



Standard Test Methods for Chemical Analysis of Graphite¹

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1. Scope

1.1 These test methods cover the chemical analysis of graphite.

1.2 The analytical procedures appear in the following order:

	Sections
Silicon by the Molybdenum Blue (Colorimetric) Test Method	8 to 14
Iron by the <i>o</i> -Phenanthroline (Colorimetric) Test Method	15 to 21
Calcium by the Permanganate (Colorimetric) Test Method	22 to 28
Aluminum by the 2-Quinizarin Sulfonic Acid Test Method	29 to 35
Titanium by the Peroxide (Colorimetric) Test Method	36 to 43
Vanadium by the 3,3'-Dimethylnaphthidine (Colorimetric) Test Method	44 to 51
Boron by the Curcumin-Oxalic Acid (Colorimetric) Test Method	52 to 59

1.3 The preferred concentration of sought element in the final solution, the limits of sensitivity, and the precision of the results are given in Table 1.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See 56.1 for specific caution statement.

2. Referenced Documents

2.1 ASTM Standards:

C 561 Test Method for Ash in a Graphite Sample²

D 1193 Specification for Reagent Water³

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials⁵

3. Significance and Use

3.1 These test methods provide a practical way to measure the concentration of certain trace elements in graphite. Many end uses of graphite require that it be free of elements which

TABLE 1 Concentration of Elements, Limits of Sensitivity, and Reproducibility

Element	Concentration Range, $\mu\text{g/mL}$ Solution	Sensitivity Limit, $\mu\text{g/mL}$ Solution	Reproducibility, Relative, % ($\sigma/x \times 100$)
Silicon	10 to 100 $\mu\text{g}/100\text{ mL}$	1 $\mu\text{g}/100\text{ mL}$	± 4
Iron	100 to 600 $\mu\text{g}/100\text{ mL}$	40 $\mu\text{g}/100\text{ mL}$	± 5
Calcium	600 to 3000 $\mu\text{g}/100\text{ mL}$	50 $\mu\text{g}/100\text{ mL}$	± 5
Aluminum	10 to 100 $\mu\text{g}/100\text{ mL}$	2 $\mu\text{g}/100\text{ mL}$	± 0.1
Titanium	600 to 3000 $\mu\text{g}/100\text{ mL}$	200 $\mu\text{g}/100\text{ mL}$	± 2
Vanadium	10 to 130 $\mu\text{g}/50\text{ mL}$	5 $\mu\text{g}/50\text{ mL}$	± 5
Boron	0.5 to 1.4 $\mu\text{g}/50\text{ mL}$	0.1 $\mu\text{g}/50\text{ mL}$	± 20

may be incompatible with certain nuclear applications. Other elemental contamination can affect the rate of oxidative degradation.

3.2 These test methods allow measurement of trace amounts of contaminants with a minimal amount of costly equipment. The colorimetric procedures used are accessible to most laboratories.

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.⁶ 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 When available, National Institute of Standards and Technology (NIST) certified reagents should be used as standards in preparing calibration curves.

4.3 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

4.4 National Institute of Standards and Technology certified reagents specified in certain steps of this procedure may no

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² *Annual Book of ASTM Standards*, Vol 05.05.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

longer be available. If NIST reagents are not available, then the highest purity reagent grade shall be substituted.

5. Sampling

5.1 The entire sample of graphite should be crushed and ground to pass a No. 60 (250- μ m) sieve in a roll crusher. The sample may have been reduced in size initially by drilling the test bar with silicon carbide-tipped drills.

6. Rounding Calculated Values

6.1 Calculated values shall be rounded to the desired number of places in accordance with Practice E 29.

7. Precision and Bias

7.1 No statement is being made about either the precision or bias of these test methods. At this time Committee C-5 is investigating new standard methods of chemical analysis of graphite that will eventually replace these test methods. For this reason, no statistical study of these test methods has been planned.

7.2 The relative reproducibility data in Table 1 has no supportive research report on file and does not conform to ASTM precision and bias standards.

SILICON BY THE MOLYBDENUM BLUE TEST METHOD

8. Summary of Test Method

8.1 Silicomolybdic acid is formed by adding ammonium molybdate to soluble silicates in acid solution. The heteropoly acid is reduced with stannous chloride to form a deep blue colloidal solution. Photometric measurement is made at 765 nm. Regular classical gravimetric methods for silica using sodium carbonate fusion followed by hydrofluoric acid volatilization may be suitable for use.

9. Stability of Color

9.1 The blue colored solution should be disposed of and the determination repeated if a period of 12 h has elapsed between color development and measurements.

