



Designation: D 6442 – 03

Standard Test Method for Determination of Copper Release Rate From Antifouling Coating Systems in Artificial Seawater¹

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1. Scope

1.1 This test method covers the laboratory determination of the rate at which copper is released from an antifouling coating in synthetic seawater using graphite furnace atomic absorption spectrophotometry (GF-AAS).

1.2 The procedure contains the preparation steps for the leach rate determination of copper from antifouling paints including apparatus, reagents, holding tank conditions, and sampling point details. Analysis for the concentration of copper in seawater requires the accurate determination of copper at the low parts per billion (ppb) level. To detect and correct for reagent impurities, acceptable analytical precision standards are necessary. Therefore, the limit of quantitation for the analytical method should be 6 ppb or less. The method of choice for most commonly available instrument with the greatest sensitivity would be GF-AAS. This procedure is written to include necessary steps to isolate the copper from seawater, thereby increasing sensitivity and eliminating salts that interfere with the use of atomic absorption techniques.

1.3 Other analytical methods may be utilized with appropriate procedural changes, as needed, to accommodate selected specific methods. Such methods must meet the limit of quantitation (6 ppb) as presented in Section 13.

1.4 This test method has not yet been validated to reflect in-situ copper release rates for antifouling products and therefore should not, at present, be used in the process of generating environmental risk assessments. In-service release rates of antifouling (AF) coatings are expected to vary with natural variability in seawater chemistry, temperature, and hydrodynamic regime.

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

1.6 *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 appro-*

priate safety practices and to determine the applicability of regulatory limits prior to use. For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

- D 1005 Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers²
- D 1141 Specification for Substitute Ocean Water³
- D 1193 Specification for Reagent Water⁴

3. Summary of Test Method

3.1 The candidate paint system is applied to cylindrical test specimens. The coated specimens are placed in a tank of synthetic seawater where the copper levels are kept below 100 $\mu\text{g/L}$ by circulating the seawater through an absorbent filter and an activated carbon filter. At specified intervals, each specimen is placed in 1500 mL of seawater (see Section 9 for details) and rotated 60 r/min for 1 h (or less, see 9.8 for further explanation and instruction). The rate of copper release from the paint is determined by measuring copper concentrations of the seawater in the individual measuring containers.

3.2 Analysis of the seawater for copper is conducted by extracting the copper with a solid state absorbent, elution with 10 % HNO_3 , and measuring for copper using GF-AAS.

4. Significance and Use

4.1 This test method is designed to provide a laboratory procedure to measure changes in the release rates of copper that occur during a period of immersion under specified conditions of constant temperature, pH, salinity, and low copper concentrations in the surrounding seawater. Quantitative measurement of the release rate is necessary to help in selection of materials, in providing quality control, and in understanding the performance mechanism.

4.2 This test method serves only as a guide for characterization of the early release pattern as well as estimating the

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² *Annual Book of ASTM Standards*, Vol 06.01.

³ *Annual Book of ASTM Standards*, Vol 11.02.

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

steady-state release of copper from antifouling coatings. Copper release rates of antifouling paint systems in service can vary over the life of the coating system depending on the formulation and the environment. Differences in berthing locations, operating schedules, length of service, condition of paint film surface, temperature, pH, and salinity can affect results. Results obtained may not reflect actual copper release rates that will occur in service, but provide reliable comparisons of the release rate characteristics of different antifouling formulations.

5. Apparatus

5.1 *Release Rate Measuring Container*—A nominal 2-L (½-gal.) polycarbonate container, approximately 13.5 cm (5.3 in.) in diameter and 19 cm (7.5 in.) high, fitted with three polycarbonate rods approximately 6 mm (nominal ¼ in.) in diameter to serve as baffles. Rods shall be evenly spaced on the inside circumference of the container to prevent swirling of the water with the test cylinder during rotation. The rods will be secured to the container walls using acetone or methylene chloride, (see Appendix X2).

5.2 *Constant Temperature Control*: A means of maintaining the release rate measuring test containers at a temperature of $25 \pm 1^\circ\text{C}$ during the spin cycle.

5.3 *Holding Tank*: An inert plastic container of such dimensions so as to permit immersion of four or more test cylinders; must be equipped with a system to continuously circulate the seawater in the tank through an absorbent filter⁵ and an activated carbon filter. Regenerate as outlined in Appendix X1. The rate of water flow and the size of the filter should be selected to maintain copper concentrations below 100 µg/L. Suggested flow rates should be set to obtain 2 to 8 turnovers per hour.

5.4 The size and geometry of the tanks as well as the positioning of the inflow and outflow ports for the water circulation system should be selected to obtain a slow, relatively uniform flow of seawater past all test cylinders in the tank. Maintain the pH of the synthetic seawater between 7.9 and 8.1 and salinity between 33 and 34 parts per thousand (ppt). The tank shall be provided with heaters to maintain the temperature at $25 \pm 1^\circ\text{C}$ ($77 \pm 2^\circ\text{F}$).

