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PHOTOMETRIC METHODS FOR THE DETERMINATION OF IRON, TITANIUM, ALUMINUM, SILICON, AND NICKEL IN BORON CARBIDE

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MATERIALS TESTING DIVISION

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Product Technical Report by

WALTER F. CZYRKLIS and THOMAS A. FERRARO, JR.

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ABSTRACT

I. INTRODUCTION

This paper presents a collection of selected wet-chemical methods which have been tested and are recommended for application to the analysis of boron carbide. Detailed procedures are given for the determination of iron, titanium, aluminum, silicon, and nickel.

The application of these methods to the analysis of a boron carbide sample comprises the initial phase of work done under an Materials Testing Technology Program Task entitled *Emission Spectroscopic Methods for Analysis of Ceramic Armor.* Initial emphasis has been placed on boron carbide because of its importance as the best armor-facing ceramic material presently produced commercially. With the application of different processes for the synthesis and forming of this material, it can be expected that the levels and types of impurity elements will vary. Chemical analysis is needed to monitor such variations in chemical composition because of their potential effect on the ballistic performance of this material.

In emission spectroscopy, the generation of spectral emission is dependent not only upon the electrical-excitation parameters but also upon the nature of the sample material. With highly refractory materials, the volatilization and excitation of constituent elements may be partially or even drastically inhibited; moreover, the extent of this matrix effect may vary widely from element to element and from matrix to matrix.

Ideally then, working curves, that is plots relating spectral line intensities with constituent concentrations, should be based on standard or reference samples of varying composition in which the matrix is identical to that of the samples to which these curves are to be applied.

In the case of boron carbide, however, standard or reference samples are not available. A boron carbide sample which has been analyzed by the methods presented herein is therefore being employed to prepare working curves for the determined elements by applying the technique of sequential dilution. Graphite and lithium carbonate are being used as diluents. Additional samples of boron carbide which have since been obtained from various sources will be analyzed by the wet-chemical methods described herein. The concentration levels of one or more constituents in these samples may prove sufficiently different to allow direct evaluation of the prepared working curves over the observed concentration ranges and may also allow the use of different ratios of sample-to-diluent to check the curves at low levels, thereby enabling the dilution effect to be evaluated.

The wet-chemical methods employed are photometric methods. Each element is determined in an aliquot portion of a sample stock solution which is prepared by fusing a weighed portion of the boron carbide sample with sodium carbonate and dissolving the melt in dilute hydrochloric acid. The methods for iron and titanium have been tested on a series of National Bureau of Standards ceramic samples. The methods for aluminum, silicon, and nickel were each tested on a series of standard solutions prepared from high-purity materials which were carried through the entire procedure.

II. ANALYTICAL PROCEDURES

A. Preparation of Sample Stock Solution

1. Mix an accurately weighed 1-g sample of pulverized boron carbide (~80 mesh) with 5 g of sodium carbonate in a platinum crucible. Cover the crucible and fuse gently over a gas burner. Maintain a low flame until the initial vigorous reactions have subsided, then very gradually increase the temperature to maximum. Allow the material to fuse for about 1/2 hr at this point, occasionally swirling the melt. Finally, transfer the hot crucible to a muffle furnace and continue the fusion at 900 to 1000 °C for 15 to 20 min.

2. Allow the melt to cool, then transfer the crucible and cover to a 250 ml pyrex beaker. Add 100 ml of hydrochloric acid (25 percent) and heat gently to dissolve the melt.

3. Cool the solution, then remove the crucible and cover after rinsing with distilled water. Transfer the solution to a 250-ml volumetric flask, dilute to volume with water, and mix. Transfer the solution to a plastic bottle and reserve.*

B. Determination of Iron by the 1,10-Phenanthroline Photometric Method

1. Scope

This method covers the determination of iron in concentrations from 0.01 to 10 percent.

