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The Chemical Determination of Boron in Boron Carbide-Zirconium, Clad with Zircaloy

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The Chemical Determination of Boron in Boron-Carbide—Zirconium, Clad with Zircaloy

J. Rynasiewicz and V. F. Consalvo

Abstract

A rapid dissolution, chemical method for the determination of boron in Zircaloy-clad, boron carbide-zirconium is described.

The sample is dissolved in a mixture of hydrofluoric plus hydrochloric acids contained in a platinum dish which is cooled in a dry-ice bed. Approximately 96 to 99% of the total boron remains undissolved. This is filtered off, ashed, fused with sodium carbonate and the boron is determined according to the classical mannitol titration method.

The acid-soluble boron is determined by a modified mannitol titration after separating the zirconium and other interfering cations with barium carbonate.

The acid-insoluble and acid-soluble boron are added to give the total boron in the sample.

The accuracy and precision of this analysis were checked on synthetic mixtures of "standard" boron carbide plus zirconium. At the 2 per cent boron carbide (1.59% B) level or

higher, the method was accurate to at least 1.15 relative per cent. The precision (95% confidence level) was ± 0.27 and ± 0.95 relative per cent based on 8 measurements or a single measurement, respectively.

"Standardization" of the boron carbide sample was performed by analyzing for boron, carbon, and impurities. A mass balance of 100.22 ± 0.69% was obtained and the boron value was considered accurate within the precision of the analytical method.

Introduction

In connection with the fabrication of Zircaloy-clad reactor materials containing 1 to 5 per cent boron carbide in zirconium, it became necessary to determine the absolute boron level and also the boron homogeneity. The boron content was required for reactor loading purposes and for vendor material acceptance. Any chemical procedure would also serve as a reference method for calibration of non-destructive instrumental monitors.

Previous experience with boron-zirconium alloys (1) indicated that a sodium carbonate fusion of finely divided material effected a good extraction of boron from the bulk of the zirconium. Various metal-boride powders and powdered boron-zirconium samples were particularly amenable to this treatment. However, coarse millings of boron-zirconium failed to fuse completely and the boron results were invariably low.

Because boron carbide is lost during the milling of boron carbide-Zircaloy, an alternate method of analysis had to be devised. Fortunately a procedure (2) had been developed for elemental boron-zirconium alloys whereby the sample was dissolved in dilute HF plus concentrated HCl. Dissolution was done in quartz, under reflux conditions to eliminate possible boron losses. The zirconium was precipitated with barium carbonate and the boron in the filtrate was titrated potentiometrically by the mannitol method between the empirically determined equivalence points, pH-6.9 to 7.5. This wet-dissolution method for elemental boron-zirconium was, therefore, adapted to the analysis of boron in boron carbide-zirconium (3). Accordingly, the acid-insoluble boron carbide was fused with sodium carbonate and analyzed separately; the acid-soluble boron was analyzed after a barium carbonate separation of the zirconium (2).

A particularly objectionable part of this analysis was the lengthy dissolution time. Sometimes one or two weeks were required for dissolving massive samples, usually ~5 g. Consequently, a rapid dissolution method (Appendix I) was developed whereby the sample was dissolved in concentrated hydrofluoric acid, in a platinum dish cooled on a dry-ice bed to minimize boron losses.

At first, the procedure was used to test the homogeneity of vendor material and of samples prepared at KAPL. The least accurate step in the analysis was believed to be the determination of the acid-soluble boron. However, less than 5 per cent of the total boron was acid-soluble and the procedure was considered adequate. The extreme pressure to turn out large numbers of analyses precluded an intensive study of the accuracy and precision. Cursory experiments indicated that the method was precise to ± 3 relative per cent. The accuracy, however, was not known because of the unknown quantity of boron in mocked-up samples of boron carbide plus zirconium. The following experimental procedures, therefore, were used to check the accuracy and precision for reactor loading purposes and for calibration of non-destructive instrumental methods.