5.5 *Test Cylinders*: Approximately 6.4 cm (nominal 2-½ in.) outside diameter by 17.8 cm (nominal 7 in.) long polycarbonate pipe or equivalent polycarbonate cylindrical shapes coated with a 10-cm (3.94 in.) band of antifouling paint around the exterior circumference of the test cylinder to provide 200 cm² of paint film that can be immersed and freely rotated in the release rate measuring container (see Note 1). A top disc, fitted with a shaft of proper diameter for rotating device, should be sealed to the cylinder. Seal the bottom of the test cylinder with a polycarbonate disc using acetone, methylene chloride or a polycarbonate cement so as to form a watertight joint. Do not coat the lower 1 to 2 cm (0.39 to 0.79 in.) of the test cylinder. The test cylinder shall be of such height so that a rotating

device can be attached to rotate the cylinder with the upper end of the cylinder above the level of the test container immersion liquid to prevent entry of the immersion liquid into the test cylinder (see Appendix X2). It is advisable to weight the cylinder by filling with water so that the unit does not have buoyancy.

NOTE 1—When coating release rates are very high, it may be desirable to use a 5-cm band (100 cm²) paint area to avoid exceeding 200 µg/L of copper in the measuring containers (see 9.8.1).

5.6 *Test Cylinder Rotating Device*: The device shall be capable of rotating the test cylinder in the release rate measuring container at 60 ± 5 r/min (0.2 ± 0.02 m/s, velocity of test cylinder surface). No part of the device shall be immersed in seawater.

5.7 *Sample Tubes*: 60-mL capacity with screw closures (or disposable bottles, culture tubes, etc.) made of polycarbonate, polypropylene or borosilicate glass.

5.8 *Vortex Mixer, or Ultrasonic Bath*.

5.9 *Dispensers*: Automatic or repeating for reagents.

5.10 *Pipets, Class A*.

5.11 *GF-AAS*, with appropriate background correction and optional automatic sampler.

5.12 *pH Meter*, with a suitable electrode.

5.13 *Appropriate Hydrometer or Salinometer*.

5.14 *Appropriate Volumetric Flasks*.

5.15 *Column Processing System*.

5.16 *Vacuum Pump*.

5.17 *Disposable Polypropylene Syringes, 60 mL*

5.18 *Syringe Filters, 0.45 µm*.

6. Reagents and Materials

6.1 *Purity of Reagents*—All reagents and cleaning agents are to be reagent grade or better.

6.2 *Purity of Water*—Distilled water conforming to Type II of Specification D 1193.

6.3 *Seawater*: Artificial ocean water in accordance with Section 6 of Specification D 1141 or a proprietary equivalent with a salinity of 33 to 34 ppt and pH 7.9-8.1.

6.4 *Extraction Media*: Ion exchange, 200 to 400 mesh analytical grade and ion exchange resin⁵, 20 to 50 mesh analytical grade.

6.5 *Copper Standards*: Prepare standards using a stock solution of copper (1,000 ppm atomic absorption standard) (see Section 9).

6.6 *Nitric Acid (HNO₃)*: High purity (grade).

6.7 *Hydrochloric Acid (HCl)*: 10 %, v/v, aqueous solution.

6.8 *Nitric Acid (HNO₃)*: 10 % vv, aqueous solution.

6.9 *Sodium Hydroxide (NaOH)*: 1N.

6.10 *Deionized Water*.

6.11 *Magnesium Nitrate Hexahydrate (Mg(NO₃)₂·6H₂O)*: 99.999 %,

6.12 *AA Modifier Solution (1 % Pd)*.

7. Hazards

7.1 **Warning**: Antifouling paints contain toxic materials that could cause skin and eye irritation on contact and adverse physiological effects if ingested or inhaled. See antifouling coating supplier's Material Safety Data Sheet.

⁵ A filter cartridge, containing Chelex ion exchange resin, 20 to 50 mesh, sufficient in size to require regeneration only once a month or less frequently should be used.

7.2 In the preparation of test specimens and the application of various types of paints, the use of appropriate protective clothing and equipment is required consistent with local, state, and federal government regulations, and recognized industrial and technical standards. Spills, overspray, and unused material should not be flushed down the drain, but should be disposed of as hazardous waste.

8. Calibration and Standardization

8.1 Pipete 5 mL of 1000 ppm copper standard into a 100-mL volumetric flask, add 3 to 4 mL of nitric acid and dilute to volume with deionized water (50 ppm). Pipete 2 mL of this solution into another 100-mL volumetric flask and dilute to volume with 10 % HNO₃ (1000 ppb). Pipete 1, 3, 5, 8 and 10 mL of this solution into separate 100-mL volumetric flasks and dilute to volume with 10 % HNO₃ (10, 30, 50, 80 and 100 ppb).

