



## Standard Test Method for Analysis of Zinc Hydroxy Phosphite Pigment<sup>1</sup>

This standard is issued under the fixed designation D 4450; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method is intended for the determination of zinc oxide and phosphorous acid content of the pigment commercially known as zinc hydroxy phosphite. The zinc content is determined by ethylenediaminetetraacetate (EDTA) titration and calculated as zinc oxide (ZnO), while the phosphorous content is determined colorimetrically and calculated as phosphorous acid ( $H_3PO_3$ ).

1.2 The analytical procedures appear in the following order:

	Sections
Zinc oxide	6 through 8
Phosphorous acid	9 through 14

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:*

D 1193 Specification for Reagent Water<sup>2</sup>

### 3. Summary of Test Method

3.1 The zinc is determined by dissolving the test sample in nitric acid, adjusting the pH of the solution to 5 to 5.5 and titrating with EDTA.

3.2 The phosphorus is determined colorimetrically with the aid of nitric acid, ammonium vanadate, and ammonium molybdate. The absorbance of the test sample is compared to a calibration curve that yields the number of milligrams of phosphorus.

### 4. Significance and Use

4.1 This test method may be used to confirm the stated zinc oxide and phosphorous acid content of zinc hydroxy phosphite pigment.

### 5. Purity of Reagents

5.1 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>3</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 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

### TOTAL ZINC AS ZINC OXIDE

### 6. Reagents

6.1 *Ammonium Hydroxide* (sp gr 0.90), concentrated ammonium hydroxide ( $NH_4OH$ ).

6.2 *Glacial Acetic Acid* (min 99.7 %), concentrated glacial acetic acid ( $CH_3COOH$ ).

6.3 *Acid Ammonium Acetate Buffer*—Mix 400 mL of distilled water and 400 mL of reagent grade ammonium hydroxide (sp gr 0.90). Add 375 mL of reagent grade glacial acetic acid slowly while stirring.

6.4 *Cupric Sulfate Solution* (0.1 M)—Dissolve 25 g of  $CuSO_4 \cdot 5H_2O$  in distilled water and dilute to 1 L.

6.5 *Disodium Ethylenediaminetetraacetate Dihydrate* (0.05 M) (EDTA Solution)—Dissolve 18.6 g of the reagent grade salt in distilled water and dilute to 1 L. Standardize the solution as follows:

6.5.1 Transfer 25 mL of lead standard (6.6) to a 400-mL beaker. Add concentrated ammonium hydroxide (6.1) dropwise until a permanent precipitate just forms. Add 25 mL of acid ammonium acetate (6.3), dilute to 200 mL, heat to boiling, add 4 drops of copper EDTA (6.7) and 12 drops of PAN (6.8), and titrate with EDTA to a clear yellow.

6.5.2 Calculate the molarity of the EDTA,  $M$ , as follows:

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

$$M = 25 \times 0.01036/L \times 0.20721 \quad (1)$$

where  $L$  = EDTA solution, mL. Also 1 mL of primary standard 0.05  $M$  lead nitrate = 0.01036 g of lead and 0.20721 is the milliequivalent weight of lead.

6.6 *Primary Standard* (0.05  $M$  lead nitrate)—Dissolve 16.5615 g reagent grade lead nitrate in distilled water and dilute to 1 L (1 mL = 0.01036 g lead).

6.7 *Copper-EDTA Solution*—Mix equivalent amounts of cupric sulfate solution (6.4) and EDTA solution (6.5) and store in a dropping bottle. The cupric sulfate EDTA equivalence may be determined as follows:

6.7.1 Pipet 10 mL of cupric sulfate into a beaker, and add concentrated ammonium hydroxide (6.1) dropwise until the precipitate that forms just redissolves. Dilute to 200 mL with water, add two Murexide indicator tablets, crush with a stirring rod to dissolve, and titrate immediately with EDTA to purple.

6.8 *Pan Indicator* [1-(2-pyridylazo)-2-naphthol]—Dissolve 0.1 g in 100 mL of ethanol.

6.9 *Murexide Indicator Tablets*—Ammonium salt of purpuric acid.

6.10 *Nitric acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ).

## 7. Procedure

7.1 Weigh accurately 0.2 g of pigment and transfer to a 400-mL beaker. Add 5 mL of nitric acid (6.10) and 50 mL of water and boil gently for 10 min. Cool, and add ammonium hydroxide (6.1) until the pH of the solution is from 5 to 5.5 (as indicated by pH paper). Add 25 mL of acid ammonium acetate (6.3), boil 5 min, dilute to 200 mL with water, heat to boiling, add 4 drops of copper-EDTA (6.7) and 12 drops of PAN (6.8), and titrate while hot with standard EDTA to a clear yellow.

## 8. Calculation

8.1 Calculate the percent zinc oxide,  $A$ , as follows:

$$A = L \times M \times 0.08137 \times 100/S \quad (2)$$

where:

- $L$  = EDTA required for titration, mL,
- $M$  = molarity of EDTA solution,
- $S$  = specimen, g, and
- 0.8137 = milliequivalent weight of zinc oxide.