2. Summary of Method

A suitable aliquot of the sample stock solution is adjusted to pH 6 after reduction with hydroxylamine hydrochloride. The color is developed with 1,10-phenanthroline, and photometric measurement is made at 500 nm (nanometers).

3. Concentration Range

The recommended concentration range is from 0.01 to 0.4 mg of iron per 100 ml of solution, using a 1-cm cell.

4. Stability of Color

The color is stable after heating the solution at 60 to 70 °C for 25 min and remains stable for several hours.

5. Interferences

None of the interfering elements are likely to be present in sufficient quantity to cause any serious error.

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*In photometric methods of analysis, it is customary to correct for reagent effects by carrying a reagent blank through the procedure. It is convenient to prepare a reagent blank stock solution concurrently with the sample stock solution. It is prepared by carrying 5 g of sodium carbonate through the above procedure.

6. Reagents

(a) Standard Iron Solution A (1 ml = 0.200 mg Fe). Dissolve 100.0 mg of iron metal (minimum purity 99.9 percent) in 20 ml of HCl (50 percent). Cool, transfer to a 500-ml volumetric flask, add 25 ml of HCl, dilute* to volume, and mix.

(b) Standard Iron Solution B (1 ml = 0.04 mg Fe). Transfer a 50-ml aliquot of iron solution A (0.200 mg Fe/ml) to a 250-ml volumetric flask, add 25 ml of HCl dilute to volume, and mix.

(c) Ammonium Tartrate Solution (100 g/liter). Dissolve 100 g of ammonium tartrate in water and dilute to one liter.

(d) Ammonium Acetate Solution (250 g/liter). Dissolve 250 g of ammonium acetate in water and dilute to one liter.

(e) Hydroxylamine Hydrochloride Solution (100 g/liter). Dissolve 10 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 100 ml. Prepare fresh as needed.

(f) 1,10-Phenanthroline Solution (10 g/liter). Dissolve 1 g of 1,10-phenanthroline monohydrate in ethanol and dilute to 100 ml with ethanol.

7. Preparation of Calibration Curve

(a) Transfer 0.00, 0.50, 1.00, 3.00, 5.00, 7.00, and 10.00 ml of iron solution B (0.04 mg/ml) to 150-ml beakers.†

(b) Add 5 ml of $NH_2OH \cdot HCl$ solution, 10 ml of ammonium tartrate solution successively, mixing well after each addition.

(c) Using a pH meter, adjust to pH 6 ± 0.1 with NH_4OH (50 percent).

(d) Add 2 ml of the 1,10-phenanthroline solution and mix. Transfer to 100-ml volumetric flasks and dilute to about 90 ml. Heat the solution in a water bath at 60 to 70 °C for 25 min. Cool, dilute to volume, and mix.

(e) Transfer a suitable portion of the reference solution (no iron added) to a 1-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 500 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

(f) Plot the net photometric readings of the calibration solutions against milligrams of iron per 100 ml of solution.

8. Procedure

(a) Transfer a suitable aliquot‡ (containing between 0.01 to 0.4 mg of iron) of the sample stock solution and an identical aliquot of the reagent blank stock solution to separate 150-ml beakers.

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*In this and subsequent procedures, distilled water is used for dilution unless indicated otherwise.

†All glassware used in this method should be cleaned with HCl and rinsed with distilled water before using.

‡Usually a 5 to 15 ml aliquot is adequate.

(b) Proceed as directed in Preparation of Calibration Curve, Steps 7.(b) through 7.(e), above.

(c) After correcting for reagent blank, convert the photometric readings to milligrams of iron by means of the calibration curve.

9. Calculations

Calculate the percentage of iron as follows:

$$\text{Iron, percent} = \frac{A}{B} \times 100$$

where:

A = milligrams of iron in aliquot,

B = sample weight in milligrams, represented in aliquot taken.

C. Determination of Titanium by the Hydrogen Peroxide Photometric Method

1. Scope

This method covers the determination of titanium in concentrations from 0.01 to 0.5 percent.