Experimental

The final accuracy (not precision) of the total boron analysis in boron-carbide-zirconium depends on the cumulative errors in the following steps of the procedure:

Standards and stoichiometry in the titration of boric acid

Standardization of the boron-carbide

Standards and Stoichiometry

The boron in a solution may be directly related to the number of gram-milliequivalents of sodium hydroxide required to react stoichiometrically with the boric acid according to the mannitol titration.

$$C_6H_8(OH)_6 + H_3BO_3 \longrightarrow C_6H_8(OH)_4 \circ HBO_3 + 2H_2O$$

$$C_6H_8(OH)_4 \circ HBO_3 + NaOH \longrightarrow C_6H_8(OH)_4 \circ NaBO_3 + H_2O$$

The sodium hydroxide solution used for this work was standardized using potassium acid phthalate as a primary standard.[a]

The accuracy of the sodium hydroxide titrant and the stoichiometry of the mannitol-boron titration was further checked against specially prepared "standards"[b] of H_3BO_3 and B_2O_3 containing either isotopically pure boron-10 or boron-11. Reagent grade[c] boric acid (natural boron) was also analyzed as a "standard". The results are found in Table I.

Table I. Analysis of H_3BO_3 and B_2O_3 Prepared from Isotopically Pure B^{10} and B^{11}

Sample	mg B Titrated	Boron Found % theor.
$H_3B^{10}O_3$	4-5	99.63 ± .13
$H_3B^{11}O_3$	4-5	100.0 ± .11
$B_2{}^{10}O_3$	4-5	99.47 ± .07
$B_2{}^{10}O_3$	4-5	99.79 ± .07
$H_3B^{n}O_3$	5	99.88[c]
"	10	99.88
"	10	99.74
"	25	99.32
"	25	99.84

Average = 99.73 ± .22 (95% confidence level)

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[a] National Bureau of Standards potassium acid phthalate sample 84C was used for this work.

[b] Prepared by W. O. Haas, Jr. and J. L. Mewherter

[c] Baker and Adams product

The magnitude and the direction of any bias calculated from the data in Table I depend on a combination of the following:

(a) Accuracy of the absolute acid equivalent of the standard potassium acid phthalate.

(b) Accuracy of the absolute boron content of the boric acid and boric oxide "standards."

(c) Accuracy in the stoichiometry of the mannitol titration for boric acid (i.e. accuracy of the method).

If (a) and (b) are 100% accurate, the bias is -0.27 relative per cent and constitutes an error for the method (c) which may be corrected on the basis of the empirical data. The boron in the boric oxide and boric acid "standards" was calculated on the basis that these materials were 100% pure[a]. Any impurities would tend to decrease the amount of boron actually taken, and thus increase the per cent recovered (Table I). Assuming (a) is known with certainty, the bias ascribed to the method should be smaller than -0.27 relative per cent.

Acid Insoluble Boron

Approximately 95% of the total boron in boron carbide-Zircaloy is acid insoluble and requires a fusion with sodium carbonate (10 parts of Na_2CO_3 to 1 part of boron carbide) which is neutralized with HCl, thereby forming a boric acid solution buffered with sodium chloride.

Possible boron losses due to the fusion with sodium carbonate and the buffering effect of the NaCl during the titration of the boric acid by the mannitol method were checked as follows:

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[a] Baker and Adams H_3BO_3, contains 0.06% impurities.

Replicate samples containing .10 grams of boron (added as boric acid), with and without spectrographically pure carbon, were fused with 1 gram of sodium carbonate at 920°C for 2-4 hours to simulate the fusion conditions for boron carbide. The flux was dissolved and analyzed for boron according to the conventional procedure. The results are given in Table II and indicate that at the .100 gram boron level, the precision and accuracy are not significantly affected by the fusion or by the buffering effect of sodium chloride.

