Designation: D6442 – 06 (Reapproved 2012)

Standard Test Method for Determination of Copper Release Rate From Antifouling Coatings in Substitute Ocean Water[1]

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 µg cm^{-2}d^{-1}. This range may be extended to 0.2 to 500 µg cm^{-2}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 µg 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 µg 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 µg 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.

1.5 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 µg 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

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[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.

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[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 ± 1°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 $\mu g\ L^{-1}$. 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 ± 1°C (77 ± 2°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 $\mu g\ L^{-1}$ 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 ± 5 rpm (0.2 ± 0.02 $m \cdot s^{-1}$, velocity of test cylinder surface). No part of the device shall be immersed in substitute ocean water.

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[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 (imminodiacetic) 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 µg 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 % ± 10 % for the 50 µg L^{-1} spike and spikes of higher concentration. Recovery must be 100 % ± 15 % for spikes with a concentration below 50 µg 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 paint applicator, or spray as recommended by the manufacturer. If the paint is marketed only in spray cans, then apply as a spray. If applied by brush, the film shall not show brush marks. After the final application, allow the paint to dry for 7 ± 1 day at 25 ± 2°C and 30 to 80 % relative humidity. 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 D1005 or other suitable non-destructive method and report the method used. Remove masking promptly after paint is dry. At the conclusion of the test, allow the cylinders to dry for at least 12 hours at ambient conditions and 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 blank (unpainted) cylinder in a holding tank. The painted surface on the cylinders must be completely submerged. Cylinders must be stationary, and positioned so that substitute ocean water moving through the tank will flow around each cylinder.

9.7 Maintain the substitute ocean water within the prescribed range (see 5.4) by monitoring and adjusting the pH, salinity, and temperature of the substitute ocean water in the holding tank at least every third day from the start through the end of the study. Monitor the pH and adjust if necessary using either dilute NaOH or dilute HCl. Monitor the salinity and adjust if necessary by adding distilled water or 5 M NaCl. Determine the copper concentration in the holding tank at each sampling point. When copper levels increase, replace or regenerate the extraction media before the copper concentration exceeds 100 µg L^{-1}.

NOTE 3—More frequent monitoring and adjustment of pH and salinity may be required to maintain the substitute ocean water within the prescribed range during the early stages of a study while the system equilibrates.

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 substitute ocean water that, prior to use, has been passed through a filter containing the extraction media. Randomly assign cylinders (control and painted) to measuring containers on each measurement day. When transferring cylinders, lift the cylinder out of the holding tank, allow substitute ocean water to drain off, install the cylinder into the rotating device and submerge the painted area into the test substitute ocean water. Immediately start rotation of the cylinder at 60 ± 5 rpm 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 minutes).

9.8.1 If, when a measurement is taken, the copper concentration in the individual measuring container is determined to be > 200 µg L^{-1}, the rotation period for the next measurement shall be reduced to less than 1 h, with the goal of ultimately building the rotation period back up to 1 h. The amount by which the rotation period is reduced shall be estimated based on familiarity with the coating being evaluated and experience with the test method, and shall take into consideration the degree to which the measurement exceeded 200 µg L^{-1}. If the next measurement also exceeds 200 µg L^{-1}, the period of rotation shall be further reduced until the result falls under 200 µg L^{-1}. Once a measurement has been taken that falls under 200 µg L^{-1}, the period of rotation shall be incrementally re-adjusted back up to a maximum of 1 h at the earliest possible point in the testing.

9.8.2 Any measurements taken where either the concentration in the individual measuring container was > 200 µg L^{-1} or where the period of rotation was less than 1 h should be used to calculate release rate, and they must be recorded in the final report.

9.9 If testing beyond the minimum 45 days requirement is desired, the study may be extended. During the extended test, remove the cylinders from the holding tank at least once every 7 days to make a measurement of the release rate in accordance with the above procedure.

9.10 At the completion of the cylinder rotation, transfer the cylinder back to the holding tank. Withdraw approximately a 100 mL subsample of the test substitute ocean water from the measuring container. Acidify the subsample by adding 0.10 mL of high purity concentrated nitric acid per 100 mL of subsample and agitate for at least 10 minutes (expected pH ≤2). Then, draw 50 mL of the acidified subsample into a plastic syringe. Filter through a 0.45-µm filter while transferring the subsample into a properly labeled sample tube (approximately 60 mL). The sample can be refrigerated (approximately 5°C) for up to 14 days if necessary before analysis.

9.11 Analyze the samples using an appropriate analytical technique. The method should have a sensitivity (LOQ) for copper in substitute ocean water of 10 µg L^{-1} or less and show spike recoveries as indicated in 8.4.2. A method using GF-AAS can be found in Appendix X1.

