.2 *Nitrogen*, prepurified grade or equivalent.<sup>21</sup>

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

### 69. Calibration of Analyzer

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

69.2 A control standard, which can be sodium tartrate dihydrate, should be analyzed at least once in each 8-h shift in which samples are analyzed.<sup>30</sup>

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

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

NOTE 48—Use only very clear crystals to avoid low results that occur when using cloudy crystals.

69.3.2 Analyze the weighed sodium tartrate dihydrate in accordance with Section 70 with the following exception: use 125 ± 5°C instead of the stated temperature in 70.2, 70.4, 70.9, and 70.15.

NOTE 49—Do not heat above 150°C because sodium tartrate dihydrate decomposes to give high results.

69.3.3 Calculate the percent water in the control standard in accordance with 71.2. The control limits are 14.8 to 16.4 %. If the result is outside, investigate and correct the problem before analyzing samples.

### 70. Procedure<sup>31</sup>

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

NOTE 50—The flow rate adjustment is not critical. Because the cell current is integrated as a function of time, the total water present is

<sup>29</sup> Du Pont Instrument Inc. CEC water analyzer, Model 26-321 AMA, has been found satisfactory for this method.

<sup>30</sup> A method of calibration using an injection of measured amounts of hydrogen that is converted to water has been used (see LA-4622, Los Alamos Scientific Laboratory, Los Alamos, N. M., March 1971). Another technique that is used is to add a measured amount of water to the analyzer by way of a capillary tube.

<sup>31</sup> If a water analyzer other than the CEC Model 26-321 AMA is used, consult the manufacturer's operation manual for the method of calibration and operation.

independent of carrier-gas flow rate. However, a flow rate less than 150 mL/min is recommended.

70.2 Set the temperature controller at 400°C.

NOTE 51—This temperature was chosen because 400°C is considered to be high enough to release all water from the sample and yet low enough to minimize the reaction of hydrogen to form water if the sample contains absorbed hydrogen.

70.3 Place an empty platinum boat in the oven.

NOTE 52—Platinum is preferred over nickel for boats because nickel may have an oxide-film coating that is a source of oxygen to react with hydrogen.

70.4 Start the timer and heat at 400°C until the count rate of the integrator decreases to a constant rate over a 10-min period.

NOTE 53—The system must be dried sufficiently at this step to permit setting the zero of the analyzer at 68.5. The count rate that indicates sufficient drying is determined by experience.

70.5 Zero the instrument at a count rate of 0.6 µg/min.

NOTE 54—Consult the manufacturer's operation manual for instructions on how to zero the analyzer.

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

70.7 Remove the boat when the oven reaches room temperature.

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

NOTE 55—The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

70.9 Heat at 400°C until the count rate of the integrator decreases to a constant rate of 0.6 µg/min.

70.10 Record the reading ( $R_b$ ) on the integrator and the time ( $T_b$ ) required to complete 70.9.

NOTE 56—If the analyzer is not used in a controlled environment, the blank will vary from day to day, particularly if the humidity varies. Therefore, with samples containing less than 30 µg of water, it is recommended that a blank be determined between each sample analysis.

70.11 Stop the timer and reset the integrator to zero.

70.12 Remove the boat when the oven reaches room temperature.

NOTE 57—The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

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

70.14 Replace the boat in the oven.

70.15 Heat at 400°C until the count rate of the integrator decreases to a constant rate of 0.6 µg/min.

70.16 Record the reading ( $R_s$ ) on the integrator and the time ( $T_s$ ) required to complete 70.15.

NOTE 58—The reading and time are  $R_c$  and  $T_c$  respectively when a control standard is analyzed.

70.17 Stop the timer and reset the integrator to zero.

70.18 Repeat 70.12-70.17 for subsequent sample analyses.

## 71. Calculation

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

$$W_H = [R_s - (B)(T_s)]/W_s \quad (12)$$

where:

$R_s$  = water from sample measurement, µg,

$B$  =  $R_b/T_b$ (see 70.10),

$T_s$  = min required for sample measurement, and

$W_s$  = sample weight, g.

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

$$W_p = [R_c - B(T_c)]/(W_c)(10^4) \quad (13)$$

where:

$R_c$  = water from control standard measurement, mg,

$B$  =  $R_b/T_b$ (see 70.10),

$T_c$  = min required for control standard measurement, and

$W_c$  = control standard weight, g.

## 72. Precision and Accuracy

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

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

## IMPURITIES BY SPECTROCHEMICAL ANALYSIS

### 73. Scope

73.1 This method covers the determination of 14 impurity elements in boron carbide in either powder or pellet form.

### 74. Summary of Method

74.1 In this spectrographic method, boron carbide samples in powdered form are mixed with a spectroscopic buffer of germanium dioxide and graphite. Excitation is done in a d-c arc by total burn technique.

74.2 The concentrations of the impurity elements are determined by visual comparison of selected-line densities from the samples and standards for a semi-quantitative analysis and by a microdensitometric comparison for a quantitative analysis (22,23).

### 75. Interferences

75.1 Interference effects depend primarily upon the resolving power of the spectrograph and the selection of the analytical lines.

### 76. Apparatus

76.1 *Mortar*, boron carbide, with a 38.1-mm (1.5-in.) diameter by 19.0-mm (0.75-in.) deep cavity mortar and a boron-carbide-tipped pestle.

76.2 *Comparator*, projection type, having a magnification of at least 15×.

76.3 *Mortar*, diamond (plattner).

76.4 *Excitation Source*—A d-c arc source capable of providing spectrographic conditions required for 79.12.

76.5 *Graphite Electrodes*:<sup>32</sup>

<sup>32</sup> AGKSP grade, National Carbon Co., has been used successfully. Anodes (cupped with center post) can be obtained as a special order item from suppliers of graphite electrodes.



76.5.1 *Anode*, cupped, with center post, machined from 6.15 mm (0.242 in.) diameter by 31.8 mm (1.25 in.) long rod. The annular cup around the center post is 3 mm (0.118 in.) deep, 2.24 mm (0.088 in.) inside diameter, and 5.08 mm (0.200 in.) outside diameter.

76.5.2 *Cathode*, 0.125-in. diameter, flat-end.

76.6 *Microdensitometer*, repeatability of 0.2 % of the full-scale reading for transmittance values between 5 and 90 %.

76.7 *Mixer Mill*, capable of handling 50.8-mm (2-in.) long, 22.2-mm (0.875-in.) diameter vials.<sup>25</sup>

76.8 *Packing Tool*, fabricated from tantalum or niobium (see Fig. 5).

76.9 *Photographic Plates*.<sup>33</sup>

76.10 *Photographic Processor*, capable of maintaining a development temperature of 20°C controlled to ±0.3°C.

