Designation: D 283 – 84 (Reapproved 1999)

Standard Test Methods for Chemical Analysis of Cuprous Oxide and Copper Pigments[1]

This standard is issued under the fixed designation D 283; 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 cuprous oxide and copper pigments.

1.2 The analytical procedures appear in the following order:

	Sections
Total Copper	7
Total Reducing Power as Cuprous Oxide	8 and 9
Metallic Copper	10 and 11
Cuprous Oxide	12
Cupric Oxide	13
Metals Other than Copper	14-16
Chlorides and Sulfates	17 and 18
Acetone-Soluble Matter	19
Water	20
Stability	21
Coarse Particles	22
Coarse Particles Insoluble in Nitric Acid	23

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.* Specific hazard statements are given in Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 185 Test Methods for Coarse Particles in Pigments, Pastes, and Paints[2]

D 1193 Specification for Reagent Water[3]

D 1208 Test Methods for Common Properties of Certain Pigments[2]

3. Significance and Use

3.1 This collection of test methods is used by pigment producers and paint manufacturers for process control, product acceptance, and research and development.

4. Treatment of Sample

4.1 Grind dry pigments, if lumpy or not finely ground, to a fine powder and thoroughly mix (Note 1). Large samples may be thoroughly mixed and a representative portion taken and powdered if lumpy or not finely ground. In all cases thoroughly mix the sample before taking portions for analysis. Preserve all samples in dry, dark, airtight and completely filled bottles or containers to prevent oxidation. Some commercial copper oxides appear to segregate or oxidize rather easily. Therefore, the thorough mixing of the sample to ensure homogeneity and the rapid handling of the sample, when exposed to light and air, are extremely important factors in obtaining accurate results.

NOTE 1—It is very important that the sample be thoroughly mixed. Some samples of cuprous oxide are not homogeneous so are likely to give trouble when an attempt is made to obtain concordant results. By placing a few grams of a sample on a sheet of white paper and drawing it out with a spatula, it is frequently found that the sample contains coarse particles of black scale, along with small balls of bright red cuprous oxide. Thus, it may be necessary to pass the pigment through a No. 60 (250-µm) sieve, break up any lumps of ground pigment by gentle pressure, and grind any coarse particles failing to pass through the sieve. Since oxidation of slight or even considerable magnitude may take place, these operations should be performed quickly, avoiding prolonged grinding and exposure to light and air.

5. Reagents

5.1 *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,

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[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 11.01.

where such specifications are available.[4] 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 reagent water conforming to Type II of Specification D 1193.

5.3 *Ammonium Sulfate*—($(NH_4)_2SO_4$).

5.4 *Nitric Acid* (sp gr 1.42)—Concentration nitric acid (HNO_3).

5.5 *Perchloric Acid* (70 %)—Concentrated perchloric acid ($HClO_4$).

6. Hazards

6.1 **Warning**—Concentrated mineral acids cause burns of the skin and eyes. Concentrated bases are also hazardous. Avoid contact with skin or eyes. In case of contact immediately flush skin or eyes with plenty of water. See appropriate MCA Safety Data Sheets for further information before handling dangerous chemicals.

6.2 Chemicals that have been declared toxic should be disposed of as hazardous chemicals and not discharged into a sink.

TOTAL COPPER

7. Procedure

7.1 Weigh accurately 1.0 g of the sample and transfer to a 300-mL electrolytic beaker. Add 10 mL of concentrated nitric acid (HNO_3) and boil several minutes. Add 10 mL of $HClO_4$ (70 %) and fume for 5 min. Cool, dilute to a volume of approximately 150 mL, and add 1 mL of HNO_3 and 1 g of $(NH_4)_2SO_4$.

7.2 Carefully weigh the platinum electrode to 0.1 mg. Electroplate the copper on a rotating platinum electrode at a current of 2 A for 2 h. Dilute with water and continue the electrolysis for 15 min. When the deposition is complete, remove the electrode, wash with water and acetone, dry, and weigh to 0.1 mg. Save the electrolyte for the determination of metals other than copper (Section 15).

