



Designation: D1844 – 86 (Reapproved 2020)

Standard Test Methods for Chemical Analysis of Basic Lead Silicochromate¹

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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 D1648).

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

1.5 *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.*

1.6 *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.*

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. Referenced Documents

2.1 ASTM Standards:²

- D185 Test Methods for Coarse Particles in Pigments
- D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments
- D281 Test Method for Oil Absorption of Pigments by Spatula Rub-out
- D387 Test Method for Color and Strength of Chromatic Pigments with a Mechanical Muller
- D1193 Specification for Reagent Water
- D1648 Specification for Basic Lead Silicochromate Pigment
- D2371 Test Method for Pigment Content of Solvent-Reducible Paints

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.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.

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

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 *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. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

5. Preparation of Sample

5.1 Thoroughly mix liquid coatings and separate in accordance with Test Method **D2371** 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.

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).

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.

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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 L.

11.5 *Disodium Ethylenediaminetetraacetate Dihydrate (0.05 M) (EDTA solution)*⁴—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

$0.05 \text{ M} \times 0.22321 = 0.01116 \text{ g PbO}$ in 1 mL of lead standard (11.14).

$25 \text{ mL} \times 0.05 \text{ M} \times 0.22321 \text{ g/mmol} = 0.2790 \text{ g PbO}$ in 25 mL of lead standard (11.14).

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

11.7 *Copper-EDTA Solution*—Mix equivalent amounts of cupric sulfate solution (11.4) and EDTA solution (11.5) and store in a dropping bottle. The cupric sulfate EDTA equivalence may be determined as follows: Pipet 10 mL of cupric sulfate into a beaker, add concentrated ammonium hydroxide dropwise until the precipitate which forms just redissolves. Dilute to 200 mL with water, add two Murexide indicator tablets, and titrate immediately with EDTA to a color change from yellow to purple.

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

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

11.10 *Hydrogen Sulfide (H_2S)*—Cylinder. Handle and use in a hood.

11.11 *Hydrogen Sulfide Wash Solution*—Add 10 mL of HCl (sp gr 1.19) to 1 L of water and saturate with H_2S .

11.12 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

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

11.14 *Primary Standard (0.05 M lead nitrate)*—Dissolve 16.5615 g of reagent grade lead nitrate in distilled water and dilute to 1 L.

$$1 \text{ mL} = 0.01116 \text{ g PbO}$$

⁴ The standardized solution may also be purchased from Corco Chemical Corp. Catalog No.—Special.

11.15 *Sulfuric Acid (1 + 1)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) with 1 volume of water.

12. Procedure

12.1 Dissolve 1 g of pigment in accordance with 8.1 and 8.2.

12.2 Cool, so that the addition of 25 mL of water does not cause excessive splattering of the sulfuric acid; the solution at this point should be water white. Add ammonium hydroxide (sp gr 0.90) until the pH of the solution is 5 to 5.5 (as indicated by pH paper). Add 50 mL of acid ammonium acetate (11.3), boil 5 min, dilute to 200 mL with water, heat to boiling, add 4 drops of copper-EDTA (11.7) and 12 drops of PAN (11.13) and titrate while hot with standard EDTA to a clear yellow.

13. Calculation

13.1 Calculate the percent lead oxide as follows:

$$\text{PbO, \%} = \frac{V \times L \times 100}{S}$$

where:

V = EDTA required for titration, mL,

L = lead equivalent of EDTA solution, and

S = specimen weight, g.

14. Precision and Bias

14.1 On the basis of an interlaboratory study of the method in which operators in three laboratories analyzed two paints containing basic lead silicochromate with iron oxide the following criteria should be used for judging the acceptability of the results at the 95 % confidence level:

14.1.1 *Repeatability*—Two results, each the mean of duplicate determinations obtained by the same operator should be considered suspect if they differ by more than the following:

Percent Absolute PbO	
28 %	0.20
45 %	0.30

14.1.2 *Reproducibility*—A realistic range could not be established for results between laboratories because of the limited number of participating laboratories.

14.1.3 *Bias*—A bias statement could not be established because of the limited number of participating laboratories.

CHROMIUM TRIOXIDE

15. Interference

15.1 Soluble Fe^{+3} will cause high results. See Section 20.

16. Reagents

16.1 *Potassium Dichromate, Standard Solution (0.1 N)*—Weigh 4.904 g of dried potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), dissolve it in water, and dilute to 1 L with water in a volumetric flask.

16.2 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of potassium iodide (KI) in water and dilute to 1 L.

16.3 *Hydrochloric Acid Mixture*—Saturate water with NaCl (about 350 g/L). To each litre of this solution add 150 mL of water and 100 mL of concentrated HCl (sp gr 1.19).