Table II. Analysis of Boric Acid with and without Added Graphite following Fusion with Sodium Carbonate[c]

Boron Added[a]	Carbon Added[b]	Boron Found	
g	g	g	% Theor.
0.1001	0.00	0.1001	100.0
0.0997	0.00	0.0996	99.9
0.1012	0.00	0.1013	100.1
0.08981	0.020	0.08980	99.99
0.08975	0.020	0.08974	99.99
0.09880	0.020	0.09881	100.01

Acid Soluble Boron

Approximately 5 per cent of the total boron in the boron carbide-Zircaloy extrusion was acid soluble under the conditions of the analytical method outlined in Appendix I.

The accuracy of this step in the procedure was checked by analyzing HF solutions containing known amounts of boron (added as H_3BO_3) and zirconium (ZE-4)[d] to simulate solutions containing

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[a] Baker and Adams reagent grade boric acid contains .06% impurities
[b] Spectrographically pure graphite
[c] 1 gram of Na_2CO_3 added. Fusion was at 920°C for 2-4 hours
[d] Sample ZE-4 is an ASTM zirconium "standard" containing ~0.5% Fe, 0.3% Ni, and 0.58% Cr as major impurities.

2 to 8% soluble boron, calculated from the total boron in a 2% boron carbide-Zircaloy sample (i.e. 0.04 to 0.16% boron based on the total sample).

The results are found in Table III and indicate that the acid soluble boron may be analyzed with an error of +22 to -6 relative per cent, but when calculated in terms of the total boron, this amounts to only +44 to -1.44 per cent relative error.

It may be noted from Table III that the boron results tend to be lower the higher the amount of acid soluble boron. If hydrochloric acid is added to the HF solution of the boron-zirconium sample, the boron results are more accurate (Table IV). The relative error computed in terms of the acid soluble boron was +29 to -0.5%; and in terms of the total boron, it was +0.58 to -0.36%.

It is believed that the presence of HCl prevents the coprecipitation of boron when the zirconium is precipitated with barium carbonate as barium fluor-zirconate.

Standardization of Boron Carbide for Total Boron

Two samples of boron carbide[a] were "standardized" by determining total boron, carbon, iron, silicon, and nitrogen by the chemical methods to be described in a separate report. Oxygen and hydrogen analyses were performed by vacuum fusion. Spectrographic analyses were performed and indicated relative amounts of other impurities in the two samples.

The compositions of the individual samples are listed in Table V. (The complete data are found in Appendix II). The deviation of the mass balance (from 100%) and the summation of the standard deviations of each element analyzed were used to evaluate the accuracy of the boron value.

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[a] Made by the Norton Co., Worcester, Mass.

Table III. Analysis of HF Soluble[a] Boron in the Presence of Zirconium

Boron Added	Boron Found	Zr Present	Acid Soluble Boron (%)[b]		Acid-Soluble Boron Found	Relative Error (%)[b]	
			of total boron	of total sample	% Theor.	of acid-soluble boron	of total boron
.080	.100 .096	.2	2.0	0.04	122	+ 22	+ 0.44
.160	.151 .151	.2	4.0	0.08	94	- 6	- 0.24
.240	.193 .193	.2	6.0	0.12	80	- 20	- 1.20
.320	.263 .259	.2	8.0	0.16	82	- 18	- 1.44

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[a] 0.8 ml conc HF/0.2 gram Zr present
[b] based on a 5 gram B_4C-Zirc sample containing 2% boron
[c] corrected for a blank containing 0.079 mg boron

Table IV. Effect of HCl[a] Addition on the Analysis of HF Soluble Boron in the Presence of Zirconium