76.11 *Plastic Funnel*.<sup>34</sup>

76.12 *Plastic Vials and Balls*—Two sizes of vials: 25-mm (1-in.) long, 13 mm (0.5 in.) diameter and 51 mm (2 in.) long, 22.22 mm (0.875 in.) diameter; 3.18-mm (0.125-in.) diameter balls.

76.13 *Sample Mixer*, dental amalgamator type for 25-mm (1-in.) long, 13-mm (0.5-in.) diameter vials.

76.14 *Spectrograph*, having a reciprocal linear dispersion of 5 Å/mm or less, a resolving power of 23 000 or greater, and a wavelength range from 2500 to 4000Å .

## 77. Reagents

77.1 *Germanium Dioxide*, 99.999 % purity.<sup>35</sup>

77.2 *Graphite Powder*.<sup>36</sup>

77.3 *Standards*—Each standard used for calibration should be a blend of 14 metal impurity elements in a matrix of boron carbide, germanium dioxide, and graphite, which is the same matrix as that obtained by treating samples according to Section 79.

## 78. Calibration

78.1 For visual comparison, a minimum of four standards covering the impurity concentration range of interest are exposed on the same plate with the sample.

78.2 For microdensitometric measurement, prepare a calibration curve for each analytical line from the full set of calibration standards for each plate. Use these curves only for the samples recorded on the same plate. Details are given in 80.2.

## 79. Procedure

79.1 Combine 300 mg of germanium dioxide and 900 mg of graphite powder in a 51-mm (2-in.) long by 20.96-mm (0.825-in.) diameter vial containing four plastic balls.

NOTE 59—The processing of calibration standards starts at 79.9.

79.2 Mix for 2 min on the mixer mill.

NOTE 60—Start analysis of pellet samples at 79.3 and powder samples at 79.7.

79.3 Crush the sample pellet in a diamond (plattner) mortar, using light hammer taps and taking fine material out of the mortar during the operation.

NOTE 61—The cycle of light hammer taps and removal of fine material should continue until the whole pellet is crushed. Grinding action must be avoided; otherwise, iron contamination of the sample might occur.

79.4 Reduce further the particle size of the crushed sample in a boron carbide mortar by using a rocking motion of the pestle.

79.5 Transfer the sample to a plastic vial and shake the vial to mix the sample.

79.6 Transfer a 100-mg portion of sample to the boron carbide mortar and grind to a fine powder.

79.7 Combine 15 mg of sample in powder form and 135 mg of the germanium dioxide—graphite powder mixture from 79.1 in a 25-mm (1-in.) by 13-mm (0.5-in.) diameter vial containing two plastic balls.

79.8 Mix for 45 s on the sample mixer.

79.9 Weigh out 20 ± 0.2-mg portions of the sample mixture from 79.8.

79.10 Transfer each portion to the cavity of an electrode using the plastic funnel, tapping the side of the electrode during the transfer to settle the material in the cavity.

NOTE 62—The number of electrodes prepared depends on the exposure required for the particular spectrograph used.

79.11 Pack the charge in each electrode with the packing tool.

79.12 Make exposures of each charge in appropriate regions of the spectrum using the following conditions as guidelines:

79.12.1 *Current*, 17 A, short circuit value.

79.12.2 *Slit*, 0.015 to 0.025 mm.

79.12.3 *Plate*, SA-1.

79.12.4 *Gap*, 4 mm.

79.12.5 *Exposure Time*, 120 s.

79.12.6 *Step Exposure*, 100 and 15 % T steps. Fifteen percent is an approximate value recommended for the weak step; it may be obtained by neutral density filter or by rotating sector.

79.12.7 *Exposure Control*—Adjust the exposure to produce a line density of approximately 1.15 (or 7 % T) for the 3082.2 Å line at a concentration of 1000 µg/g on the strong step. The Ca 3968.5 Å line should have a density of approximately 1 (or 10 % T) on the weak step at a concentration of 130 µg/g. A neutral filter of appropriate density at the plate may be used to reduce the Ca line density if required.

79.13 Develop the plate for 5 min in D-19 developer at 20 ± 0.3°C; rinse for 15 to 20 s in short stop; fix for 3 min in a rapid fixer; wash for 5 min in running water and dry.

## 80. Calculation

80.1 *Visual Comparison*:

80.1.1 Place the sample and calibration plate in the comparator.

80.1.2 Visually compare the densities of the analytical lines in the sample spectrum with the corresponding lines in the

<sup>33</sup> Kodak SA-1.

<sup>34</sup> Spex Industries No. 3001 has been used for this method.

<sup>35</sup> Germanium dioxide of this purity has been obtained from Eagle-Picher Industries, Inc.

<sup>36</sup> SP-2, grade, National Carbon Co., has been used successfully.

standard spectrum, exposed on the same plate, to obtain the concentration of each impurity. Recommended analytical lines are given in Table 1.

80.1.3 If the measured concentration of an impurity other than Cr, Fe, Mn, or Ni is 25 % or more of the specification value, proceed with a microdensitometric evaluation of that concentration. For Cr, Fe, Mn, and Ni, proceed with a microdensitometric evaluation if the concentration of any of these elements exceeds 500 µg/g.

#### 80.2 Microdensitometry:

80.2.1 Calibrate the photographic emulsion by the two-step method given in Method E 116.

NOTE 63—Calibrations are recommended for the wavelength regions 2500 to 2750, 2800 to 3300, 3375 to 3475, and 3960 to 3980 Å.

80.2.2 Measure the transmittance of the analytical lines given in Table 2, using the strong step or the weak step as stated, for both the calibration standards and the samples.

80.2.3 Measure the background associated with each line.

80.2.4 Prepare a calibration curve for each analytical line as follows:

80.2.4.1 Convert the transmittances of the lines and their backgrounds to intensities using the emulsion calibration curve.

80.2.4.2 Correct each line intensity by subtracting its corresponding background intensity.

80.2.4.3 Plot the corrected intensities versus concentrations (µg/g) on log-log paper.

80.2.5 Calculate the concentration of each impurity in the sample as follows:

80.2.5.1 Obtain the corrected line intensity for each line by following Steps 81.2.4.1 and 81.2.4.2.

80.2.5.2 Convert the corrected intensities to concentrations (µg/g) using the appropriate calibration curves.

NOTE 64—An extrapolation of 1.5 times the intensity of the highest calibration standard and 0.67 times the intensity of the lowest may be used. For such cases, indicate “extrapolation” with the reported concentration.

### 81. Precision and Accuracy

81.1 *Precision*—The relative standard deviation is 15 % or less for microdensitometric measurements. Replicate measurements made by visual comparisons will agree to within a factor of 2 (0 to 100 %) of the average(5).

