Designation: D1301 – 91 (Reapproved 2014)

Standard Test Methods for Chemical Analysis of White Lead Pigments[1]

This standard is issued under the fixed designation D1301; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover procedures for the chemical analysis of basic carbonate white lead and basic sulfate white lead.

NOTE 1—If it is necessary to separate these pigments from others, refer to Practice D215.

1.2 The analytical procedures appear in the following order:

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

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:*[2]

C25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime

D185 Test Methods for Coarse Particles in Pigments

D215 Practice for the Chemical Analysis of White Linseed Oil Paints (Withdrawn 2005)[3]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

D2371 Test Method for Pigment Content of Solvent-Reducible Paints

D2372 Practice for Separation of Vehicle From Solvent-Reducible Paints

D3280 Test Methods for Analysis of White Zinc Pigments

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

3. Significance and Use

3.1 These test methods are suitable for determining the level of purity and for determining the levels of various impurities. They may be used to establish compliance with specification requirements.

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society,

[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.

Current edition approved Dec. 1, 2014. Published December 2014. Originally approved in 1953. Last previous edition approved in 2008 as D1301 – 91 (2008). DOI: 10.1520/D1301-91R14.

[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.

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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

4.3 *Concentration of Reagents:*

4.3.1 *Concentrated Acids and Ammonium Hydroxide*—When acids and ammonium hydroxide are specified by name or chemical formula only, it shall be understood that concentrated reagents of the following specific gravities or concentrations are intended:

Acetic acid, CH_3COOH	99.5 %
Hydrochloric acid, HCl	sp gr 1.19
Hydrofluoric acid, HF	48 %
Nitric acid, HNO_3	sp gr 1.42
Sulfuric acid, H_2SO_4	sp gr 1.84
Ammonium hydroxide, NH_4OH	sp gr 0.90

The desired specific gravities or concentrations of all other concentrated acids are stated whenever they are specified. **Warning**—See Section 5.

4.3.2 *Diluted Acids and Ammonium Hydroxide*—Concentrations of diluted acids and ammonium hydroxide, except when standardized, are specified as a ratio stating the number of volumes of concentrated reagent to be diluted with a given number of volumes of water, as in the following example: HCl (1 + 99) means 1 volume of concentrated HCl (sp gr 1.19) diluted with 99 volumes of water.

5. Hazards

5.1 The concentrated acids bases and other reagents used in these test methods can be dangerous. Check their Material Safety Data Sheets, (MSDS) before use.

6. Preparation of Sample

6.1 Grind dry pigments, if lumpy or not finely ground, to a fine powder for analysis. Large samples may be thoroughly mixed and a representative portion taken and powdered if lumpy or not finely ground. Mix the sample in all cases thoroughly and comminute before taking specimens for analysis.

6.2 In cases of pastes in oil, extract the oil from the pigment as described in Test Method D2371 or Practice D2372, but without straining.

6.3 Dry pigments separated from paints or pastes in oil in an oven at 95 to 98°C (203 to 210°F) for 2 h, grind to a fine powder, pass through a No. 80 (180-µm) sieve (Note 2) to remove skins, and mix thoroughly. Such pigments, after weighing, should be moistened with a little ethyl alcohol (95 %) before adding reagents for analysis.

NOTE 2—Detailed requirements for this sieve are given in Specification E11.

6.4 Preserve all samples in stoppered bottles or containers.

BASIC CARBONATE WHITE LEAD

7. Small Amounts of Iron

7.1 *Reagents:*

7.1.1 *Ammonium Hydroxide* (sp gr 0.90). **Warning**—See 5.1.

7.1.2 *Hydrofluoric Acid* (48 %). **Warning**—See 5.1.

7.1.3 *Nitric Acid* (sp gr 1.42). **Warning**—See 5.1.

7.1.4 *Sulfuric Acid* (sp gr 1.84). **Warning**—See 5.1.

7.2 *Procedure:*

7.2.1 Weigh to 10 mg about 1 g of specimen into a 400-mL beaker. Treat the sample with 10 mL of HNO_3(1 + 1) and dilute to about 200 mL with water. If insoluble matter remains following treatment with HNO_3 and dilution, filter and wash the residue with hot water until lead free. Evaporate the filtrate and washings to about 200 mL. Add 20 mL of H_2SO_4 (1 + 1) to precipitate the bulk of the lead (it is unnecessary to evaporate down). Cool, filter, and wash with diluted H_2SO_4 (1 + 99). Save the precipitate for determination of total lead (Section 8).

