



Designation: D50 – 90 (Reapproved 2019)

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 ocher, 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
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Calcium Compounds (Reported as CaO)	13 and 14	
Sulfates Soluble in Hydrochloric Acid	15 and 16	
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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 appro-*

priate 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

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 May 1, 2019. Published May 2019. Originally approved in 1917. Last previous edition approved in 2011 as D50 – 90 (2011). DOI: 10.1520/D0050-90R19.

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 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 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 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 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 in excess. It is

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.

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 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.

Calcium Compounds (Reported as CaO)

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 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 to 0.3000 g of the NIST $\text{Na}_2\text{C}_2\text{O}_4$ in 250 mL of hot water (80 to 90°C) and add 15 mL of $\text{H}_2\text{SO}_4(1+1)$. Titrate at once with KMnO_4 solution, *stirring the liquid vigorously and continuously*. The KMnO_4 must not be added more rapidly than 10 to 15 mL/min, and the last 0.5 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 $\text{HCl}(1+1)$. 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 $\text{H}_2\text{O}_2(30\%)$. 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 $\text{H}_2\text{SO}_4(1+4)$ through the paper and wash a few times. Add about 30 mL of $\text{H}_2\text{SO}_4(1+4)$ 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

water. Dissolve the precipitate in hot HCl (1 + 1), reprecipitate with NH₄OH, and wash well with hot water.

16.2 Combine the united filtrates and make distinctly acid with HCl, boil, and add dropwise, while stirring, an excess of BaCl₂ solution. Boil about 10 min. The BaSO₄ precipitate should normally stand for 2 to 4 h before filtering in order to coagulate the precipitate. If the pad is thick enough on the Gooch crucible and filtrate is free of sulfate, then standing may not be necessary. Filter on a Gooch crucible, and wash with hot water. Ignite at 900°C, and weigh as barium sulfate (BaSO₄).

16.3 *Calculation*—Calculate the percent of SO₃, A, as follows:

$$A = [(P \times 0.343)/S] \times 100 \quad (5)$$

where:

P = weight of BaSO₄, g, and
S = weight of original sample, g.
 0.343 = SO₃/BaSO₄ = 80.06/233.42

Lead Chromate (in Ochres)

17. Procedure

17.1 Test for lead by any standard method of qualitative analysis. The following method is suggested: Dissolve a small portion of the pigment in cold nitric acid (HNO₃) (1 + 5), stirring vigorously. Add a few millilitres of potassium iodide (KI) solution (100 g/L). The appearance of yellow crystals indicates the presence of lead.

Calcium Carbonate (in Venetian Red)

18. Procedure

18.1 Determine carbon dioxide (CO₂) in accordance with Test Methods C25.

18.2 *Calculation*—Calculate the percent of calcium carbonate (CaCO₃), A, as follows:

$$A = [(W_3 \times 2.274)/S] \times 100 \quad (6)$$

where:

*W*₃ = CO₂, g, and
S = sample used, g. 2.274 = CaCO₃/CO₂ = 100.09/44.0

Manganese (in Siennas and Umbers)

19. Reagents

19.1 *Standard Potassium Permanganate Solution*(KMnO₄) (1 mL = 0.00035 g Mn)—Dissolve 1 g of KMnO₄ in 1 L of water. Age and standardize the solution as in Section 13, using one third the quantities of reagents specified therein. Calculate the manganese value of the solution as follows:

$$M = (W_4/V_3) \times 0.165 \quad (7)$$

where:

M = manganese equivalent of the KMnO₄ solution, g/mL,
*W*₄ = sodium oxalate used, g, and
*V*₃ = KMnO₄ solution required for the titration, mL.

19.2 *Sodium Bismuthate* (NaBiO₃).