81.2 *Bias*—No bias can be established because no material traceable to a national standards base is available (5).

## SOLUBLE BORON BY TITRIMETRY

### 82. Scope

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

### 83. Summary of Method

83.1 This method is empirical but has been found useful in characterizing boron carbide (5,6,7,24). It is based on the assumption that hydrochloric acid or, alternatively, water extracts only boron oxide and that nitric acid extracts both

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

### 84. Interferences

84.1 Hydrochloric and nitric acids may dissolve metallic impurities whose hydrous oxides distort the end point of the strong acid titration. This method, therefore, includes a precipitation separation for these metallic impurities.

### 85. Apparatus

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

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

85.3 *Electrode Pair*, glass and calomel.

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

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

85.6 *pH Meter*.

85.7 *Polyethylene Funnel*.

85.8 *Recording Titrator*.<sup>37</sup>

85.9 *Hot Plate*.

### 86. Reagents

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

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

86.3 *Hydrochloric Acid*, 3 M and 0.1 M.

86.4 *Mannitol*.

86.5 *Nitric Acid*, 3 M, 1.6 M, and 0.1 M.

86.6 *Sodium Hydroxide Solution*, 10 M.

86.7 *Sodium Hydroxide Solution*, 0.1 N, standardized, carbonate-free.

### 87. Precautions (see Section 23)

### 88. Standardization of Titrant

88.1 Standardize the 0.25 N NaOH solution in accordance with Section 24 using 225 to 280 mg of standard boric acid.

<sup>37</sup> A Sargent recording titrator, Model D, has been used successfully for this method. The use of a recording titrator is recommended because the presence of impurities, such as carbonate and aluminum, will be revealed by distortions in the titration curves at the end point. Such distortions may be overlooked when using manual titrations.

## 89. Blank

89.1 Add 100 mL of 1.6 M HNO<sub>3</sub> to a 200-mL flask and 100 mL of 0.1 M HCl to a second flask.

89.2 Take each flask through the analysis, starting at 90.1.3.

89.3 Calculate the reagent blank in accordance with 25.3.

## 90. Procedure

### 90.1 HCl and HNO<sub>3</sub> Soluble Boron:

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

NOTE 65—Crush pellets to a powder in accordance with Section 13.

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

NOTE 66—Take both samples through the remainder of the procedure. Exceptions or special treatments required for either sample are given at the appropriate steps.

90.1.3 Boil gently under reflux for 4 h.

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

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

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

NOTE 67—The filtrate contains solubilized boron.

NOTE 68—A retentive filter paper is necessary to retain the undissolved sample.

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

NOTE 69—The use of water as a rinse may cause the formation of colloids which pass through the filter. This has not been found to affect the results.

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

90.1.9 Let the solution stand for at least 2 h.

NOTE 70—The solution can be warmed and then allowed to stand for several hours to improve the filtering characteristics of the precipitate.

NOTE 71—After the precipitate settles, the supernate should be colorless.

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

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

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

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

NOTE 72—Dissolved carbon dioxide is removed by boiling.

90.1.14 Let the solution cool to ambient temperature.

NOTE 73—If a blank is being determined, proceed at 90.1.15; otherwise, proceed at 90.1.16.

### 90.1.15 Blank Determination:

90.1.15.1 Add 225 to 280 mg of the boric acid standard weighed to  $\pm 0.1$  mg to each beaker containing a blank and stir

the solution to dissolve the boric acid; add a similar weighed portion of the standard to another beaker containing 100 mL of cooled, freshly boiled water to which a few mL of 0.1 M HCl has been added to give a pH of 3.0  $\pm 0.1$ .

90.1.15.2 Analyze each of the above solutions as described in 90.1.16 and 90.1.17.

90.1.16 Titrate slightly beyond the first potentiometric end point with the standardized 0.1 N NaOH solution.

NOTE 74—If the end-point inflection on the titration curve is distorted or if there are multiple inflections that are severe enough to prevent a clear determination of the first end point, carbonate or hydrolyzable metals probably are present. The precipitation separation can be modified using the barium carbonate procedure described in 26.4.1. A longer boiling time or sparging with an inert gas can improve the removal of carbon dioxide.

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

## 91. Calculation

91.1 Calculate the weight percent of HNO<sub>3</sub>-soluble and HCl-soluble boron in the sample in accordance with Section 27.

## 92. Precision and Accuracy

92.1 *Precision*—The relative standard deviation for HCl and HNO<sub>3</sub> soluble boron is 3.4 % at concentration levels between 0.03 and 0.12 weight %.

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

## 93. Procedure

### 93.1 Water-Soluble Boron:

93.1.1 Weigh 3 to 4-g aliquots of sample in powder form to  $\pm 0.1$  mg and transfer to 200-mL beakers.

93.1.2 Add 75 mL of water and bring to a boil on a hot plate.

93.1.3 Heat at a slow boil for 10 min.

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

93.1.5 Cool to room temperature and titrate the soluble boron by following 90.1.16 and 90.1.17.

93.1.6 Determine the blank correction by carrying 75 mL of water through the procedure.

## 94. Calculation

94.1 Calculate the weight percent water soluble boron in the sample in accordance with Section 27.

## 95. Precision and Accuracy

95.1 *Scope*—Each of three laboratories analyzed six samples from each of two types of B<sub>4</sub>C material. In every case, the 0.1 N HCl method and the water reflux method were used and the results compared.

### 95.2 0.1 N HCL:

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

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

### 95.3 Water Reflux Method:



95.3.1 *Precision*—In the experiment, the percent relative standard deviations (coefficients of variation  $\times 100$ ) ranged from 1.1 to 5.4 % (5).

95.3.2 *Bias*—No bias can be established because no material traceable to a national standards base is available. In the experiment, however, the results for the water reflux method averaged 39.0% lower than results from the 0.1 N HCl method. (5)

## SOLUBLE CARBON BY A MANOMETRIC MEASUREMENT

### 96. Scope

96.1 This method covers the determination of soluble carbon in boron carbide. The lower limit of the method is 0.02 % with a 100-mg sample. Soluble carbon is defined as that carbon oxidized by the sodium dichromate-sulfuric acid solution under the conditions of this method.

### 97. Summary of Method

97.1 The sample in powder form is reacted with a solution of sodium dichromate in sulfuric acid and the soluble carbon is oxidized to carbon dioxide, which is measured manometrically (25,26).

97.2 The conditions selected for this method are empirical, and it is assumed that only carbon in forms other than  $B_4C$  is oxidized under the conditions prescribed. It is therefore important that the apparatus and analysis conditions are used exactly as described in this method (27,28).

