Designation: C560 – 15$^{\varepsilon 1}$

An American National Standard

Standard Test Methods for Chemical Analysis of Graphite[1]

This standard is issued under the fixed designation C560; 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 (ε) indicates an editorial change since the last revision or reapproval.

ε^1 NOTE—Subsection 1.2 was corrected editorially in February 2017.

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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	9 to 15
Iron by the *o*-Phenanthroline (Colorimetric) Test Method	16 to 22
Calcium by the Permanganate (Colorimetric) Test Method	23 to 29
Aluminum by the 2-Quinizarin Sulfonic Acid Test Method	30 to 36
Titanium by the Peroxide (Colorimetric) Test Method	37 to 44
Vanadium by the 3,3'-Dimethylnaphthidine (Colorimetric) Test Method	45 to 52
Boron by the Curcumin-Oxalic Acid (Colorimetric) Test Method	53 to 60

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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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:*[2]

C561 Test Method for Ash in a Graphite Sample

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration curve, n*—graphical or mathematical representation of the relationship between known concentrations of an element in a series of standard calibration solutions and the measured response from the measurement system.

3.1.2 *calibration solutions, n*—solutions of accurately known concentrations of the chemical element to be determined using the calibration curve method.

3.1.3 *colorimetric analysis, n*—photometric analysis method of using absorption of monochromatic light in the visible spectrum.

3.1.4 *photometric analysis, n*—analytical chemistry method for quantitative chemical analysis based on the relationship between solution concentrations and the absorption of monochromatic light, as expressed by the Beer law.

4. Significance and Use

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

4.2 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.

4.3 Other instrumental analysis techniques are available, capable of simultaneous quantitative analysis of 76 stable elements in a single run, with detectability limits in the parts per million range. Standards are currently being developed for elemental analysis of impurities in graphite using glow discharge mass spectrometry (GDMS), inductively coupled plasma optical emission spectroscopy (ICP-OES), combustion ion chromatography (CIC).

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[1] These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.F0 on Petroleum Products, Liquid Fuels, and Lubricants

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

***A Summary of Changes section appears at the end of this standard**

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

Element	Concentration Range, µg/mL Solution	Sensitivity Limit, µg/mL Solution	Reproducibility, Relative, % (σ/*x* × 100)
Silicon	10 µg ⁄100 mL to 100 µg/ 100 mL	1 µg/100 mL	±4
Iron	100 µg ⁄100 mL to 600 µg/100 mL	40 µg/100 mL	±5
Calcium	600 µg ⁄100 mL to 3000 µg/100 mL	50 µg/100 mL	±5
Aluminum	10 µg ⁄100 mL to 100 µg/ 100 mL	2 µg/100 mL	±0.1
Titanium	600 µg ⁄100 mL to 3000 µg/100 mL	200 µg/100 mL	±2
Vanadium	10 µg ⁄50 mL to 130 µg/50 mL	5 µg/50 mL	±5
Boron	0.5 µg ⁄50 mL to 1.4 µg/50 mL	0.1 µg/50 mL	±20

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

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

5.3 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

5.4 National Institute of Standards and Technology certified reagents specified in certain steps of this procedure may no longer be available. If NIST reagents are not available, then the highest purity reagent grade shall be substituted.

6. Sampling

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

NOTE 1—The 75 g to 250 g graphite should be crushed and ground to pass the 250 µm sieve, before combustion, which will eventually result in 75 g ash as needed in 13.1.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places in accordance with Practice E29.

8. Precision and Bias

8.1 No statement is being made about either the precision or bias of these test methods. At this time Committee C05 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.

8.2 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

9. Summary of Test Method

9.1 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.

10. Stability of Color

10.1 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.

11. Interferences

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

12. Reagents

12.1 *Ammonium Molybdate (50 g/L)*—Dissolve 50 g of ammonium molybdate ($(NH_4)_6$-$Mo_7O_{24}\cdot 4H_2O$) in water and dilute to 1 L.

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

12.3 *Silicon, Standard Solution (1 mL = 1 mg Si)*—Dissolve 10.1 g of sodium silicate ($Na_2SiO_3\cdot 9H_2O$) in water and dilute to 1 L in a volumetric flask. Store in a polyethylene bottle. Determine exact concentration by the standard gravimetric procedure.

12.4 *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.

12.5 *Sodium Carbonate Solution (100 g ⁄L)*—Dissolve 100 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L. Store in a polyethylene bottle.

12.6 *Stannous Chloride Solution*—Dissolve 2.5 g of stannous chloride ($SnCl_2\cdot 2H_2O$) 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.

12.7 *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.

13. Preparation of Calibration Curve

13.1 *Calibration Solutions*—Transfer 0 mL, 1.0 mL, 3.0 mL, 5.0 mL, 7.0 mL, and 10 mL of silicon working solution (1 mL = 0.01 mg Si) to 100 mL volumetric flasks. Add 5 drops of H_2SO_4 (1+3) and dilute to approximately 10 mL.