Boron Added mg	Boron[c] Found mg	Zr Present mg	Simulated Acid-Soluble Boron (%) of total boron	Simulated Acid-Soluble Boron (%) of total sample	Acid Soluble Boron Found % Theor.	Relative Error (%)[b] of acid-soluble boron	Relative Error (%)[b] of total boron
.080	.103	.2	2.0	0.04	129	+ 29	+ 0.58
.160	.159	.2	4.0	0.08	99.5	- 0.5	- 0.02
.240	.226	.2	6.0	0.12	94.0	- 6.0	- 0.36
.320	.305	.2	8.0	0.16	95.0	- 4.5	- 0.36

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[a] 5 ml conc HCl/6 ml of 1-20 HF/0.2 gram of Zr

[b] Based on a 5 gram B_4C-Zirc sample containing 2% boron

[c] Corrected for a blank containing 0.079 mg of boron

Table V. "Standardization" of Boron Carbide Samples by the Mass Balance Method

	Sample KB-325 (-150 to 200 mesh) wt. %	Sample KB-331 (-270 to 400 mesh) wt. %
boron	76.49 ± 0.26 (9)	79.73 ± 0.19 (9)
carbon	20.88 ± 0.08 (9)	19.54 ± 0.08 (9)
iron	0.46 ± 0.02 (4)	0.15 ± 0.05 (4)
silicon	0.31 ± 0.03 (6)	0.50 ± 0.18 (8)
nitrogen	0.49 ± 0.15 (3)	0.20 ± 0.18 (4)
hydrogen	0.02 ± 0.002 (1)	0.01 ± 0.001 (1)
oxygen	0.54 ± 0.05 (1)	0.09 ± 0.009 (1)
spectrographic impurities[a]		
Mass balance	99.19 ± 0.59	100.22 ± 0.69

( ) indicates the number of replicate analyses performed on individual sub-samples (<u>not aliquots of the same solution</u>)

[a] Although absolute values for the metallic impurities (except for iron and silicon) cannot be reported at this time, sample KB-325 appears to be three times "dirtier" than KB-331 with respect to the following elements: Mn, Mg, Cu, Ni, Zr, V, Al

The accuracy of the boron content of the two "standard" boron carbide samples may be more readily evaluated by regrouping the data as in Table V-a. Accordingly the boron content by direct analysis and by difference (subtracting the total impurities from 100%) gave 79.51 ± 0.50 vs. 79.73 ± 0.19% for sample KB-331, and 77.30 ± 0.33 vs. 76.49 ± 0.26% for sample KB-325. The maximum relative error in the accuracy of the boron values was calculated to be 1.15 and 1.84% for KB-331 and KB-325, respectively.

Preparation and Analysis of Synthetic Boron Carbide-Zirconium Mixtures

On the basis of the acceptable mass balance data for sample KB-331, the boron content of this sample was considered to be absolute within the limits specified above.

Nine loose mixtures of boron carbide (KB-331) plus zirconium (ZE-4) plus soluble boric acid[a] were synthesized, dissolved and analyzed according to the procedure given in Appendix I for total boron in boron carbide-Zircaloy. The results (Table VI) were treated statistically and show that the method is accurate to at least 1.15 relative per cent (95% confidence level). One of the measurements failed the "gn" test (4) and was excluded in calculating the precision and accuracy. The precision of a single measurement (95% confidence level) is ± 0.95% relative per cent; of 8 measurements, ± 0.27%.

The reliability of the data in Table VI is particularly enhanced because the total boron was calculated from the sum of two variables; i.e. the acid-soluble plus the acid-insoluble boron.

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[a] Baker and Adams reagent grade.