### 98. Interferences

98.1 Gases, including water vapor, that are present with the carbon dioxide during the manometric measurement will interfere. The method is designed to remove such interferences prior to the measurement.

### 99. Apparatus

99.1 *Soluble Carbon Apparatus*—A few of the components are given below with dimensions. The letters in parentheses refer to Fig. 6.

99.1.1 *Calibrated Volumes* ( $N$  and  $O$ ), 200 and 100-mL.

99.1.2 *Carbon Dioxide Trap* ( $L$ ), 2-mm inside diameter capillary U-tube.

NOTE 75—The tube is inverted. It is constructed so that side arms are located 32 mm below the top of the inverted U and the legs extend 150 mm into liquid nitrogen in the Dewar ( $M$ ).

99.1.3 *Condenser* ( $H$ ), Friedrichs, about 203 mm long, supplied with 5°C water cooled by a refrigerator system.

99.1.4 *Reactor Tube* ( $D$ ), 44.4-mm outside diameter by 178 mm long, with a delivery tube for nitrogen.

NOTE 76—The shape shall be conical with the end of the delivery tube being within 1 to 2 mm of the bottom. This configuration is required to provide adequate and reproducible stirring of the boron carbide during the analysis. The sample port is a 28/15 TFE-fluorocarbon coated ball-and-socket joint.

99.1.5 *Water Trap* ( $J$ ), dry ice, and acetone, 31.8-mm outside diameter by 254 mm long, filled with 3-mm glass beads.

99.1.6 *Water Trap* ( $I$ ), magnesium perchlorate, 38.1-mm outside diameter by 178 mm long, with an extra-coarse frit on the bottom of the inlet tube.

99.1.7 *McLeod Gage*, triple range,<sup>38</sup>

99.2 *Timer* for measurement of  $60 \pm 1$ -min interval.

### 100. Reagents

100.1 *Acetone*.

100.2 *Dry Ice*, crushed.

100.3 *Liquid Nitrogen*.

100.4 *Magnesium Perchlorate*, anhydrous.

100.5 *Mercury*, triple distilled or equivalent.

100.6 *Nitrogen*, prepurified grade or equivalent.<sup>21</sup>

100.7 *Reaction Solution*—Add slowly with stirring 350 mL of 18 M  $H_2SO_4$  (96 %) to 150 mL of distilled water containing 10 g of sodium dichromate dihydrate. Store in a glass container. Storage in polyethylene containers causes gradually increasing blanks because of a slow reaction between the reaction solution and the polyethylene. **Caution:** In case of accidental contact with the skin, rinse promptly with running cold water to avoid severe burns.

### 101. Calibration

101.1 Calibrate the volume of the gas-measuring part of the apparatus. This gas-measuring system contains the volume from  $S_4$  to  $S_5$ ,  $S_6$  to  $S_{10}$  and it includes the McLeod gage and the calibrated volumes  $N$  and  $O$ . This total volume of the system is designated as  $Z$ . In this procedure, volumes  $Z - (N + O)$ ,  $O$ , and  $N$  are designated as  $V_1$ ,  $V_2$ , and  $V_3$  respectively. Determine the three volumes required,  $V_1$ ,  $V_2$ , and  $V_3$ . Refer to Fig. 6.

101.2 Calculate the volume of  $N$  ( $V_3$ ) from the weight of the water required to fill  $N$ . Attach  $N$  (a glass bulb) to the apparatus. The volume of  $O$  ( $V_2$ ) can be obtained likewise, although this volume can be obtained also by using the following steps.

101.3 Flush the apparatus with nitrogen by following 103.6 and 103.7 but also by opening  $S_8$  and  $S_9$  at 103.7.

101.4 Open  $S_1$ , and close  $S_2$ ,  $S_4$ ,  $S_5$ ,  $S_{10}$ , and  $S_{11}$ .

101.5 Reduce the pressure of the gas-measuring system by opening  $S_6$  until the pressure has been reduced to about 20 torr (2.7 kPa).

101.6 Close  $S_6$  and open  $S_7$ .

101.7 Control the height of mercury in the McLeod gage by cautiously opening  $S_{11}$  to the atmosphere. Read and (see 103.18) record the pressure on the McLeod gage. This pressure is  $P_1$ .

101.8 Slowly open  $S_{11}$  to vacuum and close  $S_9$ .

101.9 Open  $S_6$  and  $S_{10}$  to evacuate the system (excluding volume  $N$ ).

101.10 Close  $S_6$ ,  $S_8$ ,  $S_{10}$ , and  $S_{11}$  and open  $S_9$ . The gas remaining in  $N$  now expands into the evacuated portion of the system.

101.11 Cautiously open  $S_{11}$  to atmosphere. Read and record the pressure on the McLeod gage. Refer to 101.7. This pressure is  $P_2$ .

<sup>38</sup> A Todd universal vacuum gage, available from laboratory supply houses, has been found satisfactory.



101.12 Slowly open  $S_{11}$  to vacuum.

101.13 Close  $S_{11}$  and open  $S_8$ .

101.14 Cautiously open  $S_{11}$  to atmosphere. Read and record the pressure on the McLeod gage. This pressure is  $P_3$ .

101.15 Calculate  $V_1$  and  $V_2$  as follows:

$$V_1 = \frac{V_3 P_1 - V_3 P_2}{P_2} \quad (14)$$

$$V_2 = \frac{V_3 P_1 - (V_3 P_3 + V_1 P_3)}{P_3} \quad (15)$$

## 102. Blank

102.1 A blank should be determined at least once in each 8-h shift in which soluble carbon analyses are made. In terms of milligrams of carbon, a range in the blank from 0.04 to 0.06 over several weeks has been typically obtained. An individual blank should be within  $\pm 0.02$  of the long-term average. A reagent blank is determined by following 103.1-103.22, omitting 103.3.

## 103. Procedure

103.1 Start heating the oil bath ( $C$ ), turn on the water ( $T$ ) to the condenser ( $H$ ), and turn on the refrigerated cooling unit.

NOTE 77—The oil bath must reach a temperature of 102°C before being used at 103.9.

103.2 Prepare a bath of dry ice and acetone in a Dewar flask ( $K$ ) and place it in position.

NOTE 78—Slowly add crushed dry ice to an acetone-water mixture until a slush is formed. Use about 10 mL of water for each 400 mL of acetone used.

103.3 Weigh to the nearest 0.1 mg a small capsule made from aluminum foil and add 25 to 100 mg of powdered sample to the capsule. Close the capsule and reweigh. Record the sample weight as  $W_s$ .

NOTE 79—A piece of foil, about 38 mm by 19 mm, is rolled into a cylinder around a glass rod.

NOTE 80—Pellets are prepared by following the instructions in Section 13.

