



Designation: D 1844 – 86 (Reapproved 1999)

Standard Test Methods for Chemical Analysis of Basic Lead Silicochromate¹

This standard is issued under the fixed designation D 1844; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the chemical analysis of the pigment commercially known as basic lead silicochromate and are applicable to pigment supplied by the manufacturer and to pigment, but not mixed pigments, separated from liquid coatings. The presence of basic lead silicochromate species shall be confirmed by X-ray diffraction analysis (see Specification D 1648).

1.2 For liquid coatings the pigment must first be separated from the vehicle before conducting the analysis.

1.3 The analytical procedures appear in the following order:

	Sections
Lead oxide	6 to 14
Chromium trioxide	15 to 23
Silica	24 to 27
Moisture and other volatile matter	28
Coarse particles	29
Oil absorption	30
Mass color and tinting strength	31

1.4 *This standard does not purport to address 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 185 Test Methods for Coarse Particles in Pigments, Pastes, and Paints²
- D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments²
- D 281 Test Method for Oil Absorption of Pigments by Spatula Rub-Out³
- D 387 Test Method for Color and Strength of Color Pigments with a Mechanical Muller³
- D 1193 Specification for Reagent Water⁴

¹ 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 Pigments Specifications.

Current edition approved April 25, 1986. Published June 1986. Originally published as D 1844 – 61 T. Last previous edition D 1844 – 78.

² Annual Book of ASTM Standards, Vol 06.03.

³ Annual Book of ASTM Standards, Vol 06.01.

⁴ Annual Book of ASTM Standards, Vol 11.01.

D 1648 Specification for Basic Lead Silicochromate Pigment²

D 2371 Test Method for Pigment Content of Solvent-Reducible Paints³

3. Significance and Use

3.1 These test methods may be used to confirm the stated lead oxide, chromium trioxide and silica content of basic lead silicochromate and is useful for quality control.

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.⁵ 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. Preparation of Sample

5.1 Thoroughly mix liquid coatings and separate in accordance with Test Method D 2371 sufficient pigment to enable the required analyses to be carried out.

5.2 Thoroughly mix pigment supplied as such and grind separated pigment to a fine powder in a mortar and pestle before taking portions for analysis.

TOTAL LEAD AS LEAD OXIDE-GRAVIMETRIC METHOD

6. Apparatus

6.1 *Glass Filtering Crucible* (medium-porosity fritted disk), dried to constant weight before use.

⁵ *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.

6.2 Platinum Dish.

7. Reagents

7.1 *Acetic Acid (Glacial).*

7.2 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH₄OH).

7.3 *Ammonium Acetate, Acid Solution*— To 300 mL of water add an equal volume of NH₄OH. Neutralize with glacial acetic acid and add 20 mL in excess.

7.4 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

7.5 *Hydrofluoric Acid* (47 %)—Concentrated hydrofluoric acid (HF).

7.6 *Hydrogen Sulfide* (H₂S)—Handle and use H₂S in hood.

7.7 *Isopropyl Alcohol* (50 and 98 %).

7.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃) (see 7.4.1).

7.9 *Potassium Dichromate Solution* (saturated)—Prepare a saturated solution of potassium dichromate (K₂Cr₂O₇) in water.

7.10 *Sulfuric Acid* (1 + 1)—Carefully mix 1 volume of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) with 1 volume of water (see 7.4.1).

8. Procedure

8.1 Weigh accurately (to 0.1 mg) 1 g of the sample into a platinum dish. Add 5 mL of HNO₃ and 10 mL of HF. Cautiously evaporate to dryness on a steam bath. Repeat the addition of HNO₃ and HF and again cautiously evaporate to dryness. Wash the sides of the dish with a little water and evaporate to dryness. Wet the residue with 5 mL of HNO₃, warm gently, and transfer the residue to a 400-mL beaker using a policeman. Neutralize with NH₄OH, and then make the solution just acid with HCl, adding 5 mL in excess. Dilute to 200 mL and heat to just below the boiling point until solution is complete.