Table V-a. Direct vs. Indirect Determination of Boron in "Standard" Boron Carbide Samples KB-331 and KB-325

	$\bar{\bar{x}}$	$s^{a}_{.95}$	$\bar{\bar{x}}$	$s^{a}_{.95}$
Iron	0.15	± .05	0.46	± .02
Silicon	0.50	± .18	0.31	± .03
Carbon	19.54	± .08	20.88	± .08
Nitrogen	0.20	± .18	0.49	± .15
Hydrogen	0.0068	± .0007	0.02	± .002
Oxygen	0.0929	± .009	0.54	± .05
Totals	20.49	± .50	22.70	± .33

	100.00	100.00
	-20.49 ± .50	-22.70 ± .33
Boron (by difference)	79.51 ± .50	77.30 ± .33
Boron (direct)	79.73 ± .19	76.49 ± .26
Max. limits of boron (by 2 methods)	79.01 to 79.92%	76.23 to 77.63%
Max. error (absolute)	0.91%	1.40%
Max. error (relative)	1.15%	1.84%

[a] All values except oxygen and hydrogen have been calculated at the 95% confidence level

Table VI. Analysis of Boron in Synthetic Mixtures of Boron Carbide, Zirconium and Boric Acid

Zirconium Present grams	Boron Carbide Added grams	Boric[a] Acid Added grams	Boron in Boron Carbide Added %	Acid-Insoluble Boron Found %	Acid Soluble Boron Found[b] %	Total Boron Found %
5.0	0.100	0.001	79.73	74.02	2.45	76.47[c]
5.0	0.100	0.001	79.73	77.40	2.42	79.82
5.0	0.100	0.001	79.73	78.78	0.93	79.71
5.0	0.100	0.001	79.73	78.06	1.84	79.90
5.0	0.100	0.001	79.73	76.87	3.11	79.96
5.0	0.100	0.001	79.73	78.25	1.40	79.65
5.0	0.100	0.001	79.73	76.20	3.48	79.68
5.0	0.100	0.001	79.73	77.09	2.14	79.23
5.0	0.100	0.001	79.73	77.00	2.06	79.06

$\bar{x}$ = 79.629

s^2 = 0.1016

s = 0.319

[a] Norton sample KB-331 boron carbide

[b] Corrected for 0.001 g. boron added as boric acid

[c] Omitted from calculations because it failed the "gn" test for extreme results.

DISCUSSION

The final phase of this experiment to prove the accuracy and precision of the analytical method for boron would be to analyze extruded boron carbide-Zircaloy "standards." Time did not allow such a study to be made; however, plans are in progress to complete the final phase of this work and to issue the findings in a separate report.

The hot extrusion process could possibly cause the formation of the following boron products, in decreasing order of probability: borides, elemental boron, boric oxide, boron nitride, boron hydride. Of these possible boron products, only the boron hydride would elude detection and estimation by the described analytical procedure.

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APPENDIX I

THE DETERMINATION OF BORON IN BORON CARBIDE-ZIRCONIUM CLAD WITH ZIRCALOY[a]

SCOPE

1. This method is recommended for the determination of boron in boron carbide-zirconium material clad with Zircaloy.

SUMMARY OF METHOD

2. The sample is dissolved in hydrofluoric acid and distilled water in a platinum dish and cooled in dry ice bed. The acid-insoluble residue is filtered, ashed and fused with sodium carbonate. The melt is dissolved in hydrochloric acid and adjusted with sodium hydroxide to precipitate any hydrolyzable elements which may interfere with the final boron titration.(1)

   The boron in the hydrofluoric acid filtrate is separated from the zirconium with a barium carbonate precipitation.(2)

   The acid-insoluble and acid-soluble boron are then determined individually by a potentiometric mannitol titration.

CONCENTRATION RANGE

3. This method is satisfactory for the determination of boron in the range of 1-5 w/o B_4C on at least a 0.2 gram sample.

INTERFERING ELEMENTS

4. Iron, aluminum and other hydrolyzable metals will interfere if present in the final boron titration. However, these should be removed by the barium carbonate or sodium carbonate precipitations.

