



## Standard Test Methods for Chemical Analysis of Graphite<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Updated 57.1 editorially in May 2010.

### 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 $\alpha$ -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 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*:<sup>2</sup>

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

<sup>1</sup> 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 and Lubricants

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<sup>2</sup> 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. 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 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.<sup>3</sup> 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 D1193.

4.4 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.

### 5. Sampling

5.1 The entire sample of graphite should be crushed and ground to pass a No. 60 (250- $\mu$ m) sieve in a roll crusher. The

<sup>3</sup> *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.

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

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

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 E29.

## 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 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.

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 ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) 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 ( $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ ) in water and dilute to 1 L in a volumetric flask. Store in a polyethylene bottle. Determine exact concentration by the standard gravimetric procedure.

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 ( $\text{Na}_2\text{CO}_3$ ) in water and dilute to 1 L. Store in a polyethylene bottle.

11.6 *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.

11.7 *Sulfuric Acid* ( $\text{H}_2\text{SO}_4$ ) (1+3)—Carefully mix 1 volume of concentrated  $\text{H}_2\text{SO}_4$ , 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  $\text{H}_2\text{SO}_4$  (1+3) and dilute to approximately 10 mL.

12.2 *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  $\text{H}_2\text{SO}_4$  (1+3), mix well, and add 5 drops of  $\text{SnCl}_2$  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  $\text{Na}_2\text{CO}_3$  passing a No. 100 (150- $\mu\text{m}$ ) sieve (see Test Method C561). Grind the resulting mixture to pass a No. 200 (75- $\mu\text{m}$ ) sieve to ensure intimate contact of the ash with the flux. Then transfer the mixture to a platinum crucible (containing 0.5 g of  $\text{Na}_2\text{CO}_3$ ) with three 0.5-g rinses of  $\text{Na}_2\text{CO}_3$ . Add sufficient  $\text{Na}_2\text{CO}_3$  to bring the total  $\text{Na}_2\text{CO}_3$  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  $\text{Na}_2\text{CO}_3$  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 (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,  $\mu\text{g}$ ,

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 ( $\text{NH}_4\text{OH}$ ) (1+1)*—Mix equal volumes of concentrated  $\text{NH}_4\text{OH}$ , 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  $\text{NH}_4\text{OH}$  (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 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,  $\mu\text{g}$ ,

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<sub>4</sub>OH<sub>2</sub>) (1+6)*—Mix 1 volume of concentrated NH<sub>4</sub>OH<sub>2</sub>, sp gr 0.90 with 6 volumes of water.

25.2 *Ammonium Oxalate Solution*—Prepare a saturated solution of ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>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 (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) 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<sub>4</sub>) in 1 L of hot water. Let stand in the dark for 12 h. Filter through inert filter medium into a dark colored bottle.

25.7.1 Standardize as follows: dissolve 3.0 g of dried NIST sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) 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<sub>2</sub>SO<sub>4</sub> (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 H<sub>2</sub>SO<sub>4</sub> (1+33). Note the volume required to impart a pink color. Calculate the normality of the permanganate solution.

25.7.2 Prepare 0.0200 N KMnO<sub>4</sub> solution by appropriate dilution of the standardized solution.

25.8 *Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) (1+3)*—Carefully mix 1 volume of concentrated H<sub>2</sub>SO<sub>4</sub>, 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 H<sub>2</sub>SO<sub>4</sub> (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<sub>4</sub> 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<sub>2</sub>-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 (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution. Add, dropwise, NH<sub>4</sub>OH (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 H<sub>2</sub>SO<sub>4</sub> (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 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

### 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