Designation: D4487 – 90 (Reapproved 2020)

Standard Test Methods for Analysis of Calcium Borosilicate[1]

This standard is issued under the fixed designation D4487; 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.

1. Scope

1.1 These test methods cover the analysis of the pigment commercially known as calcium borosilicate.

1.2 The test methods appear in the following order:

Test Methods	Sections
Silicon Dioxide (SiO_2)	6 – 9
Iron Oxide (Fe_2O_3)	10 – 13
Boron Trioxide (B_2O_3)	17 – 20
Calcium Oxide (CaO)	21 – 23
Moisture and Volatile Matter	24
Water of Hydration	25 to 26
Coarse Particles	27
Oil Absorption	28

1.3 Individual specimens may be used for the direct determinations of SiO_2, B_2O_3, and CaO. SiO_2 and Fe_2O_3 should be removed before the determination of the B_2O_3 and CaO.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D185 Test Methods for Coarse Particles in Pigments

D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments

D281 Test Method for Oil Absorption of Pigments by Spatula Rub-out

D1193 Specification for Reagent Water

3. Significance and Use

3.1 These test methods compile in one place, recommended procedures for analysis of the pigment known commercially as calcium borosilicate. This pigment is used extensively in paints and the composition is important to the user and producer.

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.[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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

4.3 *Concentration of Acids and Ammonium Hydroxide*—When acids and ammonium hydroxide are specified by name or chemical formula only, it should be understood that concentrated reagents of the following specific gravity are intended:

Hydrochloric acid (HCl)	1.19
Nitric acid, (HNO_3)	1.42
Sulfuric acid (H_2SO_4)	1.84
Ammonium hydroxide (NH_4OH)	0.90

5. Preparation of Samples

5.1 Thoroughly mix and comminute the sample before taking portions for analysis.

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

Current edition approved June 1, 2020. Published July 2020. Originally approved in 1985. Last previous edition approved in 2014 as D4487 – 90 (2014). DOI: 10.1520/D4487-90R20.

[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] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

SILICON DIOXIDE

6. Apparatus

6.1 *Evaporating Casserole,* 250-mL capacity.

6.2 *Hot Plate.*

6.3 *Porcelain Filtering Crucible,* medium porosity, 30-mL capacity.

6.4 *Drying Oven,* maintained at 100 ± 5°C.

6.5 *Muffle Furnace.*

7. Reagents

7.1 *Hydrochloric Acid* (1+1).

7.2 *Hydrochloric Acid* (1+19).

7.3 *Hydrochloric Acid* (1+99).

8. Procedure

8.1 Introduce a 1-g specimen, weighed to the nearest 0.1 mg into an evaporating casserole. Add 50 mL of HCl (1+1) and thoroughly mix.

8.2 Place the casserole on a hot plate and evaporate carefully to dryness.

8.3 Place the casserole in the oven at 100°C for 2 h. Do not allow the oven temperature to exceed 105°C at any time. Remove the casserole and allow to cool for 10 min.

8.4 Completely wet the residue with 25 mL of HCl (1+1) and cover the casserole with a watch glass. Warm just to boiling on a hot plate and maintain for 10 min.

8.5 Add 25 mL of water, free any material from the sides of the casserole with a stirring rod, and immediately filter through a tared porcelain crucible of medium porosity.

8.6 Wash the residue with two 5-mL portions of hot HCl (1+19), one 5-mL portion of hot HCl (1+99), and finally with two 5-mL portions of hot water. Save the combined filtrates for the determination of iron oxide (Sections 10 – 12).

8.7 Place the crucible containing the precipitate in the muffle furnace from 600 to 800°C and heat to constant weight (±4 mg). Cool in a desiccator and weigh.

9. Calculation

9.1 Calculate the percent of SiO_2, *A*, as follows:

$$A = R/S_1\,(100) \quad (1)$$

where:

R = weight of residue, g, and
S_1 = weight of original specimen, g.

IRON OXIDE

10. Apparatus

10.1 *Volumetric Flasks,* 250-mL and 1000-mL capacity.