7.3 Calculate the percent of total copper, Cu.

TOTAL REDUCING POWER AS CUPROUS OXIDE

8. Reagents

8.1 *Ceric Ammonium Nitrate, Standard Solution* (0.1 *N*)—Mix 54.826 g of ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) (either reagent grade or reference standard purity) with 56 mL of sulfuric acid (H_2SO_4) (1+1). Dissolve the salt and acid in water, cool to room temperature, and dilute to 1 L. Standardize this solution against analyzed bright copper foil that has been freed from all oxide coating.

8.2 *Ferric Chloride Solution*—Dissolve 75 g of ferric chloride ($FeCl_3 \cdot 6\ H_2O$) in a mixture of 150 mL of hydrochloric acid (HCl) (sp gr 1.19) and 400 mL of distilled water. Add 5 mL of hydrogen peroxide (H_2O_2) (30 %) and boil to remove the excess.

8.3 *Ferrous Ammonium Sulfate, Standard Solution* (0.03 *N*)—Dissolve 12 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$) in 200 to 300 mL of water and add 40 mL of H_2SO_4 (sp gr 1.84), while stirring constantly. Dilute to 1 L in a volumetric flask. A few pieces of mossy aluminum may be added to stabilize the solution. The solution should be restandardized frequently against 0.1 *N* ceric ammonium nitrate solution.

8.4 *Orthophenanthroline Indicator Solution* (0.5 % in water)—Orthophenanthroline ferrous complex (ferroin) shall be used as the indicator.

9. Procedure

9.1 Weigh accurately (Note 2) 0.15 g of the sample and place in a 250-mL, vented, glass-stoppered Erlenmeyer flask previously filled with carbon dioxide (CO_2) or other inert gas. Add a few small glass beads and 10 mL of $FeCl_3$ solution. Heat gently for 15 min, stirring occasionally and maintaining at all times an atmosphere of CO_2 or other inert gas.

NOTE 2—The use of a 0.4-mL micro beaker for weighing the specimen is advised. The beaker is weighed first and the sample introduced into the beaker, the correct weight obtained, and the entire beaker and its contents dropped into the flask. This eliminates errors in weighing caused by brushing the sample from glass balance pans.

9.2 After the specimen has been dissolved, cool, add 50 mL of distilled water, and titrate at once with 0.1 *N* ceric ammonium nitrate solution until near the end point. Add 2 drops of orthophenanthroline indicator solution and complete the titration. A sharp, distinct color change from orange to pale green occurs at the end point. Back-titrate with 0.03 *N* ferrous ammonium sulfate solution to the orange color.

9.3 *Calculation*—Calculate the percent of total reducing power, *A*, as cuprous oxide (Cu_2O) as follows:

$$A = \frac{V_1N_1 - V_2N_2 \times 0.07154}{S_1} \times 100 \tag{1}$$

where:

V_1 = $Ce(NH_4)_2(No3)_6$ solution required to titrate the specimen, mL,

N_1 = normality of the $Ce(NH_4)_2(No3)_6$ solution,

V_2 = $Fe(NH_4)_2(SO_4)_2$ solution required for the back-titration, mL,

N_2 = normality of the $Fe(NH_4)_2(SO_4)_2$ solution,

S_1 = specimen weight, g, and

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[4] *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.

0.07154 = equivalent weight of Cu_2O/1000.

METALLIC COPPER[5]

10. Reagents

10.1 *Ceric Ammonium Nitrate, Standard Solution* (0.1 *N*)—See 8.1.

10.2 *Denatured Alcohol (Formula No. 2B)*

10.3 *Extraction Solution*—Add 40 mL of HCl (sp gr 1.19) to 1 L of denatured alcohol. Mix thoroughly. Add 40 g of stannous chloride ($SnCl_2 \cdot 2H_2O$) and stir until completely dissolved.

10.4 *Ferric Chloride Solution*—See 8.2.

10.5 *Orthophenanthroline Indicator*— See 5.4.

11. Procedure

11.1 Add approximately 20 mL of 4-mm diameter glass beads to a 250-mL Phillips beaker (assay flask). Weigh accurately 0.15 g of sample on a tared, glazed paper approximately ½ in. (13 mm) square or a small watch glass that will fit into the Phillips beaker, and transfer the specimen and paper or watch glass to the beaker.