10. Interferences

10.1 There is no interference from the ions usually present in graphite.

11. Reagents

11.1 *Ammonium Molybdate* (50 g/L)—Dissolve 50 g of ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) in water and dilute to 1 L.

11.2 *Hydrochloric Acid* (HCl) (1+1)—Mix equal volumes of concentrated HCl, sp gr 1.19 and water.

11.3 *Silicon, Standard Solution* (1 mL = 1 mg Si)—Dissolve 10.1 g of sodium silicate (Na₂SiO₃·9H₂O) in water and dilute to 1 L in a volumetric flask. Store in a polyethylene bottle. Determine *exact* concentration by the standard gravimetric procedure.

11.4 *Silicon, Working Solution* (1 mL = 0.01 mg Si)—Dilute 10 mL of standard silicon solution (1 mL = mg Si) to 1 L in a volumetric flask. Transfer to a polyethylene bottle.

11.5 *Sodium Carbonate Solution* (100 g/L)—Dissolve 100 g of sodium carbonate (Na₂CO₃) in water and dilute to 1 L. Store in a polyethylene bottle.

11.6 *Stannous Chloride Solution*—Dissolve 2.5 g of stannous chloride (SnCl₂·2H₂O) in 5 mL of hot concentrated HCl (sp gr 1.19) and dilute to 250 mL with water. Prepare a fresh solution every 2 weeks.

11.7 *Sulfuric Acid* (H₂SO₄) (1+3)—Carefully mix 1 volume of concentrated H₂SO₄, sp gr 1.84 with 3 volumes of water.

12. Preparation of Calibration Curve

12.1 *Calibration Solutions*—Transfer 0, 1.0, 3.0, 5.0, 7.0, and 10 mL of silicon working solution (1 mL = 0.01 mg Si) to 100-mL volumetric flasks. Add 5 drops of H₂SO₄ (1+3) and dilute to approximately 10 mL.

12.2 *Color Development*—Add 2.5 mL of (NH₄)₆Mo₇O₂₄ solution to each flask and let stand 5 min. Then add 5.0 mL of H₂SO₄ (1+3), mix well, and add 5 drops of SnCl₂ solution. Dilute to volume and let stand 5 min.

12.3 *Photometry*—Transfer a suitable portion of the reagent blank solution to a 1-cm absorption cell and adjust the photometer to the initial setting, using a wavelength of 765 nm. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

12.4 *Calibration Curve*—Plot the photometric readings (absorbance) of the calibration solution against micrograms of silicon per 100 mL of solution.

13. Procedure for Carbonate Fusion

13.1 *Sample Solution*—Rinse the ash (from a 50 to 75-g ash sample) from the platinum dish into a mullite mortar with three 0.5-g portions of Na₂CO₃ passing a No. 100 (150- μ m) sieve (see Test Method C 561). Grind the resulting mixture to pass a No. 200 (75- μ m) sieve to ensure intimate contact of the ash with the flux. Then transfer the mixture to a platinum crucible (containing 0.5 g of Na₂CO₃) with three 0.5-g rinses of Na₂CO₃. Add sufficient Na₂CO₃ to bring the total Na₂CO₃ content to 6 g. Cover the crucible, and fuse gently over a bunsen burner.

13.1.1 When fusion is complete (usually 30 min to 1 h), remove the crucible from the burner, swirl to distribute the melt on the sides of the crucible, and allow to cool. Then place the crucible and contents in a 200-mL high-form beaker and add 25 mL of water. Cover the beaker with a watch glass, and cautiously add HCl (1+1) to decompose the melt. When solution of the melt is complete, boil for several minutes on a hot plate and cool.

13.1.2 Transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer a suitable aliquot of this solution to a 100-mL volumetric flask.

13.2 *Color Development*—Adjust the pH of the aliquot to 6 to 8 with Na₂CO₃ solution, then proceed in accordance with 13.2.

13.3 *Photometry*—Proceed in accordance with 12.3.

13.4 *Calibration*—Convert the photometric reading of the sample solution to micrograms of silicon by means of the calibration curve.

14. Calculation

14.1 Calculate the parts per million of silicon in the original sample as follows:

$$\text{Silicon, ppm } (A \times B)/W$$

where:

- A = silicon per 100 mL of solution found in the aliquot used, μg ,
- B = aliquot factor = original volume divided by aliquot taken for analysis, and
- W = original sample weight, g.

IRON BY THE ORTHO-PHENANTHROLINE (PHOTOMETRIC) TEST METHOD

15. Summary of Test Method

15.1 After suitable dilution of an aliquot from the carbonate fusion is adjusted to a pH of 3.0, the iron is reduced with hydroxylamine hydrochloride. The ferrous ortho-phenanthroline complex is formed, and its absorption is measured at a wavelength of 490 nm.

