Standard Test Methods for Chemical Analysis of Acid Copper Chromate[1]

This standard is issued under the fixed designation D 1627; 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 solid acid copper chromate and solutions of this material.

1.1.1 Test Method D 38 covers the sampling of wood preservatives prior to testing.

1.2 The analytical procedures appear in the following order:

	Sections
Copper (calculated as CuO)	7 to 10
Hexavalent chromium (calculated as CrO_3)	11 to 13
pH of solution	14

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:*

D 38 Test Methods for Sampling Wood Preservatives Prior to Testing[2]

D 1003 Test Method for Haze and Luminous Transmittance of Transparent Plastics[3]

D 1035 Test Methods for Chemical Analysis of Fluor-Chrome-Arsenate-Phenol[2]

D 1193 Specification for Reagent Water[4]

D 1326 Methods for Chemical Analysis of Ammoniacal Copper Arsenate[2]

D 1624 Specification for Acid Copper Chromate[2]

D 1628 Test Methods for Chemical Analysis of Chromated Copper Arsenate[2]

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode[5]

2.2 *Other Standard:*

AWPA A2 Standard Methods for Analysis of Waterborne Preservatives and Fire-Retardant Formulations[6]

3. Summary of Test Methods

3.1 *Copper*—A measured sample is reacted with Hydrochloric Acid and Potassium Iodide to complex the copper ion. The solution is then titrated with a standard solution of Sodium Thiosulfate. The Copper is calculated as CuO.

3.2 *Chromium*—A diluted and chemically treated sample is reacted with an excess of Ferrous Ammonium Sulfate. The unreacted Ferrous Ammonium Sulfate is titrated with a standard solution of Potassium Dichromate to determine the consumed chromium. Hexavalent Chromium is calculated as CrO_3.

3.3 *pH*—The solution is measured for pH with a glass electrode.

4. Significance and Use

4.1 Acid copper chromate for use in the preservative treatment of wood must conform with Specification D 1624.

5. Purity of Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[7] 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

6. Sampling

6.1 When the material to be sampled is a water solution, it shall be mixed to ensure uniformity and the sample shall be at

---

[1] These test methods are under the jurisdiction of ASTM Committee D-7 on Wood and are the direct responsibility of Subcommittee D07.06 on Treatments for Wood Products.

Current edition approved July 15, 1994. Published September 1994. Originally published as D 1627 – 59. Last previous edition D 1627 – 87.

The analytical methods and sampling procedures are substantially the same as those given in the American Wood-Preservers' Association Standard Methods for Analysis of Water-Borne Preservatives and Fire-Retardant Formulations (A2 – 84). Acknowledgment is made to the American Wood-Preservers' Association for its development of the subject matter covered in this standard.

[2] *Annual Book of ASTM Standards*, Vol 04.10.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 15.05.

[6] Available from American Wood-Preservers' Assn., P.O. Box 286, Woodstock, MD 21163-0286.

[7] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

least a pint and preferably a quart. The sample shall be representative and taken by a “thief” or other device. The sample shall be collected and stored in properly closed containers of glass or other suitable material.

6.2 When the material to be sampled consists of solids, a sample at least 5 lb (2.3 kg) in weight shall be taken from various points in the container or containers so that a representative sample is obtained. It shall be kept in an airtight container to prevent changes in composition by reason of moisture absorption or loss or chemical action of the air.

6.3 The analytical procedures given in these methods specify samples containing between 0.1 and 1.0 g of the ingredient to be determined. If the sample is solid, unless it is dry and finely pulverized, it is preferable to weigh a larger sample than specified and dissolve this in a definite quantity of water from which aliquots containing the specified quantity may be taken for analysis. Prepared samples or solutions having a content of 10 to 20 g of solid preservative equivalent per litre are usually convenient. Samples of solution from working tanks or plant equipment shall be filtered at working temperature immediately on obtaining, and shall not be filtered at the time the analysis is performed. Should any precipitate or solid adhering to the container be present when the sample is analyzed, the solution and any such precipitate or solid shall be thoroughly intermixed before analysis in order to obtain a proper sample.