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

13.2 *Color Development*—Add 2.5 mL of $(NH_4)_6Mo_7O_{24}$ solution to each flask and let stand 5 min. Then add 5.0 mL of H_2SO_4 (1+3), mix well, and add 5 drops of $SnCl_2$ solution. Dilute to volume and let stand 5 min.

13.3 *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.

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

14. Procedure for Carbonate Fusion

14.1 *Sample Solution*—Rinse the ash (from a 50 g to 75 g ash sample) from the platinum dish into a mullite mortar with three 0.5 g portions of Na_2CO_3 passing a No. 100 (150 µm) sieve (see Test Method C561). Grind the resulting mixture to pass a No. 200 (75 µm) sieve to ensure intimate contact of the ash with the flux. Then transfer the mixture to a platinum crucible (containing 0.5 g of Na_2CO_3) with three 0.5 g rinses of Na_2CO_3. Add sufficient Na_2CO_3 to bring the total Na_2CO_3 content to 6 g. Cover the crucible, and fuse gently over a bunsen burner.

NOTE 2—In order to get 75 g ash, one needs to combust 250 kg high puruty graphite (300 ppm ash) or 75 kg low purity graphite (1000 ppm ash).

14.1.1 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.

14.1.2 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.

14.2 *Color Development*—Adjust the pH of the aliquot to 6 to 8 with Na_2CO_3 solution, then proceed in accordance with 14.2.

14.3 *Photometry*—Proceed in accordance with 13.3.

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

15. Calculation

15.1 Calculate the parts per million (ppm) of silicon in the original sample as follows:

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

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

16. Summary of Test Method

16.1 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.

17. Stability of Color

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

18. Interferences

18.1 No interfering elements are normally present in graphite.

19. Reagents

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

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

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

19.4 *Hydroxylamine Hydrochloride Solution*—Dissolve 10 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in water and dilute to 100 mL. Discard the solution if color develops on standing for long periods of time.

19.5 *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.

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

19.7 *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.

20. Preparation of Calibration Curve

20.1 *Calibration Solutions*—Transfer 0.0, mL 1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL, 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 ($Fe(OH)_3$) 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 $NH_2OH{\cdot}HCl$ solution.

20.2 *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.

20.3 *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.

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

21. Procedure

21.1 *Sample Solution*—Proceed in accordance with 14.1.

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

21.3 *Photometry*—Proceed in accordance with 20.2.

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

22. Calculation

22.1 Calculate the ppm 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

23. Summary of Test Method

23.1 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.

24. Stability of Color

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

25. Interferences

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

26. Reagents

26.1 *Ammonium Hydroxide (NH_4OH_2) (1+6)*—Mix 1 volume of concentrated NH_4OH_2, sp gr 0.90 with 6 volumes of water.

26.2 *Ammonium Oxalate Solution*—Prepare a saturated solution of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot 2H_2O$).

26.3 *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.

26.4 *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.

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

26.6 *Oxalate, Standard Solution (1 mL = 0.125 mg Ca)*—Dry approximately 2 g of sodium oxalate ($Na_2C_2O_4$) 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.

26.7 *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 inert filter medium into a dark colored bottle.

26.7.1 Standardize as follows: dissolve 3.0 g of dried NIST sodium oxalate ($Na_2C_2O_4$) 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 H_2SO_4 (1+33), heat to 55 °C 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 H_2SO_4 (1+33). Note the volume required to impart a pink color. Calculate the normality of the permanganate solution.

26.7.2 Prepare 0.0200 *N* $KMnO_4$ solution by appropriate dilution of the standardized solution.

26.8 *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.

27. Preparation of Calibration Curve

27.1 *Calibration Solutions*—Transfer 0.0 mL, 5.0 mL, 10.0 mL, 15.0 mL, and 25.0 mL of standard oxalate solution into 100 mL volumetric flasks. Add 40 mL of H_2SO_4 (1+3) and 10 mL of boiled and cooled water. Place the flasks in a water bath at 55 °C to 60 °C for 5 min.

27.2 *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.

27.3 *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.

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

28. Procedure

28.1 *Sample Solution*—Proceed in accordance with 14.1. 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 $(NH_4)_2C_2O_4$ 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 min 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 H_2SO_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 °C to 60 °C for 5 min.

28.2 *Color Development*—Proceed in accordance with 27.2.

28.3 *Photometry*—Proceed in accordance with 27.3.

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

29. Calculation

29.1 Calculate the ppm 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

30. Summary of Test Method

30.1 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.

31. Stability of Color

31.1 The solution is stable for at least 24 h.

32. Interferences

32.1 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.

33. Reagents

33.1 *Aluminum, Standard Solution (1 mL = 1 mg Al)*—Weigh out 6.95 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), 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.

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

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

33.4 *Methanol, Absolute.*

33.5 *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.

34. Preparation of Calibration Curve

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

34.2 *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.

34.3 *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.

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

35. Procedure

35.1 *Ash Dissolution*—Proceed in accordance with 14.1. 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 mL 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.

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

35.3 *Photometry*—Proceed in accordance with 34.2.

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

36. Calculation

36.1 Calculate the ppm 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 = liquot factor = original volume a divided by the aliquot taken for analysis, and
W = original sample weight, g.