2. Summary of Method

A suitable aliquot of the sample stock solution is treated with sulfuric acid, and the yellow-colored complex of titanium is formed with hydrogen peroxide. Photometric measurement is made at approximately 400 nm.

3. Concentration Range

The recommended concentration range is from 0.01 to 0.10 mg of titanium per 25 ml of solution, using a 5-cm cell.*

4. Stability of Color

The color is stable for at least one hr.

5. Interferences

The elements ordinarily present in boron carbide do not interfere.

6. Reagents

(a) Standard Titanium Solution A (1 ml = 1.000 mg). Fuse 0.1668 g of titanium dioxide (previously heated to 500 °C) with 2 g potassium pyrosulfate in a quartz crucible. Add 50 ml of H_2SO_4 (20 percent) and heat gently to dissolve the melt. Cool the solution, then transfer to a 100-ml volumetric flask, dilute to volume, and mix.

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*This procedure has been written for a 5-cm cell. Cells having other dimensions may be used and the concentration range extended, provided suitable adjustments can be made in the amounts of sample and reagents used.

(b) Standard Titanium Solution B (1 ml = 0.010 mg). Transfer a 10-ml aliquot of titanium solution A (1 mg Ti/ml) to a 1-liter volumetric flask, dilute to volume, and mix.

7. Preparation of Calibration Curve

(a) Transfer 0.00, 1.00, 3.00, 5.00, 7.00, and 10.00 ml of titanium solution B (0.01 mg/ml) to 25-ml volumetric flasks.

(b) Add 5 ml of H_2SO_4 (50 percent) and 5 ml of H_3PO_4 (20 percent), dilute to approximately 20 ml, and mix. Add 1 ml of H_2O_2 (30 percent), dilute to volume, and mix.

(c) Transfer a suitable portion of the reference solution (no titanium added) to a 5-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 400 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

(d) Plot the net photometric readings of the calibration solutions against milligrams of titanium per 25 ml of solution.

8. Procedure

(a) Transfer two suitable aliquots (containing between 0.01 and 0.10 mg of titanium) of the sample stock solution and an identical aliquot of the reagent blank stock solution to separate 150-ml beakers.

(b) Add 5 ml of H_2SO_4 (50 percent) and evaporate on a hot-plate until sulphur trioxide fumes appear. Cool the solutions, rinse the cover glasses and beakers, then heat to fumes again to insure the complete removal of HCl. Cool the solutions and dilute to approximately 10 ml. Heat if necessary to dissolve any soluble salts.

(c) Transfer to 25-ml volumetric flasks, add 5 ml of H_3PO_4 (20 percent), and dilute to 20 ml if necessary. Add 1 ml H_2O_2 (30 percent) to one of the two sample solutions and to the reagent blank. The other sample solution is used as a sample blank to correct for the absorption due to species other than the titanium peroxide complex. Dilute the solutions to volume and mix.

(d) Proceed as directed in Preparation of Calibration Curve, Step 7.(c), above.

(e) After correcting for reagent and sample blanks, convert the photometric readings to milligrams of titanium by means of the calibration curve.

9. Calculations

Calculate the percentage of titanium as follows:

$$\text{Titanium, percent} = \frac{A}{B} \times 100$$

where:

A = milligrams of titanium in aliquot,

B = sample weight in milligrams, represented in aliquot taken.

D. Determination of Aluminum by the Chloroform 8-Quinolinol Extraction, Photometric Method

1. Scope

This method covers the determination of aluminum in concentrations from 0.01 to 0.5 percent.

2. Summary of Method

A suitable aliquot of the sample stock solution is treated with diethyldithiocarbamate and chloroform to extract interfering elements. The yellow-colored aluminum complex formed with 8-quinolinol is extracted with chloroform and measured photometrically at approximately 390 nm.

3. Concentration Range

The recommended concentration range is from 0.01 to 0.10 mg of aluminum per 50 ml of solution, using a 1-cm cell.