16. Stability of Color

16.1 The color becomes stable within 15 min and does not change for at least 48 h.

17. Interferences

17.1 No interfering elements are normally present in graphite.

18. Reagents

18.1 *Ammonium Hydroxide* (NH_4OH) (1+1)—Mix equal volumes of concentrated NH_4OH , sp gr 0.90 and water.

18.2 *Bromine Water*—Add 10 mL of bromine to 1 L of water. Allow to stand for 24 h.

18.3 *Hydrochloric Acid* (HCl) (1+1)—Mix equal volumes of concentrated HCl, sp gr 1.19 and water.

18.4 *Hydroxylamine Hydrochloride Solution*—Dissolve 10 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in water and dilute to 100 mL. Discard the solution if color develops on standing for long periods of time.

18.5 *Iron, Standard Solution* (1 mL = 0.1 mg Fe)—Into a 100-mL beaker, weigh 0.1000 g of iron wire. Dissolve the wire in 50 mL of HCl (1+1). Add 1 mL of bromine water to oxidize the iron to the ferric state. Boil the solution to expel the excess bromine and dilute to 1 L in a volumetric flask.

18.6 *Iron Wire*, primary standard, over 99.9 % pure.

18.7 *o-Phenanthroline*—Dissolve 2 g of 1,10-phenanthroline in ethyl alcohol and dilute to 250 mL with ethyl alcohol in a volumetric flask. Discard this solution if color develops upon long standing.

19. Preparation of Calibration Curve

19.1 *Calibration Solutions*—Transfer 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 mL of iron solution (1 mL = 0.1 mg Fe) to 100-mL volumetric flasks. Add NH_4OH (1+1) until the brown hydrous precipitate of ferric hydroxide ($\text{Fe}(\text{OH})_3$) is just visible. Then add HCl (1+1) drop-wise, while stirring, until the precipitate

just dissolves. Bring the pH of the solution to 3.0 by adding 2 additional drops of HCl (1+1). Then add 2 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution.

19.2 *Color Development*—Heat the solutions in the flasks almost to boiling. Add 1 mL of *o*-phenanthroline solution and allow the solutions to cool. Then dilute to the mark with water.

19.3 *Photometry*—Transfer a suitable portion of the reagent blank solution to a 1-cm absorption cell, and adjust the spectrophotometer to the initial setting using a wavelength of 490 nm. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

19.4 *Calibration Curve*—Plot the absorbance of the calibration solution against micrograms of iron per 100 mL of solution.

20. Procedure

20.1 *Sample Solution*—Proceed in accordance with 13.1.

20.2 *Color Development*—Proceed in accordance with 19.2.

20.3 *Photometry*—Proceed in accordance with 19.2.

20.4 *Calibration*—Convert the photometric reading of the sample solution to micrograms of iron by means of the calibration curve.

21. Calculation

21.1 Calculate the parts per million of iron in the original sample as follows:

$$\text{Fe, ppm } (A \times B)/W$$

where:

- A = iron per 100 mL of solution in the aliquot used, μg ,
- B = aliquot factor = original volume divided by aliquot taken for analysis, and
- W = original sample weight, g.

CALCIUM BY THE PERMANGANATE (COLORIMETRIC) TEST METHOD

22. Summary of Test Method

22.1 Calcium is precipitated as the oxalate, filtered off, and dissolved in sulfuric acid. The acid solution is added to a dilute potassium permanganate solution, and the decrease in absorption is measured at a wavelength of 528 nm.

23. Stability of Color

23.1 Potassium permanganate solution is decomposed rapidly by exposure to air or light. Photometric readings should be made at once.

24. Interferences

24.1 Ashed graphite samples are normally free of significant concentrations of possible interfering ions.

25. Reagents

25.1 *Ammonium Hydroxide* (NH_4OH) (1+6)—Mix 1 volume of concentrated NH_4OH , sp gr 0.90 with 6 volumes of water.

25.2 *Ammonium Oxalate Solution*—Prepare a saturated solution of ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$).

25.3 Bromocresol Green Indicator Solution—Use the water soluble sodium salt. Dissolve 0.040 g in water and dilute to 100 mL. Store in a glass-stoppered brown bottle.

25.4 Formate Buffer Solution (pH 3.7)—Dissolve 31.5 g of ammonium formate in about 200 mL of water and transfer to a 1-L volumetric flask. Add 20.8 mL of formic acid, dilute to volume, and mix well.

