



Standard Test Methods for Chemical Analysis of Blue Pigments¹

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This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover procedures for the chemical analysis of blue pigments known commercially as iron blue, copper phthalocyanine blue, and ultramarine blue.

1.2 The analytical procedures appear in the following order:

	Sections
IRON BLUE PIGMENTS	
Identification	6
Moisture by the Brabender Moisture Tester	7 and 8
Moisture by Toluene Distillation	9
Water-Soluble Matter by Extraction	10
Water-Soluble Salts by Electrical Conductivity	11
Detection of Acid-Insoluble Extenders	1213
Detection of Acid-Soluble Extenders	14 to 17
Detection of Organic Colors and Lakes	18
COPPER PHTHALOCYANINE BLUE PIGMENTS	
Identification	19
Moisture and Other Volatile Matter	20
Detection of Basic Dye Derivatives	21
Detection of Other Organic Coloring Matter	22
Detection of Ultramarine Blue	23
Detection of Iron Blue	24
ULTRAMARINE BLUE	
Identification	25
Moisture and Other Volatile Matter	26
Water-Soluble Matter	27
Detection of Basic Dye Derivatives	28
Detection of Other Organic Coloring Matter	29

1.3 *This standard does not purport to address the safety concerns 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 280 Test Methods for Hygroscopic Moisture (and Other

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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Matter Volatile Under the Test Conditions) in Pigments²
D 1193 Specification for Reagent Water³

D 1208 Test Methods for Common Properties of Certain Pigments²

D 2448 Test Method for Water-Soluble Salts in Pigments by Measuring the Specific Resistance of the Leachate of the Pigment²

E 11 Specification for Wire-Cloth Sieves for Testing Purposes⁴

3. Significance and Use

3.1 These test methods are suitable for determining if impurities are present and establishing that the required pigments are present. These test methods may be used for manufacturing quality control.

4. Purity of Reagents and Water

4.1 *Purity of Reagents*—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.

5. Preparation of Sample

5.1 Mix the sample thoroughly and take a representative portion for analysis. Reduce any lumps or coarse particles to a fine powder by grinding.

5.2 Grind extracted pigments to pass a No. 80 (180-μm)

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

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

sieve.⁶ Discard any skins that do not pass through the sieve. Mix the finely ground pigment thoroughly.

IRON BLUE

(Prussian Blue, Chinese Blue, Milori Blue)

IDENTIFICATION

6. Procedure

6.1 To approximately 0.1 g of pigment in a 50-mL beaker, add 15 mL of NaOH solution (50 g/L). Heat to boiling. In a few minutes the blue color should be completely destroyed, giving in its place the characteristic reddish brown precipitate of ferric hydroxide. Add HCl (1+1) until faintly acid to litmus. The iron blue should be reformed, yielding again the characteristic blue color.

NOTE 1—If the NaOH treatment does not completely destroy the blue color, the evidence is strong that a foreign pigment is present. If this occurs, it is best to filter the alkaline solution, weakly acidify the filtrate

with HCl (1+1), and add approximately 2 mL of a ferric salt solution (ferric sulfate or ferric alum (20 g/L)). The formation of a blue precipitate established the pigment as consisting, at least in part, of iron blue.

MOISTURE BY THE BRABENDER MOISTURE TESTER

7. Apparatus

7.1 *Brabender Moisture Tester*—The Brabender moisture tester (Fig. 1) consists of a constant-temperature oven with weighing apparatus attached. Specimens placed in the oven may be weighed without opening the oven door or removing the specimen from the oven, as the balance scale is calibrated to read directly in percent of moisture.



FIG. 1 Brabender Moisture Tester

8. Procedure

8.1 Set the temperature control at 160°C and allow the oven to reach this temperature before checking or making any weighing. Check the scale by placing a sample dish containing 9.200 g standard analytical balance weights in the oven. The apparatus should read 8.0 % moisture. If it does not, adjust to a reading of 8.0 % by turning either the right hand or left hand foot screw.

8.2 Weight 10.000 g of the sample in the aluminum dish and place in the oven. For a series of specimens, all should be placed in the oven at as nearly the same time as possible. No specimen should occupy the position directly in front of the door. Weigh the specimen at the end of each hour for 5 h. After each weighing, return the specimen to its original place in the oven.

NOTE 2—The dried pigment is very hygroscopic. In order to obtain consistent results, the specimen position must not be changed and the oven door must not be opened.