8.2 Prepare a spike in seawater at appropriate levels, based on expected copper concentration in the test tank.

8.3 Operate the graphite furnace in accordance with the manufacturer's instructions. Modifications may be needed with respect to drying, pre-ash, ashing and atomization time cycles to achieve optimum results.

8.4 At the beginning of each instrument run, analyze the 10 % HNO₃ blank and standards in order to establish that the response of the instrument is linear. Plot separate calibration curves for each analysis of the standards (peak area (abs-sec) versus copper concentration) and calculate the slope, intercept, and correlation coefficient for each curve using least squares fit or another appropriate procedure.

8.5 Analyze the following:

8.5.1 *Seawater blank*: Extract and analyze as specified for the test samples, to establish baseline.

8.5.2 *Spiked Seawater Samples*: Extract and analyze as specified for test samples to determine extraction efficiency. Recovery must be 100 % ± 10 %.

8.5.3 If changing the graphite tube during a run is necessary, the blank and standards should be analyzed to ensure proper response and linearity before continuing the sample analyses.

8.6 Determine the copper concentration of individual test samples with reference to the 50 µg/litre calibrating standard, analyzed immediately before those test samples.

9. Procedure

9.1 Clean polycarbonate ware with tap water then rinse with deionized water. All glass laboratory ware used for copper release measurements must be treated as follows: clean thoroughly by soaking in 10 % HCl for a minimum of 6 h. Cleaning can also be accomplished by soaking in concentrated HCl for ½ h. Rinse laboratory ware thoroughly with deionized or distilled water and allow to dry. Prepare all samples, blanks and standards in laboratory ware treated in this manner. Disposable materials (pipetes, tips, centrifuge tubes, etc.) do not have to be acid-washed before use.

9.2 Prepare the exposure surfaces of three replicate test cylinders to provide a suitable surface for adhesion of the paint system to be applied. The surface area to be painted may be lightly abraded with 200-grit sandpaper to promote adhesion. Before coating, wipe abraded area to remove dust. Mask the surfaces to remain uncoated (including the bottom 1 to 2 cm of

the exterior circumferential surface of the test cylinder). Identify each cylinder to agree with coating sample code or designation.

9.3 Paints shall be manufactured a minimum of seven days prior to testing. Also, test paints shall not be allowed to age beyond the manufacturer's recommended shelf life. Provide typical storage conditions during aging, that is, sealed in a container commonly used for sale and held at 20 to 30°C.

9.4 Apply antifouling paint to the exterior circumferential surface of three replicate test cylinders to produce a continuous band of antifouling paint with an exposure surface of 200 cm² or alternative area and a dry film thickness as recommended by manufacturer. To ensure complete surface coverage, a finished dry film coating of 100 µm (0.004 in.) minimum is recommended. Follow manufacturer's instructions with respect to mixing and drying. At a minimum, mechanically shake until the paint appears homogeneous. Apply using a sponge paint applicator or spray as recommended by the manufacturer. If the paint is marketed only in spray cans, then apply as a spray. After the final application, allow the paint to dry for 7 ± 1 day at 25 ± 2°C. Include application method and coating thickness in report.

9.5 Measure the initial dry film thickness using a suitable non-destructive procedure found in Test Method D 1005. Remove masking promptly after paint is dry. At the conclusion of the test, measure the film thickness again.

9.6 After the drying period, place one or more sets of three replicate cylinders coated with a test paint, and one control (unpainted) cylinder in a holding tank. The painted surface on the cylinders must be completely submerged. Cylinders must be stationary, and positioned so that seawater moving through the tank will flow around each cylinder.

9.7 Monitor the pH (using a pH meter with a suitable electrode) and the temperature of the seawater in the holding tank every 1 to 2 days. Adjust the pH if necessary using either dilute NaOH or dilute HCl. Quantitate salinity (by measuring specific gravity or with a salinometer) every 1 to 2 days and adjust if necessary by adding distilled water to compensate for evaporation losses. Determine copper concentrations at each sampling point. When copper levels increase, change both filters before the copper concentration exceeds 100 µg/litre.

9.8 At 1, 3, 7, 10, 14, 21, 24, 28, 31, 35, 38, 42 and 45 day intervals, transfer all cylinders in a given set from the holding tank(s) into individual measuring containers, each containing 1500 mL of seawater that, prior to use, has been passed through an ion exchange resin and activated carbon filter. Randomly assign cylinders (control and painted) to measuring containers at each leaching point. When transferring cylinders, lift the cylinder out of the holding tank, allow seawater to drain off, install the cylinder into the rotating device and submerge the painted area into the test seawater. Immediately start rotation of the cylinder at 60 ± 5 r/min and continue rotation for 1 h (see 9.8.1). When transferring the cylinders do not touch, or in any way damage, the paint film and do not allow the paint surface to dry. The transfer should be completed as quickly as possible (generally in less than 5 min).