103.4 Place the capsule into the reaction tube ( $D$ ).

103.5 Add 25 mL of the reaction solution to the reaction tube and close the sample port.

103.6 Start the nitrogen gas flow with  $S_1$  open,  $S_{12}$  opened to the reaction tube, and  $S_2$  closed. Flush for at least 2 min.

NOTE 81—The flow rate should be about 160 mL/min.

NOTE 82—At this point, stopcocks  $S_2$  through  $S_9$  must be closed.  $S_{10}$  and  $S_{11}$  are open to vacuum.

103.7 Close  $S_1$  and open  $S_2$ ,  $S_3$ ,  $S_4$ , and  $S_5$ ; let the nitrogen purge the apparatus for 3 min.

103.8 Place a Dewar flask containing liquid nitrogen ( $M$ ) around the carbon dioxide trap ( $L$ ) and wait 2 min.

103.9 Place the oil bath, at a temperature of 102°C, around the reaction tube and start the timer.

NOTE 83—To heat the sample in a reproducible manner, a liquid hot-bath must be used. Heating tapes or heating mantles are not suitable. With a bath temperature of 100 to 102°C, it takes less than 10 min for the temperature of the reaction solution to reach 98 to 101°C. to 2-degree

temperature drop between the bath and reaction solution is expected. Either the temperature of the reaction solution or the bath may be controlled.

103.10 Maintain the temperature of the oil bath at 102°C for  $60 \pm 1$  min.

103.11 Remove the oil bath; close  $S_2$  and open  $S_1$ .

103.12 Close  $S_4$ ,  $S_5$ ,  $S_{10}$ ,  $S_{11}$ . Open  $S_8$ ,  $S_9$  and  $S_6$  to vacuum.

103.13 Evaluate the apparatus for 3 min, opening  $S_7$  during the last minute. Then close  $S_6$ ,  $S_8$ , and  $S_9$ .

103.14 Open  $S_{11}$  to atmosphere and adjust the middle column of mercury on the McLeod gage to its reference point.

NOTE 84—The adjustment is made by opening  $S_{11}$  to either the atmosphere or vacuum as required to adjust the column. Final adjustment must be made by opening  $S_{11}$  to the atmosphere.

103.15 Read and record the pressure ( $P_B$ ) from the left-hand column of mercury on the McLeod gage. This pressure is the blank ( $P_B$ ).

103.16 Slowly open  $S_{11}$  to vacuum and then close  $S_{11}$ . **Caution:** Open  $S_{11}$  to vacuum slowly to avoid blowing mercury from the McLeod gage into the gas-measuring system.

103.17 Remove the liquid nitrogen from the carbon dioxide trap and heat the trap to room temperature by immersing in warm water. The frozen carbon dioxide is evaporated and it expands as a gas through volume  $V_1$  of the gas-measuring system.

103.18 Slowly open  $S_{11}$  to the atmosphere and adjust the left-hand column of mercury to one of the following, depending upon the pressure level:

103.18.1 Adjust to the appropriate reference point to read the pressure on the right-hand column of mercury.

103.18.2 Adjust to the appropriate reference point to read the pressure on the middle column of mercury.

103.19 Read and record the pressure ( $P_s$ ) of the carbon dioxide.

NOTE 85—If the pressure is too high to read, use volumes  $O$  ( $V_2$ ) and  $N$  ( $V_3$ ) as necessary. Record which volumes are used in the gas measuring system. Refer to 101.1.

103.20 Measure and record the room temperature ( $T$ ) near the gas-measuring section.

103.21 Slowly open  $S_{10}$  and  $S_{11}$  to vacuum to evacuate the McLeod gage.

NOTE 86— $S_{10}$  and  $S_{11}$  may be left open to evacuate the McLeod gage continuously during steps 103.3-103.11.

103.22 Discard the contents of the reaction tube to waste by opening  $S_{12}$  to vacuum ( $R$ ) and rinse the reaction tube with distilled water.

103.23 Repeat steps 103.3-103.22 to analyze additional samples.

## 104. Calculations

104.1 Calculate the amount of carbon dioxide in samples or blanks from pressure, volume, and temperature measurements as follows:

$$n = PV/RT \quad (16)$$

where:

$n$  = micromoles of carbon dioxide,

- $P$  = pressure measured by mercury manometer, torr =  $P_S - P_B$ ,  
 $P_S$  = pressure for sample, torr,  
 $P_B$  = pressure for blank, torr,  
 $R$  = gas constant, 0.0624 (torr) (mL)/(mol) (K),  
 $T$  = temperature of the gas, K, and  
 $V$  = volume occupied by the gas, mL. This will be the sum of the volumes  $V_1$ ,  $V_2$  and  $V_3$  which were used.

NOTE 87—Within the pressure range measured, the deviation of carbon dioxide from the ideal gas equation is insignificant.

104.2 Calculate the concentration of soluble carbon in the samples as follows:

$$\text{Soluble carbon, \%} = \frac{(n_s - n_b)(10^{-6}) \times 100}{W_s} \quad (17)$$

where:

- $n_s$  = carbon dioxide in sample,  $\mu$  mol,  
 $n_b$  = carbon dioxide in reagent blank,  $\mu$ mol, and  
 $W_s$  = sample weight, g.

104.3 To simplify the calculations, a calibration curve of weight of carbon versus pressure can be prepared for each combination of volumes  $V_1$ ,  $V_2$ , and  $V_3$ .

### 105. Precision and Bias

105.1 *Precision*—The relative standard deviation is 12 % at concentration levels between 0.6 and 1.2 weight %.

105.2 *Bias*—The average percent recovery obtained from analyzing LASL control standards over a two-year period was 97 %. This method is empirical and consequently precision and bias depend on strict adherence to the prescribed analysis conditions (5).

## METALLIC IMPURITIES BY A DIRECT READER SPECTROMETRIC METHOD

### 106. Scope

106.1 This method is applicable to the determination of metallic impurities in samples of boron carbide powder and pellets. From 20 to 5000  $\mu$ g of many of the impurities per gram of sample can be determined.

### 107. Summary

107.1 Impurity elements are determined by a direct-reading emission spectrometer using a mixture of germanium oxide and graphite as a buffer. Concentrations of impurity elements are printed directly in micrograms per gram after computer calculation of the data supplied by the spectrograph. The number of elements measured by the direct reader will depend on the need and instrument design. This procedure describes the measurement of 13 impurity elements.

### 108. Interferences

108.1 Interference effects depend primarily upon the resolving power of the spectrometer and the selection of the analytical lines.

### 109. Apparatus

- 109.1 *Boron Carbide Mortar and Pestle*.  
 109.2 *Computer*, with at least 8k memory.