11.2 Add 25 mL of denatured alcohol and swirl vigorously for approximately 1 min to remove any surface coating and break up lumps. While swirling the flask, slowly add 100 mL of the extraction solution.

11.3 After the addition of the extraction solution, swirl the flask vigorously for 5 min, adding lumps of dry ice (solid carbon dioxide) (Note 3) continuously during this time to lower the temperature of the solution to approximately −10°C. Break up any lumps in the solution with a glass rod or policeman.

11.4 Filter off the metallic copper-cupric oxide residue using a 125-mm close-texture paper, a filter cone to support the paper, and suction (Note 4). Continue the addition of dry ice to the flask and filter paper during the filtration to keep the solution cold. Wash the flask and filter paper with 150 to 200 mL of denatured alcohol, continuing the use of suction.

NOTE 3—During the 5-min swirling period approximately 25 to 30 g of dry ice is added in approximately 5-g portions. The initial lumps of dry ice volatilize rapidly due to the temperature of the solution. Approximately 15 g of dry ice is added in the first 2 min with a subsequent temperature drop to 0°C. The remaining 15 g volatilizes more slowly and gradually lowers the temperature to the vicinity of −10°C. These directions are not critical, but merely serve as a guide. The solution must be kept very cold in order to obtain correct and reproducible results. During the filtration period, additions of dry ice to the flask should be continued to keep the solution cold until all of the extraction solution has been filtered.

NOTE 4—In the great majority of cases, the metallic copper-cupric oxide residue is completely retained by the use of a suitable close-texture filter paper. The filtration is rapid and can be readily completed in 5 min with proper suction. The filtrate should be carefully examined for the presence of finely divided particles of copper. In the event that extremely finely divided particles of copper are present and pass through the filter paper, as evidenced by the presence in the filtrate of a reddish color, which may be transient, the following method of filtration should be used: Place a 25-mm diameter, beveled-edge, perforated porcelain filter disk in a 60°, 75-mm diameter glass funnel. Using suction, prepare an asbestos filter pad on the porcelain disk of sufficient thickness and retentiveness to hold the finely divided residue. Wash the asbestos pad several times with denatured alcohol to remove all water from the pad. Filter the metallic copper-cupric oxide residue on this asbestos pad with the suction on at the start of the filtration. Keep the solution cold by the addition of dry ice and proceed with washing the residue, transferring it to the original extraction flask, and the subsequent titration as directed in Section 11.

11.5 Transfer the entire residue, filter paper, and beads to the original extraction flask and dissolve the residue in 25 mL of $FeCl_3$ solution, keeping an atmosphere of CO_2 above the sample by addition of dry ice. Heat on a steam bath to dissolve the copper. Add 50 mL of distilled water and 3 drops of orthophenanthroline indicator solution. Titrate with 0.1 *N* ceric ammonium nitrate solution until the color changes from orange to pale green.

11.6 *Calculation*—Calculate the percent of metallic copper content, *B*, as follows:

$$B = \frac{V_3 C}{S_2} \times 100 \qquad (2)$$

where:

V_3 = ceric ammonium nitrate solution required for titration of the sample, mL,

C = copper equivalent of the ceric ammonium nitrate solution, g/mL, and

S_2 = specimen weight, g.

CUPROUS OXIDE

12. Calculation

12.1 Calculate the percent of cuprous oxide (Cu_2O), *D*, as follows:

$$D = A - 2.252B \qquad (3)$$

where:

A = total reducing power as cuprous oxide (Section 9), %, and

B = metallic copper (Section 11), %.

CUPRIC OXIDE

13. Calculation

13.1 Calculate the percent of cupric oxide (CuO), *E*, as follows:

$$E = 1.252(F - B) - 1.112D \qquad (4)$$

where:

F = total copper (Section 7), %,

B = metallic copper (Section 11), %, and

D = cuprous oxide (Section 12),% .

METALS OTHER THAN COPPER

14. Reagents

14.1 *Ceric Ammonium Nitrate, Standard Solution* (0.1 *N*)—See 8.1.

14.2 *Diphenylamine Indicator*—Dissolve 1 g of diphenylamine in 100 mL of H_2SO_4 (sp gr 1.84).