APPARATUS

5. (a) Corning 728 low-boron glass beakers (400-600 ml)
   (b) 5 ml buret - 0.02 ml buret
   (c) 25 ml buret - 0.1 ml buret
   (d) Polyethylene funnels for 11 cm filter paper
   (e) 250 ml quartz volumetric flask
   (f) Polyethylene beakers - 250 ml
   (g) Schleicher and Schuell blue and white label filter paper
   (h) Flat bottom platinum dishes (100 ml) and covers
   (i) Platinum crucibles (30 ml) and covers

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[a] KAPL Master Analytical Manual, KAPL-AC-7 Rev. 1

(j) Gooch crucibles (medium porosity)

(k) Suction flasks - 500 ml

(l) pH meter - Beckman line operated

(m) Large pyrex dish - 12" x 17"

(n) Paper pulp

REAGENTS

(Should be reagent grade, low in boron)

6. (a) Conc hydrochloric acid

(b) Hydrofluoric acid

(c) Barium carbonate -

(d) Mannitol

(e) 20% sodium hydroxide
Dissolve 100 grams in 500 ml of distilled water

(f) 0.1% methyl red
Dissolve 0.5 gram of methyl red in 500 ml of 95% ethyl alcohol

(g) 1:5 conc hydrochloric acid

(h) 0.1 N sodium hydroxide
Use Acculute solutions and standardize with NBS potassium acid phthalate. Weigh out 2-5 grams of potassium acid phthalate and dissolve in 50 ml of distilled water. Add 3-4 drops of 1% phenolphthalein indicator and titrate with NaOH solution to faint pink color.

$$N_{NaOH} = \frac{\text{grams potassium acid phthalate}}{(.2042)\ \text{ml NaOH}}$$

(i) Phenolphthalein - .5%
Dissolve 2.5 grams of phenolphthalein in 500 ml of ethyl alcohol

(j) 0.02 N sodium hydroxide
Take 200 ml of standardized 0.1 N sodium hydroxide and dilute to 1000 ml

PROCEDURE

7. Transfer at least 0.2 gram sample to a platinum dish. Place the platinum dish in a dry ice bed. Add 5 ml of distilled water and 2-5 ml of hydrofluoric acid in 2 ml increments. Place platinum cover on platinum dish. When the sample has dissolved, warm to room temperature. (If the sample is greater than 0.5 gram, add proportionally larger amounts of acid. Keep concentration of HF at a minimum. For 1 gram add 2-5 ml HF; 5 grams add 20 ml of HF).

Filter the acid insoluble residue using 11 cm fine texture filter paper (plus filter paper pulp) fitted to a polyethylene funnel. (Use paper pulp to police platinum dish). Catch the filtrate in a 400 ml low-boron beaker and save.

Ash the filter paper in a platinum crucible at 500°C. Mix the ash with approximately 10 times as much sodium carbonate. Fuse the sample in a covered crucible at 900°C for 2 to 4 hours.

Transfer the platinum cover, crucible and cooled melt to a 600 ml low-boron beaker. Cover the crucible with water and heat gently until the flux dissolves or otherwise becomes loosened from the crucible. Add a few drops of methyl red. Neutralize the solution with conc hydrochloric acid (red color) and then add 1 ml of acid in excess. Heat solution gently for 1/2 hour and neutralize with 20% NaOH to precipitate zirconium and other metals (pH-7).

Filter the solution into a 600 ml low-boron beaker.[a] Adjust the volume to ~250 ml with distilled water. Add a few drops of methyl red, and adjust to the red end point with 1:5 hydrochloric acid. Add 2-3 drops of acid in excess. Allow the solution to boil on the hot plate for approximately 10-15 minutes to expel carbon dioxide.

Cool the solution to room temperature in cool water and then in ice bath.[b] Neutralize the solution with 0.1 N sodium hydroxide exactly to yellow end point. Note buret reading. Dissolve approximately 20 grams of mannitol in the solution and titrate with standard 0.1 N sodium hydroxide until a lemon color is observed. Add 20 drops of phenolphthalein indicator and continue the titration to the pink-phenolphthalein end point. Note the volume of titrant used after adding the mannitol.