109.3 *Counter Electrode*, ASTM C-6 in accordance with Practice E 130 or equivalent.

109.4 *Diamond (Plattner) Mortar*.

109.5 *Direct-Reading Optical Emission Spectrometer*, with at least 0.5 nm/mm reciprocal linear dispersion.

109.6 *Mixer, Dental Amalgamator*,<sup>39</sup> to hold 25.4 by 12.7-mm plastic vials using 9.6-mm plastic balls.

109.7 *Mixer Mill*,<sup>39</sup> to hold 60 by 27-mm plastic vials using 9.6-mm plastic balls.

109.8 *Power Supply*, to provide 15-A d-c arc.

109.9 *Readout System*, to provide conversion of electrical signals from the spectrometer into digital form.

109.10 *Sample Electrode*, AGK SP,<sup>40</sup> Type SP 9036 or equivalent.

109.11 *Teletypewriter*, to provide print-out of results.

## 110. Reagents and Standards

110.1 *Spectroscopic Buffer*—Combine 2 g of germanium dioxide (99.99 % purity) and 6 g of graphite powder (SP-2 Grade),<sup>39</sup> in a 60 by 27-mm plastic vial containing a plastic ball. Mix for 10 min on the mixer mill.

110.2 *Standards*—A minimum of four standards covering the impurity concentration range of interest should be prepared. Each standard used for calibration should be a blend of 13 metal impurity elements in a matrix of boron carbide, germanium dioxide, and graphite, which is the same matrix as that obtained by treating samples according to Section 112.

## 111. Calibration

111.1 Analyze the standards by following the instructions in 112.2.

111.2 *Initial Calibration*—Analyze each standard and measure the output signal versus the concentration for each impurity element. Enter data from the calibration into the computer to determine coefficients for each curve. Store the calibration data in the computer for future use.

111.3 *Calibration Check*—Analyze at least one standard with each set of samples. If the results of this calibration check do not agree with previous calibrations, investigate and resolve the problem before completing the analysis of samples.

## 112. Analysis

112.1 *Sample Preparation*—Sections 112.1.1-112.1.5 are used to reduce pellets to powder. For powder samples, begin their preparation at 112.1.6.

112.1.1 Crush a pellet in diamond mortar using a few, light hammer blows.

NOTE 88—Grinding action must be avoided to prevent iron contamination of the sample.

112.1.2 Remove the finer material.

112.1.3 Repeat 112.1.1 and 112.1.2 until several hundred milligrams of the finer material is obtained.

<sup>39</sup> The Wig-L-Bug and mixer-mill of Spex Industries, Scotch Plains, N. J., have been found to be satisfactory.

<sup>40</sup> Electrodes from National Carbon Company, 120 South Riverside Plaza, Chicago, Ill., 60606, have been found to be satisfactory.

112.1.4 Reduce the particle size of finer crushed material in the boron carbide mortar by using a rocking motion of the pestle.

112.1.5 Grind a 100-mg portion from 112.1.4 to a fine powder in the boron carbide mortar.

112.1.6 Combine 20 mg with 180 mg of the spectroscopic buffer in a plastic vial containing a plastic ball.

112.1.7 Mix for 45 s on the mixer.

112.2 *Sample Analysis:*

112.2.1 Weigh duplicate 20-mg portions of powdered sample into separate sample electrodes.

112.2.2 Make duplicate exposures of each sample using the following conditions: current, 15-A d c; analytical gap, 4 mm; exposure, 20 s.

### 113. Calculations

113.1 The digital information from the detection system is processed by the instruments' computer. The signals are

matched with the appropriate calibration curve, background corrected and the concentration printed in  $\mu\text{g/g}$  of sample. Table 3 lists the wavelength and concentration range for 13 elements determined by this method.

### 114. Precision and Bias

114.1 *Precision*—For LASL control standards analyzed over a two-year period, the relative standard deviations range between 18 and 49

for eight impurity elements, which were Al, Ca, Fe, Si, Mn, Ni, Ti, and V. Concentration levels ranged from about 50 to 1000  $\mu\text{g/g}$ .

114.2 *Bias*—Average percent recoveries obtained analyzing the standards in 114.1 varied between 35 and 80 %.

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**TABLE 1 Analytical Lines for Visual Comparison**

Element	Analytical Line, Å	Concentration Range, µg/g	Element	Analytical Line, Å	Concentration Range, µg/g
Al	3082.2	90 to 4000	Mg	2795.5	20 to 2000
	3092.7	50 to 4000		2802.7	20 to 2000
Bi	3067.7	25 to 1000	Mn	2576.1	50 to 2000
	2898.0	500 to 1000		2801.1	50 to 2000
Ca	3968.5	50 to 450	Ni	3012.0	40 to 4000
	3179.3	450 to 4000		3002.5	40 to 4000
Co	3453.5	50 to 2000	Si	2881.6	150 to 6000
	3044.0	200 to 2000		2514.3	300 to 12 000
Cr	2835.6	200 to 4000	Ti	3088.0	50 to 2000
	2843.2	200 to 4000		3234.5	50 to 2000
Cu	3274.0	20 to 20 000	V	3110.7	40 to 4000
	3247.5	20 to 20 000		3118.4	40 to 4000
Fe	2599.4	200 to 20 000	Zr	3392.0	40 to 4000
	2746.5	1000 to 20 000		3438.2	100 to 4000

**TABLE 2 Analytical Lines for Microdensitometry**

Element	Analytical Line, Å	Concentration Range, µg/g
Al	3082.2	90 to 2050 SS <sup>A</sup>
		1050 to 4050 WS <sup>A</sup>
Bi	3067.7	25 to 1000 SS
Ca	3968.5	50 to 450 WS
		3179.3 <sup>B</sup>
Co	3453.5	20 to 200 SS
		3044.0
Cr	2835.6	400 to 4000 SS
Cu	3274.0	20 to 500 WS
		2599.4
Fe	2746.5	5000 to 20 000 WS
		2000 to 20 000 SS
Mg	2802.7	100 to 1000 WS
Mn	2576.1	100 to 1000 WS
Ni	3012.0	200 to 4000 SS
Si	2881.6	450 to 6150 WS
Ti	3088.0	100 to 2000 SS
V	3110.7	40 to 2000 SS
Zr	3392.0	40 to 440 SS
		240 to 2040 WS