4. Stability of Color

The color develops almost immediately and is stable for at least 2 hrs.

5. Interferences

The elements that interfere (iron, manganese, titanium, and nickel) are removed by extraction with diethyldithiocarbamate and chloroform.

6. Reagents

(a) Standard Aluminum Solution A (1 ml = 0.200 mg). Dissolve 100.0 mg of aluminum metal (minimum purity 99.9 percent) in 50 ml of HCl (50 percent). Cool, transfer to a 500-ml volumetric flask, dilute to volume, and mix.

(b) Standard Aluminum Solution B (1 ml = 0.010 mg). Transfer a 25-ml aliquot of aluminum solution A (0.200 mg/ml) to a 500-ml volumetric flask, add 25 ml of HCl, dilute to volume, and mix.

(c) Sodium Acetate Solution (270 g/liter). Dissolve 270 g of sodium acetate in water and dilute to one liter.

(d) Sodium Diethyldithiocarbamate Solution (10 g/liter). Dissolve 1 g of sodium diethyldithiocarbamate in water and dilute to 100 ml. Prepare fresh as needed.

(e) 8-Quinolinol Solution (10 g/liter). Dissolve 1 g of 8-hydroxyquinoline in chloroform ($CHCl_3$) and dilute to 100 ml with $CHCl_3$.

7. Preparation of Calibration Curve

(a) Transfer 0.00, 1.00, 3.00, 5.00, 7.00, and 10.00 ml of aluminum solution B (0.010 mg/ml) to separatory funnels.

(b) To each funnel add 10 ml of sodium acetate solution followed by 10 ml of sodium diethyldithiocarbamate solution, mixing well after each addition. Add 5 ml of $CHCl_3$.

(c) Shake thoroughly, allow the layers to separate and discard the $CHCl_3$ layer. Repeat with 5-ml portions of $CHCl_3$ until the $CHCl_3$ layer remains colorless. Finally, rinse the stem of the funnel with the same solvent.

(d) Adjust the aqueous phase to pH 9-9.5 with NaOH (30 percent). By pipet, add 10 ml of 8-quinolinol solution. Shake thoroughly for 1 to 2 min. Allow the layers to separate and draw off the $CHCl_3$ layer, collecting it in a 50-ml volumetric flask. Repeat at least twice with 5-ml portions of $CHCl_3$ to ensure a complete extraction. Dilute the solution to volume with acetone and mix.

(e) Transfer a suitable portion of the reference solution (no aluminum added) to a 1-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 390 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

(f) Plot the net photometric readings of the calibration solutions against milligrams of aluminum per 50 ml of solution.

8. Procedure

(a) Transfer a suitable aliquot (containing between 0.01 to 0.10 mg of aluminum) of the sample stock solution and an identical aliquot of the reagent blank stock solution to separatory funnels.

(b) Proceed as directed in Preparation of Calibration Curve, Steps 7.(b) through 7.(e), above.

(c) After correcting for reagent blank, convert the photometric readings to milligrams of aluminum by means of the calibration curve.

9. Calculations

Calculate the percentage of aluminum as follows:

$$\text{Aluminum, percent} = \frac{A}{B} \times 100$$

where:

A = milligrams of aluminum in aliquot,

B = sample weight in milligrams, represented in aliquot taken.

E. Determination of Silicon by the Molybdenum - Blue Photometric Method

1. Scope

This method covers the determination of silicon in concentrations from 0.01 to 1.0 percent.

2. Summary of Method

A suitable aliquot of the sample stock solution is adjusted to pH 1, and treated with sodium molybdate, oxalic acid, and ferrous ammonium sulfate to form the blue silicomolydate complex. Photometric measurement is made at 650 nm.

3. Concentration Range

The recommended concentration range is from 0.01 to 0.2 mg of silicon per 100 ml of solution, using a 2-cm cell.