Make the filtrate (containing the HF soluble boron) to 250 ml (quartz flask). Take an aliquot containing approximately 250 milligrams of the sample and transfer to a 600 ml beaker (low-boron). Dilute to approximately 200 ml and add 5 ml conc HCl. Heat the solution to 80°C and add 3 drops of methyl red.

Neutralize the solution with barium carbonate powder. Add a slight excess leaving a layer of barium carbonate on the bottom of the beaker. (Methyl red color changes to yellow). Heat and digest without bumping for 1/2 hour.

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[a] If the sample taken for analysis contained more than 25 mg total boron, make this filtrate to 200 ml and select a convenient aliquot containing $\lesssim$ 25 mg boron.

[b] Caution: Corning 728 glass has a relatively low coefficient of thermal expansion. Rapid cooling will crack the beakers.

Suction-filter the sample through a Gooch crucible containing a mat of paper pulp plus a layer of barium carbonate. Wash the beaker and precipitate well with hot water. Transfer the filtrate to a low-boron beaker. Adjust the pH of the sample to 3.3 using a pH meter. Boil for 10 minutes. Cool the solution carefully.

Titrate the solution potentiometrically to pH 6.9 with standard 0.1 N NaOH. Note buret reading. Add 20 grams of mannitol (color change, yellow to red). Titrate to pH ~6 with 0.02 NaOH and add 20 drops of phenolphthalein. Continue titration to pH 7.5. Note buret reading (color change - yellow to red).

Record the volume of titrant used after adding the mannitol.

Correct the boron found in the acid soluble fraction of the sample by analyzing a solution containing 6 ml 1-20 HF, 5 ml conc HCl, and 250 mg of boron-free zirconium - starting with the barium carbonate precipitation step. The blank contains ~0.08 mg of boron.

CALCULATIONS

8. % total boron % acid-soluble B + % acid-insoluble B

$$\frac{\%\ \text{acid-soluble or}}{}\! \quad$$

$$\begin{array}{l}\%\ \text{acid-soluble or}\\ \%\ \text{acid-insoluble boron}\end{array} = \frac{x\ (\text{N NaOH})\ (.01082) \times 100}{\text{wt sample in grams}}$$

where x = ml of standard NaOH used after addition
of the mannitol

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APPENDIX II

Analysis of "Standard" Boron Carbide Samples KB-331 and KB-325

KB-331

	Boron wt %	Iron wt %	Silicon wt %	Carbon wt %	Nitrogen wt %	Hydrogen wt %	Oxygen wt %	Mass Balance wt %
	79.85	0.13	0.82	19.37	0.16	0.0068	0.0929	
	79.79	0.13	0.64	19.54	0.35			
	79.21	0.20	0.58	19.63	0.21			
	79.92	0.14	0.28	19.43	0.08			
	79.98		0.70	19.63				
	79.99		0.20	19.54				
	79.61		0.35	19.65				
	79.54		0.46	19.62				
	79.71			19.49				
$\bar{x}$ =	79.73	0.15	0.50	19.54	0.20	0.0068	0.0929	100.22 ± 0.69
$s_{.95}$ =	± .19	0.05	0.18	0.08	0.18	0.0007	0.009	0.69

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	76.17	0.45	0.28	20.70	0.45	0.0196	0.5415	
	76.05	0.48	0.25	20.92	0.60			
	76.97	0.46	0.30	20.90	0.42			
	76.04	0.45	0.36	20.83				
	76.65		0.34	20.99				
	76.90		0.31	20.90				
	76.52			20.78				
	76.48			21.03				
	76.59			20.86				
$\bar{x}$ =	76.49	0.46	0.31	20.88	0.49	0.02	0.54	99.19 ± 0.59
$s_{.95}$ =	± .26	0.02	0.03	0.08	0.15	0.002	0.05	0.59