25.5 Hydrochloric Acid (HCl) (1+1)—Mix equal volumes of concentrated HCl, sp gr 1.19 and water.

25.6 Oxalate, Standard Solution (1 mL = 0.125 mg Ca)—Dry approximately 2 g of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) at 105°C for 1 h, and cool in a desiccator. Weigh accurately 0.2090 g into a 250-mL beaker, dissolve in boiled water, and dilute to 500 mL in a volumetric flask.

25.7 Potassium Permanganate, Standard Solution—Dissolve 3.25 g of NIST potassium permanganate (KMnO_4) in 1 L of hot water. Let stand in the dark for 12 h. Filter through asbestos into a dark colored bottle.

25.7.1 Standardize as follows: dissolve 3.0 g of dried NIST sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) in boiled water and dilute to 500 mL in a volumetric flask. Pipet 25-mL aliquots of the oxalate solution into 600-mL beakers. Add 250 mL of $\text{H}_2\text{SO}_4(1+33)$, heat to 55 to 60°C, and titrate to a faint pink end point that persists for 30 s. For a blank, add permanganate solution, dropwise, to 250 mL of $\text{H}_2\text{SO}_4(1+33)$. Note the volume required to impart a pink color. Calculate the normality of the permanganate solution.

25.7.2 Prepare 0.0200 NKMnO_4 solution by appropriate dilution of the standardized solution.

25.8 Sulfuric Acid (H_2SO_4) (1+3)—Carefully mix 1 volume of concentrated H_2SO_4 , sp gr 1.84 with 3 volumes of water.

26. Preparation of Calibration Curve

26.1 Calibration Solutions—Transfer 0.0, 5.0, 10.0, 15.0, and 25.0 mL of standard oxalate solution into 100-mL volumetric flasks. Add 40 mL of $\text{H}_2\text{SO}_4(1+3)$ and 10 mL of boiled and cooled water. Place the flasks in a water bath at 55 to 60°C for 5 min.

26.2 Color Development—Pipet into each flask 10.0 mL of the 0.0200 N KMnO_4 solution. Remove from the bath and allow to stand at room temperature for 5 min for the color change to be completed. Place in a cold-water bath, and cool to room temperature. Dilute to volume with CO_2 -free water and mix.

26.3 Photometry—Transfer a portion of the reagent blank solution to a 1-cm absorption cell. Transfer a portion of the first standard into a second absorption cell. Adjust the spectrophotometer to zero, with the standard in the light path. Then measure the absorbance of the reference solution. Repeat the procedure using the other standard solutions.

26.4 Calibration Curve—Plot the absorption of the calibration solutions against micrograms of calcium per 100 mL of solution.

27. Procedure

27.1 Sample Solution—Proceed in accordance with 13.1. However, after the sample solution has been diluted to volume and mixed, proceed as follows: pipet a suitable aliquot (usually 25 mL) into a 50-mL beaker. Add 1 or 2 drops of bromocresol

green indicator, 1 mL of formate buffer, and 1 mL of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution. Add, dropwise, NH_4OH (1+6) to the appearance of a faint blue color (pH = about 4.6). Then add HCl (1+1) dropwise with stirring, to obtain a very light yellow color (pH = 3.8). Digest in a water bath at a temperature of 90°C for 10 to 15 min. Remove from the water bath and allow to digest at room temperature for at least 30 min. Filter through a 15-mL, medium-porosity fritted-glass crucible, and wash with four 2-mL portions of cold water. Remove the crucible from the holder and rinse off the outside and bottom thoroughly. Discard all filtrates and washings. Place the crucible back on the filtration assembly. Pour four 10-mL portions of hot $\text{H}_2\text{SO}_4(1+3)$ (slowly with stirring) into the beaker and then into the crucible. Collect the solution and four 2.5-mL hot water washings in a 100-mL volumetric flask, and place in a hot water bath at 55 to 60°C for 5 min.

27.2 Color Development—Proceed in accordance with 26.2.

27.3 Photometry—Proceed in accordance with 26.3.

27.4 Calibration—Convert the photometric reading of the sample solution to micrograms of calcium by means of the calibration curve.

28. Calculation

28.1 Calculate the parts per million of calcium in the original sample as follows:

$$\text{Ca, ppm} = (A \times B)/W$$

where:

A = calcium per 100 mL of solution in the aliquot used, μg ,

B = aliquot factor = original volume divided by the aliquot taken for analysis, and

W = original sample weight, g.