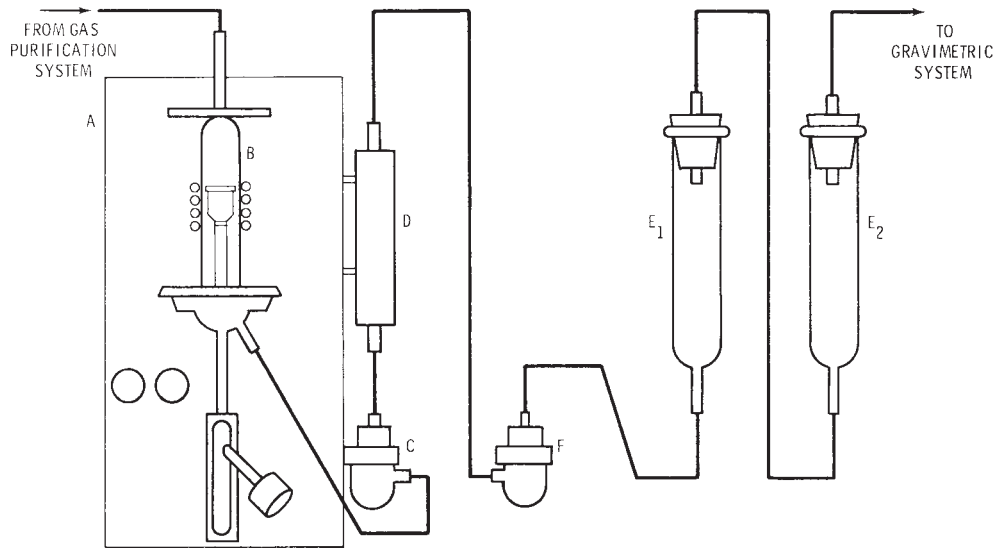
<sup>A</sup>SS means strong (dark) step of the spectrum; WS means weak (light) step.

<sup>B</sup>This analytical line has a weak interfering line for which no correction is made because it is considered to contribute an equal intensity for samples as well as calibration standards.

**TABLE 3 Analytical Lines and Concentration Ranges**

Element	Wavelength, nm	Concentration Range, µg/g
Al	338.289	40–4000
Ca	422.673	100–4000
Co	345.350	20–2000
Cr	425.435	40–4000
Cu	327.396	20–2000
Fe	259.940	200–10 000
Mg	280.270	20–2000
Mn	257.610	10–2000
Na	588.995	50–7000
Ni	305.082	40–4000
Si	251.611	200–6000
Ti	364.268	50–2000
V	310.230	40–4000

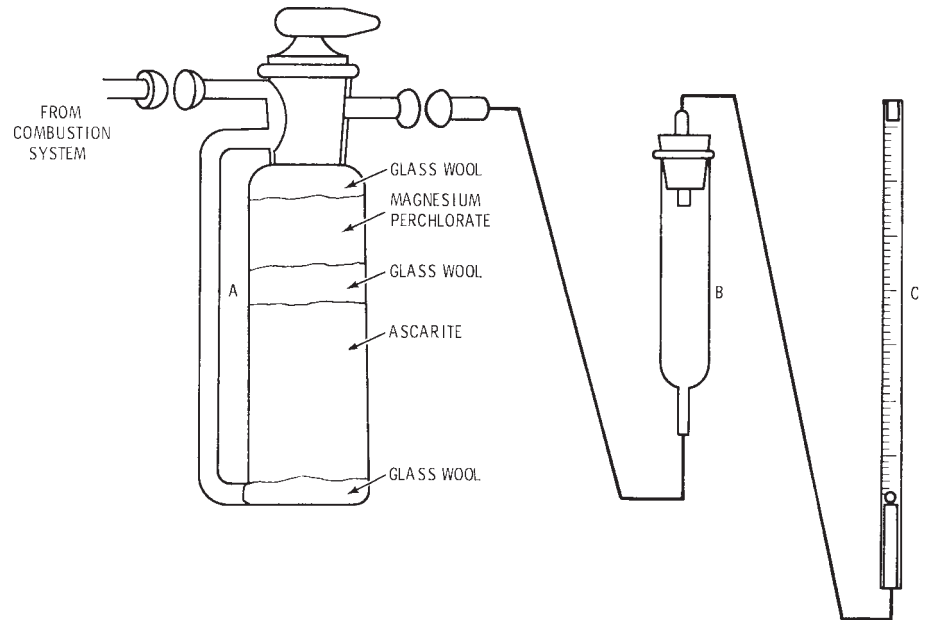




- A. Induction furnace
- B. Combustion tube
- C. Dust trap
- D. Catalyst furnace

- E<sub>1</sub>. Magnesium perchlorate tube
- E<sub>2</sub>. Drierite tube
- F. Sulfur trap

FIG. 1 Combustion System



- A. Nesbitt absorption bulb
- B. Magnesium perchlorate, Drierite and Ascarite tube
- C. Flowmeter