8.3 *Calculation and Report*—Plot time against percent loss in weight on rectilinear cross-section paper. Extrapolate the linear portion of the curve to zero time. That portion beyond about 2 h will be essentially linear. Report the percent loss in weight at the extrapolated zero time as the percent moisture in the pigment.

NOTE 3—The pigment undergoes a slight loss in weight due to decomposition during the heating. The method of plotting and extrapolation corrects for this loss. An approximate value for moisture content may be obtained by taking the reading at the end of the first hour's heating. An occasional pigment may decompose rapidly at the oven temperature. In such cases, determine moisture by the toluene distillation method (Section 9).

MOISTURE BY TOLUENE DISTILLATION

9. Procedure

9.1 Determine the moisture content in accordance with Sections 7 and 8 of Test Method D 1208, but using 25 g of pigment and 200 mL of toluene and adjusting the calculation accordingly.

WATER-SOLUBLE MATTER BY EXTRACTION

10. Procedure

10.1 Determine whether or not the pigment is easily wet by water at room temperature by adding a little to some water in a beaker. If it tends to float on top of the water with very little, if any, tendency to sink to the bottom or disperse throughout the solution, even after agitation, it contains a hydrophobic treating agent.

10.2 Weigh to 1 mg about 2.5 g of the pigment into a 250-mL volumetric flask. If the pigment is hydrophobic as tested above, moisten thoroughly with a few mL of ethyl alcohol (Note 4). If the pigment is easily wet with water, no alcohol is necessary. Fill the flask about half full with water and shake to disperse the pigment thoroughly. Fill to the mark and again shake. Allow to remain at room temperature for not less than 15 h, shaking from time to time, preferably with an automatic shaking device.

NOTE 4—Ethyl alcohol denatured with acetone (Formula No. 23A) or

denatured with methyl alcohol (Formula No. 3A) has been found suitable.

10.3 Let settle, filter through a dry filter paper, and discard the first 20 mL of the filtrate. Transfer 100 mL of the clear filtrate to a weighed dish, and evaporate to dryness on a steam bath. Dry for 1 h in an oven at $105 \pm 2^\circ\text{C}$, cool, and weigh.

10.4 *Calculation*—Calculate the percent of water-soluble matter as follows:

$$\text{Water-soluble matter, \%} = \text{grams of residue} \times 100$$

WATER-SOLUBLE SALTS BY ELECTRICAL CONDUCTIVITY

11. Procedure

11.1 Determine water soluble salt content in accordance with Test Method D 2448.

DETECTION OF ACID-INSOLUBLE EXTENDERS

12. Scope

12.1 Acid-insoluble extenders include barium sulfate, silica, and silicates. Alumina may also be found, in part, with this group.

13. Procedure

13.1 Ignite about 1 g (weighed to 0.1 mg) of the sample at a low temperature, just enough to decompose the last trace of pigment but not high enough to render the iron difficultly soluble in HCl (Note 5). Cool, and add 15 mL of HCl (sp gr 1.19) and a few drops of bromine. Cover with a watch glass and evaporate to a sirup. Add about 15 mL of water, and boil. It may be necessary to add a drop or two of HCl to effect complete solution of the ferric iron residue. Filter and wash with hot water. Save the filtrate for the determination of alumina hydrate (Section 16).

NOTE 5—The ignition can conveniently be carried out in a 250-mL beaker or a porcelain dish over a free flame. Oxidation of the specimen is evidenced by a dull glowing. While being heated, it is advisable to roll the specimen around in the beaker or dish exposing all of the surface to the oxygen of the air. A moderately low flame should be used and the ignition is complete when the specimen ceases to glow and acquires a uniform brown color.

13.2 A residue of less than 3 mg that appears as small black specks can be neglected, since quite frequently a small amount of iron is rendered insoluble or a small amount of blue pigment escapes destruction. Ignite the residue and weigh. If appreciably more than 3 mg are present, extenders should be suspected, and if it is required to know which extenders are present, analyze the residue for silica, barium sulfate, and alumina.

NOTE 6—If alumina is present, it may appear both with the acid-insoluble and acid-soluble extenders. As a rule, most of it will appear with the acid-soluble extenders.

DETECTION OF ACID-SOLUBLE EXTENDERS

14. Scope

14.1 Acid-soluble extenders include the alkaline earth carbonates or sulfates, magnesium carbonate, and alumina hydrate.

15. Reagents

15.1 *Ammonium Oxalate Solution*—Dissolve 40 g of ammonium oxalate monohydrate in warm water and dilute to 1 L.

