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Standard Test Methods of Chemical Analysis of Red Lead[1]

This standard is issued under the fixed designation D49; 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.

1. Scope

1.1 These test methods cover procedures for the chemical analysis of red lead having the approximate formula Pb_3O_4 (probably $PbO_2·2PbO$).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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:*[2]

D50 Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese

D215 Practice for the Chemical Analysis of White Linseed Oil Paints (Withdrawn 2005)[3]

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

D1193 Specification for Reagent Water

D1208 Test Methods for Common Properties of Certain Pigments

D1301 Test Methods for Chemical Analysis of White Lead Pigments

D1959 Test Method for Iodine Value of Drying Oils and Fatty Acids (Withdrawn 2006)[3]

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.[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.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

5. Moisture

5.1 Determine moisture content with a 2-g specimen in accordance with Method A of Test Methods D280. 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

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[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] The last approved version of this historical standard is referenced on www.astm.org.

[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.

used, taking into account the nature of the pigment involved (**1**,**2**,**3**).[5]

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 insoluble matter is present, add 25 mL of water, boil, filter, and wash with hot water. The insoluble matter contains free SiO_2 and should be examined for $BaSO_4$ and silicates, if appreciable.

7.2 To the original solution or filtrate from the insoluble matter add 20 mL of H_2SO_4 (sp gr 1.84) and evaporate to 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 $PbSO_4$. Calculate to PbO.

7.3 Red lead is rarely adulterated, but should the specimen contain soluble barium compounds, the $PbSO_4$ obtained in 8.2 will contain $BaSO_4$. In this case, precipitate the lead as sulfide from a slightly acid (HCl) solution, dissolve the PbS in hot diluted HNO_3, and determine the lead as sulfate or chromate.

7.4 If the specimen contains significant amounts of calcium or magnesium, boil the $HNO_3 - H_2O_2$ solution (7.1) until all the lead is converted into nitrate and then determine the lead as $PbCrO_4$.

7.5 If soluble barium, calcium, or magnesium are to be determined, precipitate the lead as sulfide from a slightly acid solution (HCl), dissolve the PbS in hot diluted HNO_3, and determine the lead as sulfate. Boil the filtrate from the PbS to expel H_2S, add a little bromine water to oxidize iron (if present), boil to expel bromine, and precipitate the barium with a few millilitres of H_2SO_4 (1 + 3). Filter and weigh as $BaSO_4$. Calculate to BaO or $BaCO_3$. To the filtrate from the $BaSO_4$ add NH_4OH in slight excess, filter off any precipitate of $Fe(OH)_3 + Al(OH)_3$, wash with hot water. Manganese, if present, can be precipitated by adding bromine and NH_4OH and warming. Filter, wash with hot water, ignite, and weigh as Mn_3O_4. Unite all the filtrates, make slightly acid with acetic acid, heat to boiling and pass H_2S into the hot solution until saturated (20 to 30 min); add 5 g of NH_4Cl and let stand 5 h, filter off any ZnS, wash with H_2S water, dissolve the ZnS in hot diluted HCl and determine the zinc by titration with $K_4Fe(CN)_6$. Or, boil off the H_2S, filter out any separated sulfur and determine the zinc as $Zn_2P_2O_7$. Calcium may be determined in the filtrate from the ZnS by expelling H_2S and then adding NH_4OH and ammonium oxalate. Titrate the calcium oxide precipitate using the procedure described in 13.3 of Test Methods D50. In the filtrate from calcium determine magnesium by precipitating with sodium phosphate solution, finally weighing as $Mg_2P_2O_7$.

8. Lead Peroxide (PbO_2) and True Red Lead (Pb_3O_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 PbO_2 to 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 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 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* (0.1*N*)—Dissolve 24.83 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), 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 CO_2, or let stand 8 to 14 days before standardizing, as described in Section 5 of Test Method D1959.

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 D1959.

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 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* $Na_2S_2O_3$ 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 $Na_2S_2O_3$ 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 $Na_2S_2O_3$ that had been added.

10. Calculation

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

$$PbO_2 = I \times 0.942$$
$$Pb_3O_4 = PbO_2 \times 2.866 = I \times 2.7$$

where: I = iodine value of the $Na_2S_2O_3$ solution,

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[5] The boldface numbers in parentheses refer to a list of references at the end of these test methods.

$$0.942 = \frac{PbO_2}{I_2} = \frac{239.19}{253.81}, \text{ and} \quad (1)$$

$$2.86616 = \frac{Pb_3O_4}{PbO_2} = \frac{685.57}{239.19}$$

11. Zinc

11.1 If the volume is appreciable, evaporate off the alcohol from the filtrate from total lead, make alkaline with NH_4OH, then acid with HCl (sp gr 1.19), add 3 mL more of HCl, dilute to about 250 mL with water, heat nearly to boiling and titrate with standard $K_4Fe(CN)_6$ solution in accordance with 16.1.11 of Practice D215. Report as ZnO (includes cadmium). Iron, copper, or other interfering substances should first be removed as described in 25.2.3 of Practice D215.

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 D1208 or determine in accordance with Test Methods D1301.

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_3 (1 + 1). Evaporate to dryness to dehydrate. Cool, treat with hot water and HNO_3, boil, filter, wash with hot acid ammonium acetate solution, then dilute HCl and finally hot water. Ignite and weigh as SiO_2. The residue may be treated with H_2SO_4 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_4Cl, 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_2CO_3, 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 $BaCl_2$ solution (10 %). Let stand on a steam bath for 1 h. Filter and wash with hot water. Ignite and weigh as $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2).

15.2 Or, dissolve 0.5 g of the sample in 25 mL of water, 10 mL of NH_4OH (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 $BaCl_2$ solution (10 %), let stand on a steam bath for 1 h, filter, wash with hot water, ignite, and weigh as $BaSO_4$ (any $SrSO_4$ present is not decomposed in this method).[6]

16. Iron Oxide

16.1 Determine iron oxide in accordance with Section 12 of Test Methods D50, or in a large beaker, treat 20 g of the sample with 20 mL of water, 20 mL of HNO_3 (sp gr 1.42), and 3 mL of formaldehyde solution. Warm until all PbO_2 is dissolved, dilute with water, warm, filter off insoluble matter, and wash with hot water. Ignite filter and insoluble matter, and evaporate with H_2SO_4 and HF. To filtrate from insoluble matter add 14 mL of H_2SO_4 (1 + 1), filter off $PbSO_4$, and wash. Dissolve the residue from HF and H_2SO_4 in H_2SO_4 and add to the filtrate from $PbSO_4$. Dilute to 500 mL and determine iron colorimetrically in an aliquot, using the same amounts of HNO_3, H_2SO_4, and formaldehyde in the comparison solution Ref (**7**). Calculate to Fe_2O_3.

17. Keywords

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

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[6] The solubility of $BaSO_4$ is increased by the presence of aluminum chloride (**6**).

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(6) Skoog, D. A. and West, D. M., *Fundamentals of Analytical Chemistry*, Holt, Rinehart and Winston, Inc., New York, 1969, p. 192.

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

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