ALUMINUM BY THE 2-QUINIZARAN SULFONIC ACID(PHOTOMETRIC) TEST METHOD

29. Summary of Test Method

29.1 The bulk of the water is removed by evaporation, and the moist residue is taken up in absolute methanol. The color reagent is added, and the “pH” is adjusted with concentrated hydrochloric acid, if necessary. The absorption of the colored solution is measured at a wavelength of 560 nm.

30. Stability of Color

30.1 The solution is stable for at least 24 h.

31. Interferences

31.1 Iron and titanium are the only ions that might interfere. However, they do not interfere in the amounts usually present in graphite. If a sample contains more than 500 ppm of iron, or more than 40 ppm of titanium, they are removed by electrolysis in a mercury cell.

32. Reagents

32.1 Aluminum, Standard Solution (1 mL = 1 mg Al)—Weigh out 6.95 g of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and transfer to a 500-mL volumetric flask. Cover the salt with 200 mL of absolute methanol. Add 10 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to dissolve the salt, and dilute to

volume with absolute methanol. For use dilute 10 mL of this solution to 1 L with absolute methanol (1 mL = 0.01 mg Al) for a working aluminum solution.

32.2 *Hydrochloric Acid* (HCl) (sp gr 1.19)—Concentrated HCl.

32.3 *Hydrochloric Acid* (1+1)—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

32.4 *Methanol, Absolute*.

32.5 *2-Quinizarin Sulfonic Acid Solution*—Dissolve 0.16 g of 2-quinizarin sulfonic acid in absolute methanol, dilute to 500 mL with absolute methanol, and store in a polyethylene bottle.

33. Preparation of Calibration Curve

33.1 Transfer 0.0, 1.0, 3.0, 5.0, 7.0 and 10.0 mL of the working aluminum solution to 100-mL volumetric flasks.

33.2 *Color Development*—Add 10 mL of 2-quinizarin sulfonic acid solution, dilute to volume with absolute methanol, and mix. The acidity should be within the desired limits of pH 0.3 to 0.5, as measured with a pH meter. (If the solution is on the basic side, adjust to the desired range with concentrated HCl (sp gr 1.19). Let stand 1 h.

33.3 *Photometry*—Transfer a portion of the reference solution to a 1-cm absorption cell and adjust the photometer to the initial setting, using a wavelength of 560 nm. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

33.4 *Calibration Curve*—Plot the absorbance of the calibration solutions against the micrograms of aluminum per 100 mL of solution.

34. Procedure

34.1 *Ash Dissolution*—Proceed in accordance with 13.1. Transfer the aliquot from the sample solution to a platinum dish, add 1 drop of HCl (1+1), and evaporate the solution to a volume of 0.5 to 1.0 mL on a sand bath. Remove, cool, and add 5 mL of absolute methanol to the dish. Rub with a policeman to ensure complete solution of the aluminum salt. Transfer the solution to a 100-mL volumetric flask, and rinse the dish with three 5-mL portions of absolute methanol, adding these to the solution in the volumetric flask.

34.2 *Color Development*—Proceed in accordance with 33.2.

34.3 *Photometry*—Proceed in accordance with 33.2.

34.4 *Calibration*—Convert the photometric reading of the sample to micrograms of aluminum by means of the calibration curve.

35. Calculation

35.1 Calculate the parts per million of aluminum in original sample as follows:

$$\text{Aluminum, ppm} = (A \times B)/W$$

where:

A = aluminum per 100 mL of solution in the aliquot used, μg ,

B = aliquot factor = original volume a divided by the aliquot taken for analysis, and

W = original sample weight, g.

TITANIUM BY THE PEROXIDE (COLORIMETRIC) TEST METHOD

36. Summary of Test Method

36.1 Hydrogen peroxide is added to form the peroxy-titanium complex. The absorption of the yellow solution is measured at a wavelength of 409 nm.

37. Stability of Color

37.1 The yellow colored complex is stable for over 2 years.

38. Interferences

38.1 No interfering ions are normally present in ashed graphite samples.

39. Reagents

39.1 *Hydrochloric Acid* (HCl) (1+1)—Mix equal volumes of concentrated HCl, sp gr 1.19 and water.

39.2 *Hydrogen Peroxide* (H_2O_2) (30 %)—Concentrated H_2O_2 .

39.3 *Potassium Pyrosulfate* ($\text{K}_2\text{S}_2\text{O}_7$).

39.4 *Sodium Carbonate Solution* (Na_2CO_3) (100 g/L)—Dissolve 100 g of Na_2CO_3 in water and dilute to 1 L.

39.5 *Sodium Hydroxide Solution* (NaOH) (100 g/L)—Dissolve 100 g of NaOH in water and dilute to 1 L.

