



Designation: D 1326 – 94 (Reapproved 2000)

Standard Test Methods for Chemical Analysis of Ammoniacal Copper Arsenate and Ammoniacal Copper Zinc Arsenate^{1, 2}

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1. Scope

1.1 These test methods cover the determination of the chemical analysis of commercial solutions of ammoniacal copper arsenate.

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
Ammonium bicarbonate (calculated as carbonate)	20 to 22
Ammonia (calculated as anhydrous ammonia)	6 to 9
Arsenic (calculated as arsenic pentoxide)	10 to 11
Copper (calculated as copper oxide)	13 to 16
Zinc (calculated as zinc oxide)	17 to 19

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 Testing³

D 1193 Specification for Reagent Water⁴

D 1325 Specification for Ammoniacal Copper Zinc Arsenate³

D 3873 Test Method for Valency State of the Arsenic Component of Ammoniacal Copper Arsenate Solutions³

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.

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² The analytical methods and sampling procedures are essentially the same as those given in the American Wood-Preservers' Assn. Standard Methods for Analysis of Water-Borne Preservatives and Fire-Retardant Formulations (A2-91). Acknowledgment is made to the American Wood-Preservers' Association for its development of the subject matter covered in this test.

³ *Annual Book of ASTM Standards*, Vol 04.10.

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

2.2 AWPA Standard:

AWPA A2 Standard Methods for Analysis of Waterborne Preservatives and Fire-Retardant Formulations⁵

3. Summary of Test Methods

3.1 *Ammonia*—Ammonia is freed from a caustic solution of the sample by distillation and absorbed in a measured excess of sulfuric acid solution. The unreacted sulfuric acid solution is titrated with standardized NaOH solution to determine the ammonia reacted with sulfuric acid.

3.2 *Arsenic*—A diluted sample is acidified with hydrochloric and hypophosphorous acid to precipitate the arsenic. The arsenic is volatilized by heating in the presence of sulfuric acid, which is then diluted with water and titrated with a standard solution of potassium bromate. Arsenic is calculated as As_2O_5 .

3.3 *Copper*—A measured sample is dissolved in hydrochloric acid and reacted with 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.

3.4 *Zinc*—A diluted and chemically treated sample is treated with a standard solution of potassium ferrocyanide in the presence of an oxidation-reduction indicator (diphenylamine). The zinc is calculated as ZnO.

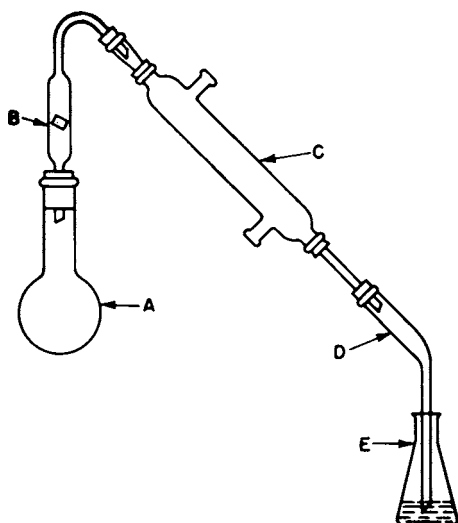
4. Significance and Use

4.1 Ammoniacal copper arsenate and ammoniacal copper zinc arsenate for use in the preservative treatment of wood must conform with Specification D 1325.

5. Purity of Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such

⁵ Available from American Wood-Preservers' Association, P.O. Box 286, Woodstock, MD 21163-0286.



A—Round-bottom flask, 500-mL
 B—Distillation trap.
 C—Condenser.
 D—Delivery tube.
 E—Erlenmeyer flask, 500-mL.

FIG. 1 Distillation Apparatus for Determination of Ammonia in Ammoniacal Copper Arsenate and Ammoniacal Copper Zinc Arsenate

specifications are available.⁶ Other grades shall only be used when 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 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

AMMONIA

6. Apparatus

6.1 A typical apparatus for the distillation of ammonia is shown in Fig. 1.

7. Reagents

7.1 *Methyl Purple or Methyl Red Indicator Solution*—Suitable prepared solutions of methyl purple can be purchased. To prepare the methyl red indicator solution, dissolve 0.1 g of methyl red in 50 mL of alcohol (90 %), dilute to 100 mL with water, and filter if necessary.

7.2 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of alcohol.

7.3 *Sodium Hydroxide Standard Solution (0.1 N)*—Dissolve 4 g of NaOH in CO₂-free water and dilute to 1 L with CO₂-free water. Standardize as follows: Place 2 0.8000-g portions of potassium acid phthalate (National Bureau of Standards standard sample No. 84) in volumetric flasks, and add 100 mL of

freshly boiled water and 2 drops of phenolphthalein indicator solution to each flask. Titrate with the NaOH solution to the appearance of a faint, persistent pink color. The titrations should agree within 0.1 mL; record the average. Calculate the normality of the NaOH solution as follows:

$$\text{Normality of NaOH solution} = 3.920/V \quad (1)$$

where V = mL of NaOH solution required.

7.4 *Sulfuric Acid, Standard (0.1 N)*—To 100 mL of water in a 1000-mL volumetric flask, add 3.3 mL of H₂SO₄ (sp gr 1.84); mix and cool to 20°C. Dilute to the mark with water. Standardize as follows: Pipet 25 mL of the H₂SO₄ solution into a 500-mL Erlenmeyer flask, and add 100 mL of water and 2 drops of phenolphthalein indicator solution. Titrate with the 0.1 N NaOH solution to the appearance of a faint, persistent pink color. Calculate the normality of the H₂SO₄ as follows:

$$\text{Normality of H}_2\text{SO}_4 = VN/25 \quad (2)$$

where:

V = NaOH solution required, mL, and

N = normality of the NaOH solution.

