



Standard Test Methods for Chemical Analysis of Graphite¹

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^ε1 NOTE—Subsection 1.2 was corrected editorially in February 2017.

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 α -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

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.

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

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

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.

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 ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) 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 ($\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$) 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 ($\text{SnCl}_2\cdot 2\text{H}_2\text{O}$) 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.

13.2 *Color Development*—Add 2.5 mL of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ 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 purity 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:

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

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

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 ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in water and dilute to 100 mL. Discard the solution if color develops on standing for long periods of time.

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, 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 ($\text{Fe}(\text{OH})_3$) 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.

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 (NH₄OH₂) (1+6)*—Mix 1 volume of concentrated NH₄OH₂, sp gr 0.90 with 6 volumes of water.

26.2 *Ammonium Oxalate Solution*—Prepare a saturated solution of ammonium oxalate ((NH₄)₂C₂O₄·2H₂O).

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 (Na₂C₂O₄) 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 (KMnO₄) 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 (Na₂C₂O₄) 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 H₂SO₄ (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 H₂SO₄ (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 KMnO₄ solution by appropriate dilution of the standardized solution.

26.8 *Sulfuric Acid (H₂SO₄) (1+3)*—Carefully mix 1 volume of concentrated H₂SO₄, 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 H₂SO₄ (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 KMnO₄ 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 CO₂-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 (NH₄)₂C₂O₄ solution. Add, dropwise, NH₄OH (1+6) to the