4. Stability of Color

The color develops almost immediately after the addition of ferrous ammonium sulfate and is stable for at least 40 min.

5. Interferences

None of the elements commonly found in boron carbide interfere.

6. Reagents

(a) Standard Silicon Solution A (1 ml = 0.05 mg Si). Fuse 0.1070 g of anhydrous silicon dioxide (SiO_2) with 1.0 g of sodium carbonate (Na_2CO_3) in a platinum crucible. Cool the melt, dissolve completely in hot water in a Teflon beaker, remove the crucible, rinse, and cool the solution. Transfer to a 1-liter volumetric flask, dilute to volume, and mix. Immediately transfer to a polyethylene bottle.

(b) Standard Silicon Solution B (1 ml = 0.02 mg Si). Using a pipet, transfer 200 ml of silicon solution A (1 ml = 0.05 mg Si) to a 500-ml volumetric flask, dilute to volume, and mix. Immediately transfer to a polyethylene bottle. Prepare fresh, just before use.

(c) Sodium Molybdate Solution (100 g/liter). Dissolve 100 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in water and dilute to one liter.

(d) Oxalic Acid Solution (100 g/liter). Dissolve 100 g of oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$) in water and dilute to one liter.

(e) Ferrous Ammonium Sulfate Solution (62.5 g/liter). Dissolve 62.5 g of ferrous ammonium sulfate hexahydrate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] in 100 ml of H_2SO_4 (10 percent), and dilute to one liter.

7. Preparation of Calibration Curve

(a) Transfer 0.00, 0.50, 1.00, 3.00, 5.00, 7.00, and 10.00 ml of silicon solution B (0.02 mg Si/ml) to polyethylene beakers and dilute to 10 ml.

(b) Using plastic pipets, add while swirling 10 ml of sodium molybdate solution. Adjust the pH to 1.0 ± 0.1 with NaOH (10 percent) or HCl (10 percent) and dilute to 25 ml, if necessary. Allow solution to stand 15 min.

(c) Add 18 ml of HCl (50 percent). Using plastic pipets, add 10 ml of oxalic acid solution, then immediately add 2 ml of ferrous ammonium sulfate solution, mixing during each addition.

(d) Transfer to 100-ml volumetric flasks, dilute to volume, and mix. Allow to stand 10 min.

(e) Transfer a suitable portion of the reference solution (no silicon added) to a 2-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 650 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

(f) Plot the net photometric readings of the calibration solutions against milligrams of silicon per 100 ml of solution.

8. Procedure

(a) Transfer an aliquot of the sample stock solution containing between 0.01 to 0.2 mg of silicon (usually 5 to 15 ml) and an identical aliquot of the reagent blank stock solution to 100-ml polyethylene beakers. Transfer a second aliquot of the sample stock solution to a 100-ml pyrex beaker. The second sample solution is used as a sample blank to correct for absorption due to species other than the silicomolybdate complex. To the polyethylene beakers add 10 ml of sodium molybdate solution, using a plastic pipet, and mixing during the addition (if the sample solution turns turbid at this point, it is an indication that too much silicon is present and a smaller aliquot portion should be taken). To the pyrex beaker, add 10 ml of oxalic acid solution, again using a plastic pipet. Adjust the pH to 1.0 ± 0.1 with NaOH (10 percent) or HCl (10 percent) and dilute to 25 ml, if necessary. Allow to stand 15 min.

(b) To each beaker add 18 ml of HCl (50 percent) and mix. To the polyethylene beakers add 10 ml of oxalic acid solution and immediately 2 ml of ferrous ammonium sulfate solution, using plastic pipets and mixing while adding. To the pyrex beaker add 10 ml of sodium molybdate solution and 2 ml of ferrous ammonium sulfate solution, again using plastic pipets and mixing while adding.

(c) Transfer the solutions to 100-ml volumetric flasks, dilute to volume, and mix. Allow to stand 10 min.

