



Designation: D50 – 90 (Reapproved 2023)

Standard Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese¹

This standard is issued under the fixed designation D50; 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.

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

1. Scope

1.1 These test methods cover procedures for the chemical analysis of yellow, orange, red, and brown pigments containing iron and manganese. The test methods apply specifically to the following pigments: synthetic hydrated yellow iron oxide, yellow ochre, red and brown iron oxides, raw and burnt umber, raw and burnt sienna, and venetian red.

1.2 The analytical procedures appear in the following order:

Dry Pigments	Sections	ASTM Method References
Moisture and Other Volatile Matter	6	D280
Loss on Ignition	7	
Coarse Particles	8	D185
Matter Soluble in Water	9	D1208
Organic Coloring Matter	10	
Iron Oxide	11 and 12	
Calcium Compounds (Reported as CaO)	13 and 14	
Sulfates Soluble in Hydrochloric Acid	15 and 16	
Lead Chromate (in Ochres)	17	
Calcium Carbonate (in Venetian Red)	18	C25
Manganese (in Siennas and Umbers)	19 and 20	
Pigment Pastes in Oil		
Pigment Content	21	D1208
Moisture and Other Volatile Matter	22	D1208
Nonvolatile Matter in Vehicle	23	
Moisture by Distillation	24	D1208
Coarse Particles and Skins	25	D185
Consistency (Stormer)	26	D562

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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*

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.

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

1.5 *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

- C25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
- D185 Test Methods for Coarse Particles in Pigments
- D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments
- D562 Test Method for Consistency of Paints Measuring Krebs Unit (KU) Viscosity Using a Stormer-Type Viscometer
- D1193 Specification for Reagent Water
- D1208 Test Methods for Common Properties of Certain Pigments
- E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

3. Significance and Use

3.1 These test methods compile in one place, recommended procedures for analyzing inorganic colored pigments. These pigments are used extensively in paints, and for this reason their compositions are important to the formulators and user.

4. Preparation of Sample

4.1 Mix the sample thoroughly and take a representative portion for analysis. Reduce any lumps or coarse particles to a fine powder by grinding. Grind extracted pigments to pass a No. 80 (180 μ m) sieve (see Specification E11 for detailed

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.

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

5. Purity of Reagents

5.1 *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.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.

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

DRY PIGMENTS

Moisture and Other Volatile Matter

6. Procedure

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

Loss on Ignition

7. Procedure

7.1 Weigh accurately approximately 1 g of pigment into a previously weighed and ignited porcelain crucible (**Note 1**). Cover and ignite to constant weight over a bunsen or Meker burner or in an electric furnace at a temperature of approximately 900 °C. Cool in a desiccator, weigh, and calculate the percent loss on ignition. This figure may include combined water, carbon dioxide (CO₂), organic matter, and some sulfuric oxide (SO₃) if much calcium sulfate (CaSO₄) is present. The CO₂ may be determined on a separate portion if desired.

NOTE 1—It is inadvisable to use platinum unless it is known that attacking substances are absent.

Coarse Particles

8. Procedure

8.1 Determine coarse particles in accordance with Test Methods **D185**.

Matter Soluble in Water

9. Procedure

9.1 Determine matter soluble in water in accordance with Test Methods **D1208**.

Organic Coloring Matter

10. Procedure

10.1 Boil 2 g of the sample with 25 mL of water, let settle, and decant the supernatant liquid. Boil the residue with 25 mL

of ethyl alcohol (95 %) and decant as before. Boil the residue with 25 mL of 1 N alcoholic sodium hydroxide (NaOH) solution and again decant. Boil another 2 g portion of the sample with 25 mL of chloroform, let settle, and decant the supernatant liquid. If any one of the above solutions is colored, organic coloring matter is indicated (**Note 2**). If the solutions remain colorless, organic colors are probably absent, but may be tested for by reference to procedures given in standard reference works, taking into account the nature of the pigment involved.⁴

NOTE 2—With this class of pigments indication of presence of an organic color may often be noted by the characteristic odor given off on ignition.