7.2.2 Ignite the HNO_3-insoluble matter and treat with HF and H_2SO_4. Bring into solution, filter (any precipitate is probably $BaSO_4$), and add to the $PbSO_4$ filtrate.

7.2.3 Colorimetrically determine iron in the combined filtrates by the thiocyanate method,[5] using the same amounts of reagents in preparing the reference standards. If copper is present in the filtrate, as shown by the characteristic blue-green or yellow color, remove it by precipitating the iron with NH_4OH, filtering, washing, redissolving the $Fe(OH)_3$ in 10 mL of HNO_3 (1 + 1), and diluting to about 200 mL before proceeding with the thiocyanate method.

8. Total Lead

8.1 *Apparatus:*

8.1.1 *Gooch Crucible,* prepared prior to use.

8.2 *Reagents:*

8.2.1 *Acetic Acid (glacial)*—**Warning**—See 5.1.

8.2.2 *Ammonium Hydroxide (sp gr 0.90)*—**Warning**—See 5.1.

8.2.3 *Ethyl Alcohol (95 volume %)*—**Warning**—See 5.1.

8.2.4 *Potassium Dichromate Solution* (100 g $K_2Cr_2O_7$/L)—**Warning**—See 5.1.

8.3 *Procedure:*

8.3.1 Ignite the $PbSO_4$ precipitate and filter paper from 7.2.1 at or below 550°C (1020°F), and transfer the residue to a 400-mL beaker. (If preferred, a new 1-g specimen of pigment may be weighed to 10 mg into a 400-mL beaker. Proceed to 8.3.2.)

8.3.2 Moisten with water and add 5 mL of glacial acetic acid. Warm to dissolve the material and dilute to about 200 mL

[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.

[5] Described in Scott, *Standard Methods of Chemical Analysis*, Fifth Edition, D. Van Nostrand Co., New York, NY, 1939, p. 486.

with water. Neutralize the solution with NH_4OH and then make slightly acid with acetic acid, adding about 3 mL excess. Filter off any insoluble residue and wash thoroughly with hot water.

8.3.3 Unite the filtrate and washings, heat to boiling, and add 15 mL of $K_2Cr_2O_7$ solution. Stir and heat until the yellow precipitate assumes an orange color. Let settle and filter on a weighed Gooch crucible. Wash by decantation with hot water until the washings are colorless. Finally transfer all the precipitate from the beaker to the crucible and wash with ethyl alcohol (95 %). Dry at 105 ± 2°C (220 ± 4°F) for 1 h. Cool in a desiccator and weigh as $PbCrO_4$.

8.4 *Calculation:*

$$\text{PbO, \%} = (P \times 0.691/S) \times 100$$

where:

P = $PbCrO_4$ precipitate, g,
S = specimen, g, and
0.691 = $PbO/PbCrO_4$ = 223.19/323.18.

9. Moisture and Other Volatile Matter

9.1 *Procedure*—Determine moisture and other volatile matter in accordance with Method A of Test Methods D280.

10. Carbon Dioxide (Evolution Method)

10.1 *Apparatus*—Knorr type of CO_2 evolution apparatus with dropping funnel, condenser, and suitable purifying train.

NOTE 3—A description of a suitable purifying train, is found in the Carbon Dioxide Standard Method section of Test Methods C25.

10.2 *Reagent:*

10.2.1 *Nitric Acid* (1 + 19).

10.3 *Procedure*—Transfer about 2 g of the sample, weighed to 10 mg, to a clean, dry evolution flask. Connect the evolution flask to the absorption train, which previously has been flushed free of any CO_2, and add 100 mL of HNO_3, (1 + 19) through a separatory funnel. When all of the HNO_3 has been introduced into the flask, close the stopcock from the separatory funnel. Heat the solution in the flask to gentle boiling and boil for 5 min. Turn off the heat and aspirate CO_2 free air through the system for 20 min. Remove the absorbing tube from the system, seal, cool in a desiccator, and weigh. The increase in weight is CO_2.

10.4 *Calculation*—Calculate the percent of carbon dioxide as follows:

$$CO_2, \% = (C_1/S_1) \times 100$$

where:

C_1 = CO_2, g, and
S_1 = specimen, g.

