Designation: D3280 – 85 (Reapproved 2020)

Standard Test Methods for Analysis of White Zinc Pigments[1]

This standard is issued under the fixed designation D3280; 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 analysis of white zinc pigments.

1.2 The analytical procedures appear in the following order:

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 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]

D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments

D1193 Specification for Reagent Water

D1394 Test Methods for Chemical Analysis of White Titanium Pigments

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

3. Summary of Test Method

3.1 *Zinc Oxide:*

3.1.1 *Total Zinc*—Determined using diphenylamine as an internal indicator and also using uranyl acetate as an external indicator. Total impurities are calculated.

3.1.2 *Total Sulfur*—Determined as $BaSO_4$ and calculated to sulfur.

3.1.3 *Moisture and Volatile Matter*—Determined in accordance with Method A of Test Methods D280.

3.2 *Leaded Zinc Oxide:*

3.2.1 *Total Lead*—Determined as $PbSO_4$ and calculated to percent PbO.

3.2.2 *Total Zinc*—Determined on the filtrate from procedure in 13.2.1 in accordance with methods in Sections 7 or 8.

3.2.3 *Total Sulfur*—Determined as $BaSO_4$ and calculated to percent SO_3.

3.2.4 *Total Impurities*—Calculated from compositional data.

3.2.5 *Moisture and Other Volatile Matter*—Determined in accordance with Method A of Test Methods D280.

3.2.6 *Water Soluble Salts*—Determined gravimetrically.

3.3 *Zinc Sulfide:*

3.3.1 *Total Zinc*—Determined using uranyl acetate external indicator in accordance with Section 9.

3.3.2 *Zinc Sulfide*—Determined in accordance with Sections 8 or 9 and calculating ZnO to ZnS.

3.3.3 *Water Soluble Salts*—Determined in accordance with Section 18.

[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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[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.

3.3.4 *Moisture*—Determined in accordance with Method A of Test Methods D280.

3.3.5 *Barium Sulfate*—The sample is treated with N_2SO_4 and Na_2CO_3 and the residue of $BaCO_3$ is dissolved in NCl and $(NH_4)_2SO_4$ added to precipitate $BaSO_4$, which is weighed.

3.3.6 *Titanium Dioxide*—Determined in accordance with Test Methods D1394.

4. Significance and Use

4.1 White zinc pigments find considerable use in white paints, and as such it is useful to formulators and users to be able to monitor the amounts of these pigments in whole paints. It is also of interest to raw material suppliers and paint producers to check the specifications of each pigment.

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.[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 grade water conforming to Specification D1193.

5.3 *Concentration of Reagents:*

5.3.1 *Concentrated Acids and Ammonium Hydroxide*—When acids and ammonium hydroxide are specified by name or chemical formula only it should be understood that concentrated reagents of the following specific gravities or concentrations are intended:

Acetic acid, $HC_2H_3O_2$	99.5 %
Hydrochloric acid, HCl	sp gr 1.19
Hydrofluoric acid, HF	48 %
Nitric acid, HNO_3	sp gr 1.42
Sulfuric acid, H_2SO_4	sp gr 1.84
Ammonium hydroxide, NH_4OH	sp gr 0.90

The desired specific gravities or concentrations of all other concentrated acids are stated whenever they are specified.

5.3.2 *Diluted Acids and Ammonium Hydroxide*—Concentrations of diluted acids and ammonium hydroxide, except when standardized, are specified as a ratio stating the number of volumes of the concentrated reagents to be diluted with a given number of volumes of water, as in the following example: HCl (1+99) means 1 volume of concentrated HCl (sp gr 1.19) diluted with 99 volumes of water.

6. Preparation of Sample

6.1 Grind dry pigments, if lumpy or not finely ground, to a fine powder for analysis. Large samples may be thoroughly mixed and a representative portion taken and powdered if lumpy or not finely ground. Mix the sample in all cases thoroughly before taking specimens for analysis.