39.6 *Sulfuric Acid* (H_2SO_4) (1+7)—Carefully mix 1 volume of concentrated H_2SO_4 , sp gr 1.84 with 7 volumes of water.

39.7 *Sulfuric Acid* (1+33)—Carefully mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) with 33 volumes of water.

39.8 *Titanium, Standard Solution* (1 mL = 0.6 mg Ti)—Fuse 0.5 g of titanium dioxide (TiO_2) with 10 to 12 g of potassium hydrogen sulfate (KHSO_4) in a platinum dish, keeping at fusion heat until the oxide has dissolved. Avoid heating to high temperature. Allow the melt to cool, dissolve in 20 to 25 mL of H_2SO_4 (1+7), and dilute to volume with H_2SO_4 (1+7) in a 500-mL volumetric flask.

40. Preparation of Sample

40.1 Add sufficient sample of graphite to give at least 50 mg of ash (see Test Method C 561). Fuse the ash with Na_2CO_3 as described in 13.1. After the fusion has cooled, place the crucible and lid in a 250-mL high-form glass beaker, add 100 mL of water, and digest on a sand bath until solution is complete. Dissolve any residual melt in the crucible by adding several drops of HCl (1+1) and rinse into the main solution. Then add 1 mL of NaOH solution (100 g/L) and boil the solution for 15 min. Remove from the hot plate and cool the solution to room temperature. (The solution must be cooled before filtering to prevent loss of TiO_2 through solution in hot carbonate solution.) Filter the solution through rapid-filtering paper, wash the precipitate twice with Na_2CO_3 solution (100 g/L), and three times with cold water. Collect the filtrate and washings and reserve for the determination of vanadium.

40.2 Dissolve the precipitate on the paper with HCl (1+1), collecting the solution in a 100-mL volumetric flask. (Keep the final volume below 75 mL.) If any residue remains on the paper, transfer the filter paper to a platinum crucible, burn off the paper, and ignite to completely ash the paper. Allow the crucible to cool, then add 5 g of $\text{K}_2\text{S}_2\text{O}_7$ to the residue. Slowly

heat the crucible to the lowest temperature that will melt the pyrosulfate. Maintain at this temperature until the fusion is complete. Remove the crucible from the flame and allow to cool. Then dissolve the melt in 10 mL of $\text{H}_2\text{SO}_4(1+33)$. When solution is complete, add it to the acid solution in the 100-mL volumetric flask. Rinse the crucible with three 2-mL portions of $\text{H}_2\text{SO}_4(1+33)$ and add to the main solutions. Dilute to volume with $\text{H}_2\text{SO}_4(1+33)$.

41. Preparation of Calibration Curve

41.1 *Calibration Solutions*—Transfer 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 mL of titanium standard solution (1 mL = 0.6 mg Ti) to 100-mL volumetric flasks. Dilute nearly to volume with $\text{H}_2\text{SO}_4(1+33)$.

41.2 *Color Development*—Add 2 mL of concentrated $\text{H}_2\text{O}_2(30\%)$ to each flask, and dilute to 100 mL with $\text{H}_2\text{SO}_4(1+33)$.

41.3 *Photometry*—Transfer a portion of the reagent blank solution to a 1-cm absorption cell, and adjust the photometer to the initial setting, using a wavelength of 409 nm. While maintaining this setting, take the photometric readings of the calibration solutions.

41.4 *Calibration Curve*—Plot the absorbance of the calibration solutions against micrograms of titanium per 100 mL of solution.

42. Procedure

42.1 Transfer a suitable aliquot, usually 50 mL of the sample solution, to a 100-mL volumetric flask. Dilute nearly to volume with $\text{H}_2\text{SO}_4(1+33)$.

42.2 *Color Development*—Proceed in accordance with 41.2.

42.3 *Photometry*—Proceed in accordance with 41.3.

42.4 *Calibration*—Convert the photometric reading of the sample solution to micrograms of titanium by means of the calibration curve.

43. Calculation

43.1 Calculate the parts per million of titanium in the original sample as follows:

$$\text{Titanium, ppm} = (A \times B)/W$$

where:

A = titanium per 100 mL of solution in the aliquot used, μg ,

B = aliquot factor = original volume divided by the aliquot taken for analysis, and

W = original sample weight, g.

VANADIUM BY THE 3,3'-DIMETHYLNAPHTHIDINE (COLORIMETRIC) TEST METHOD

44. Summary of Test Method

44.1 Vanadium in solution reacts with 3,3'-dimethylnaphthidine to form a stable, colored solution. This method is much more sensitive and much freer from interferences than is the classical phosphotungstate method.