10.2 *Buret,* 10-mL capacity.

11. Reagents

11.1 *Potassium Iodate* (0.01878 *N*)—Dry 1.0 g of KIO_3 at 120°C for 2 h in a drying oven. After cooling, weigh 0.6700 g and dissolve it in 100 mL of water. Dilute the solution to 1 L in a volumetric flask. 1 mL = 0.001500 g Fe_2O_3.

11.2 *Potassium Iodide (KI)*—Iodate free.

11.3 *Starch Indicator Solution*—Make a homogeneous paste of 10 g of soluble starch in cold water. Add to this 1 L of boiling water, stir rapidly, and cool. Salicylic acid (1.25 g/L) may be added to preserve the indicator. If long storage is required, the solution should be kept in a refrigerator at 4 to 10°C. Prepare fresh indicator when the end point of the titration from blue to colorless fails to be sharp.

11.4 *Sulfuric acid* (H_2SO_4) (1+18).

11.5 *Sodium Thiosulfate, Standard Solution* (0.025 *N*)—Dissolve 1.5 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 50 mL of water and dilute to 250 mL. Standardize as follows: Pipet 10 mL of the KIO_3 solution into each of three 150-mL beakers. Dilute each to 100 mL with water, add 2 g of KI and 5 mL of H_2SO_4 (1+18), and dissolve the KI with stirring. Titrate the liberated iodine with 0.025 N $Na_2S_2O_3$ solution until the color of the solution becomes pale yellow. Add 2 mL of starch indicator and continue the titration dropwise until the color changes from blue to colorless.

$$I = 1 \text{ mL } Na_2S_2O_3 = 0.01500/V_1 \text{ g } Fe_2O_3 \quad (2)$$

where:

I = iron oxide equivalent of $Na_2S_2O_3$ solution,
V_1 = $Na_2S_2O_3$ required for titrations, mean, mL, and
0.01500 = (10.00 mL KIO_3) × (0.001500 g Fe_2O_3/mL KIO_3).

12. Procedure

12.1 Dilute the solution obtained from the procedure in 8.6 to 100 mL with water. Add 10 mL of HCl and 5 g KI. Dissolve the KI with stirring.

12.2 Titrate with 0.025 N $Na_2S_2O_3$ solution until the color becomes a pale yellow. Add 2 mL of starch indicator solution and continue the titration until the color changes from blue to colorless.

13. Calculation

13.1 Calculate the percent of iron oxide, *D*, as follows:

$$D = (I \times V_2)/S_1\,(100) \quad (3)$$

where:

V_2 = $Na_2S_2O_3$ solution required for titration, mL, and
S_1 = weight of original specimen, g.

SOLUTION OF PIGMENT FOR THE DETERMINATION OF BORON TRIOXIDE AND CALCIUM OXIDE

14. Apparatus

14.1 *Boiling Flask*—300-mL capacity with ground glass connection.

14.2 *Büchner Funnel,* 56-mm diameter.

14.3 *Filter Paper,* 55-mm diameter.[4]

14.4 *Filter Flask,* 250-mL capacity.

14.5 *Hot Plate/Stirrer.*

14.6 *pH Meter.*

14.7 *Reflux Condenser,* with ground glass connection, water cooled.

14.8 *Sintered Glass Crucible,* 50-mL capacity, medium porosity.

14.9 *Volumetric Flask,* 250-mL capacity.

15. Reagents

15.1 *Hydrochloric Acid* (1+1).

15.2 *Hydrochloric Acid* (1+25).

15.3 *Nitric Acid* (1+1).

15.4 *Potassium Hydroxide,* pellets.

15.5 *Potassium Hydroxide Solution,* 28 g/L.

16. Procedure

16.1 Introduce 2.5 g of sample, weighed to 0.1 mg, into the 300-mL boiling flask.

16.2 Add 50 mL of HCl (1+1) and 2 drops HNO_3 (1+1). Place a magnetic stirring bar in the flask, connect the reflux condenser to the flask, and reflux for 1 h on the hotplate with constant stirring.

