



# Standard Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese<sup>1</sup>

This standard is issued under the fixed designation D 50; 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 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	D 280
Loss on Ignition	7	
Coarse Particles	8	D 185
Matter Soluble in Water	9	D 1208
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	C 25
Manganese (in Siennas and Umbers)	19 and 20	
Pigment Pastes in Oil		
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Moisture and Other Volatile Matter	22	D 1208
Nonvolatile Matter in Vehicle	23	
Moisture by Distillation	24	D 1208
Coarse Particles and Skins	25	D 185
Consistency (Stormer)	26	D 562

1.3 *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:

C 25 Test Methods for Chemical Analysis of Limestone,

Quicklime, and Hydrated Lime<sup>2</sup>

D 185 Test Methods for Coarse Particles in Pigments, Pastes, and Paints<sup>3</sup>

D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments<sup>3</sup>

D 562 Test Method for Consistency of Paints Using the Stormer Viscometer<sup>4</sup>

D 1193 Specification for Reagent Water<sup>5</sup>

D 1208 Test Methods for Common Properties of Certain Pigments<sup>3</sup>

E 11 Specification for Wire Cloth Sieves for Testing Purposes<sup>6</sup>

## 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-μm) sieve (see Specification E 11 for detailed 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.<sup>7</sup> Other grades may be used, provided it is first ascertained that the

<sup>2</sup> Annual Book of ASTM Standards, Vol 04.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 06.03.

<sup>4</sup> Annual Book of ASTM Standards, Vol 06.01.

<sup>5</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>6</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>7</sup> 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.

<sup>1</sup> 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 Specification.

Current edition approved May 25, 1990. Published July 1990. Originally published as D 50 – 17 T. Last previous edition D 50 – 81.

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 D 1193.

## 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 D 280.

### *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 (CO<sub>2</sub>), organic matter, and some sulfuric oxide (SO<sub>3</sub>) if much calcium sulfate (CaSO<sub>4</sub>) is present. The CO<sub>2</sub> 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 Method D 185.

### *Matter Soluble in Water*

## 9. Procedure

9.1 Determine matter soluble in water in accordance with Test Methods D 1208.

### *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.<sup>8</sup>

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* (SnCl<sub>2</sub>·2H<sub>2</sub>O)—Dissolve 50 g of SnCl<sub>2</sub>·2H<sub>2</sub>O 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* (HgCl<sub>2</sub>)—Prepare a saturated solution of HgCl<sub>2</sub> (60 to 100 g/L).

11.3 *Sulfuric-Phosphoric Acid Mixture*—Mix 150 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (sp gr 1.84) with 150 mL of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (85 %) and dilute with water to 1 L.

11.4 *Diphenylamine Indicator*—Dissolve 1 g of diphenylamine in 100 mL of H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84).

11.5 *Standard Potassium Dichromate Solution* (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) (0.1 N)—Dissolve 4.904 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water and dilute to 1 L. Standardize against the National Bureau of Standards standard sample No. 27 of Sibley iron ore.

11.6 *Potassium Ferricyanide Solution* (K<sub>3</sub>Fe(CN)<sub>6</sub>)—A very dilute solution is most satisfactory. Dissolve approximately 0.01 g of K<sub>3</sub>Fe(CN)<sub>6</sub> 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 SnCl<sub>2</sub> 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 SnCl<sub>2</sub> 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 best to keep the watchglass on the beaker while adding the SnCl<sub>2</sub> solution, with agitation of the hot iron solution after each addition. If too much SnCl<sub>2</sub> is added by mistake, add potassium permanganate (KMnO<sub>4</sub>) to the solution until a yellow color appears, then again add SnCl<sub>2</sub> 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<sub>2</sub> 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 H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub> mixture and 3 drops of diphenylamine indicator solution. Titrate with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, taking the sudden change of the dark green color to a blue-black color as the end point.

12.4 If preferred, K<sub>3</sub>Fe(CN)<sub>6</sub> may be used as an external indicator. In this case omit the addition of the H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>

<sup>8</sup> Reference may be made to the following: Payne, H. F., "Organic Coatings Technology," Vol II, John Wiley & Sons, Inc., New York, N. Y., 1961.

mixture and the diphenylamine indicator. Titrate with the  $K_2Cr_2O_7$  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  $K_3Fe(CN)_6$  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  $K_2Cr_2O_7$  solution, g/mL,

$V$  =  $K_2Cr_2O_7$  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 [ $(NH_4)_2C_2O_4 \cdot H_2O$ ] 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 ( $Na_2C_2O_4$ ) as follows: In a 400-mL beaker dissolve 0.2500 to 0.3000 g of the NIST  $Na_2C_2O_4$  in 250 mL of hot water (80 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 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 asbestos-covered 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.

$$0.4185 = CaO/Na_2C_2O_4 = 56.08 / 134.01 \quad (3)$$

## 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:

$$A = (V_2C/0.5) \times 100 \quad (4)$$

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 ( $BaCl_2 \cdot 2H_2O$ ) 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  $NH_4OH$ , 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  $BaCl_2$  solution. Boil about 10 min. The  $BaSO_4$  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 ( $BaSO_4$ ).