45. Stability of Color

45.1 The colored complex is stable for at least 24 h.

46. Interferences

46.1 Heavy metal oxides interfere. However, these elements are absent when the filtrate obtained in accordance with 40.1 is used for the vanadium determination.

47. Reagents

47.1 *3,3'-Dimethylnaphthidine Solution*—Dissolve 0.5 g of 3,3'-dimethylnaphthidine in approximately 400 mL of glacial acetic acid. Warm gently until the reagent dissolves, cool and dilute to volume with glacial acetic acid in a 500-mL volumetric flask.

47.2 *Hydrochloric Acid (HCl) (1+1)*—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

47.3 *Perchloric Acid (60 %)*—(HClO_4).

47.4 *Phosphoric Acid (H_3PO_4) (1+1)*—Mix equal volumes of concentrated H_3PO_4 , 85 % and water.

47.5 *Vanadium, Standard Solution* (1 mL = 10 μg V)—Weigh 0.2296 g of NIST ammonium vanadate (NH_4VO_3) into a 250-mL beaker. Add 10 mL of $\text{HClO}_4(60\%)$ and heat to strong fumes. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Dilute 50 mL of this solution to 500 mL in a volumetric flask. This working solution contains 10 ppm of vanadium.

48. Preparation of Sample

48.1 See 40.1 and 40.2.

49. Preparation of Calibration Curve

49.1 *Calibration Solutions*—Transfer 0.0, 1.0, 4.0, 7.0, 10.0, and 13.0 mL of the vanadium solution to 50-mL volumetric flasks. Bring this volume in the flasks to 25 mL with water and add 6 mL of $\text{HClO}_4(60\%)$ and 10 mL of $\text{H}_3\text{PO}_4(1+1)$.

49.2 *Color Development*—Add 5 mL of 3,3'-dimethylnaphthidine solution to each flask, dilute to volume, and mix. Let stand for 15 min.

49.3 *Photometry*—Transfer a portion of the reference solution to a 1-cm absorption cell and adjust the photometer to the initial setting using a wavelength of 550 nm. While maintaining this photometer adjustment, measure the absorbance of the calibration solutions.

49.4 *Calibration Curve*—Plot the absorbance of the calibration solutions against the micrograms of vanadium per 50 mL of solution.

50. Procedure

50.1 Acidify the filtrate obtained in accordance with 40.1 with HCl (1+1), and evaporate to a volume of 70 to 80 mL. Cool, and transfer to a 100-mL volumetric flask. Adjust the solution to pH 6 with HCl using test paper, dilute to volume with water, and mix. Transfer an aliquot equivalent to 1 or 2 g of the original sample into a 50-mL volumetric flask. Bring the volume to 25 mL and add 6 mL of $\text{HClO}_4(60\%)$ and 10 mL of $\text{H}_3\text{PO}_4(1+1)$.

50.2 *Color Development*—Proceed in accordance with 49.2.

50.3 *Photometry*—Proceed in accordance with 49.3.

50.4 *Calibration*—Convert the photometric reading of the sample solution to micrograms of vanadium by means of the calibration curve.

51. Calculation

51.1 Calculate the parts per million of vanadium in the original sample as follows:

$$\text{Vanadium, ppm} = (A \times B)/W$$

where:

- A = vanadium per 50 mL of solution in the aliquot used, μg ,
 B = aliquot factor = original volume divided by the aliquot taken for analysis, and
 W = original sample weight, g.

BORON BY THE CURCUMIN-OXALIC ACID (COLORIMETRIC) TEST METHOD

52. Summary of Test Method

52.1 After ashing the sample, the residue is acidified and the color is developed by adding curcumin-oxalic acid solution and evaporating to dryness on a water bath. The colored complex is extracted with alcohol, and the absorption of the complex is measured at 555 nm.

53. Stability of Color

53.1 The colored complex is stable for several hours if kept dry. After extracting with alcohol, photometer readings must be made within 2 h.

54. Interferences

54.1 No interfering ions are usually present in the ashed graphite samples.

55. Reagents

55.1 *Boron, Standard Solution* (1 mL = 200 μg B)—Dissolve 1.1435 g of boric acid in water, dilute to 1 L in a volumetric flask, and mix thoroughly. For use, dilute 5.0 mL of this solution to volume in a 1-L volumetric flask for a working boron solution (1 mL = 1 μg B).