8.2 Pass H₂S through the solution for about 20 min. Filter, using paper pulp. Wash the precipitate five to six times with water just acid with HCl and saturated with H₂S. Transfer the paper and precipitate to the original beaker, add 25 mL of HNO₃, boil until the residue is white, then add 10 mL of H₂SO₄ (1 + 1). Destroy the organic material by evaporating the solution to dense white fumes, making further additions of HNO₃ until there is no charring.

8.3 Cool the solution, add 10 mL of water, and evaporate to fumes. Repeat the addition of water and the evaporation. Cool the solution, add 40 mL of water, and bring the solution to boiling. Cool the solution and add 50 mL of isopropyl alcohol (98 %), stir, and allow the solution to stand cold for at least 4 h. Filter, using paper pulp, and wash once with cold isopropyl alcohol (50 %) containing 10 mL of H₂SO₄ (sp gr 1.84)/100 mL.

8.4 Transfer the precipitate to the original beaker with 150 mL of water, add 50 mL of the ammonium acetate solution, and boil the solution until the lead sulfate dissolves. Filter while hot through the original paper and wash well (6 to 8 washes) with hot water. To the filtrate add 5 mL of glacial acetic acid, heat the solution to boiling, and add 20 mL of saturated K₂Cr₂O₇ solution. Boil the solution until the precipitate turns orange, and allow to stand on a warm plate for at least 2 h. Filter

through a glass filtering crucible (medium-porosity fritted disk), wash three times with hot water, and finally once with alcohol. Dry in an oven at 105°C for 2 h, cool, and weigh.

9. Calculation

9.1 Calculate the percent of total lead as lead oxide (PbO) as follows:

$$\text{PbO, \%} = (P \times 69.06) / S$$

where:

P = lead chromate (PbCrO₄) precipitate, g,

S = sample used, g, and

$$\frac{\text{molecular weight (PbO)}}{\text{molecular weight (PbCrO}_4\text{)}} = \frac{223.21}{323.21} = 0.6906 \times 100 \text{ (for percent)} = 69.06$$

69.06 represents the gravimetric factor to convert grams of PbCrO₄ to grams of PbO.

This gravimetric factor has led to high results due to the presence of mixed lead chromates and an empirical factor can be used to compensate:

$$\text{Empirical factor} = 69.06 \times 0.9944 = 68.67$$

ALTERNATIVE METHOD FOR TOTAL LEAD AS LEAD OXIDE—TITRIMETRIC METHOD

10. Apparatus

10.1 *Platinum Dish.*

10.2 *Filter Paper*, ashless, medium texture, or paper pulp.

11. Reagents

11.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH₄OH).

11.2 *Glacial Acetic Acid* (min 99.7 %)—Concentrated glacial acetic acid (CH₃COOH).

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

11.4 *Cupric Sulfate Solution* (0.1 M)—Dissolve 25 g of CuSO₄ · 5H₂O in distilled water and dilute to 1 L.

11.5 *Disodium Ethylenediaminetetracetate Dihydrate* (0.05 M) (EDTA solution)⁶—Dissolve 18.6 g of the salt in distilled water and dilute to 1 L. Standardize the solution as follows: Transfer 25 mL of lead standard (11.14) to a 400-mL beaker. Add concentrated ammonium hydroxide (11.1) dropwise until a permanent precipitate just forms. Add 25 mL of acid ammonium acetate (11.3), dilute to 200 mL, heat to boiling, add 4 drops of copper EDTA (11.7) and 12 drops of PAN (11.13) and titrate with the EDTA to a clear yellow.

$$1 \text{ mL Na}_2 \text{ EDTA} = 0.2790 / V \text{ g PbO}$$

where:

V = EDTA required for titration, mL

g = lead oxide, g, and

⁶ The standardized solution may also be purchased from Corco Chemical Corp. Catalog No.—Special.