6.2 Separate pigments from paints or pastes, grind to a fine powder, pass through a 180-µm (No. 80) sieve (Note 1) to remove any skins, thoroughly mix, and oven dry at 105°C. Moisten such pigments after weighing with a little alcohol before adding reagents for analysis.

NOTE 1—Detailed requirements for this sieve are given in Specification E11.

6.3 Preserve all samples in stoppered bottles or containers.

ZINC OXIDE

7. Total Zinc, Using Diphenylamine as Internal Indicator

7.1 *Reagents:*

7.1.1 *Diphenylamine Indicator Solution (10 g/L))*—Dissolve 1 g of diphenylamine in 100 mL of H_2SO_4.

7.1.2 *Potassium Ferrocyanide (1 mL = 0.008 g Zn)*—Dissolve 35 g of $K_4Fe(CN)_6{\cdot}3H_2O$ in water and dilute to 1 L and add 0.3 g of potassium ferricyanide ($K_3Fe(CN)_6$). Standardize the solution by titrating against zinc (320 to 340 mg), following the procedure described in 7.2. Calculate the grams of zinc equivalent to 1.00 mL of the solution.

7.2 *Procedure*—Weigh to 0.1 mg about 0.4 g of the sample into a tall form 400-mL beaker. Moisten with about 20 mL of water, and dissolve in 15 mL of HCl. Neutralize with NH_4OH, using litmus as the indicator. Add an excess of 15 mL of H_2SO_4 (1+2) and dilute to 200 mL. Heat to approximately 60°C, add 2 drops of diphenylamine indicator solution and while stirring vigorously, titrate with $K_4Fe(CN)_6$ solution to the color change from purple to a persistent yellowish green.

NOTE 2—The true end point is a sharp, persistent change from a purple to a yellowish green. At the beginning of the titration, a deep blue color is developed after addition of a few millilitres of $K_4Fe(CN)_6$ solution. About 0.5 to 1.0 mL before the true end point is reached, the solution changes from a blue to a purple color. After the purple color is developed, the titration should be continued dropwise to the persistent yellowish green end point.

7.3 *Calculation*—Calculate the percent total zinc as ZnO, *A*, as follows:

$$A = \left[\frac{V_2 Z \times 1.245}{S_1}\right] \times 100 \quad (1)$$

where:

V_2 = $K_4Fe(CN)_6$ solution required for titration of the specimen, mL,
Z = zinc equivalent of the $K_4Fe(CN)_6$ solution, g/mL,
S_1 = specimen weight, and
1.245 = molecular weight ZnO (81.38)/molecular weight Zn (65.38).

8. Total Zinc, Using Uranyl Acetate as External Indicator

8.1 *Reagents:*

8.1.1 *Uranyl Acetate Indicator Solution (50 g/L)*—Dissolve 5 g of $UO_2(C_2H_3O_2)_2{\cdot}2H_2O$ in 100 mL of water and make slightly acid with acetic acid.

[3] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

8.1.2 *Potassium Ferrocyanide, Standard Solution* (1 mL = 0.008 g Zn)—Prepare and standardize as in 7.1.2. Run a blank titration with the same amounts of reagents and water. Calculate the zinc equivalent of the solution as follows:

$$Z = W/(V - B) \quad (2)$$

where:

Z = zinc equivalent of the $K_4Fe(CN)_6$ solution, g/mL,
W = zinc used,
V = $K_4Fe(CN)_6$ solution required for titration of the zinc, mL, and
B = $K_4Fe(CN)_6$ solution required for titration of the blank, mL.

8.2 *Procedure:*

8.2.1 Weigh to 0.1 mg about 0.4 g of the sample into a tall-form 400-mL beaker. Moisten with about 20 mL of water and dissolve by adding 10 mL of HCl. Add NH_4OH until slightly alkaline to litmus paper. Add HCl until just acid, and then add 3 mL in excess. Dilute to about 250 mL with hot water and heat nearly to boiling. Titrate with $K_4Fe(CN)_6$ solution, stirring constantly, until a drop of uranyl acetate indicator tested in a white porcelain spot plate shows a brown tinge after standing 1 min.

