



Standard Test Methods for Analysis of Calcium Borosilicate¹

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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 ₂ O ₃)	10-13
Boron Trioxide (B ₂ O 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 SiO₂, B₂O₃, and CaO. SiO₂ and Fe₂O₃ should be removed before the determination of the B₂O₃ and CaO.

1.4 *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:

- D 185 Test Methods for Coarse Particles in Pigments, Pastes, and Paints²
- D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments²
- D 281 Test Method for Oil Absorption of Pigments by Spatula Rub-Out³
- D 1193 Specification for Reagent Water⁴

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.

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

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² *Annual Book of ASTM Standards*, Vol 06.03.

³ *Annual Book of ASTM Standards*, Vol 06.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

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.⁵ 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 D 1193.

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 ₂ SO ₄)	1.84
Ammonium hydroxide (NH ₄ OH)	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*.
- 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).

⁵ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

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 SiO₂, *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 KIO₃ 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 Fe₂O₃.

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* (H₂SO₄) (1+18).

11.5 *Sodium Thiosulfate, Standard Solution* (0.025 *N*)—Dissolve 1.5 g of sodium thiosulfate (Na₂S₂O₃·5H₂O) in 50 mL of water and dilute to 250 mL. Standardize as follows: Pipet 10 mL of the KIO₃ solution into each of three 150-mL beakers. Dilute each to 100 mL with water, add 2 g of KI and 5 mL of H₂SO₄ (1+18), and dissolve the KI with stirring.

Titrate the liberated iodine with 0.025 *N* Na₂S₂O₃ 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.

$$I = 1 \text{ mL Na}_2\text{S}_2\text{O}_3 = 0.01500/V_1 \text{ g Fe}_2\text{O}_3 \quad (2)$$

where:

I = iron oxide equivalent of Na₂S₂O₃ solution,

*V*₁ = Na₂S₂O₃ required for titrations, mean, mL, and

0.01500 = (10.00 mL KIO₃) × (0.001500 g Fe₂O₃/mL KIO₃).

12. Procedure

12.1 Dilute the solution obtained from the procedure in 7.6 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* Na₂S₂O₃ 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 = Na₂S₂O₃ 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.⁶

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.

⁶ 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

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 HNO₃ (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 paper⁶ 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 B₂O₃). 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.

$$B = 1 \text{ mL NaOH} = 0.07000/V_3 \text{ g B}_2\text{O}_3 \quad (4)$$

where:

$$\begin{aligned} B &= \text{B}_2\text{O}_3 \text{ equivalent of NaOH solution,} \\ V_3 &= \text{NaOH used in standardization titrations, mean,} \\ &\quad \text{mL, and} \\ 0.07000 &= (25.00 \text{ mL KHP}) \times (0.002800 \text{ g B}_2\text{O}_3/\text{mL KHP}). \end{aligned}$$

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:

$$E = B \times V_4/S_2 (500) \quad (5)$$

where:

$$\begin{aligned} V_4 &= \text{NaOH used in titrations, mean, mL, and} \\ S_2 &= \text{weight of original specimen, g.} \end{aligned}$$

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 NH₄OH, add 5 mL of concentrated ammonium sulfide, and dilute to 500 mL with water.
- 21.6 Calcium Standard—Dry 7 g of calcium carbonate (CaCO₃) at 105°C for 2 h. Weigh 6.2461 g of the dried CaCO₃ into a 500-mL flask. Slowly add HCl (1+1) until all the CaCO₃ has dissolved. Add 200 mL of water and boil for a few minutes to expel CO₂. Cool and adjust the pH from 5 to 6 by adding NH₄OH (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 Na₂CO₃ in water and dilute to 1 L.

21.8 *Sodium Carbonate* (10 g/L)—Dissolve 10 g Na₂CO₃ 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 (Na₂CO₃) solution. Dilute to 100 mL with isopropanol. Adjust the pH to 9.0 with Na₂CO₃ 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 (MgCl₂), 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.

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

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:

$$F = C \times V_6/S_2 (500) \quad (7)$$

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 D 280.

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 D 185.

28. Oil Absorption

28.1 Determine the oil absorption of the pigment in accordance with Test Method D 281.

29. Precision⁷

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 % SiO₂, 16.5 and 10.6 % B₂O₃ and 40.7 and 44.1 % CaO, the within-laboratory pooled standard deviations were found to be 0.27 % for SiO₂, 0.13 % for B₂O₃, 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 % SiO₂, 0.48 % B₂O₃, and 1.01 % CaO at levels of 32 to 40 % SiO₂, 10.5 to 16.5 % B₂O₃ 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 % SiO₂, 0.88 % B₂O₃, 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

⁷ Supporting data are available from ASTM Headquarters. Request RR: D01-1047.

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