15.2 Ammonium Phosphate Solution—Dissolve 100 g of $(\text{NH}_4)_2\text{HPO}_4$ in water and dilute to 1 L.

16. Procedure for Alumina Hydrate

16.1 To the filtrate from 13.1, add NaOH solution (50 g/L) until just alkaline; then add 5 mL excess. Boil for about 2 min and let stand in a warm place until the hydrous iron oxide is coagulated. Filter through a rapid filter paper, wash a few times with hot water, and discard the precipitate.

16.2 To the filtrate add 7 mL of HCl (1+1). Add NH_4OH (1+4) until just ammoniacal. Boil about 2 min. If no precipitate is apparent, allow to stand about $\frac{1}{2}$ h. If the solution is still clear, no alumina hydrate is present. A white gelatinous precipitate indicates alumina hydrate. Filter and save the filtrate for the detection of alkaline earth and magnesium salts (Section 17).

16.3 If a rough estimate of the amount of alumina hydrate is desired, the residue may be washed, dried, ignited, and weighed as Al_2O_3 .

17. Procedure for Alkaline Earth and Magnesium Salts

17.1 To the filtrate from Section 16, add HCl (1+1) until faintly acid. Divide the filtrate into two portions.

17.2 To one portion of the filtrate, add 15 mL of $(\text{NH}_4)_2\text{HPO}_4$ solution and neutralize with NH_4OH (sp gr 0.90). Add 10 mL excess NH_4OH . If no precipitate forms immediately, let stand for a short time in a cool place with occasional vigorous stirring. Rub the inside of the beaker from time to time with a

glass rod to initiate crystallization. A white microcrystalline precipitate indicates the presence of magnesium salts and possibly some alkaline earth salts as well.

17.3 To the other portion of the filtrate, add 5 mL of ammonium oxalate solution. Make slightly alkaline with NH_4OH (sp gr 0.90). If no precipitate forms immediately, warm on a hot plate and let stand for a short time. A white microcrystalline precipitate indicates the presence of alkaline earth salts. If it is required to know specifically which acid soluble extenders are present, any of the established tests for these metal salts may be employed.

DETECTION OF ORGANIC COLORS AND LAKES

18. Procedure

18.1 Boil 2 g of the sample for 2 min with 25 mL of water. Let settle and decant the supernatant liquid. Similarly, boil the residue with 25 mL of denatured ethyl alcohol (95 %) and decant as before. Likewise boil with 25 mL of chloroform and again decant. If any one of the above solutions is colored, organic colors are present. If all solutions remain colorless, disregarding a slight yellowish cast, organic colors are presumably absent. The presence of organic colors resistant to the above reagents is unlikely, but may be tested by reference to procedures given in standard reference works.⁶

⁶ Reference may be made to the following: Payne, H. F., "Organic Coatings Technology," Vol II, John Wiley & Sons, Inc., New York, NY, 1961.

COPPER PHTHALOCYANINE BLUE

IDENTIFICATION

19. Procedure

19.1 To about 0.05 g of the sample in a 50-mL beaker, add 30 mL of H_2SO_4 (sp gr 1.84). Stir occasionally for 15 min; the sample should dissolve, forming a dark greenish yellow solution (color best seen on the side of the beaker). Pour the solution into 250 mL of water and stir. The copper phthalocyanine should immediately precipitate as a brilliant blue flocculent mass.

19.2 Filter off the precipitate, washing once or twice with water. Scrape a small amount of the precipitate off the filter, place on a clean platinum wire moistened with HCl, and subject it to the low flame of a bunsen burner. As the precipitate burns, a light blue-green flame should be clearly evident. This indicates organically combined copper.

NOTE 7—Characteristic spectrophotometric absorption spectra in the near infrared range (700 to 900 nm) are exhibited by dilute solutions of copper phthalocyanine blue pigments in H_2SO_4 (sp gr 1.84) (2 to 50 mg/L). The absorption maxima are so sharp and well defined that they may be used for positive qualitative identification of the various phthalocyanine pigments.

MOISTURE AND OTHER VOLATILE MATTER

20. Procedure

20.1 Determine moisture in accordance with Method A of Test Methods D 280.

DETECTION OF BASIC DYE DERIVATIVES

21. Procedure

21.1 Add to 1 g of the sample, 50 mL of a mixture of equal parts of NH_4OH (sp gr 0.90) and denatured ethyl alcohol (95 %). Warm gently and filter. Neutralize the filtrate with tartaric acid solution (200 g/L) until slightly acid to litmus. If the solution is colorless, discounting a slight yellow tinge, no basic dye is present.