7.5 *Sodium Hydroxide Solution (100 g/L)*—Dissolve 100 g of NaOH in water and dilute to 1 L.

8. Procedure

8.1 Transfer a portion of the sample containing not more than 0.15 g of NH₃ (Note 1) to the 500-mL distillation flask. Dilute with water to a volume of about 200 mL. Add a few glass beads to prevent bumping. Add 20 mL of NaOH solution (100 g NaOH/L) and immediately close the flask with a rubber stopper through which a spray trap has been inserted. The spray trap shall previously have been connected to a vertical condenser. Place 100 mL of 0.1 N H₂SO₄ in a 400-mL beaker. Adjust the tip of the condenser so that it just dips into the H₂SO₄. Add 4 to 5 drops of methyl purple or methyl red indicator solution to the H₂SO₄.

NOTE 1—If this procedure is used for testing a solution of treating strength, use an accurately measured volume of the filtered solution equivalent to the appropriate amount of the element to be determined.

8.2 After making sure all the connections are airtight, commence heating the mixture of sample and NaOH solution. Distill slowly at first, and finally boil rather vigorously. Distill off about 150 mL of solution. Adjust the height of the beaker throughout the distillation so that the tip of the condenser is always near the surface of the liquid in the receiving vessel. If the indicator starts to turn color, add a measured amount of additional 0.1 N H₂SO₄. When distillation is complete, turn out the flame and lower the receiving vessel. Wash down the condenser tube and its tip into the receiver.

8.3 Titrate the excess acid with 0.1 N NaOH solution.

9. Calculation

9.1 Calculate the percentage of ammonia as NH₃, as follows:

$$\text{NH}_3, \% = [(AB - CD) \times 1.703]/E \quad (3)$$

⁶ *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.

where:

A = H_2SO_4 added to the receiving vessel, mL,

B = normality of the H_2SO_4 ,

C = NaOH solution used for titration of the excess H_2SO_4 , mL,

D = normality of the NaOH solution, and

E = sample used, g.

ARSENIC

10. Reagents

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

10.2 *Hypophosphorous Acid (50 %)*.

10.3 *Methyl Orange Indicator Solution*—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

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

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

11. Procedure

11.1 Transfer a portion of the sample containing arsenic equivalent to about 0.17 g As_2O_5 (see **Note 1**) 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_3PO_2 , mix thoroughly, and warm the solution on a steam bath until a precipitate forms. Boil gently for about 15 min. With the aid of suction, filter the hot solution through a 10-mL Gooch crucible containing a mat of medium fiber, acid-washed asbestos, washing the flask and precipitate thoroughly with water.

11.2 Place the crucible containing the precipitate in the flask in which the precipitation was carried out. Discard the filtrate. Pour 10 mL of H_2SO_4 into the flask and while agitating, heat over an open flame in a hood until dense white fumes are evolved. 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 and titrate immediately with KBrO_3 solution. When the solution becomes colorless, the end point has been reached.

12. Calculation

12.1 Calculate the percentage of arsenic as As_2O_5 , as follows:

$$\text{As}_2\text{O}_5, \% = 0.5746 A/B \quad (4)$$

where:

A = KBrO_3 solution required for titration of the sample, mL, and

B = sample used, g.

COPPER

13. Reagents

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

13.2 *Potassium Chlorate-Nitric Acid Mixture*—Dissolve 5 g of KClO_3 in 100 mL of HNO_3 (sp gr 1.42). Prepare this solution just before use and do not save any surplus for use later.

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

13.4 *Sodium Hydroxide Solution (100 g/L)*—Dissolve 100 g of NaOH in water and dilute to 1 L.

13.5 *Sodium Thiosulfate, Standard Solution (0.0500 N)*—Dissolve 12.4103 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in water and dilute to 1 L in a volumetric flask.

13.6 *Starch Indicator Solution*—Make a paste of 1 g of soluble starch in about 5 mL of water, add 100 mL of water, and boil for 1 min while stirring. Cool and add 1 drop of chloroform. This solution is subject to decomposition and fresh solution shall 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 drop of the starch indicator solution.

14. Procedure for New Solutions

14.1 Transfer a portion of the sample containing the equivalent of about 0.11 g CuO to a 300-mL Erlenmeyer flask, and add 10 mL of water and 10 mL of HCl (sp gr 1.19). Wash down the side of the flask with water, boil for 1 min, and neutralize with NaOH solution until a permanent precipitate just forms. Add HCl (sp gr 1.19) dropwise until the precipitate just dissolves. Cool to below 20°C. The solution volume should be 20 to 30 mL.

14.2 Add 10 mL of KI solution and mix thoroughly by rotating the flask. Titrate with 0.05 N $\text{Na}_2\text{S}_2\text{O}_3$ solution, adding 2 mL of starch solution just before the brownish color of the iodine disappears. Stop the titration when the color changes from dark blue to cream color.

14.3 If poor end points or checks are obtained in the titrations (12.2), repeat the determination following the procedure described in Section 13.

15. Procedure for Used Solutions Contaminated with Organic Matter

15.1 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 ion. When dry, bake the residue over an open flame for about 1 min. Cool, then add 20 mL water and 10 mL of HCl (sp gr 1.19). Warm, if necessary, to effect complete solution.

15.2 Cool the solution and proceed in accordance with Section 14, starting with the second sentence of 15.1.

16. Calculation

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

$$\text{CuO}, \% = (A/B) \times 7.96 \quad (5)$$