## TOTAL PHOSPHORUS AS PHOSPHOROUS ACID

### 9. Reagents

9.1 *Standard Phosphorus Solution*—Dissolve 0.9156 g of secondary sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) in about 200 mL of water. Add 20 mL of nitric acid (sp gr 1.42), dilute to 1 L, and mix. 1 mL = 0.0002 g P.

9.2 *Ammonium Vanadate Solution*—Dissolve 2.5 g of ammonium vanadate ( $\text{NH}_4\text{VO}_3$ ) in 500 mL of hot water. When solution is complete, add 10 mL nitric acid (sp gr 1.42), cool, dilute to 1 L, and mix.

9.3 *Ammonium Molybdate Solution*—Dissolve 100 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) in 800 mL of water and dilute to 1 L. Filter before use.

9.4 *Bromine*, reagent grade.

9.5 *Bromine Water*, distilled water saturated with bromine.

9.6 *Nitric Acid* (sp gr 1.42), concentrated nitric acid ( $\text{HNO}_3$ ).

9.7 *Nitric Acid* (2:3)—Dilute 200 mL of nitric acid (sp gr 1.42) to 500 mL with water.

## 10. Apparatus

10.1 *Photoelectric Colorimeter*, either a single- or double-beam spectrophotometer with a wavelength capability of 465  $\mu\text{m}$ .

10.2 *Volumetric Flasks*, 100-mL.

10.3 *Tubes*, 10-mm or 20-mm.

10.4 *Filter Paper*, medium texture.

## 11. Calibration Curve

11.1 Transfer from a pipet 0.0, 1.0, 3.0, 7.0, 10.0, 15.0, and 20.0-mL aliquots of standard phosphorus solution (9.1) to a 100-mL volumetric flask. To each flask add 10 mL of nitric acid (9.7), 10 mL of ammonium vanadate (9.2), and 10 mL of ammonium molybdate (9.3), dilute to the mark, and mix. Allow solutions to stand 20 min and transfer to a 20-mm tube. Read the absorbance of the solution at 465  $\mu\text{m}$ . Construct a calibration curve for phosphorus by plotting the absorbance versus milligrams of phosphorus in 100 mL of solution for each standard solution.

## 12. Procedure

12.1 Weigh accurately 0.2 g of pigment and transfer to a 150-mL beaker. Add 25 mL of bromine water (9.5), 10 mL nitric acid (9.6), and 0.5 mL bromine (9.4), and mix the solution. Allow to stand in a warm place for about 1/2 h, and then gently boil off the bromine until the solution is clear.

12.2 Cool the solution and transfer to a 100-mL volumetric flask. Make to the mark with water and mix.

12.3 Pipet 10 mL of the solution into a 100-mL volumetric flask and add 10 mL nitric acid (9.7), 10 mL of ammonium vanadate (9.2), and 10 mL of filtered ammonium molybdate (9.3).

12.4 Dilute the sample to the mark, mix, and allow to stand for 20 min, and transfer to a 20-mm tube.

12.5 Read the absorbance of the sample at 465  $\mu\text{m}$  and from the calibration curve, read the number of milligrams of phosphorus in the test solution.

12.6 Run a blank with the sample.

TABLE 1 Standard Deviation

	Within-laboratory		Between-laboratory	
	$s_w$	DF	$s_b$	DF
$\text{H}_3\text{PO}_3$	0.198	8	0.515	6
ZnO	0.193	8	0.42	8

## 13. Calculation

13.1 Calculate the percent phosphorus acid,  $C$ , as follows:

$$C = A - B \times 2.646/S \times 10 \quad (3)$$

where:

- $A$  = phosphorus in test solution, mg,
- $B$  = phosphorus in reagent blank, mg,
- $S$  = specimen in aliquot, g and

2.646 = gravimetric factor to convert phosphorus to phosphorous acid.

#### 14. Precision <sup>4</sup>

14.1 In an interlaboratory study of this test method, in which two samples containing 18.5 to 19.0 % H<sub>3</sub>PO<sub>3</sub> and 77.0 to 78.0 % ZnO were analyzed by one operator in each of four laboratories for H<sub>3</sub>PO<sub>3</sub> and five laboratories for ZnO, the within-laboratory and between-laboratories pooled standard deviations, after discarding one day's results from one laboratory for both samples of ZnO (see Table 1). Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

14.1.1 *Repeatability*—Two results, each the mean of two runs, obtained by the same operator should be considered suspect if they differ by more than 0.65 % absolute at H<sub>3</sub>PO<sub>3</sub> contents of 18 to 20 % and more than 0.63 % absolute at ZnO contents of 75 to 80 %.

14.1.2 *Reproducibility*—Two results, each the mean of two runs, obtained by operators in different laboratories should be considered suspect if they differ by more than 1.78 % absolute for H<sub>3</sub>PO<sub>3</sub> and 1.37 % absolute for ZnO at the same contents as in 14.1.1.

#### 15. Keywords

15.1 phosphorus acid; pigment analysis; zinc; zinc hydroxy phosphite; zinc oxide

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<sup>4</sup> Supporting data are available from ASTM International Headquarters. Request RR:D01.1048.

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