(d) Proceed as directed in Preparation of Calibration Curve, Step 7.(e), above.

(e) After correcting for reagent and sample blanks, convert the photometric readings to milligrams of silicon by means of the calibration curve.

9. Calculations:

Calculate the percentage of silicon as follows

$$\text{Silicon, percent} = \frac{A}{B} \times 100$$

where:

A = milligrams of silicon in aliquot,

B = sample weight in milligrams, represented in aliquot taken.

F. Determination of Nickel by the Dimethylglyoxime Photometric Method

1. Scope

This method covers the determination of nickel in concentrations from 0.01 to 0.5 percent.

2. Summary of Method

A suitable aliquot of the sample stock solution is treated with nitric acid, and the soluble red-colored nickel-dimethylglyoxime complex is formed after oxidation with ammonium persulfate. Photometric readings are taken at approximately 520 nm.

3. Concentration Range

The recommended concentration range is from 0.01 to 0.10 mg of nickel per 100 ml of solution, using a 5-cm cell.*

4. Stability of Color

The color develops in approximately 1 hr and is stable for at least 30 min after.

5. Interferences

The elements ordinarily present in boron carbide do not interfere.

6. Reagents

(a) Standard Nickel Solution A (1 ml = 0.200 mg). Dissolve 100.0 mg of nickel metal (minimum purity 99.9 percent) in 50 ml of HNO (50 percent). Boil to expel oxides of nitrogen. Cool, transfer to a 500-ml volumetric flask, dilute to volume, and mix.

(b) Standard Nickel Solution B (1 ml = 0.010 mg). Transfer a 25-ml aliquot of nickel solution A (0.200 mg/ml) to a 500-ml volumetric flask, dilute to volume, and mix.

(c) Ammonium Persulfate Solution (100 g/liter). Dissolve 10 g of ammonium persulfate [$(NH_4)_2S_2O_8$] in water and dilute to 100 ml. Prepare fresh as needed.

(d) Ammonium Citrate Solution (250 g/liter). Dissolve 250 g of ammonium citrate in water and dilute to one liter.

(e) Dimethylglyoxime, Alcoholic Solution (10 g/liter). Dissolve 10 g of dimethylglyoxime in ethanol and dilute to one liter with ethanol.

7. Preparation of Calibration Curve

(a) Transfer 0.00, 1.00, 3.00, 5.00, 7.00, and 10.00 ml of nickel solution B (0.010 mg/ml) to 150-ml beakers.

(b) Add 5 ml of [$(NH_4)_2S_2O_8$] solution, mix and allow to stand 5 min. Add 10 ml of ammonium citrate solution, mix, then dilute to 70 to 80 ml. Using a pH meter, adjust the pH to 10 ± 0.1 with NaOH (30 percent).

(c) Transfer to 100-ml volumetric flasks, add 2 ml of dimethylglyoxime solution, dilute to volume, and mix. Allow to stand 1 hr.

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*This procedure has been written for a 5-cm cell. Cells having other dimensions may be used and the concentration range extended, provided suitable adjustments can be made in the amounts of sample and reagents used.

(d) Transfer a suitable portion of the reference solution (no nickel added) to a 5-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 520 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

(e) Plot the net photometric readings of the calibration solutions against milligrams of nickel per 100 ml of solution.

8. Procedure

(a) Transfer a suitable aliquot (containing between 0.01 to 0.10 mg of nickel) of the sample stock solution and an identical aliquot of the reagent blank stock solution to 150-ml beakers.

(b) Add 5 ml of HNO_3 and evaporate almost to dryness (2 to 3 ml). Dilute to 20 ml and heat if necessary to dissolve soluble salts. Cool the solution.

(c) Proceed as directed in Preparation of Calibration Curve, Steps 7.(b) through 7.(d), above.

(d) After correcting for reagent blank, convert the photometric readings to milligrams of nickel by means of the calibration curve.

