



## Standard Test Methods of Chemical Analysis of Red Lead<sup>1</sup>

This standard is issued under the fixed designation D 49; 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 These test methods cover procedures for the chemical analysis of red lead having the approximate formula  $Pb_3O_4$  (probably  $PbO_2 \cdot 2PbO$ ).

1.2 *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 50 Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese<sup>2</sup>

D 215 Practice for the Chemical Analysis of White Linseed Oil Paints<sup>3</sup>

D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments<sup>2</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

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

D 1301 Test Methods for Chemical Analysis of White Lead Pigments<sup>2</sup>

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids<sup>2</sup>

### 3. Treatment of Sample

3.1 If the pigment is lumpy or not finely ground, grind it to a fine powder and mix thoroughly. Large samples may be thoroughly mixed and a representative portion taken and powdered if lumpy or not finely ground. The sample in all cases shall be thoroughly mixed before taking portions for analysis. All samples shall be preserved in stoppered bottles or containers.

### 4. Purity of Reagents

4.1 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>5</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.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

### 5. Moisture

5.1 Determine moisture content with a 2-g specimen in accordance with Method A of Test Methods D 280. The specimen is dried for 2 h at 105°C. The loss in weight is considered as moisture.

### 6. Organic Color

6.1 Boil 2 g of the sample with 25 mL of 95 % ethyl alcohol, let settle, decant the supernatant liquid; boil the residue with 25 mL of distilled water and decant as before; boil the residue with 25 mL of diluted  $NH_4OH$  (1 + 4) 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. If the solutions remain colorless, organic colors are probably absent.

NOTE 1—If it is desired to test for organic colors resistant to the above reagents, the test procedures described in the following books may be used, taking into account the nature of the pigment involved (1,2,3).<sup>6</sup>

### 7. Total Lead and Insoluble Matter

7.1 Treat 1 g of the sample with 15 mL of  $HNO_3$ (1 + 1) and sufficient  $H_2O_2$  to dissolve all  $PbO_2$  on warming. If any

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>5</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>6</sup> The boldface numbers in parentheses refer to a list of references at the end of these test methods.

insoluble matter is present, add 25 mL of water, boil, filter, and wash with hot water. The insoluble matter contains free  $\text{SiO}_2$  and should be examined for  $\text{BaSO}_4$  and silicates, if appreciable.

7.2 To the original solution or filtrate from the insoluble matter add 20 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) and evaporate to  $\text{SO}_3$  fumes. Cool, add 150 mL of water, and 150 mL of 95 % ethyl alcohol, let stand *cold* for 2 h, filter, on a Gooch crucible, wash with 95 % alcohol, dry at 105 to 110°C, and weigh as  $\text{PbSO}_4$ . Calculate to  $\text{PbO}$ .

7.3 Red lead is rarely adulterated, but should the specimen contain soluble barium compounds, the  $\text{PbSO}_4$  obtained in 8.2 will contain  $\text{BaSO}_4$ . In this case, precipitate the lead as sulfide from a slightly acid ( $\text{HCl}$ ) solution, dissolve the  $\text{PbS}$  in hot diluted  $\text{HNO}_3$ , and determine the lead as sulfate or chromate.

7.4 If the specimen contains significant amounts of calcium or magnesium, boil the  $\text{HNO}_3 - \text{H}_2\text{O}_2$  solution (7.1) until all the lead is converted into nitrate and then determine the lead as  $\text{PbCrO}_4$ .

7.5 If soluble barium, calcium, or magnesium are to be determined, precipitate the lead as sulfide from a slightly acid solution ( $\text{HCl}$ ), dissolve the  $\text{PbS}$  in hot diluted  $\text{HNO}_3$ , and determine the lead as sulfate. Boil the filtrate from the  $\text{PbS}$  to expel  $\text{H}_2\text{S}$ , add a little bromine water to oxidize iron (if present), boil to expel bromine, and precipitate the barium with a few millilitres of  $\text{H}_2\text{SO}_4$  (1 + 3). Filter and weigh as  $\text{BaSO}_4$ . Calculate to  $\text{BaO}$  or  $\text{BaCO}_3$ . To the filtrate from the  $\text{BaSO}_4$  add  $\text{NH}_4\text{OH}$  in slight excess, filter off any precipitate of  $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ , wash with hot water. Manganese, if present, can be precipitated by adding bromine and  $\text{NH}_4\text{OH}$  and warming. Filter, wash with hot water, ignite, and weigh as  $\text{Mn}_3\text{O}_4$ . Unite all the filtrates, make slightly acid with acetic acid, heat to boiling and pass  $\text{H}_2\text{S}$  into the hot solution until saturated (20 to 30 min); add 5 g of  $\text{NH}_4\text{Cl}$  and let stand 5 h, filter off any  $\text{ZnS}$ , wash with  $\text{H}_2\text{S}$  water, dissolve the  $\text{ZnS}$  in hot diluted  $\text{HCl}$  and determine the zinc by titration with  $\text{K}_4\text{Fe}(\text{CN})_6$ . Or, boil off the  $\text{H}_2\text{S}$ , filter out any separated sulfur and determine the zinc as  $\text{Zn}_2\text{P}_2\text{O}_7$ . Calcium may be determined in the filtrate from the  $\text{ZnS}$  by expelling  $\text{H}_2\text{S}$  and then adding  $\text{NH}_4\text{OH}$  and ammonium oxalate. Titrate the calcium oxide precipitate using the procedure described in 13.3 of Test Methods D 50. In the filtrate from calcium determine magnesium by precipitating with sodium phosphate solution, finally weighing as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