Iron Oxide

11. Reagents

11.1 *Stannous Chloride Solution (SnCl₂·2H₂O)*—Dissolve 50 g of SnCl₂·2H₂O in 300 mL of hydrochloric acid (HCl) (sp gr 1.19) and dilute with water to 500 mL. Keep the clear solution in a tightly stoppered bottle containing some metallic tin.

11.2 *Mercuric Chloride Solution (HgCl₂)*—Prepare a saturated solution of HgCl₂ (60 g/L to 100 g/L).

11.3 *Sulfuric-Phosphoric Acid Mixture*—Mix 150 mL of sulfuric acid (H₂SO₄) (sp gr 1.84) with 150 mL of phosphoric acid (H₃PO₄) (85 %) and dilute with water to 1 L.

11.4 *Diphenylamine Indicator*—Dissolve 1 g of diphenylamine in 100 mL of H₂SO₄ (sp gr 1.84).

11.5 *Standard Potassium Dichromate Solution (K₂Cr₂O₇) (0.1 N)*—Dissolve 4.904 g of K₂Cr₂O₇ in water and dilute to 1 L. Standardize against the National Institute of Standards and Technology standard sample No. 27 of Sibley iron ore.

11.6 *Potassium Ferricyanide Solution (K₃Fe(CN)₆)*—Optional. Dissolve approximately 0.01 g of K₃Fe(CN)₆ in 50 mL of water. This solution must be made fresh when wanted because it does not keep.

12. Procedure

12.1 According to the amount of iron in the pigment, weigh 0.3 g to 1.0 g of the pigment and ignite in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 400 mL beaker and add 25 mL of HCl (sp gr 1.19). Cover with a watchglass and digest just short of boiling (80 °C to 90 °C) until no dark specks can be seen in the insoluble residue. The addition of a few drops of SnCl₂ solution after adding the acid greatly assists dissolving of the iron. When the residue is light in color, the solution of iron may be considered complete. This may take from 15 min to 1 h, or longer.

12.2 Add 25 mL to 50 mL of water and heat to gentle boiling (avoid vigorous prolonged boiling). Slowly add SnCl₂ solution dropwise until the last drop makes the solution colorless or free from any tinge of yellow, then add 1 or 2 drops

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.

⁴ Reference may be made to the following: Payne, H. F., "Organic Coatings Technology," Vol II, John Wiley & Sons, Inc., New York, N. Y., 1961.

in excess. It is best to keep the watchglass on the beaker while adding the SnCl_2 solution, with agitation of the hot iron solution after each addition. If too much SnCl_2 is added by mistake, add potassium permanganate (KMnO_4) to the solution until a yellow color appears, then again add SnCl_2 dropwise until the yellow color just disappears, again adding one or two drops in excess. Dilute with 200 mL of cold water; then add all at once with vigorous stirring 15 mL of HgCl_2 solution. Let stand 3 min to 4 min. A slight white precipitate should form. If none, or a heavy grayish precipitate forms, the determination should be discarded and repeated.

12.3 Add 15 mL of $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ mixture and 3 drops of diphenylamine indicator solution. Titrate with $\text{K}_2\text{Cr}_2\text{O}_7$ solution, taking the sudden change of the dark green color to a blue-black color as the end point.

12.4 If preferred, $\text{K}_3\text{Fe}(\text{CN})_6$ may be used as an external indicator. In this case omit the addition of the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ mixture and the diphenylamine indicator. Titrate with the $\text{K}_2\text{Cr}_2\text{O}_7$ solution as in 12.3, except toward the end take out a very small drop of the solution being titrated and touch this to a drop of the $\text{K}_3\text{Fe}(\text{CN})_6$ solution, best placed on a paraffined surface. Toward the end point the blue is replaced by a bluish-green coloration, perceptible at the junction of the two solutions. Take as the end point when no trace of the bluish-green coloration can be detected.

12.5 *Calculation*—Calculate the percent of iron oxide (Fe_2O_3), A , as follows:

$$A = (FV/S) \times 100 \quad (1)$$

where:

F = Fe_2O_3 equivalent of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution, g/mL,
 V = $\text{K}_2\text{Cr}_2\text{O}_7$ solution required, mL, and
 S = sample used, g.

