Designation: D 1628 – 94 (Reapproved 2000)

Standard Test Methods for Chemical Analysis of Chromated Copper Arsenate[1]

This standard is issued under the fixed designation D 1628; 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 chromated copper arsenate 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 occur in the following order:

	Sections
Pentavalent Arsenic (calculated as As_2O_5)	7-9
Copper (calculated as CuO)	10-13
Hexavalent Chromium (calculated as CrO_3)	14-16

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.* Specific precautionary statements are given in 8.2, 12.1.2, and in accordance with the safety precautions section of Test Method D 4278.

2. Referenced Documents

2.1 *ASTM Standards:*

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

D 1033 Methods of Chemical Analysis of Chromated Zinc Chloride[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 and Ammoniacal Copper Zinc Arsenate[2]

D 1625 Specification for Chromated Copper Arsenate[2]

D 1627 Methods for Chemical Analysis of Acid Copper Chromate[2]

D 4278 Test Method for Wet Ashing Procedure for Preparing Wood Samples for Inorganic Chemical Analysis[2]

3. Summary of Test Methods

3.1 Add 20 mL of tartaric acid solution to a 250-mL Erlenmeyer flask, then add 2 mL of the ACA concentrate. The resulting solution should become light blue-green. Twenty millilitres of sodium bicarbonate solution is then added and the solution will turn light blue. Two millilitres of the starch indicator is added. To this solution, one drop of iodine solution from a buret is added. If the solution turns a dark blue and remains, then the aeration is complete.

4. Significance and Use

4.1 These test methods test the completion of aeration which is used to convert trivalent arsenic to pentavalent arsenic.

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.[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.

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 least 0.45 L and preferably 0.9 L. 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.

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[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 D1628 – 59 T. Last previous edition D1628 – 90.

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 (A2-82). Acknowledgment is made to the American Wood-Preservers’ Association for its development of the subject matter covered in these test methods.

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

[3] Discontinued—See *1992 Annual Book of ASTM Standards*, Vol 04.09.

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

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

6.2 When the material to be sampled consists of solids, a sample at least 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 test 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 a 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.

ARSENIC

NOTE 1—This procedure is essentially the same as the procedure for arsenic Method D 1326.

7. Reagents

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

7.2 *Hypophosphorous Acid* (50 %)—Concentrated hypophosphorous acid ($H_3 PO_2$).

7.3 *Methyl Orange Indicator Solution* (0.1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 1 L.

7.4 *Potassium Bromate, Standard Solution* (0.1000 *N*)—Dissolve 2.784 g of potassium bromate ($KBrO_3$) in water and dilute to 1 L in a volumetric flask.

7.5 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid ($H_2 SO_4$).

8. Procedure

8.1 Transfer a measured portion of the sample containing arsenic equivalent to about 0.17 g of $As_2 O_5$ to a 250-mL wide-mouth Erlenmeyer flask and dilute with water to about 50 mL. Add 50 mL of HCl and 20 mL of $H_3 PO_2$, mix thoroughly, and warm the solution on a steam bath until a precipitate forms. Boil gently for about 15 min.

8.2 **Warning**—If the sample being analyzed is a wood sample digested with a perchloric acid mixture it now contains perchloric acid and a strong reducing agent, hypophosphorus acid. If it is evaporated too much, *it may explode with dangerous violence.* Do not boil longer than the specified time and cover the mouth of the Erlenmeyer flask with a small watchglass to minimize evaporation.

8.3 With the aid of suction, filter the hot solution, using a 10-mL Gooch crucible containing a mat of medium fiber, acid-washed asbestos, and washing the flask and precipitate thoroughly with water.

8.4 Place the crucible containing the precipitate in the flask in which the precipitation was carried out. Discard the filtrate. Pour 10 mL of $H_2 SO_4$ into the flask and, while agitating, heat over an open flame in a hood until dense white fumes are evolved.

8.5 Allow the flask and contents to cool, and then add 100 mL of water very slowly and carefully, especially at first, since heat is generated during this addition. Next, add 5 mL of HCl and 2 drops of methyl orange indicator solution and titrate immediately with 0.1000 *N* $KBrO_3$ solution. When the solution becomes colorless, the end point has been reached.

9. Calculation

9.1 Calculate the percentage of pentavalent arsenic, $As_2 O_5$, as follows:

$$As_2 O_5, \% = 0.5746\, A/B \quad (1)$$

where:

A = 0.1000 *N* $KBrO_3$ solution required for titration of the sample, mL, and

B = sample used, g.

COPPER

NOTE 2—This procedure is essentially the same as the procedure for copper in Test Methods D 1326 and D 1627.

10. Reagents

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

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

10.3 *Methanol.*

10.4 *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.

10.5 *Copper Foil or Shot.*

10.6 *Nitric Acid,* concentrated (sp gr 1.42).

10.7 *Urea Solution,* 5 %. Dissolve 5 g urea in 95 mL water.

10.8 *Acetic Acid,* glacial.

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

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

10.11 *Sodium Thiosulfate, Standard Solution* (0.1 N)—Dissolve 24.85 g of dry but not effloresced sodium thiosulfate ($Na_2 S_2 O_3 \cdot 5H_2 O$) and 1.0 g of sodium carbonate ($Na_2 \cdot CO_3$) in water and dilute to 1 L.

