



Standard Test Method for Total Copper in Antifouling Paints¹

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1. Scope

1.1 This test method is for the analytical determination of copper in liquid samples of antifouling coatings. The procedure outlines in detail equipment, reagents, and necessary steps to satisfactorily determine the concentration of copper in paint. Conversion to specific copper compounds can be made by appropriate gravimetric factors.

1.2 The values stated in SI units are to be regarded as standard. The inch-pound units given in parenthesis are for information only.

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 283 Test Methods for Chemical Analysis of Cuprous Oxide and Copper Pigments²

3. Summary of Test Method

3.1 Samples of the paint are weighed into beakers and solvent is allowed to evaporate. Dry ashing is done at 600°C to destroy organic materials, followed by acid digestion. Solutions are diluted, filtered to remove insolubles and electrolyzed to deposit the copper onto platinum gauze. Recovered copper is determined as percentage of sample weight and calculated to original compound.

4. Significance and Use

4.1 This test method allows the accurate determination of copper content in formulated paints as a means of verifying composition (see Test Methods D 283).

5. Apparatus

5.1 *Pyrex Beakers*, tall-form, 400-mL with spout.

5.2 *Magnetic Stirrer* and TFE-fluorocarbon-coated stirring bar.

5.3 *D.C. Power Supply* to deliver approximately 3 V and approximately 2 A.

5.4 *Two Electrode Holders*.

5.5 *Platinum Gauze Electrodes*, cathode and anode.

5.6 *Glass Filter Funnels*.

5.7 *Hot Plate*.

5.8 *Analytical Balance*.

5.9 *Graduated Cylinders*.

6. Reagents and Materials

6.1 *Concentrated Nitric Acid* (HNO₃), reagent-grade.

6.2 *Perchloric Acid* (HClO₄), 69 to 72 %, reagent-grade.

6.3 *Deionized or Distilled Water*.

6.4 *Alcohol or Acetone*.

6.5 *Ammonium Sulfate*.

6.6 *Filter Paper, Glass Fiber*, approximately 1.5 μ m, of suitable diameter to fit funnel.

7. Procedure

7.1 Thoroughly mix the paint and place a U-shaped stirrer into the container and while stirring, transfer and accurately weight approximately 1 g into each of two tared 400-mL beakers.

7.2 Allow samples to dry overnight, vaporizing solvent.

7.3 Place beakers into a muffle furnace and dry ash at 600°C overnight to remove acid resistant organic matter.

7.4 In a laboratory hood, add 10 mL of concentrated nitric acid to each beaker to dissolve the copper-based ingredient, heating on a hot plate to dissolve sample. Boil for several minutes with watch glass in place to reflux acid.

7.5 Remove from hot plate and add 10 mL of perchloric acid, fume, and reflux on hot plate for 15 min. If insolubles remain, dilute to approximately 100 mL with water and filter through a glass fiber filter having approximately 1.5- μ m particle retention into a 400-mL tall-form beaker. If no insolubles are present, dilute directly to approximately 200 mL and continue as in 7.7.

7.6 Wash filter thoroughly to recover all soluble salts, diluting up to a volume of approximately 200 mL.

7.7 Add 1 mL HNO₃ and 1 g of ammonium sulfate to each collected sample, swirl to mix. Add a magnetic stirring bar to each beaker.

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.45 on Marine Solvents.

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² *Annual Book of ASTM Standards*, Vol 06.03.

7.8 Record tare weight of each clean, dry platinum gauze cylindrical cathode.

7.9 Follow the power source manual, set maximum amperage to 5.00, then adjust voltage to approximately 4 V.

7.10 Attach platinum cathode unit to negative electrode holder. Place anode in center of cathode and attach to positive electrode holder.

7.11 Immerse electrodes into the beaker containing the filtrate and washings, allow enough bottom clearance for stirring bar. Place magnetic stirring platform under beaker and adjust stirrer control to achieve moderate mixing.

7.12 Dilute with distilled water so that approximately 6.3 mm (¼ in.) of cathode is above solution level. Turn on power source, adjust voltage to approximately 3 V, if necessary.

7.13 Electrolyze for 2 h, copper will then deposit on platinum gauze cathode. Add water to cover cathode and container, electrolyzing for an additional 15 min.

7.14 With power on, swing stirrer platform away while holding beaker. Slowly lower beaker while washing cathode with deionized or distilled water from a wash bottle. Do not let cathode and anode touch each other.

7.15 Turn off power switch, quickly detach cathode, wash in water, then dip in acetone or alcohol. Place cathode in a 100°C oven to dry for approximately 15 min.

7.16 Remove cathode from oven, cool, weigh and record weight.

7.17 Clean cathode and anode in 1-1 nitric acid; wash with water, dip in alcohol or acetone and dry for re-use.

8. Calculation

8.1 Factor percent copper to copper compound used in paint (where Wt stands for weight), with appropriate gravimetric conversion factor as follows:

% Copper

$$= \frac{\text{Gross Wt of Plated Cathode, g} - \text{Tare Wt of Cathode, g}}{\text{Sample Wt, g}} \times 100 \quad (1)$$

9. Precision and Bias

9.1 *Precision*—Ten replicate samples of a representative cuprous oxide based antifouling paint were analyzed using this test method. Average value for copper converted to cuprous oxide was determined to be 38.82 % with a RSD of 0.43.

9.2 *Bias*—Has not been established. A round robin is planned.

10. Keywords

10.1 antifouling coatings; copper; cuprous oxide

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