16.4 *Sodium Thiosulfate Solution (0.1 N)*—Dissolve 24.8 g of reagent grade $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in recently boiled water and dilute to 1 L with additional recently boiled water. To standardize, pipet 25 mL of the standard potassium dichromate solution (exactly 0.1000 *N*) into a 250-mL Erlenmeyer flask. Add 100 mL of water, 15 mL of potassium iodide solution, and 15 mL of concentrated hydrochloric acid (sp gr 1.19). Titrate the liberated iodine with sodium thiosulfate solution until the reddish-brown color becomes quite faint. Add 5 mL of starch solution and continue the titration dropwise until the blue color changes to a pale green. Calculate the normality of the sodium thiosulfate solution as follows:

$$N = \frac{2.5000}{M}$$

where:

N = normality, and

M = sodium thiosulfate solution, mL,

16.5 *Starch Indicator Solution*—Make a homogeneous paste of 10 g of soluble starch in cold water. Add to this 1 L of boiling water, stir rapidly, and cool. Salicylic acid (1.25 g/L) may be added to preserve the indicator. If long storage is required, the solution should be kept in a refrigerator at 4 to 10°C (40 to 50°F). Prepare fresh indicator when the end point of the titration from blue to colorless or blue to light green fails to be sharp.

17. Procedure

17.1 Weigh to 0.1 mg about 1 g of sample into a 500-mL Erlenmeyer flask. Add 100 mL of NaCl-HCl solution and dissolve the sample without heat, keeping the solution cold. (Silica will not dissolve, but it does not interfere with the analysis.) Add 10 mL of KI solution and titrate with 0.1 *N* sodium thiosulfate solution until the reddish-brown color is almost gone. Add 5 mL of starch solution and titrate slowly, dropwise, until the blue color changes to a light green.

18. Calculation

18.1 Calculate the percent of chromium trioxide (CrO_3) as follows:

$$\text{CrO}_3, \% = [(V_1 N \times 0.03334) / S_2] \times 100$$

where:

*V*₁ = sodium thiosulfate solution required for titration of the specimen, mL

N = normality of the sodium thiosulfate solution,

*S*₁ = sample used, g, and

$$\begin{aligned} &+ 6 \\ &\text{CrO}_3 \rightarrow \text{Cr}^{+3} \\ &\text{milliequivalent weight} \\ &= \frac{\text{molecular weight (CrO}_3\text{)}}{1000 \times 3 \text{ (valence)}} \\ &= \frac{99.99}{1000 \times 3} = 0.03334 \end{aligned} \quad (1)$$

ALTERNATIVE METHOD FOR CHROMIUM TRIOXIDE

19. Scope

19.1 This test method determines total chromium as chromium trioxide. Iron oxide interference is masked by the use of EDTA. This procedure is not applicable when chromium oxide green (Cr_2O_3) is present. This test method is limited to basic lead silicochromate pigments with or without iron oxide.

19.2 The perchloric acid is employed as an oxidizing agent to ensure complete oxidation of any reduced chromium. When perchloric acid is used, concentrated nitric acid must also be used. The use of a perchloric acid hood is optional since the specimen is covered with a watch glass and is being oxidized, not wet ashed.

20. Reagents

20.1 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

20.2 *Disodium Ethylenediaminetetracetate Dihydrate (0.05 M) (EDTA)*—Dissolve 18.6 g of the reagent grade salt in distilled water and dilute to 1 L. See 11.5 for standardization.

20.3 *Hydrochloric Acid Mixture*—See 16.3.

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

20.5 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

20.6 *Perchloric Acid (sp gr 1.67)*—Concentrated perchloric acid (HClO_4).

20.7 *Potassium Dichromate, Standard Solution (0.1 N)*—See 16.1.

20.8 *Potassium Iodide Solution (150 g/Litre)*—See 16.2.

20.9 *Sodium Thiosulfate Solution (0.1 N)*—See 16.4.

20.10 *Starch Indicator Solution*—See 16.5.

21. Procedure

21.1 Transfer 0.5 g of pigment to a 500-mL high-silica Erlenmeyer flask.⁵ Add 10 mL of nitric acid (sp gr 1.42), and 10 mL of perchloric acid (sp gr 1.67) and cover with a watch glass. Evaporate to fumes (flask will fill with white vapor) of perchloric acid, cool, add 15 mL of water, and evaporate to fumes. Continue fuming for 15 to 20 min (the specimen should be red-orange color). Cool immediately by placing the flask in a cold water bath.

21.2 Wash down the cover glass and sides of the flask with water. Add 50 mL of HCl mixture and 50 mL of 0.05 *M* EDTA solution. Adjust to pH 8 (determined with pH paper) with ammonium hydroxide (sp gr 0.90) and add 50 mL of HCl mixture (16.3). Cool the flask to 20 to 25°C, add 10 mL of potassium iodide solution, 10 mL of starch solution, and titrate immediately with standard sodium thiosulfate solution to a

⁵ Vycor has been found suitable for this purpose.