COPPER

NOTE 1—This procedure is essentially the same as the procedure for copper in Methods D 1326, and Test Methods D 1628.

7. Reagents

7.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide ($NH_4 \cdot OH$).

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

7.3 *Methanol*.

7.4 *Potassium Chlorate–Nitric Acid Mixture*—Dissolve 5 g of potassium chlorate ($KClO_3$) in 100 mL of concentrated nitric acid (HNO_3, sp gr 1.42). Prepare this solution just before use and do not save any surplus solution for use later.

7.5 *Potassium Dichromate* ($K_2Cr_2O_7$)—This reagent is used for standardization purposes only.

7.6 *Potassium Iodide Solution* (200 g/L)—Dissolve 200 g of potassium iodide (KI) in water and dilute to 1 L.

7.7 *Sodium Thiocyanate Solution* (200 g/L)—Dissolve 200 g of sodium thiocyanate (NaCNS) in water and dilute to 1 L.

7.8 *Sodium Thiosulfate*, *Standard Solution* (0.0500 N)—Dissolve 12.4103 g of dry but not effloresced sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) and 0.2 g of sodium carbonate ($Na_2 \cdot CO_3$) in water and dilute to 1 L. Sodium thiosulfate solution prepared as above is usually close enough to 0.0500 *N* and stable enough to give reasonable service. However, on standing, particularly at elevated laboratory temperatures, the titer of the solution may change. For referee work, therefore, it is desirable to standardize the solution as follows:

7.8.1 Weigh 0.1000 g of $K_2Cr_2O_7$ into a 150-mL glass-stoppered Erlenmeyer flask. Add 50 mL of water and 5 mL of HCl slowly with agitation. Cool to 20° C. Add 10 mL of KI solution and mix thoroughly by rotating the flask with the stopper in place. Titrate with the $Na_2 \cdot S_2O_3$ solution, adding 2 mL of starch solution just before the brownish color of the iodine disappears. Stop the titration when the color first changes from deep blue to green. Disregard any reappearance of the blue color.

7.8.2 Calculate the normality of the thiosulfate solution as follows:

$$\text{Normality} = 2.039/\text{m}L \text{ of } Na_2S_2O_3 \text{ solution} \tag{1}$$

7.9 *Starch Indicator Solution* (10 g/L)—Make a paste of 1 g of soluble starch in about 5 mL of water, dilute to 100 mL, and boil for 1 min with stirring. Cool and add 1 drop of chloroform. This solution is subject to decomposition, and fresh solution should be prepared if a dark blue color is not produced with a drop of tincture of iodine in 100 mL water on addition of a few drops of the starch indicator solution.

7.10 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

8. Procedure for Solid Preservative or New Solutions

8.1 Transfer a sample, containing the equivalent of about 0.11 g of copper oxide (CuO) to a 300-mL Erlenmeyer flask, and add 10 mL of water if the sample is in the solid form. Add 10 mL of HCl and a few glass beads.

8.2 Add 15 mL of methanol carefully, warm to boiling, and heat until all chromium is reduced, as evidenced by a clear bluish-green color with no yellow tinge.

8.3 Wash down the side of the flask with water, boil for 1 min, and neutralize cautiously with NH_4OH until a permanent precipitate just forms. Cool, add H_2SO_4 dropwise until the precipitate just dissolves. Boil down to a volume of 30 mL cool to 20°C, and dilute to 125 mL.

8.4 Add 10 mL of KI solution and 5 mL of NaCNS solution and mix thoroughly by rotating the flask. Titrate with 0.05 *N* $Na_2S_2O_3$ solution, adding 2 mL of starch solution just before the brownish color of the iodine disappears. Stop the titration when the color first changes from dark blue to light green. Disregard any reappearance of the blue color.