16.3 *Calculation*—Calculate the percent of  $SO_3$ ,  $A$ , as follows:

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

where:

$P$  = weight of  $BaSO_4$ , g, and

$S$  = weight of original sample, g.

$$0.343 = SO_3/BaSO_4 = 80.06/233.42$$

### *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 (HNO<sub>3</sub>) (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 (CO<sub>2</sub>) in accordance with Test Methods C 25.

18.2 *Calculation*—Calculate the percent of calcium carbonate (CaCO<sub>3</sub>), A, as follows:

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

where:

$W_3$  = CO<sub>2</sub>, g, and

$S$  = sample used, g.  $2.274 = \text{CaCO}_3/\text{CO}_2 = 100.09/44.0$

#### *Manganese (in Siennas and Umbers)*

### 19. Reagents

19.1 *Standard Potassium Permanganate Solution* (KMnO<sub>4</sub>) (1 mL = 0.00035 g Mn)—Dissolve 1 g of KMnO<sub>4</sub> 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 KMnO<sub>4</sub> solution, g/mL,

$W_4$  = sodium oxalate used, g, and

$V_3$  = KMnO<sub>4</sub> solution required for the titration, mL.

19.2 *Sodium Bismuthate* (NaBiO<sub>3</sub>).

19.3 *Ferrous Ammonium Sulfate Solution*— To 12 g of ferrous ammonium sulfate (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) add 25 mL of H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) and 25 mL of H<sub>3</sub>PO<sub>4</sub> (85 %) and dilute to 1 L with water. Each day the solution is used run a blank titration against the KMnO<sub>4</sub> as follows: Measure into a 200-mL Erlenmeyer flask 50 mL of HNO<sub>3</sub> (1 + 3), cool, and add about 0.2 g of NaBiO<sub>3</sub>. Dilute with 50 mL of HNO<sub>3</sub> (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 HNO<sub>3</sub> (3 + 97). Run in exactly 25 mL of the ferrous solution and titrate to a faint pink color with the KMnO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84), 20 mL of HF (48 %), and a few drops of H<sub>2</sub>SO<sub>3</sub>. Evaporate until the H<sub>2</sub>SO<sub>4</sub> fumes freely, cool, and add 25 mL of HNO<sub>3</sub> (1 + 3). If no appreciable residue remains, transfer to a 100-mL volumetric flask, using 25 mL of HNO<sub>3</sub> (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 (Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>) or potassium pyrosulfate (K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>). Dissolve in water, with the

addition of a little HNO<sub>3</sub>, add to the main filtrate, and evaporate nearly to dryness. Take up in HNO<sub>3</sub> (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 HNO<sub>3</sub> (sp gr 1.42). Add about 0.5 g of NaBiO<sub>3</sub> and heat for a few minutes, or until the pink color has disappeared with or without the precipitation of magnesium dioxide (MnO<sub>2</sub>). Add a few small crystals of sodium nitrite (NaNO<sub>2</sub>) or potassium nitrite (KNO<sub>2</sub>) to dissolve the MnO<sub>2</sub> and boil the solution several minutes to expel nitrous oxide fumes (a little anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) 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 HNO<sub>3</sub> (3 + 97), filter by suction through an asbestos felt into a 300-mL Erlenmeyer flask, and wash with 50 to 100 mL of the HNO<sub>3</sub> (3 + 97). Run in exactly 25 mL of ferrous ammonium sulfate solution and titrate to a faint pink color with KMnO<sub>4</sub> 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:

$B_2$  = KMnO<sub>4</sub> solution required for titration of the blank (19.2), mL,

$V_4$  = KMnO<sub>4</sub> solution required for back-titration of the specimen (19.2), mL,

$M$  = manganese equivalent of the KMnO<sub>4</sub> 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 D 1208.

### 22. Moisture and Other Volatile Matter

22.1 Determine moisture and other volatile matter in accordance with Test Methods D 1208.

### 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 D 1208.

### 25. Coarse Particles and Skins

25.1 Determine coarse particles and skins in accordance with Test Methods D 185.

### 26. Consistency (Stormer)

26.1 Determine consistency in accordance with Test Method D 562.

**27. Keywords**

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

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