55.2 *Calcium Hydroxide Suspension*—Ignite approximately 10 g of calcium carbonate (CaCO_3) in a platinum dish at a temperature of 950°C for 1 h. Cool in a desiccator, and grind in a mullite mortar to pass a No. 200 (75- μm) sieve. Add 2.8 g of the calcium oxide (CaO) to 1 L of water. Store in a tightly stoppered plastic bottle.

55.3 *Curcumin-Oxalic Acid Reagent*—Prepare “standard” alcohol by adding 35 mL of water to 1 L of anhydrous ethanol. Dissolve 7.50 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in about 350 mL of the “standard” alcohol, then add 12.5 mL of concentrated hydrochloric acid (HCl, sp gr 1.19), 37.5 mL of water, and 0.1750 g of finely ground curcumin. Dilute to 500 mL with “standard” alcohol. (Filter if cloudy.) Store in a plastic bottle in a dark place. Make a fresh solution every ten days.

55.4 *Extraction Alcohol*—Add 200 mL of water to 800 mL of anhydrous ethanol. Mix thoroughly and store in a plastic bottle.

55.5 *Hydrochloric Acid* (1+11)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 11 volumes of water.

56. Preparation of Calibration Curve

56.1 Transfer 0.0, 0.5, 1.0, 2.0, 3.0, and 4.0 mL of the working boron solution (1 mL = 1 μg B) to 100-mL platinum dishes. Stir the calcium hydroxide (Ca(OH)_2) suspension, and rapidly transfer 10.0 mL of the suspension to each dish. Swirl the mix, and evaporate to dryness on a sand bath. (**Caution:** see Note.) Transfer the dishes to a muffle furnace and heat at 650°C until all of the carbon has burned off. (The ashing can be accelerated by admitting air into the furnace through a tube connected to the compressed air line. However, the flow must be carefully adjusted to prevent the material in the dishes from being blown out of the dishes.) After all the carbon has been burned off (requires about 18 h), remove the dishes from the furnace and cool in a desiccator.

NOTE 1—**Caution:** Avoid spattering during the evaporation.

56.2 *Color Development*—Add 6 drops of HCl (1+11) to the residues in the dishes, swirling to dissolve all of the material. Then add 1 mL of a saturated alcoholic solution of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and 5.0 mL of curcumin-oxalic acid reagent. Float the dishes on the surface of a water bath maintained at 55 to 60°C. When dry, allow the dishes to remain 3 min longer, then remove and cool. The water bath shall be enclosed so that a constant humidity can be maintained. Extract the colored complex with about 10 mL of the extraction alcohol, rubbing with a policeman to assist complete solution. Transfer the extract to a 50-mL volumetric flask, and rinse the dish thoroughly with small portions of the extraction alcohol. Make sure that *all* of the colored material has been rinsed from the platinum dish. Then dilute to volume with extraction alcohol and mix.

56.3 *Reference Solution*—Stir the Ca(OH)_2 suspension and transfer 10.0 mL to a platinum dish. Then proceed in accordance with 56.1.

56.4 *Photometry*—Filter a portion of the reference solution through a rapid-filtering paper directly into a 1-cm absorption cell, and adjust the photometer to the initial setting, using a wavelength of 555 nm. While maintaining this photometric adjustment, measure the absorbance of the calibration solutions.

56.5 *Calibration Curve*—Plot the absorbance of the calibration solutions against the micrograms of boron per 50 mL of solution.

56.5.1 The analytical recovery of boron involves serious problems of reproducibility with respect to the effect of changes in humidity, evaporation rate, etc. on the solutions. It is necessary, therefore, that a new calibration curve be drawn for each set of samples. An alternative is to include a standard sample of graphite of known boron content with each set of samples. The calibration curve is drawn from the absorbance obtained.

57. Procedure

57.1 Weigh a 3.0000-g sample of graphite into a tared platinum dish. Proceed in accordance with 56.1.

57.2 *Color Development*—Proceed in accordance with 56.2.

57.3 *Reference Solution*—Proceed in accordance with 56.3.

57.4 *Photometry*—Proceed in accordance with 56.4.

57.5 *Calibration*—Convert the photometric reading of the sample solution to micrograms of boron by means of the calibration curve.

58. Calculation

58.1 Calculate the parts per million of boron in the original sample as follows:

$$\text{Boron, ppm} = (A \times B)/W$$

where:

A = boron per 50 mL of solution in the aliquot used, µg,

B = aliquot = original volume divided by the aliquot taken for analysis, and

W = original sample weight, g.

59. Report

59.1 The report shall include the following:

59.1.1 Proper identification of the sample, and

59.1.2 Results obtained from at least two analytical determinations, and their average.

60. Keywords

60.1 calibration; calibration solutions; chemical analysis; color development; graphite; photometry

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