16.3 Remove the hotplate and place an ice bath under the flask. After the solution has cooled, wash the condenser down with a small amount of water (10 mL) and remove from the flask.

16.4 Filter the mixture through a Büchner funnel equipped with filter paper[4] into a 250-mL filter flask. Wash the boiling flask with several 5-mL portions of hot water to transfer all the material to the filter.

16.5 Cool the filtrate in an ice bath to a temperature of approximately 10°C, add 15 g of KOH pellets and swirl to dissolve them. Using the pH meter, neutralize the solution to a pH from 6.0 to 7.0, adding first KOH pellets and finally either KOH (28 g/L) or HCl (1+25). Be careful not to add appreciably to the volume of the solution, nor to exceed a pH of 7.0.

16.6 After neutralizing the solution, warm it gently on a hot plate to coagulate the iron precipitate. Filter off the iron precipitate with a medium-porosity sintered glass filter into a clean 250-mL filter flask.

16.7 Replace the sintered glass crucible on the original filter flask and add 10 mL of water. Dissolve the iron precipitate by the dropwise addition of HCl (1+1) and constant stirring. Filter with suction and wash the crucible with two 5-mL portions of hot water. Swirl the acidic solution around in the flask to dissolve any iron precipitate adhering to the sides of the flask.

16.8 Repeat the neutralization step (16.5) and filter the solution through the sintered glass crucible into the flask containing the first filtrate (16.7).

16.9 Wash the flask used in the neutralization with two 5-mL portions of water, and then wash the precipitate in the crucible.

16.10 Transfer the filtrate quantitatively to a 250-mL volumetric flask and dilute to volume. Use this filtrate for the determination of boron trioxide (Sections 17 – 19) and calcium oxide (Sections 20 – 22).

BORON TRIOXIDE

17. Apparatus

17.1 *pH Meter.*

17.2 *Buret,* 25-mL capacity.

17.3 *Volumetric Flasks,* 1000-mL and 100-mL capacity.

17.4 *Drying Oven,* maintained at 105 ± 2°C.

18. Reagents

18.1 *Hydrochloric Acid* (1+19).

18.2 *Mannitol.*

18.3 *Phenolphthalein Indicator Solution*—Dissolve 0.10 g phenolphthalein in 50 mL of ethyl alcohol. Dilute to 100 mL with water.

18.4 *Thymol Blue Indicator Solution*—Dissolve 0.1 g of thymol blue in 50 mL of 0.01 *N*sodium hydroxide. Dilute to 100 mL with ethyl alcohol.

18.5 *Mixed Indicator Solution*—Mix 25 mL of thymol blue indicator solution with 75 mL of phenolphthalein indicator solution. Adjust the pH from 6.0 to 7.0 on a pH meter with either HCl (1+19) or NaOH (0.1 *N*).

18.6 *Potassium Hydrogen Phthalate* (KHP)—Acidimetric standard.

18.7 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Dissolve 4.0 g of NaOH pellets in 100 mL of water and dilute to 1 L in a volumetric flask. Standardize as follows: Dry 2.0 g of KHP for 2 h at 105°C in the oven and cool. Weigh 1.6420 g and dissolve in 50 mL of water. Transfer quantitatively to a 100-mL volumetric flask and dilute to volume with water (1 mL = 0.002800 g B_2O_3). Pipet 25 mL of the KHP solution into each of three 150-mL beakers. Add 3 drops of phenolphthalein indicator and titrate with 0.1 *N* NaOH until the color changes from colorless to red.

$$B = 1 \text{ mL NaOH} = 0.07000/V_3 \text{ g } B_2O_3 \quad (4)$$

where:

B = B_2O_3 equivalent of NaOH solution,
V_3 = NaOH used in standardization titrations, mean, mL, and
0.07000 = (25.00 mL KHP) × (0.002800 g B_2O_3/mL KHP).

[4] The sole source of supply of Whatman No. 50 Filter Paper, known to the committee at this time is Whatman, Inc. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, [1] which you may attend.