10.11.1 Sodium thiosulfate solution prepared in accordance with 10.11 is usually close enough to 0.1 *N* and stable enough to give reasonable service. However, on standing, particularly at elevated laboratory temperatures, the titer of the solution may change. Therefore it is desirable to standardize the solution.

10.12 For standardization of the 0.1 *N* sodium thiosulfate solution, dissolve in a 250-mL Erlenmeyer flask an accurately weighed portion of pure copper foil or shot (about 0.25 g) in 10 mL of concentrated nitric acid. Evaporate the solution until

about 3 to 4 mL remains. Cool. Wash down the sides of the flask with distilled water. Add 10 mL of 5 % urea solution and boil 3 min. Cool the solution to room temperature and add concentrated ammonium hydroxide cautiously until the solution just turns to a deep blue color. The use of a dropping bottle facilitates this step. Add 5 mL of glacial acetic acid, swirl, and wash down the sides of the flask with distilled water. Dilute to 50 mL with distilled water and cool to room temperature. Add 10 mL of 20 % potassium iodide solution, do not swirl, and 5 mL of 20 % sodium thiocyanate solution. Titrate with sodium thiosulfate solution. When about 20 mL of sodium thiosulfate have been added, swirl the flask and continue the titration until the solution color changes from dark brown to light tan. Add 5 mL of fresh starch indicator solution and continue the titration until the solution color just changes from blue to cream-white.

10.13 Calculate the standardization of the sodium thiosulfate as follows:

$$\text{Normality of sodium thiosulfate solution} = \frac{\text{grams copper} \times 15.74}{\text{mL titration}} \quad (2)$$

10.14 *Starch Indicator Solution*—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 of water on addition of a few drops of the starch indicator solution.

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

11. Procedure for Solid Preservative or New Solutions

11.1 Transfer a sample, containing the equivalent of about 0.2 g of 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.

11.2 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.

11.3 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.

11.4 Add 10 mL of KI solution and 5 mL of NaCNS solution and mix thoroughly by rotating the flask. Titrate with 0.1 *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.

11.5 If poor end points or checks are obtained, this may be due to contaminating organic matter. Repeat the determination, using the procedure described in Section 12.

12. Procedure for Used Solutions Contaminated with Organic Matter

12.1 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:

12.1.1 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.

12.1.2 **Warning**—If the sample being analyzed is a wood sample digested with a perchloric acid mixture, it now contains perchloric acid and a strong reducing agent, alcohol. If it is evaporated too much, *it may explode with dangerous violence*. Keep the Erlenmeyer flask covered and boil gently in 12.1.1 to minimize evaporation.

12.2 Cool the solution and proceed in accordance with 11.2-11.4.

13. Calculation

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

$$CuO, \% = (7.96A \times B)/C \quad (3)$$

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 3—This procedure is essentially the same as the procedures for chromium in Test Methods D 1033, D 1035, and D 1627.

14. Reagents

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

14.2 *Ferrous Ammonium Sulfate Solution* (50 g/L)—Dissolve 50 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.

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

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

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

15. Procedure

15.1 Transfer a sample (see Note 4), prepared in accordance with Section 6, 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 4—The analysis for chromium should be performed as soon as possible after sampling.

15.2 Add 3 mL of H_3PO_4 and 6 mL of H_2SO_4 (1+1) and stir the solution well. Pipet 10.0 mL of ferrous ammonium sulfate solution into the sample solution and add 10 drops of barium diphenylamine sulfonate indicator. Titrate immediately with 0.2000 *N* $K_2Cr_2O_7$ solution to a deep purple or deep green end point.

15.3 *Blank*—Pipet 10.0 mL of the same ferrous ammonium sulfate solution as used in 15.2 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 solution, and titrate with 0.2000 *N* $K_2Cr_2O_7$ solution as described in 15.2. Ferrous ammonium sulfate solutions change strength quite rapidly; the blank determination should therefore be repeated at frequent intervals.

16. Calculation

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

$$CrO_3, \% = [0.6668\ (A - B)/C] \quad (4)$$

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.

17. Precision and Bias

17.1 *Chromated Copper Arsenate in Solution*—The following statements and tables should be used to judge the acceptability of analysis on duplicate samples under the conditions following:

17.1.1 *Repeatability*—Duplicate single determination on the same sample by the same operator using the same equipment should not be suspect at the 95 % confidence level if they do not differ from one another by equal to or less than the limiting percentages shown in Table 1.

TABLE 1 Precision

Element	Expressed As Oxide	Solution Oxide Concentration Level,%	Limiting Percentages Repeatability	Limiting Percentages Reproducibility
Chromium		0 to 0.95	0.021	0.045
Chromium	CrO_3	0.96 to 2.50	0.027	0.040
Chromium		2.51 to 4.00	0.041	0.121
Copper		0 to 0.45	0.008	0.038
Copper	CuO	0.46 to 1.05	0.021	0.085
Copper		1.06 to 1.60	0.014	0.236
Arsenic		0 to 1.00	0.029	0.036
Arsenic	As_2O_5	1.01 to 2.20	0.020	0.050
Arsenic		2.21 to 3.00	0.071	0.330

17.1.2 *Reproducibility*—Duplicate single determinations on the same sample made by different operators in different laboratories should not be considered suspect at the 95 % confidence level if they do not differ from one another by equal to or less than the limiting percentages shown in Table 1.

18. Keywords

18.1 chemical analysis; chromated copper arsenate