FIG. 2 Gravimetric System

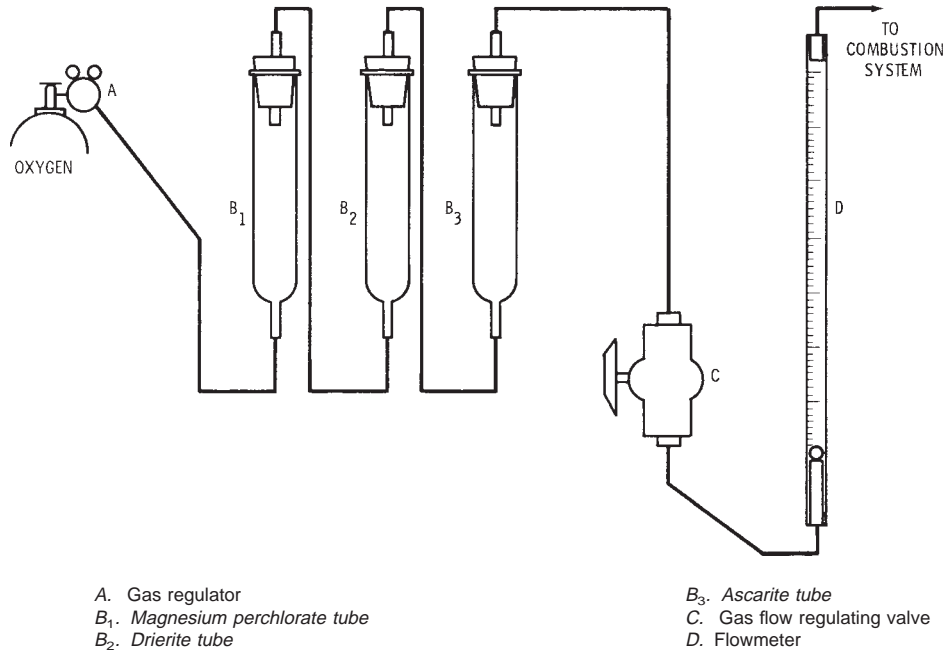


FIG. 3 Oxygen Purification System

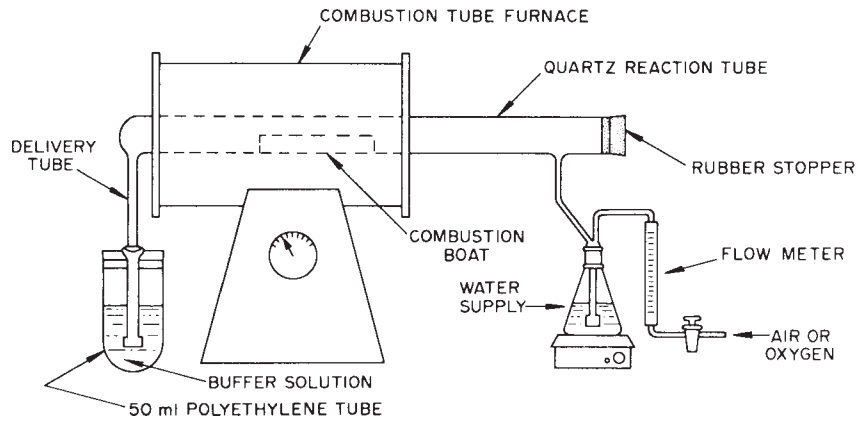


FIG. 4 Pyrohydrolysis Apparatus

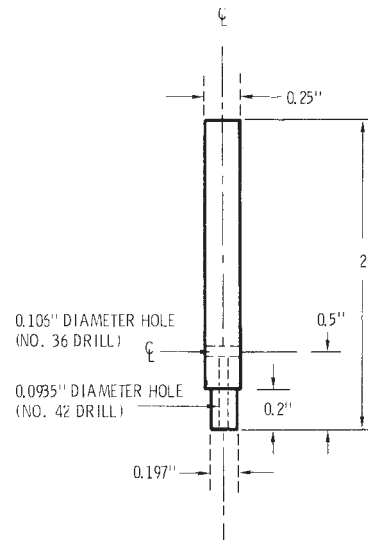
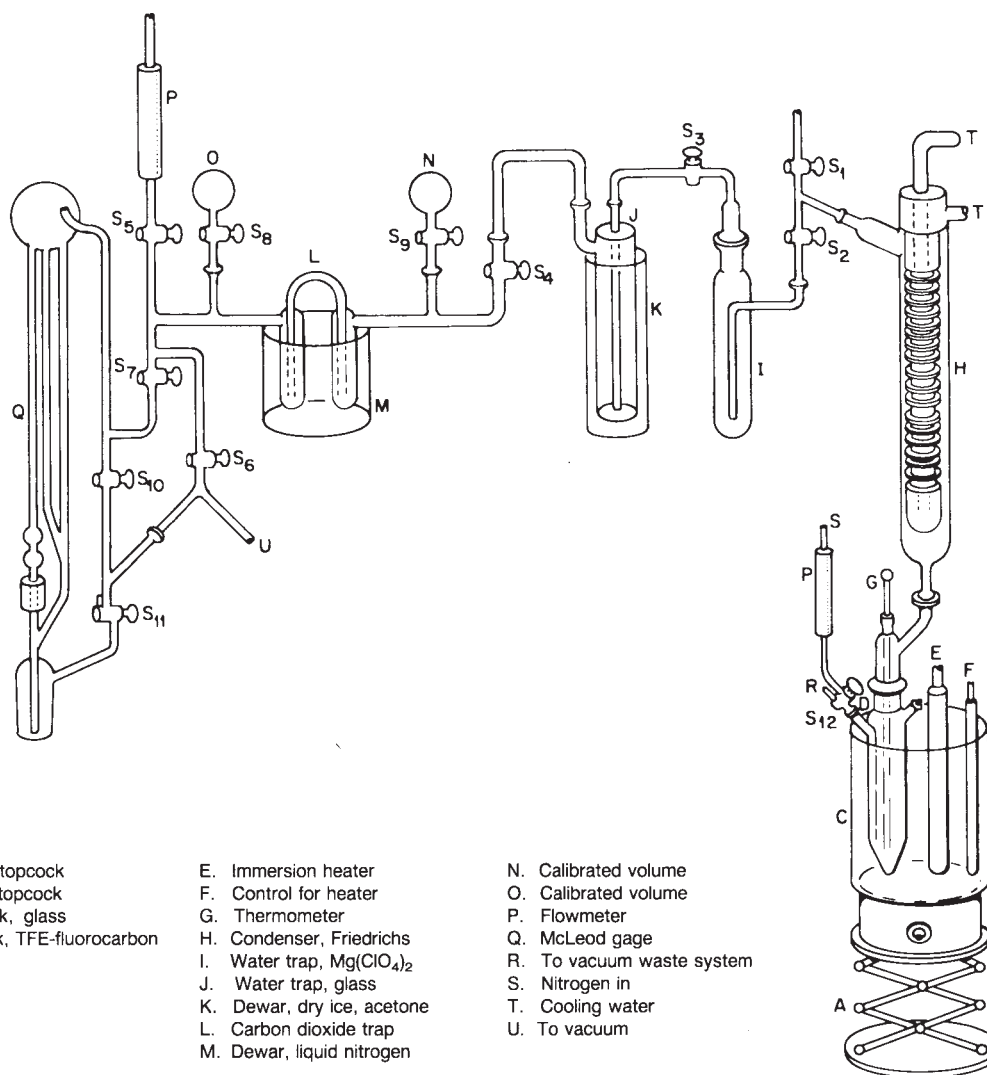


FIG. 5 Packing Tool



- |   |   |                           |
|---|---|---------------------------|
| S <sub>1</sub> -S <sub>9</sub> 5-mm O-Ring stopcock | E. Immersion heater                               | N. Calibrated volume      |
| S <sub>10</sub> Straight-bore stopcock              | F. Control for heater                             | O. Calibrated volume      |
| S <sub>11</sub> 3-Way stopcock, glass               | G. Thermometer                                    | P. Flowmeter              |
| S <sub>12</sub> 3-Way stopcock, TFE-fluorocarbon    | H. Condenser, Friedrichs                          | Q. McLeod gage            |
| A. Power jack                                       | I. Water trap, Mg(ClO <sub>4</sub> ) <sub>2</sub> | R. To vacuum waste system |
| B. Stirrer  | J. Water trap, glass                              | S. Nitrogen in            |
| C. Oil bath   | K. Dewar, dry ice, acetone                        | T. Cooling water          |
| D. Reaction tube                                    | L. Carbon dioxide trap                            | U. To vacuum              |
|   | M. Dewar, liquid nitrogen                         |                           |

FIG. 6 Soluble Carbon Apparatus

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