19.3 *Ferrous Ammonium Sulfate Solution*—To 12 g of ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O) add 25 mL of H₂SO₄ (sp gr 1.84) and 25 mL of H₃PO₄ (85 %) and dilute to 1 L with water. Each day the solution is used run a blank titration against the KMnO₄ as follows: Measure into a 200-mL Erlenmeyer flask 50 mL of HNO₃ (1 + 3), cool, and add about 0.2 g of NaBiO₃. Dilute with 50 mL of HNO₃ (3 + 97), filter by suction through Gooch crucible with a medium-porosity fritted disk into a 300-mL Erlenmeyer flask, and wash with 50 mL of HNO₃ (3 + 97). Run in exactly 25 mL of the ferrous solution and titrate to a faint pink color with the KMnO₄ solution.

20. Procedure

20.1 Ignite 1 g of the sample in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a platinum dish and add 10 mL of water, 4 mL of H₂SO₄(sp gr 1.84), 20 mL of HF (48 %), and a few drops of H₂SO₃. Evaporate until the H₂SO₄ fumes freely, cool, and add 25 mL of HNO₃(1 + 3). If no appreciable residue remains, transfer to a 100-mL volumetric flask, using 25 mL of HNO₃(1 + 3) to rinse the dish, dilute to the mark with water, and mix thoroughly. If there is an appreciable residue, filter through a small qualitative filter paper and wash with water. Ignite the residue in a platinum crucible, and fuse with a little sodium pyrosulfate (Na₂S₂O₇) or potassium pyrosulfate (K₂S₂O₇). Dissolve in water, with the addition of a little HNO₃, add to the main filtrate, and evaporate nearly to dryness. Take up in HNO₃ (1 + 3) and transfer to the flask as before.

20.2 Pipet a 10-mL aliquot into a 200-mL Erlenmeyer flask and add 30 mL of water and 10 mL of HNO₃ (sp gr 1.42). Add about 0.5 g of NaBiO₃ and heat for a few minutes, or until the pink color has disappeared with or without the precipitation of magnesium dioxide (MnO₂). Add a few small crystals of sodium nitrite (NaNO₂) or potassium nitrite (KNO₂) to dissolve the MnO₂ and boil the solution several minutes to expel nitrous oxide fumes (a little anhydrous sodium carbonate (Na₂CO₃) will aid this). Add water to bring the volume up to 50 mL and cool to about 15°C. Add about 0.5 g of bismuthate and shake the flask well. Add 50 mL of HNO₃ (3 + 97), filter by suction through a medium-porosity fritted disk into a 300-mL Erlenmeyer flask, and wash with 50 to 100 mL of the HNO₃ (3 + 97). Run in exactly 25 mL of ferrous ammonium sulfate solution and titrate to a faint pink color with KMnO₄ solution.

NOTE 3—If 25 mL of ferrous ammonium sulfate solution is not sufficient to decolorize the solution, add a further 10 mL or more as required. Adjust the blank (19.3) accordingly.

20.3 *Calculation*—Calculate the percent of manganese, A, as follows:

$$A = [(B_2 - V_4)M/W_5] \times 100 \quad (8)$$

where:

*B*₂ = KMnO₄ solution required for titration of the blank (19.2), mL,
*V*₄ = KMnO₄ solution required for back-titration of the specimen (19.2), mL,
M = manganese equivalent of the KMnO₄ solution, g/mL, and

W_5 = sample in the aliquot, g.

PIGMENT PASTES IN OIL

21. Pigment Content

21.1 Determine pigment content in accordance with Test Methods **D1208**.

22. Moisture and Other Volatile Matter

22.1 Determine moisture and other volatile matter in accordance with Test Methods **D1208**.

23. Nonvolatile Matter in Vehicle

23.1 Subtract the percent pigment content and percent volatile matter from 100 and report as percent vehicle.

24. Moisture by Distillation

24.1 Determine moisture by distillation in accordance with Test Methods **D1208**.

25. Coarse Particles and Skins

25.1 Determine coarse particles and skins in accordance with Test Methods **D185**.

26. Consistency (Stormer)

26.1 Determine consistency in accordance with Test Method **D562**.

27. Keywords

27.1 brown pigment (iron and manganese); calcium; colored pigment; iron oxide; red pigment; soluble sulfate; yellow pigment

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