11. Carbon Dioxide and Combined Water (Combustion Method)

11.1 *Apparatus—Combustion Train,* consisting of the following parts connected in the order specified; tank of purified compressed nitrogen, purifying jars including a CO_2 absorption jar, drying tube, combustion tube, tube furnace provided with suitable controls to maintain the temperature from 450 to 550°C (840 to 1020°F), absorption bulb for water, and an absorption bulb for CO_2.

11.2 *Procedure:*

11.2.1 Heat the furnace, without the combustion tube, from 450 to 550°C (840 to 1022°F). Connect the combustion tube beside the furnace, connect the absorption tubes to the nitrogen supply, and pass a slow stream of nitrogen (about 30 mL/min) through them, to clear out any residual moisture and CO_2. Accurately weigh the absorption bulbs and reconnect them in the train. Transfer 1 g of the specimen, weighed to 10 mg, to a combustion boat that has been previously ignited and cooled.

11.2.2 With the nitrogen still flowing, disconnect the train and place the boat containing the specimen in the middle of the tube with the aid of a hooked wire. Flush the combustion tube thoroughly with nitrogen and reconnect with the train. Place the tube in the furnace.

11.2.3 Continue the combustion for 30 min, or until the water that condenses in the inlet arm of the first absorption bulb has been completely swept into the bulb. Disconnect the absorption bulbs from the combustion tube, after closing all stopcocks, place in a desiccator to cool, and then weigh.

11.3 *Calculation:*

$$\text{Carbon dioxide, \%} = 100 \times C_1$$

$$\text{Combined water, \%} = 100\,W_1 - M$$

$$\text{Combined water as Pb(OH)}_2\text{, \%} = (100\,W_1 - M) \times 13.39$$

where:

C_1 = CO_2, g,
W_1 = total water, g,
M = free moisture, %, and
13.39 = $Pb(OH)_2/H_2O$ = 241.20/18.015.

12. Lead Carbonate

12.1 *Calculation*—Calculate the percent of $PbCO_3$ from the CO_2 content, as follows:

$$PbCO_3, \% = C_1 \times 6.071/S_2 \times 100$$

where:

C_1 = CO_2 (10.4 or 11.3), g,
S_2 = specimen weight used in the CO_2 determination, g, and
6.071 = $PbCO_3/CO_2$ = 267.20/44.01.

13. Total Matter Insoluble in Acetic Acid

13.1 *Apparatus—Gooch Crucible,* prepared and weighed prior to use.

13.2 *Reagent—Acetic Acid* (3 + 2).

13.3 *Procedure*—Transfer 10 g of the sample, weighed to 10 mg, to a 250-mL beaker and add 40 mL of acetic acid (2 + 3). Heat until solution is complete and filter through a previously prepared and weighed Gooch crucible. Wash thoroughly with hot water, dry at 105 ± 2°C (220 ± 4°F) for 1 h, cool, and weigh.

13.4 *Calculation*—Calculate the percent of total matter insoluble in acetic acid as:

$$(R/S_3) \times 100$$

where:

R = residue, g, and
S_3 = specimen, g.

14. Total Matter Insoluble in Acid Ammonium Acetate

14.1 *Apparatus—Gooch Crucible,* prepared and weighed prior to use.

14.2 *Reagent—Acid Ammonium Acetate Solution*—Mix 150 mL of acetic acid (3 + 2) with 100 mL of water and then with 95 mL of NH_4OH (sp gr 0.90).

14.3 *Procedure*—Transfer about 10 g of the sample, weighed to 10 mg, to a 250-mL beaker. Add 40 mL of acid ammonium acetate solution and heat until solution is complete. Filter through a previously prepared and weighed Gooch crucible and wash thoroughly with hot water. Dry at 105 to 110°C for 1 h, cool, and weigh.

14.4 *Calculation*—Calculate the percent of total matter insoluble in acid ammonium acetate as:

$$(R/S_4) \times 100$$

where:

R_1 = residue, g, and
S_4 = specimen, g.

15. Total Impurities Other Than Moisture

15.1 *Calculations:*

15.1.1 Calculate the percent of total impurities other than moisture as:

$$100 - (L + C + H + M)$$

where:

L = PbO % (8.4),
C = CO_2 % (10.4 or 11.3),
H = combined water, % (11.3), and
M = free moisture, % (9.1).

