



Designation: D 283 – 84 (Reapproved 1999)

## Standard Test Methods for Chemical Analysis of Cuprous Oxide and Copper Pigments<sup>1</sup>

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 approval. A superscript epsilon ( $\epsilon$ ) 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<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 1208 Test Methods for Common Properties of Certain Pigments<sup>2</sup>

<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 Specifications.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

### 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- $\mu$ m) 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,

where such specifications are available.<sup>4</sup> 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*— $(\text{NH}_4)_2\text{SO}_4$ .

5.4 *Nitric Acid* (sp gr 1.42)—Concentration nitric acid ( $\text{HNO}_3$ ).

5.5 *Perchloric Acid (70 %)*—Concentrated perchloric acid ( $\text{HClO}_4$ ).

## 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 ( $\text{HNO}_3$ ) and boil several minutes. Add 10 mL of  $\text{HClO}_4$  (70 %) and fume for 5 min. Cool, dilute to a volume of approximately 150 mL, and add 1 mL of  $\text{HNO}_3$  and 1 g of  $(\text{NH}_4)_2\text{SO}_4$ .

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 ( $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ ) (either reagent grade or reference standard purity) with 56 mL

of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (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 ( $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ) 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 ( $\text{H}_2\text{O}_2$ ) (30 %) and boil to remove the excess.

8.3 *Ferrous Ammonium Sulfate, Standard Solution (0.03 N)*—Dissolve 12 g of ferrous ammonium sulfate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ) in 200 to 300 mL of water and add 40 mL of  $\text{H}_2\text{SO}_4$  (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 ( $\text{CO}_2$ ) or other inert gas. Add a few small glass beads and 10 mL of  $\text{FeCl}_3$  solution. Heat gently for 15 min, stirring occasionally and maintaining at all times an atmosphere of  $\text{CO}_2$  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 ( $\text{Cu}_2\text{O}$ ) as follows:

$$A = \frac{V_1 N_1 - V_2 N_2 \times 0.07154}{S_1} \times 100 \quad (1)$$

where:

$V_1$  =  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  solution required to titrate the specimen, mL,

$N_1$  = normality of the  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  solution,

$V_2$  =  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution required for the back-titration, mL,

$N_2$  = normality of the  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution,

$S_1$  = specimen weight, g, and

<sup>4</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.