8.5 If poor end points or checks are obtained, this may be due to contaminating organic matter. Repeat the determination, using the procedure described in 9.

9. Procedure for Used Solutions Contaminated with Organic Matter

9.1 In used solutions, the accumulation of organic matter may interfere with the copper analysis, resulting in inconsistent titrations in the determination of copper. In such cases, the organic matter may be destroyed as follows: Place the sample in a 300-mL Erlenmeyer flask, add 10 mL of the $KClO_3$ HNO_3 mixture, and boil to dryness, with constant agitation. When dry, bake the residue over an open flame for about 1 min. Cool and add 20 mL of water and 10 mL of HCl. Boil to destroy excess chlorate and dissolve the salts.

9.2 Cool the solution and proceed in accordance with 8.2 to 8.5.

10. Calculation

10.1 Calculate the percentage of copper as CuO, as follows:

$$\mathrm{CuO}, \% = (7.96\,A \times B)/C \tag{2}$$

where:

A = sodium thiosulfate solution required for titration of the sample, mL.

B = normality of the sodium thiosulfate solution, and

C = sample used, g

HEXAVALENT CHROMIUM

NOTE 2—This procedure is essentially the same as the procedures for chromium in Methods D 1003, D 1035, and D 1628.

11. Reagents

11.1 *Barium Diphenylamine Sulfonate Indicator Solution* (2 g/L)—Dissolve 0.20 g of barium diphenylamine sulfonate in water and dilute to 100 mL.

11.2 *Ferrous Ammonium Sulfate Solution* (140 g/L)—Dissolve 140 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in 900 mL of water and 25 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84). Dilute to 1 L.

11.3 *Phosphoric Acid* (85 %)—Concentrated phosphoric acid (H_3PO_4).

11.4 *Potassium Dichromate, Standard Solution* (0.2000 *N*)—Dissolve 9.807 g of potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1 litre in a volumetric flask.

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

12. Procedure

12.1 Transfer a sample (Note 1), prepared in accordance with Section 4 and containing hexavalent chromium equivalent to about 0.17 g of CrO_3, to a 500-mL Erlenmeyer flask and dilute with water to about 200 mL.

NOTE 3—The analysis for chromium should be performed as soon as possible after sampling.

12.2 Add 3 mL of H_3PO_4 and 6 mL of H_2SO_4 (1 + 1) and stir the solution well. Pipet 25.0 mL of ferrous ammonium sulfate solution into the sample solution and add 10 drops of barium diphenylamine sulfonate indicator. Titrate with 0.2000 *N* $K_2Cr_2O_7$ solution to a deep purple or green end point.

12.3 *Blank*—Pipet 25.0 mL of the same ferrous ammonium sulfate solution as used in 10.2 into another 500-mL Erlenmeyer flask. Dilute with water to about 200 mL, add 3 mL of H_3PO_4 and 10 drops of barium diphenylamine sulfonate indicator, and titrate with 0.2000 *N* $K_2Cr_2O_7$ solution as described in 12.2. Ferrous ammonium sulfate solutions change strength quite rapidly; the blank determination should therefore be repeated at frequent intervals.

13. Calculation

13.1 Calculate the percentage of hexavalent chromium as CrO_3, as follows:

$$\mathrm{CrO_3}, \% = [0.6668\,(A - B)]/C \tag{3}$$

where:

A = 0.2000 *N* $K_2Cr_2O_7$ solution required for the blank, mL,

B = 0.2000 *N* $K_2Cr_2O_7$ solution required for titration of the sample, mL, and

C = sample used, g.

pH OF SOLUTION

14. Procedure

14.1 Determine the pH of the treating solution by means of the glass electrode method, in accordance with Test Method E 70, or by any other conventional method or procedure giving results agreeing within 0.1 pH of the value determined in accordance with Test Method E 70.

15. Precision and Bias

15.1 Data are presently not available to develop a precision and bias statement.

16. Keywords

16.1 acid copper chromate; chemical analysis