Designation: D4487 – 90 (Reapproved 2014)

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

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.

SILICON DIOXIDE

6. Apparatus

6.1 *Evaporating Casserole,* 250-mL capacity.

6.2 *Hot Plate.*

---

[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 Dec. 1, 2014. Published December 2014. Originally approved in 1985. Last previous edition approved in 2008 as D4487 – 90 (2008). DOI: 10.1520/D4487-90R14.

[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] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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:

$$A = R/S_1\,(100) \tag{1}$$

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.

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

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:

$$D = (I \times V_2)/S_1\,(100) \tag{3}$$

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.

---

[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.

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.

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

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).

19. Procedure

19.1 Pipet 50 mL of the filtrate from the procedure in 16.10, which has been diluted to volume, into each of two 150-mL beakers.

19.2 With the pH meter, adjust the pH of each solution to 6.0 using either HCl (1+19) or 0.1 *N* NaOH. Add 10 g of mannitol and dilute to 100 mL with water.

19.3 Add 1 mL of mixed indicator solution and titrate with 0.1 *N* NaOH. The end point is when the color changes from yellow to dark violet.

20. Calculation

20.1 Calculate the percent of boron trioxide, *E*, as follows:

$$E = B \times V_4 / S_2 \,(500) \tag{5}$$

where:

V_4 = NaOH used in titrations, mean, mL, and
S_2 = weight of original specimen, g.

CALCIUM OXIDE

21. Apparatus

21.1 *Buret,* 25-mL capacity.

21.2 *Volumetric Flasks,* 500-mL and 1000-mL capacity.

21.3 *Reagents.*

21.4 *Ammonium Hydroxide* (1+4).

21.5 *Buffer Solution*—Dissolve 33.75 g of ammonium chloride in 285 mL of NH_4OH, add 5 mL of concentrated ammonium sulfide, and dilute to 500 mL with water.

21.6 *Calcium Standard*—Dry 7 g of calcium carbonate ($CaCO_3$) at 105°C for 2 h. Weigh 6.2461 g of the dried $CaCO_3$ into a 500-mL flask. Slowly add HCl (1+1) until all the $CaCO_3$ has dissolved. Add 200 mL of water and boil for a few minutes to expel CO_2. Cool and adjust the pH from 5 to 6 by adding NH_4OH (1+4) or HCl (1+1). Transfer solution to a 1000-mL volumetric flask and dilute to volume. 1 mL = 0.003500 g CaO.

21.7 *Sodium Carbonate (0.2 %)*—Dissolve 2 g Na_2CO_3 in water and dilute to 1 L.

21.8 *Sodium Carbonate (10 g/L)*—Dissolve 10 g Na_2CO_3 in water and dilute to 1 L.

21.9 *Eriochrome Black T Indicator Solution*—Dissolve 1.0 g of Eriochrome Black T in 30 mL of 0.2 % sodium carbonate (Na_2CO_3) solution. Dilute to 100 mL with isopropanol. Adjust the pH to 9.0 with Na_2CO_3 solution (10 g/L). Indicator shelf life: 2 months.

21.10 *EDTA, Standard Solution* (0.17 *N*)—Weigh 63.3 g of disodium ethylenediamine tetraacetate (EDTA) and 0.1 g magnesium chloride ($MgCl_2$), and dissolve in 500 mL of NaOH (20 g/L) solution and dilute to 1 L with water. Standardize as follows: Pipet 50 mL of calcium standard into each of three 150-mL beakers. Add 15 mL of buffer solution and 3 to 4 drops of indicator solution to each beaker. Titrate immediately with EDTA solution (0.17 *N*) until the color changes from red to a definite blue.

$$C = 1 \text{ mL EDTA} = 0.1750 / V_5 \text{ g CaO} \tag{6}$$

where:

C = CaO equivalent of EDTA solution,
V_5 = EDTA required for titrations, mean, mL, and
0.1750 = (50 mL Ca Standard) × (0.003500 g CaO/mL).

22. Procedure

22.1 Pipet 50 mL of the filtrate from the procedure in 15.10 into each of two 150-mL beakers. Add 25 mL of buffer and 3 to 4 drops of indicator solution to each beaker.

22.2 Immediately titrate with EDTA until the color changes from red to a definite blue.

23. Calculation

23.1 Calculate the percent of calcium oxide, *F*, as follows:

$$F = C \times V_6 / S_2 \,(500) \tag{7}$$

where:

V_6 = EDTA required for titrations, mean, mL, and
S_2 = weight of original specimen, g.

MOISTURE AND OTHER VOLATILE MATTER

24. Procedure

24.1 Determine moisture and other volatile matter in accordance with Method A of Test Methods D280.

WATER OF HYDRATION

25. Apparatus

25.1 *Casserole.*

25.2 *Muffle Furnace,* preferably electrically heated maintained at a temperature of 450 ± 10°C.

26. Procedure

26.1 Place the casserole in the muffle furnace and heat at 450°C for 30 min. Remove to a desiccator, cool, and weigh to the nearest 0.1 mg.

26.2 Remove the weighing bottle containing approximately 3 to 5 g of previously dried pigment (Section 24) from the desiccator. Transfer most of the pigment to the casserole and weigh to 0.1 mg. Subtract the weight of the dish from the total weight to obtain the specimen weight.

26.3 Place the dish containing the specimen in the muffle furnace heated at a temperature of about 250°C and raise the temperature to 450°C. Maintain temperature at 450°C for 1 h. Remove the dish from the furnace to the desiccator and allow to cool to room temperature. Weigh to the nearest 0.1 mg. Heat again at 450°C for 15 min to check the loss in weight. The two weights should not differ by more than 4 mg.

26.4 Calculate the percent water of hydration on the basis of dried pigment to 0.01 %.

COARSE PARTICLES

27. Procedure

27.1 Determine the percent of coarse particles in the pigment in accordance with Test Methods D185.

28. Oil Absorption

28.1 Determine the oil absorption of the pigment in accordance with Test Method D281.

29. Precision[5]

29.1 In an interlaboratory study of this test method in which operators at four locations made single analyses on two days of two pigments containing 32.9 and 39.3 % SiO_2, 16.5 and 10.6 % B_2O_3 and 40.7 and 44.1 % CaO, the within-laboratory pooled standard deviations were found to be 0.27 % for SiO_2, 0.13 % for B_2O_3, and 0.31 % for CaO, each with 8 df, and the equivalent between-laboratories standard deviations 0.346 %, 0.255 % and 0.495 %, with 6 df each. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

29.1.1 *Repeatability*—Two results, each single determinations, obtained by the same operator on different days should be considered suspect if they differ in percent absolute by more than 0.88 % SiO_2, 0.48 % B_2O_3, and 1.01 % CaO at levels of 32 to 40 % SiO_2, 10.5 to 16.5 % B_2O_3 and 40 to 45 % CaO.

29.1.2 *Reproducibility*—Two results, each single determinations, obtained by operators in different laboratories should be considered suspect if they differ in percent absolute by more than 1.20 % SiO_2, 0.88 % B_2O_3, and 1.72 % CaO at the same levels as in 29.1.1.

30. Keywords

30.1 boron trioxide; calcium borosilicate pigment analysis; calcium oxide; iron oxide; silicon dioxide; water of hydration

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1047. Contact ASTM Customer Service at service@astm.org.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/