9. Calculations

Calculate the percentage of nickel as follows:

$$\text{Nickel, percent} = \frac{A}{B} \times 100$$

where:

A = milligrams of nickel in aliquot,

B = sample weight in milligrams, represented in aliquot taken.

III. RESULTS AND DISCUSSION

As stated earlier, the procedures for iron and titanium were tested on a series of National Bureau of Standards standard ceramic samples. Table I summarizes the results obtained by the recommended procedures for these standard samples and the boron carbide sample which is designated as E-1 for identification.

TABLE I. RESULTS FOR IRON AND TITANIUM

Sample	Type	Iron, %		Titanium, %	
		Certificate Value	Found	Certificate Value	Found
1A	Argillaceous limestone	1.14	1.11	0.10	0.12
69A	Bauxite	4.07	4.04	1.67	1.70
77	Burnt refractory	0.63	0.58	1.76	1.76
78	Burnt refractory	0.55	0.51	2.02	1.99
98	Plastic clay	1.43	1.42	0.86	0.88
E-1	Boron carbide	-	0.34	-	0.12

The results obtained on the standard samples are all within the range of results reported by cooperating laboratories and listed on the Bureau of Standards Certificates.

The concentration levels of aluminum and silicon in the Bureau of Standards samples cited in Table I are too high to allow proper evaluation of the recommended photometric procedures which are intended for low-level applications. Nickel, on the other hand, is not present in these materials. To evaluate the procedures recommended for these elements, therefore, synthetic standards were prepared and carried through the procedures. To simulate the composition of actual boron carbide sample stock solutions, boric acid was mixed with the sodium carbonate prior to fusion and leaching as prescribed. Aliquot portions of standard solutions of aluminum, silicon, and nickel and the simulated sample stock solution were combined to prepare the synthetic standards which were then carried through the analytical procedures.

Table II summarizes the results obtained on the synthetic samples and the boron carbide sample E-1.

TABLE II. RESULTS FOR ALUMINUM, SILICON AND NICKEL

	Synthetic Standards			Boron Carbide E-1
Aluminum, % Added	0.027	0.133	0.266	-
Found	0.026	0.126	0.266	0.297
Silicon, % Added	0.032	0.158	0.316	-
Found	0.032	0.157	0.317	0.087
Nickel, % Added	0.005	0.026	0.052	-
Found	0.005	0.026	0.053	0.028

For each element, the recommended procedure provided quantitative recoveries from the synthetic standards.

According to test results, there is no doubt that the proposed procedures can be applied to provide reliable determinations of iron, titanium, aluminum, silicon, and nickel in boron carbide within the indicated concentration ranges. However, each of these elements is determined in an aliquot portion of the sample stock solution which is prepared from a single sample. Therefore, precautions to be exercised in sample preparation cannot be overemphasized.

Samples of boron carbide submitted for analysis are usually provided in the form of solid pieces. These pieces must be pulverized until the entire sample can be passed through a No. 80 Sieve (U.S. Sieve Series). This is necessary to allow intimate mixing of the sample with sodium carbonate prior to fusion. If a steel mortar and pestle are used to crush the sample, as has been the procedure in this laboratory, it is essential that a magnet be passed through the sample several times to insure complete removal of metal particles.

Care must be taken to avoid loss of material during sample preparation due to spattering while fusing, incomplete fusion, and incomplete dissolution of the fused melt. Spattering losses can be avoided by keeping the crucible well covered and keeping the flame temperatures down, especially at the initial stage.

The molten flux should finally be examined to insure that there are no undecomposed particles remaining – the flux should be clear. Finally, complete dissolution on leaching should be verified by removal and careful examination of the crucible. Reflected light will reveal any undissolved material at the bottom edge of the crucible.

Although the photometric methods described herein were selected and evaluated primarily to provide samples of analyzed boron carbide to be used in setting up emission spectroscopic methods, it is recommended that the former methods be adopted for general use in this laboratory until reliable spectroscopic methods are established.