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[5] This test method is based on the procedure described by Irvin Baker and R. Stevens Gibbs, "Determination of Metallic Copper in Cuprous Oxide—Cupric Oxide Mixtures," *Industrial and Engineering Chemistry*, Analytical Edition, Vol 13, February 15, 1946, p. 124.

14.3 *Potassium Ferricyanide Solution* (50 g/L)—Dissolve 5 g of potassium ferricyanide ($K_3Fe(CN)_6$), in 100 mL of distilled water. Keep tightly stoppered in a dark bottle.

14.4 *Potassium Ferrocyanide, Standard Solution* (1 mL = 0.001 g Zn)—Dissolve 5.0 g of potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) in distilled water and dilute to 1 L. Standardize with analyzed reagent grade zinc prior to use.

15. Procedure

15.1 Filter the electrolyte from the determination of total copper (Section 7). Add 5 mL of H_2SO_4 (sp gr 1.84) and evaporate just to dryness to remove all $HClO_4$ and HNO_3. Add approximately 150 mL of water and neutralize with NH_4OH (sp gr 0.90), adding 5 mL in excess. Add 10 g of NH_4Cl. Boil the solution gently for several minutes and allow the precipitate to settle. Filter through a close-texture paper, and wash the precipitate with 50 mL of hot NH_4Cl solution (20 g/L).

15.2 *Determination of Iron*—Dissolve the precipitate from the filter paper with hot HCl (1+1). Determine iron by the procedure of reduction with $SnCl_2$ solution, followed by addition of $HgCl_2$ and titration with 0.1 *N* ceric ammonium nitrate solution.

15.2.1 *Calculation*—Calculate the percent of iron, *G*, as follows:

$$G = \frac{V_4 N_1 \times 0.056}{S} \times 100 \tag{5}$$

where:

V_4 = ceric ammonium nitrate solution required to titrate the specimen, mL,

N_1 = normality of the ceric ammonium nitrate solution, and

S = specimen weight (Section 7), g.

15.3 *Determination of Cobalt and Nickel*— Evaporate the filtrate (see 15.1) to 15 to 20 mL. If the solution is colored, the presence of nickel or cobalt, or both, may be indicated. If present, they must be removed before determining zinc, determined by any standard procedure and reported as percent of cobalt or nickel, or both.

15.4 *Determination of Zinc*—Neutralize the solution (see 15.4) with H_2SO_4 (1+2) and add 15 mL in excess. Dilute to 300 mL with water. Add 10 drops of $K_3Fe(CN)_6$ solution and 5 drops of diphenylamine indicator solution. Heat to 75°C and titrate with standard $K_4Fe(CN)_6$ solution. A color change from blue to greenish yellow occurs at the end point.

15.4.1 *Calculation*—Calculate the percent of zinc, *H*, as follows:

$$H = \frac{V_5 Z}{S} \times 100 \tag{6}$$

where:

V_5 = $K_4Fe(CN)_6$ solution required for titration of the specimen, mL,

Z = zinc equivalent of the $K_4Fe(CN)_6$ solution, and

S = specimen weight (Section 7), g.

16. Report

16.1 Report as percent of metals other than copper the total percent of metals determined in accordance with Section 15.

CHLORIDES AND SULFATES

17. Reagents

17.1 *Barium Chloride Solution* (100 g/L)—Dissolve 117 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 L.

17.2 *Silver Nitrate Solution*—Dissolve 5 g of silver nitrate ($AgNO_3$) in 100 mL of water.

17.3 *Sodium Carbonate Solution*—Prepare a saturated solution of sodium carbonate (Na_2CO_3) that is free of both chlorine (Cl) and sulfate (SO_4).

18. Procedure

18.1 Weigh accurately approximately 10 g of the sample, add an excess of concentrated HNO_3, and heat gently until the sample is decomposed. Dilute with water to approximately 150 mL. Add an excess of Na_2CO_3 solution (16.3), and bring to a boil. Transfer to a 500-mL volumetric flask and dilute to the mark with water. Let settle.