21.2 If the solution is colored beyond a slight yellow tinge, add about 5 mL of 0.1 N TiCl_3 solution (Note 8). If a basic dye is present, the color will lighten significantly. If no basic dye is present, no significant color change will occur.

NOTE 8—Titanium trichloride is marketed as a 16 % solution in HCl. Mix 7 mL of this solution with 90 mL of HCl (1+2) to obtain a reagent approximately 0.1 N. Protect from oxidation.

DETECTION OF OTHER ORGANIC COLORING MATTER

22. Procedure

22.1 Weigh about 0.05 g of the sample into each of two 50-mL beakers. Add 25 mL (at room temperature) of denatured ethyl alcohol (95 %) to one beaker and about 25 mL of acetone to the other. Stir each well for a few minutes, and let stand for about 2 h. Filter through two thicknesses of medium-texture, qualitative filter paper. If neither filtrate possesses more than an

extremely slight pink, yellow, or blue cast, organic colors are presumably absent, but may be tested for by procedures given in standard reference works.⁷

DETECTION OF ULTRAMARINE BLUE

23. Procedure

23.1 Warm gently about 1 g of the sample with HCl (1+1). Decomposition of the ultramarine blue takes place with evolution of H₂S. This may be detected by either its odor or a brown coloration appearing on a strip of moistened lead acetate paper.

ULTRAMARINE BLUE

IDENTIFICATION

25. Procedure

25.1 Warm gently approximately 0.1 g pigment with HCl (1+1). If the pigment is ultramarine blue, the color will be completely destroyed with the liberation of sulfur and H₂S, which may be detected by its characteristic odor or by a brown coloration appearing on a strip of moistened lead acetate paper when held above the beaker. Quite frequently warming is not necessary, the destruction taking place at room temperature.

NOTE 9—If any color remains after this treatment, it can be construed as evidence that a foreign pigment is present.

MOISTURE AND OTHER VOLATILE MATTER

26. Procedure

26.1 Determine moisture in accordance with Method A of Test Methods D 280.

WATER-SOLUBLE MATTER

27. Procedure

27.1 Establish whether or not the pigment is easily wet by water by adding a little to some water in a beaker. If it tends to float on top with little tendency to sink to the bottom or disperse through the solution it contains a hydrophobic treating agent.

27.2 Transfer 2.5 g (weighed to 1 mg) of the sample to a 400-mL beaker. If the pigment is hydrophobic as tested above, moisten thoroughly with a few millilitres of ethyl alcohol (Note 4). If the pigment is easily wet with water, the alcohol is not necessary. Add 250 mL of water and boil for 5 min with good agitation.

DETECTION OF IRON BLUE

24. Procedure

24.1 To 1 g of the sample in a 100-mL beaker, add 25 mL of NaOH solution (50 g/L). Boil for about 1 min. Dilute to approximately 40 mL and filter.

24.2 Add HCl (1+1) to the filtrate until faintly acid to litmus. Add 2 mL of a ferric iron solution (ferric sulfate or ferric alum (20 g/L)). The development of a blue color reveals the presence of ferrocyanide, and hence iron blue in the original pigment. For amounts around 0.05 % iron blue, the color may take 2 to 3 h to develop.

27.3 Cool and transfer to a 250-mL volumetric flask. Dilute to the mark with wash water from the beaker; complete transfer of the pigment to the flask is not necessary. After thorough shaking, allow to settle somewhat and filter the supernatant liquid through a dry paper, discarding the first 20 mL. Evaporate 100 mL of the clear filtrate to dryness in a weighed dish. Heat for 1 h at 105 ± 2°C, cool, and weigh.

27.4 *Calculation*—Calculate the percent of water-soluble matter as follows:

$$\text{Water-soluble matter, \%} = \text{grams of residue} \times 100$$

DETECTION OF BASIC DYE DERIVATIVES

28. Procedure

28.1 Determine basic dye derivatives in accordance with Section 21.

DETECTION OF OTHER ORGANIC COLORING MATTER

29. Procedure

29.1 Determine other organic coloring matter in accordance with Section 22.

30. Precision and Bias

30.1 Precision and Bias have not been determined.

31. Keywords

31.1 blue pigment, chemical analysis of; Brabender moisture tester; copper phthalocyanine blue, identification of; moisture, Brabender tester; moisture, toluene distillation; pigment, acid soluble extenders; ultramarine blue pigment, identification of

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