8.2.2 *Blank*—Run a blank titration with the same amounts of reagents and water.

8.3 *Calculation*—Calculate the percent total zinc as ZnO, A, as follows:

$$A = \left[\frac{((V - B)Z \times 1.245)}{S}\right] \times 100 \quad (3)$$

where:

V = $K_4Fe(CN)_6$ solution required for titration of the sample, mL,
S = sample used, g, and
1.245 = molecular weight ZnO (81.38)/molecular weight Zn (65.38).

9. Total Impurities

9.1 *Calculation*—Calculate the percent total impurities, A, as follows:

$$A = 100 - (L + Z_1 + S_5) \quad (4)$$

where:

L = total lead as PbO, %,
Z_1 = total zinc as ZnO, %, and
S_5 = total sulfur as SO_3, %.

10. Total Sulfur

10.1 *Reagents:*

10.1.1 *Bromine Water (saturated).*

10.1.2 *Aluminum*—Reagent grade granular aluminum.

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

10.2 *Procedure:*

10.2.1 Weigh to 0.1 g about 10 g of the sample into a 400-mL beaker. Add 50 mL of saturated bromine water, 100 mL of water, and 35 mL of HCl. Boil until all the bromine has been expelled, cool, and add 3 to 5 g of granular aluminum. Heat to boiling, filter, and wash well with hot water.

10.2.2 Dilute the filtrate to 300 mL with water, neutralize with NH_4OH, and add 6 drops of HCl. Heat to boiling and add 25 mL of hot $BaCl_2$ solution dropwise, with constant stirring. Allow to stand in a warm place for at least 2 h.

10.2.3 Filter, using a weighed Gooch crucible, or a fine textured filter paper and wash well with hot water. Dry and ignite in a muffle furnace for 30 min. Cool and weigh as $BaSO_4$.

10.3 *Calculation*—Calculate the percent sulfur, A, as follows:

$$A = \left[\frac{(P \times 0.1374)}{S_2}\right] \times 100 \quad (5)$$

where:

P = $BaSO_4$ precipitate, g,
S_2 = specimen weight, g, and
0.1374 = molecular weight of sulfur (32.064)/molecular weight $BaSO_4$ (233.43).

11. Moisture and Other Volatile Matter

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

LEADED ZINC OXIDE

12. Total Lead

12.1 *Procedure:*

12.1.1 Weigh to the nearest 0.1 mg about 0.5 g of the sample into a 400-mL beaker. Dissolve in 250 mL of water and 20 mL of HNO_3 (Note 2). Add 5 mL of H_2SO_4 and evaporate to dense white fumes. Cool, add 50 mL of 95 % alcohol and 200 mL of water, and let stand cold 1 to 2 h. Filter, using a weighed Gooch crucible. Wash the precipitate with H_2SO_4 (1+99) and combine the filtrate and washings. If the zinc content of the sample is known to be 40 % or over, reserve the filtrate and washings for the determination of total zinc (Section 13).

NOTE 3—If the sample contains calcium or barium, the lead and zinc should be separated by precipitation with H_2S after solution in HCl, making alkaline with NH_4OH and then acid with acetic acid. Dissolve the PbS and ZnS in dilute HNO_3 and determine the lead and zinc as above.

12.1.2 Ignite the precipitate in the crucible at dull red heat (550 ± 50°C) for 20 min, cool, and weigh.

12.2 *Calculation*—Calculate the percent total lead as PbO, A, as follows:

$$A = \left[\frac{(P_1 \times 0.736)}{S_3}\right] \times 100 \quad (6)$$

where:

P_1 = $PbSO_4$ precipitate, g,
S_3 = sample used, g, and
0.736 = molecular weight PbO (223.21)/molecular weight $PbSO_4$ (303.28).

13. Total Zinc

13.1 *Reagents*—See 7.1 or 8.1, whichever is applicable.

13.2 *Procedure:*