18.2 Draw off two separate 50-mL aliquots of the clear solution. Make each slightly acid with HNO_3.

18.3 *Determination of Chlorides*—To one of the 50-mL aliquots (18.2), add a few drops of $AgNO_3$ solution. If no precipitate forms, report no chlorides present. If a precipitate forms, add slowly an excess of $AgNO_3$ solution. Heat to boiling after the precipitate has settled, filter through a Gooch crucible, and wash with cold water. Dry at 130°C, cool, and weigh.

18.3.1 *Calculation*—Calculate the percent of chlorides as Cl, *J*, as follows:

$$J = \frac{P_1 \times 0.247}{S_3 \times 0.1} \times 100 \tag{7}$$

where:

P_1 = AgCl, g, and

S_3 = specimen weight, g.

18.4 *Determination of Sulfates*—Dilute the second 50-mL aliquot (18.1) to approximately 200 mL. Add approximately 1 mL of HCl (1+1). Heat to boiling and add slowly an excess (10 mL) of $BaCl_2$ solution. Let settle, filter through a Gooch crucible, and wash. Dry, ignite at full red heat, cool in a desiccator, and weigh.

18.4.1 *Calculation*—Calculate the percent of sulfates as SO_4, *K*, as follows:

$$K = \frac{P_2 \times 0.412}{S_3 \times 0.1} \times 100 \tag{8}$$

where:

P_2 = $BaSO_4$, g, and

S_3 = specimen weight, g.

ACETONE-SOLUBLE MATTER

19. Procedure

19.1 Weigh accurately 5.0 g of the well-mixed sample and transfer to a 250-mL glass stoppered Erlenmeyer flask. Add 100 mL of acetone and shake vigorously for 15 min. Allow to settle and filter through a double, close-texture paper into a 250-mL Griffin beaker. Wash the flask and paper well with acetone to remove all acetone-soluble matter.

19.2 Evaporate the acetone on a water bath to a low volume and transfer to a 15 by 55-mm weighed aluminum moisture dish. Wash out the beaker with a small amount of acetone. Finally evaporate all acetone and heat the residue for 30 min in an oven at 105°C.

19.3 Report the weight of the dried residue as acetone-soluble matter.

WATER

20. Procedure

20.1 Determine the water content in accordance with Test Methods D 1208.

STABILITY

21. Procedure

21.1 Spread approximately 100 g of the sample on a watch glass and heat in an oven at a temperature of 100°F (40°C) and approximately 95 % relative humidity for a period of 72 h. Remove from the oven. Note any change in color of the pigment. Determine its total reducing power in accordance with Section 9.

21.2 Determine the percent of moisture on 50 g of the sample remaining from the test described in 18.1 using the distillation method specified in Section 20.

21.3 *Calculation*—Calculate the percent decrease in total reducing power, L, as follows:

$$L = \frac{N}{100 - M} \tag{9}$$

where:
L = total reducing power after stability test calculated on dry basis,
N = total reducing power after stability test as determined in 21.1, and
M = moisture (21.2),% .

$$L = \frac{A - E}{A} \times 100 \tag{10}$$

where:
L = decrease in total reducing power (from stability test), % and
A = total reducing power before stability test as calculated in 9.3.

COARSE PARTICLES

22. Procedure

22.1 Determine the percent of coarse particles on a 25-g specimen as described in Test Methods D 185 using both a No. 200 (75-µm) and a No. 325 (45-µm) sieve.

COARSE PARTICLES INSOLUBLE IN NITRIC ACID

23. Procedure

23.1 Transfer the residue retained on a No. 200 (75-µm) sieve to a beaker, add 50 mL of HNO_3 (1+3), and boil for 5 min. Cool and filter through a tared Gooch crucible, previously washed with HNO_3 (1+3), or a fritted-glass filter of appropriate porosity. Wash the insoluble residue on the filter with hot water. Dry the crucible or fritted-glass filter and contents at 105 to 110°C and weigh.

23.2 *Calculation*—Calculate the percent of coarse particles insoluble in nitric acid, T, as follows:

$$T = \frac{R}{S} \times 100 \tag{11}$$

where:
R = weight of residue, g, and
S = weight of original specimen, g.

24. Precision

24.1 Precision data are not available at this time. When available the appropriate precision statements will be added.

25. Keywords

25.1 chemical analysis; copper pigments; cuprous oxide pigments