TITANIUM BY THE PEROXIDE (COLORIMETRIC) TEST METHOD

37. Summary of Test Method

37.1 Hydrogen peroxide is added to form the peroxytitanium complex. The absorption of the yellow solution is measured at a wavelength of 409 nm.

38. Stability of Color

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

39. Interferences

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

40. Reagents

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

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

40.3 *Potassium Pyrosulfate* ($K_2S_2O_7$).

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

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

40.6 *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.

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

40.8 *Titanium, Standard Solution (1 mL = 0.6 mg Ti)*—Fuse 0.5 g of titanium dioxide (TiO_2) with 10 g 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 mL 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.

41. Preparation of Sample

41.1 Add sufficient sample of graphite to give at least 50 mg of ash (see Test Method C561; this would be 166 g of high purity (300 ppm) graphite). Fuse the ash with Na_2CO_3 as described in 14.1. 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.

41.2 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 $K_2S_2O_7$ 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 H_2SO_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 H_2SO_4 (1+33) and add to the main solutions. Dilute to volume with H_2SO_4 (1+33).

42. Preparation of Calibration Curve

42.1 *Calibration Solutions*—Transfer 0.0 mL, 1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, and 5.0 mL of titanium standard solution (1 mL = 0.6 mg Ti) to 100 mL volumetric flasks. Dilute nearly to volume with H_2SO_4 (1+33).

42.2 *Color Development*—Add 2 mL of concentrated H_2O_2 (30 %) to each flask, and dilute to 100 mL with H_2SO_4 (1+33).

42.3 *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.

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

43. Procedure

43.1 Transfer a suitable aliquot, usually 50 mL of the sample solution, to a 100 mL volumetric flask. Dilute nearly to volume with H_2SO_4 (1+33).

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

43.3 *Photometry*—Proceed in accordance with 42.3.

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

44. Calculation

44.1 Calculate the ppm 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

45. Summary of Test Method

45.1 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.

46. Stability of Color

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

47. Interferences

47.1 Heavy metal oxides interfere. However, these elements are absent when the filtrate obtained in accordance with 41.1 is used for the vanadium determination.

48. Reagents

48.1 *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.

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

48.3 *Perchloric Acid (60 %)*—($HClO_4$).

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

48.5 *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 $HClO_4$ (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.

49. Preparation of Sample

49.1 See 41.1 and 41.2.

50. Preparation of Calibration Curve

50.1 *Calibration Solutions*—Transfer 0.0 mL, 1.0 mL, 4.0 mL, 7.0 mL, 10.0 mL, 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 $HClO_4$ (60 %) and 10 mL of H_3PO_4 (1+1).

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

50.3 *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.

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

51. Procedure

51.1 Acidify the filtrate obtained in accordance with 40.1 with HCl (1+1), and evaporate to a volume of 70 mL 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 g or 2 g of the original sample into a 50 mL volumetric flask. Bring the volume to 25 mL and add 6 mL of $HClO_4$ (60 %) and 10 mL of H_3PO_4 (1+1).

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

51.3 *Photometry*—Proceed in accordance with 50.3.

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

52. Calculation

52.1 Calculate the ppm 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

53. Summary of Test Method

53.1 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.

54. Stability of Color

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

55. Interferences

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

56. Reagents

56.1 *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).

56.2 *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.

56.3 *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 ($H_2C_2O_4{\cdot}2H_2O$) 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.

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

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

57. Preparation of Calibration Curve

57.1 Transfer 0.0 mL, 0.5 mL, 1.0 mL, 2.0 mL, 3.0 mL, 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—** Avoid spattering during the evaporation.) 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.

57.2 *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 $H_2C_2O_4{\cdot}2H_2O$, and 5.0 mL of curcumin-oxalic acid reagent. Float the dishes on the surface of a water bath maintained at 55 °C 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.

57.3 *Reference Solution*—Stir the $Ca(OH)_2$ suspension and transfer 10.0 mL to a platinum dish. Then proceed in accordance with 57.1.

57.4 *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.

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

57.5.1 The analytical recovery of boron involves serious problems of reproducibility with respect to the effect of changes in humidity, evaporation rate, and so forth 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.

58. Procedure

58.1 Weigh a sample of graphite approximately 3 g to an accuracy of 0.1 mg into a tared platinum dish. Proceed in accordance with 57.1.

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

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

58.4 *Photometry*—Proceed in accordance with 57.4.

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

59. Calculation

59.1 Calculate the ppm 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.

60. Report

60.1 The report shall include the following:

60.1.1 Proper identification of the sample, and

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

61. Keywords

61.1 calibration curve; calibration solutions; colorimetric analysis; graphite; photometric anaylsis

SUMMARY OF CHANGES

Subcommittee D02.F0 has identified the location of selected changes to this standard since the last issue (C560 – 88 (2010)$^{\varepsilon 1}$) that may impact the use of this standard. (Approved Oct. 1, 2015.)

(1) Added new Terminology section (Section 3).
(2) Added new Note 1 and Note 2.
(3) Added new subsection 4.3.
(4) Revised subsection 41.1 and Section 61.

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