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Standard Test Methods for Chemical Analysis of Basic Lead Silicochromate[1]

This standard is issued under the fixed designation D1844; 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 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 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]

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.

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.

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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] *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 (NH_4OH).

7.3 *Ammonium Acetate, Acid Solution*—To 300 mL of water add an equal volume of NH_4OH. 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 (H_2S)*—Handle and use H_2S in hood.

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

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

7.9 *Potassium Dichromate Solution (saturated)*—Prepare a saturated solution of potassium dichromate ($K_2Cr_2O_7$) in water.

7.10 *Sulfuric Acid (1 + 1)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, 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 HNO_3 and 10 mL of HF. Cautiously evaporate to dryness on a steam bath. Repeat the addition of HNO_3 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 HNO_3, warm gently, and transfer the residue to a 400-mL beaker using a policeman. Neutralize with NH_4OH, 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 H_2S 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 H_2S. Transfer the paper and precipitate to the original beaker, add 25 mL of HNO_3, boil until the residue is white, then add 10 mL of H_2SO_4 (1 + 1). Destroy the organic material by evaporating the solution to dense white fumes, making further additions of HNO_3 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 H_2SO_4 (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 $K_2Cr_2O_7$ 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 ($PbCrO_4$) 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 $PbCrO_4$ 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 LEADOXIDE—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 (NH_4OH).

11.2 *Glacial Acetic Acid (min 99.7 %)*—Concentrated glacial acetic acid (CH_3COOH).

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 $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 L.

11.5 *Disodium Ethylenediaminetetracetate 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,

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

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 M × 0.22321 = 0.01116 g PbO in 1 mL of lead standard (11.14).

25 mL × 0.05 M × 0.22321g/mmol = 0.2790 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.

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

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 ($K_2Cr_2O_7$), 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 $Na_2S_2O_3{\cdot}5H_2O$ 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:

$$CrO_3,\ \% = \left[(V_1 N \times 0.03334)/S_2 \right] \times 100$$

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

$$\overset{+6}{CrO_3} \rightarrow Cr^{+3} \qquad (1)$$

milliequivalent weight

$$= \frac{\text{molecular weight } (CrO_3)}{1000 \times 3 \text{ (valence)}}$$

$$= \frac{99.99}{1000 \times 3} = 0.03334$$

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 sharp change in the starch indicator. (The final solution color may be lavender or green depending on the composition of the sample).

21.3 Add 2 to 3 mL of HF, (20.4) stir for ½ min and if the indicator changes color titrate to the endpoint.

22. Calculation

22.1 Calculate the percent chromium trioxide (CrO_3) as follows:

$$CrO_3,\ \% = \left[(V_2 N_1 \times 0.03334)/S_3 \right] \times 100$$

where:

V_2 = sodium thiosulfate solution required for titration of the specimen, g,
N_1 = normality of the sodium thiosulfate solution, and
S_3 = sample used, g.

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[5] Vycor has been found suitable for this purpose.

23. Precision and Bias

23.1 On the basis of an interlaboratory study of this test 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.

23.1.1 *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 CrO_3
3 % CrO_3	0.15
5 % CrO_3	0.40

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

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

SILICA

24. Apparatus

24.1 *Platinum Crucible.*

25. Reagents

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

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

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

25.4 *Nitric Acid (1 + 19)*—Mix 1 volume of concentrated HNO_3 (sp gr 1.42) with 19 volumes of water.

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

25.6 *Sulfuric Acid (1 + 4)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84)[4] with 4 volumes of water.

26. Procedure

26.1 Weigh 0.5 g of pigment and transfer to a 400-mL beaker. Add 10 mL each of HCl (sp gr 1.19) and HNO_3 (sp gr 1.42). Warm slightly, if necessary, to dissolve the chromate. Add 50 mL of $HClO_4$ and fume for 15 to 20 min. Wash the sides of the beaker down with 30 to 40 mL of water, evaporate, and fume for 10 min. Cool and dilute to 200 mL with water. Filter through a double acid-washed quantitative paper and wash eight times with hot water, once with HNO_3 (1 + 19) and finally again with hot water.

26.2 Dry and ignite the paper and precipitate in a platinum crucible. Cool in a desiccator and weigh the crucible and contents. To the crucible add 2 drops of H_2SO_4 (1 + 4) and 15 mL of HF. Evaporate cautiously on a hot plate and ignite at 1000°C for approximately 5 min. Cool in a desiccator and weigh to constant weight.

27. Calculation

27.1 Calculate the percent of silica (SiO_2) as follows:

$$\mathrm{SiO}_2, \% = \left[(W_1 - W_2)/S_4\right] \times 100$$

where:

W_1 = weight of crucible and contents before HF treatment, g,

W_2 = weight of crucible and contents after HF treatment, g, and

S_4 = weight of sample used, g.

MOISTURE AND OTHER VOLATILE MATTER

28. Procedure

28.1 Determine moisture and other volatile matter in accordance with Method A of Test Methods D280.

COARSE PARTICLES

29. Procedure

29.1 Determine the percent coarse particles in the pigment as received in accordance with Test Methods D185.

OIL ABSORPTION

30. Procedure

30.1 Determine the oil absorption of the pigment in accordance with Test Method D281.

MASS COLOR AND TINTING STRENGTH

31. Procedure

31.1 Determine the mass color and tinting strength in accordance with Test Method D387.

32. Precision and Bias

32.1 Precision and bias have not been determined.

33. Keywords

33.1 basic lead silicochromate; chromium in basic lead silicochromate; lead in basic lead silicochromate; lead oxide; pigment; silica in basic lead silicochromate

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