



Standard Test Method for Determination of Copper Release Rate From Antifouling Coatings in Substitute Ocean Water¹

This standard is issued under the fixed designation D6442; 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 This test method covers the laboratory determination of the rate at which copper is released from an antifouling (AF) coating in substitute ocean water. The practical limits for quantifying copper release rates by this method are from 1.8 to 500 $\mu\text{g cm}^{-2}\text{d}^{-1}$. This range may be extended to 0.2 to 500 $\mu\text{g cm}^{-2}\text{d}^{-1}$ if the analytical procedure described in [Appendix X1](#) is followed.

NOTE 1—The term “substitute ocean water” is used throughout this standard to refer to artificial or synthetic seawater prepared in accordance with Practice [D1141](#).

1.2 The procedure contains the preparation steps for the release rate determination of copper from antifouling paints including apparatus, reagents, holding tank conditions, and sampling point details. Analysis for the concentration of copper in substitute ocean water requires the accurate determination of copper at the low parts $\mu\text{g L}^{-1}$ (parts per billion, ppb) level. To detect and correct for reagent impurities, acceptable analytical precision standards are necessary. Therefore, the limit of quantitation (LOQ) for copper in substitute ocean water for the analytical method shall be 10 $\mu\text{g L}^{-1}$ (10 ppb) or less. The procedure for determining the LOQ for copper in substitute ocean water for the analytical method is found in [Annex A2](#).

1.3 A suitable method is described in [Appendix X1](#) (graphite furnace atomic absorption spectroscopy, GF-AAS). Other analytical methods may be utilized with relevant procedural changes, as needed, to accommodate selected specific methods. Such methods must meet the limit of quantitation for copper in substitute ocean water of 10 $\mu\text{g L}^{-1}$ (10 ppb) or less. See [1.2](#).

1.4 This results of this test method do not reflect environmental copper release rates for antifouling products, and are not suitable for direct use in the process of generating environmental risk assessments, environmental loading estimates, or for establishing release rate limits for regulatory purposes. See also [Section 4](#) on Significance and Use.

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 Coatings.

Current edition approved June 1, 2012. Published August 2012. Originally approved in 1999. Last previous edition approved in 2006 as D6442 – 06. DOI: 10.1520/D6442-06R12.

1.5 The values stated in SI units are to be regarded as the standard. The values 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 appropriate 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:²

[D1005](#) Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers

[D1141](#) Practice for the Preparation of Substitute Ocean Water

[D1193](#) Specification for Reagent Water

3. Summary of Test Method

3.1 The candidate paint is applied to cylindrical test specimens. The coated specimens are placed in a tank of substitute ocean water where the copper levels are kept below 100 $\mu\text{g L}^{-1}$ by circulating the substitute ocean water through a suitable filtration system (see [5.3](#)). At specified intervals, each specimen is placed in 1500 mL of substitute ocean water (see [Section 9](#) for details) and rotated at 60 revolutions per minute (rpm) 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 substitute ocean water in the individual measuring containers.

3.2 [Appendix X1](#) provides an analytical procedure for measuring copper concentrations in substitute ocean water.

4. Significance and Use

4.1 This test method is designed to provide a laboratory procedure to quantify and characterize the release rates of copper from antifouling coatings in substitute ocean water over

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

a period of immersion under specified laboratory conditions of constant temperature, pH, salinity, and low copper concentration. 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 Results from this test method establish a pattern of copper release from an antifouling coating over a minimum of 45 days exposure under controlled laboratory conditions. Copper release rates from antifouling paints in-service vary over the life of the coating system depending on the formulation and on the physical and chemical properties of the environment. Factors such as differences in berthing locations, operating schedules, length of service, condition of paint film surface, temperature, pH, and salinity influence the actual release rate under environmental conditions. Results obtained using this test method do not reflect actual copper release rates that will occur in-service, but provide comparisons of the release rate of different antifouling formulations in substitute ocean water under the prescribed laboratory conditions.

4.3 By comparison with copper release rate measurements obtained either by direct measurements of copper release rate from AF coating systems on ship hulls, or copper release rate measurements from AF coating systems from harbor exposed panels, all available data indicate that the results of this test method (Test Method D6442) significantly overestimate the release rate of copper when compared to release rates under in-service conditions. Published results demonstrate that this test method produces higher measurements of copper release rate than from direct in-situ measurements for the same coating on in-service ship hulls and harbor-exposed panels. The difference between the results of this test method and the panel and ship studies was up to a factor of about 30 based on data for several commercial antifouling coatings.^{3,4} Realistic estimates of the copper release from a ship's hull under in-service conditions can only be obtained from this test method where the difference between the results obtained by this test method and the release rate from an AF coating in-service is taken into account.

4.4 Where the results of this test method are used in the process of generating environmental risk assessments, for environmental loading estimates, or for regulatory purposes, it is most strongly recommended that the relationship between laboratory release rates and actual environment inputs is taken into account to allow a more accurate approximation of the copper release rate from antifouling coatings under real-life conditions. This can be accomplished through the application of appropriate correction factors.⁴

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 [Annex A1](#)).

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 rotation period (see [9.8](#)).