## 8. Lead Peroxide ( $\text{PbO}_2$ ) and True Red Lead ( $\text{Pb}_3\text{O}_4$ )

NOTE 2—Method of Diehl (4) modified by Topf (5)—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given, or substances such as metallic lead which reduce  $\text{PbO}_2$  to  $\text{PbO}$  without the liberation of iodine.

8.1 *Solutions Required:* (a) *Red Lead Solution*—Dissolve in 1-L beaker 600 g of crystallized sodium acetate and 48 g of  $\text{KI}$  in about 500 mL of acetic acid (1 + 3) (made by mixing 150 mL of glacial acetic acid with 450 mL of water). Warm the beaker and contents on a steam bath, stirring occasionally, until a clear solution is obtained. Cool this solution to room temperature, dilute to exactly 1000 mL with the acetic acid (1 + 3) and mix thoroughly. If preferred, the red lead solution may be prepared separately for each titration, as follows: Dissolve 30 g of the crystallized sodium acetate and 2.4 g of  $\text{KI}$

in 25 mL of the acetic acid (1 + 3), warming gently and stirring until a clear solution is obtained. Cool this solution to room temperature, dilute to 50 mL with the acetic acid solution (1 + 3), and mix thoroughly.

8.2 *Sodium Thiosulfate Solution (0.1N)*—Dissolve 24.83 g of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), freshly pulverized and dried between filter paper, and dilute with water to 1 litre at the temperature at which the titrations are to be made. The solution is best made with well-boiled water free from  $\text{CO}_2$ , or let stand 8 to 14 days before standardizing, as described in Section 5 of Test Method D 1959.

8.3 *Starch Solution*—Stir 2 to 3 g of potato starch with 100 mL of salicylic acid solution (1 %), and boil the mixture until the starch is practically dissolved, then dilute to 1 L (Note 3), or prepare as described in 7.8.2 of Test Method D 1959.

NOTE 3—*Lead Peroxide*—If the pigment contains an appreciable amount of nitrite (nitrate has no effect on the method), leach out water-soluble matter as below, dry the residue and determine  $\text{PbO}_2$  as above, calculating to basis of original specimen.

## 9. Procedure

9.1 Weigh 1 g of the finely ground sample, transfer to a 200-mL Erlenmeyer flask, add 20 mL of water; then add as quickly as possible 40 mL of the “red lead solution” at room temperature. If the sample is red lead that has been extracted from a paint or paste, in place of the water use 10 mL of a mixture of 7 parts by volume of chloroform and 3 parts by volume of glacial acetic acid, and then add without delay the red lead solution. Add 30 mL of water containing 5 or 6 g of sodium acetate and titrate at once with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub-up any undissolved particles with the rod until free iodine no longer forms, wash off rod, add the  $\text{Na}_2\text{S}_2\text{O}_3$  solution until *pale yellow*, add starch solution, and titrate until colorless. Add the 0.1 N iodine solution until blue color is just restored and subtract the amount used for the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  that had been added.