13. Reagents

13.1 *Ammonium Oxalate Saturated Solution*—Heat to boiling 5 g powdered ammonium oxalate [$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$] and 100 mL of water. Allow to cool.

13.2 *Hydrogen Peroxide* (H_2O_2) (30 %).

13.3 *Potassium Permanganate, Standard Solution*—(KMnO_4) (0.1 N)—Dissolve 3.16 g of KMnO_4 in water and dilute to 1 L. Let stand 8 days to 14 days, siphon off the clear solution (or filter through a medium-porosity fritted disk), and standardize against the National Institute of Standards and Technology (NIST) standard sample No. 40 of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) as follows: In a 400 mL beaker dissolve 0.2500 g to 0.3000 g of the NIST $\text{Na}_2\text{C}_2\text{O}_4$ in 250 mL of hot water (80 °C to 90 °C) and add 15 mL of H_2SO_4 (1 + 1). Titrate at once with KMnO_4 solution, *stirring the liquid vigorously and continuously*. The KMnO_4 must not be added more rapidly than 10 mL/min to 15 mL/min, and the last 0.5 mL to 1 mL must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution shall not be below 60 °C by the time the end point has been reached. (More rapid cooling may be prevented by allowing

the beaker to stand on a small hot plate during the titration.) The use of a small thermometer (nonmercury type) as a stirring rod is most convenient. Keep the KMnO_4 solution in a glass-stoppered bottle painted black to keep out light, or in a brown glass bottle stored in a dark place.

13.4 Calculate the calcium oxide (CaO) value of the solution as follows:

$$C = (W_1 \times V_1) \times 0.4185 \quad (2)$$

where:

C = CaO equivalent of the KMnO_4 solution, g/mL,
 W_1 = sodium oxalate used, g, and
 V_1 = KMnO_4 solution required for the titration, mL.

$$0.4185 = \text{CaO}/\text{Na}_2\text{C}_2\text{O}_4 = 56.08/134.01 \quad (3)$$

14. Procedure

14.1 Weigh 2.5 g of sample, transfer to a porcelain crucible, and ignite at a dull red heat to destroy organic matter. Cool, transfer to a 600 mL beaker, and add 100 mL of HCl (1 + 1). Digest just short of boiling until no dark specks can be seen in the insoluble residue. Add ammonium hydroxide (NH_4OH) (sp gr 0.90) in slight excess and about 2 mL of H_2O_2 (30 %). Cool, transfer to a 500 mL graduated flask, and dilute to 500 mL. Mix thoroughly and filter through a dry paper.

14.2 Take 100 mL of the filtrate (corresponding to 0.5 g of sample), add a few drops of NH_4OH , heat to boiling, and add an excess of saturated ammonium oxalate solution. Continue the boiling until the precipitate becomes granular. Let stand about 30 min, filter, and wash three times with 20 mL aliquots of hot water until free of ammonium oxalate.

14.3 Place the beaker in which precipitation was made under the funnel, pierce the apex of the filter with a stirring rod, and wash the precipitate into the beaker with hot water. Pour warm H_2SO_4 (1 + 4) through the paper and wash a few times. Add about 30 mL of H_2SO_4 (1 + 4) and dilute to about 250 mL. Heat to 90 °C and titrate at once with KMnO_4 solution. (The temperature of the solution should not be below 60 °C when the end point is reached.)

14.4 *Calculation*—Calculate the percent of calcium compounds, A , in terms of CaO , as follows:

$$A = (V_2 C / 0.5) \times 100 \quad (4)$$

where:

V_2 = KMnO_4 solution required by the specimen, mL, and
 C = CaO equivalent of the KMnO_4 solution, g/mL.

Sulfates Soluble in Hydrochloric Acid

15. Reagent

15.1 *Barium Chloride Solution*—Dissolve 117 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 L.

16. Procedure

16.1 Weigh 1 g of the sample and add 30 mL of HCl (sp gr 1.19). Boil 10 min, add about 50 mL of water, boil, filter, and wash with hot water. Heat the solution to boiling, add NH_4OH in excess, filter, and wash the precipitate several times with hot