15.1.2 In the case of extracted pigments where direct determination of combined water cannot be made conveniently, calculate the impurities other than moisture as: 100 (L + 1.205 D + M) where L, D, are as defined in 15.1.1 and 1.025 = 2 CO_2 + H_2O/2 CO_2 = 106.035/88.02.

16. Coarse Particles

16.1 *Procedure*—Determine coarse particles in accordance with Test Methods D185.

BASIC SULFATE WHITE LEAD

17. Small Amounts of Iron

17.1 *Procedure*—Determine small amounts of iron in accordance with Section 7.

18. Total Lead

18.1 *Procedure*—Determine total lead in accordance with Section 88.

19. Moisture and Other Volatile Matter

19.1 *Procedure*—Determine moisture and other volatile matter in accordance with Method A of Test Methods D280.

20. Total Sulfate

20.1 *Apparatus—Gooch Crucible,* ignited and weighed prior to use.

20.2 *Reagents:*

20.2.1 *Barium Chloride Solution (100 g $BaCl_2$/L)*—Dissolve 117 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 L).

20.2.2 *Bromine Water* (saturated).

20.2.3 *Hydrochloric Acid* (1+1).

20.2.4 *Sodium Chloride.*

20.2.5 *Sodium Carbonate Solution* (saturated).

20.3 *Procedure:*

20.3.1 Transfer 0.625 g of the sample to a 400-mL beaker. Add 2 g of NaCl, 3 to 4 mL of bromine water, and 25 mL of HCl (1+1), and heat over a low flame until solution is complete. Dilute to 75 mL with water and bring to boiling to expel the bromine. Cool somewhat, but not enough for the $PbCl_2$ to separate, and then cautiously add, by means of a pipet, Na_2CO_3 solution until decidedly alkaline. Bring to boiling and transfer to a 250-mL volumetric flask. Cool to room temperature, dilute to the mark, and mix. Filter through a dry paper, discarding the first 15 to 20 mL of filtrate. Measure exactly 200 mL in a volumetric flask and transfer to a 600-mL beaker. The test solution will now be equivalent to 0.5 g of the original specimen.

20.3.2 Carefully add HCl (sp gr 1.19) from a pipet to the alkaline solution until the solution is neutral, and add 0.4 mL excess for each 100 mL of solution. Bring to boiling to expel the CO_2 and then add to the boiling solution, drop by drop, 20 to 25 mL of a $BaCl_2$ solution. Allow to stand in a warm place for at least 2 h. Filter on a previously ignited and weighed Gooch crucible or a fine-textured filter paper and wash with hot water. Dry and ignite. Cool, and weigh as $BaSO_4$.

20.4 *Calculations:*

$$\text{Total sulfate as } SO_3\,\% = 68.6 \times P$$

$$\text{Total sulfate as } PbSO_4\,\% = 259.8 \times P$$

where:

P = $BaSO_4$ precipitate, g.
68.6 = $SO_3/BaSO_4 \times 100/0.5 = 80.06/233.40 \times 200$
259.8 = $PbSO_4/BaSO_4 \times 100/0.5 = 303.25/233.40$

21. Zinc Oxide

21.1 *Procedure*—Determine zinc oxide in accordance with Test Methods D3280.

22. Basic Lead Oxide

22.1 *Calculation*—Calculate the percent of basic lead oxide as follows:

$$\text{Basic PbO, \%} = L = Su_1(0.736)$$

where:

L = total lead as PbO, % (Section 18),
Su_1 = total sulfate as $PbSO_4$, % (20.4), and
0.736 = $PbO/PbSO_4 = 233.19/303.25$.

23. Total Impurities

23.1 *Calculation*—Calculate the percent of total impurities as follows:

$$\text{Total impurities, \%} = 100 - \left(L + Su_2 + Z\right)$$

where:

L = total lead as PbO, % (Section 18),
Su_2 = total sulfate as SO_3, % (20.4), and
Z = zinc oxide, % (Section 21).

24. Coarse Particles

24.1 *Procedure*—Determine coarse particles in accordance with Test Methods D185.

PRECISION

25. Precision

25.1 Data are not available to determine the precision of these test methods. There are no plans at present to obtain such data. The test methods have been in use for many years and are considered acceptable.

26. Keywords

26.1 ammonium acetate soluble; basic carbonate; basic lead oxide pigment; basic sulfate white lead; carbon dioxide; chemical analysis; lead carbonate pigment ; pigment; white lead; white lead pigment