## 10. Calculation

10.1 Calculate the lead peroxide and true red lead contents as follows:

$$\text{PbO}_2 = I \times 0.942$$

$$\text{Pb}_3\text{O}_4 = \text{PbO}_2 \times 2.866 = I \times 2.7$$

where:  $I$  = iodine value of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution,

$$0.942 = \frac{\text{PbO}_2}{I} = \frac{239.19}{253.81}, \text{ and} \quad (1)$$

$$2.86616 = \frac{\text{Pb}_3\text{O}_4}{\text{PbO}_2} = \frac{685.57}{239.19}$$

## 11. Zinc

11.1 If the volume is appreciable, evaporate off the alcohol from the filtrate from total lead, make alkaline with  $\text{NH}_4\text{OH}$ , then acid with  $\text{HCl}$  (sp gr 1.19), add 3 mL more of  $\text{HCl}$ , dilute to about 250 mL with water, heat nearly to boiling and titrate with standard  $\text{K}_4\text{Fe}(\text{CN})_6$  solution in accordance with 16.1.11 of Practice D 215. Report as  $\text{ZnO}$  (includes cadmium). Iron,

copper, or other interfering substances should first be removed as described in 25.2.3 of Practice D 215.

## 12. Matter Soluble in Water

12.1 Determine the amount of water soluble material present in accordance with the procedure in Section 5 of Test Methods D 1208 or determine in accordance with Test Methods D 1301.

## 13. Total Silica

13.1 Digest 5 g of the sample in a covered casserole with 5 mL of HCl and 15 mL of HNO<sub>3</sub> (1 + 1). Evaporate to dryness to dehydrate. Cool, treat with hot water and HNO<sub>3</sub>, boil, filter, wash with hot acid ammonium acetate solution, then dilute HCl and finally hot water. Ignite and weigh as SiO<sub>2</sub>. The residue may be treated with H<sub>2</sub>SO<sub>4</sub> and HF in cases of doubt as to purity.

## 14. Carbon Dioxide

14.1 Determine carbon dioxide by the evolution method, using diluted HCl and stannous chloride.

## 15. Soluble Sulfates

15.1 *Sulfates Other Than Barium Sulfate*—Treat 0.5 g of the sample with 5 mL of water, 3 g of NH<sub>4</sub>Cl, and 5 mL of HCl saturated with bromine. Digest (covered) on steam bath about 15 min. Add 25 mL of water, neutralize with dry Na<sub>2</sub>CO<sub>3</sub>, and add about 2 g more. Boil 10 to 15 min, let settle, dilute with hot water, filter, and wash with hot water. Redissolve in HCl, reprecipitate as above, and wash thoroughly with hot water. Acidify the united filtrates with HCl, adding a slight excess; boil and add a slight excess of BaCl<sub>2</sub> solution (10 %). Let stand on a steam bath for 1 h. Filter and wash with hot water. Ignite and weigh as BaSO<sub>4</sub>. Calculate to SO<sub>3</sub> (includes SO<sub>3</sub> formed from SO<sub>2</sub>).

15.2 Or, dissolve 0.5 g of the sample in 25 mL of water, 10 mL of NH<sub>4</sub>OH (sp gr 0.90) and HCl in slight excess; dilute to about 150 mL with water and add a piece of aluminum foil which should about cover the bottom of the beaker (being held on the bottom by means of a stirring rod). Heat gently till all lead is precipitated, decant through a filter, pressing the lead sponge with a flattened rod, and washing with hot water. Add to the filtrate a little bromine water, boil until bromine is expelled, add 15 mL of BaCl<sub>2</sub> solution (10 %), let stand on a steam bath for 1 h, filter, wash with hot water, ignite, and weigh as BaSO<sub>4</sub> (any SrSO<sub>4</sub> present is not decomposed in this method).<sup>7</sup>

## 16. Iron Oxide

16.1 Determine iron oxide in accordance with Section 12 of Test Methods D 50, or in a large beaker, treat 20 g of the sample with 20 mL of water, 20 mL of HNO<sub>3</sub> (sp gr 1.42), and 3 mL of formaldehyde solution. Warm until all PbO<sub>2</sub> is dissolved, dilute with water, warm, filter off insoluble matter, and wash with hot water. Ignite filter and insoluble matter, and evaporate with H<sub>2</sub>SO<sub>4</sub> and HF. To filtrate from insoluble matter add 14 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1), filter off PbSO<sub>4</sub>, and wash. Dissolve the residue from HF and H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> and add to the filtrate from PbSO<sub>4</sub>. Dilute to 500 mL and determine iron colorimetrically in an aliquot, using the same amounts of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and formaldehyde in the comparison solution Ref (7). Calculate to Fe<sub>2</sub>O<sub>3</sub>.

## 17. Keywords

17.1 chemicals analysis; lead dioxide; red lead; tetra lead oxide

<sup>7</sup> The solubility of BaSO<sub>4</sub> is increased by the presence of aluminum chloride (6).

## REFERENCES

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- (7) Lunge-Berl, "Chemische-technisch Untersuchungs-Methoden," Vol 2, p. 95, 6th Ed.

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