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 substitute ocean water in the tank through an activated carbon filter and optionally an absorbent filter.⁵ If an absorbent filter is used, regenerate the ion-exchange resin following the manufacturer's instructions and wash the resin with substitute ocean water prior to use. The rate of water flow and the size of the filter(s) shall be selected to maintain copper concentrations below $100 \mu\text{g L}^{-1}$. 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 shall be selected to obtain a slow, relatively uniform flow of substitute ocean water past all test cylinders in the tank. Maintain the pH of the substitute ocean water between 7.9 and 8.1, the salinity between 33 and 34 parts per thousand (ppt), and temperature at $25 \pm 1^\circ\text{C}$ ($77 \pm 2^\circ\text{F}$).

5.5 *Test Cylinders*—Approximately 6.4 cm (nominal 2½ 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 cm^2 of paint film that can be immersed and freely rotated in the release rate measuring container (see [Note 2](#)). A top disc, fitted with a shaft of proper diameter for the 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 [Annex A1](#)). It is advisable to weight the cylinder by filling with water so that the unit does not have buoyancy.

NOTE 2—When coating release rates are very high, it may be desirable to use a 5 cm band (100 cm^2) paint area to avoid exceeding $200 \mu\text{g L}^{-1}$ 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 $60 \pm 5 \text{ rpm}$ ($0.2 \pm 0.02 \text{ m}\cdot\text{s}^{-1}$, velocity of test cylinder surface). No part of the device shall be immersed in substitute ocean water.

³ Valkirs, A. O, Seligman, P. F., Haslbeck, E., and Caso, J. S., Marine Pollution Bulletin, Vol 46 (2003), pp 763–779.

⁴ Finnie, A. A., "Improved Estimates of Environmental Copper Release Rates from Antifouling Products," *Biofouling*, Vol. 22 (2006). In press.

⁵ A filter cartridge, containing a chelating iminodiacetic (alternative spelling – imminodiacetic) acid ion-exchange resin on a styrene support (nominal particle size range approximately 0.300 to 0.850 mm (20 to 50 mesh)) of sufficient capacity to require regeneration only once a month or less frequently, has been found suitable.

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 *Dispensers*—Automatic or repeating for reagents.

5.9 *pH Meter*, with a suitable electrode.

5.10 *Appropriate Hydrometer or Salinometer*.

5.11 *Appropriate Volumetric Flasks*.

5.12 *Disposable Polypropylene Syringes*, 60 mL.

5.13 *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 **D1193**.

6.3 *Substitute Ocean Water*—Artificial ocean water in accordance with Practice **D1141**, section on Preparation of Substitute Ocean Water, or a proprietary equivalent with a salinity of 33 to 34 ppt and pH 7.9 to 8.1.

6.4 *Extraction Media*—Activated carbon and, optionally, a chelating ion-exchange resin,⁵ iminodiacetic (iminodiacetic) acid exchange resin on a styrene support, nominal particle size range approximately 0.300 to 0.850 mm (20 to 50 mesh) (see **5.3**).

6.5 *Copper Standards*—Prepare standards using a stock solution of copper, 1000 mg L^{-1} (1000 ppm), or other concentration suitable to the selected analytical technique (see Section **8**).

6.6 *Nitric Acid (HNO_3)*—Concentrated, high purity grade.

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

6.8 *Sodium Hydroxide (NaOH)*, 1 N, aqueous solution.

6.9 *Deionized Water*.

6.10 *Sodium Chloride (NaCl)*, 5 M, aqueous solution.

7. Hazards

7.1 **Warning**—Antifouling paints may 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.

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 Prepare five suitable standards from the copper stock solution (see **6.5**) in a medium appropriate to the analytical method.

8.2 Prepare spikes in substitute ocean water at 10, 50 and 200 $\mu\text{g L}^{-1}$ to cover the working range of the method.

Additional spikes may be prepared at appropriate levels and appropriate to the analytical technique being used.

8.3 At the beginning of each instrument run, analyze a suitable 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 (instrument response versus copper concentration) and calculate the slope, intercept, and correlation coefficient for each curve using least squares fit or another appropriate procedure.

8.4 Analyze the following:

8.4.1 *Substitute Ocean Water Blank*: Acidify, extract and analyze as specified (see **9.10** and **9.11**) for test samples, to establish baseline.

8.4.2 *Spiked Substitute Ocean Water Samples*: Acidify, extract and analyze as specified (see **9.10** and **9.11**) for the test samples to determine extraction efficiency. Recovery must be 100 % \pm 10 % for the 50 $\mu\text{g L}^{-1}$ spike and spikes of higher concentration. Recovery must be 100 % \pm 15 % for spikes with a concentration below 50 $\mu\text{g L}^{-1}$.

9. Procedure

9.1 Clean polycarbonate ware with tap water then rinse with deionized water. All glass laboratory ware used for copper release rate 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 (pipettes, 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 to be applied. The surface area to be painted shall 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 cm^2 . Ensure surface is completely covered with finished dry film coating of 100 to 200 μm (0.004 to 0.008 in.). If, during the test, the film thickness is expected to fall below 50 μm , then a greater thickness of paint should be applied. Alternative surface areas are allowed when 200 cm^2 is not appropriate – deviations from the 200 cm^2 surface area shall be noted in the final report. Follow manufacturer's instructions with respect to mixing and drying. At a minimum, mechanically shake until the paint appears homogeneous. Apply using a brush, sponge