10. Calculation

10.1 Calculate the copper concentration in each acidified subsample (see 9.10) based on instrument response for samples and blanks.

NOTE 4—If copper is detected in the substitute ocean water used to fill the individual sampling containers, this shall be reflected in the calculation.

10.2 Calculation of the release rate at each data point (sampling day):

10.2.1 Calculate the release rate (µg $cm^{-2}d^{-1}$) for each individual test cylinder.

$$\begin{aligned} R_{cyl} &= (C_{Cu} \times V \times D)/(T \times A) \qquad (1) \\ &= (C_{Cu} \times 1.5 \times 24)/(1 \times 200) \\ &= C_{Cu} \times 0.18\ (for\ 200\ cm^2\ paint\ area) \end{aligned}$$

where:

C_{Cu} = concentration of copper in substitute ocean water, µg L^{-1},
V = substitute ocean water volume in measuring container, litres,
D = hours per day (24),

T = rotation period, hours, and
A = area of paint, cm^2.

10.2.2 Calculate the mean release rate at each data point (sampling day) for each set of triplicate test cylinders.

10.3 Calculation of cumulative copper release:

10.3.1 Calculate the cumulative release of copper from the start of the trial through to Day 45 as follows:

$$R_{0,45} = \sum \bar{R}_{i,j}\,(j-i) = \sum \frac{(R_i+R_j)}{2}(j-i) \qquad (2)$$

where:

$R_{0,45}$ = the cumulative release (µgCu cm^{-2}) from the start of the trial through to Day 45,
$\bar{R}_{i,j}$ = the mean release rate (µgCu cm^{-2}d^{-1}) between consecutive sampling days i and j for all data points between the start of the trial and Day 45,
i and j = time elapsed (days) since the start of the trial for each pair of consecutive data points, specifically 0 and 1, 1 and 3, 3 and 7 days, etc., respectively, and
R_i and R_j = the mean release rates (µgCu cm^{-2}d^{-1}) for each set of triplicate test cylinders for each pair of consecutive days from the start of the trial through to Day 45, specifically Days 0 and 1, Days 1 and 3, Days 3 and 7, etc., respectively, and where the release rate on Day 0 (R_0) is taken as 0 µgCu cm^{-2}d^{-1}.

10.3.2 The cumulative release of copper for other periods of time may be calculated if required as follows:

$$R_{x,y} = \sum \bar{R}_{i,j}\,(j-i) = \sum \frac{(R_i+R_j)}{2}(j-i) \qquad (3)$$

where:

$R_{x,y}$ = the cumulative release (µgCu cm^{-2}) from Day x through to Day y,
$\bar{R}_{i,j}$ = the mean release rate (µgCu cm^{-2}d^{-1}) between consecutive sampling days i and j for all data points from Day x through to Day y,
i and j = time elapsed (days) since the start of the trial for each pair of consecutive data points, for example 0 and 1, 1 and 3, 3 and 7 days, etc., respectively, and
R_i and R_j = the mean release rates (µgCu cm^{-2}) for each set of triplicate test cylinders for each pair of consecutive data points from Day x through to Day y, for example on Days 0 and 1, Days 1 and 3, Days 3 and 7, etc., respectively, and where Day 0 is included, the release rate on Day 0 (R_0) is taken as 0 µgCu cm^{-2}d^{-1}.

NOTE 5—Previous editions of this standard calculated the cumulative copper release as being equal to $R_1 + 2(R_3) + 4(R_7) + 3(R_{10}) + 4(R_{14}) + 7(R_{21}) + 3(R_{24}) + 4(R_{28}) + 3(R_{31}) + 4\,(R_{35}) + 3(R_{38}) + 4(R_{42}) + 3(R_{45})$, where R_1, R_3, R_7, R_{10}, etc., are the release rates for sampling days 1, 3, 7, 10, etc., respectively. The current data treatment provides a more accurate calculation of the cumulative release. However, the formulae presented in 10.3.1 and 10.3.2 are still simple representations of cumulative release and may not provide a fully accurate estimation of cumulative release under the test conditions, particularly if the rate of release is changing rapidly over the test period.[6]

10.4 Mean release rate:

10.4.1 Calculate the mean release rate (µgCu cm^{-2}d^{-1}) from Day 21 through to the end of the trial as follows:

$$\bar{R}_{21,end} = \frac{\sum \bar{R}_{i,j}\,(j-i)}{\sum (j-i)} = \frac{\sum \frac{(R_i+R_j)}{2}(j-i)}{\sum (j-i)} \qquad (4)$$

where:

$\bar{R}_{21,end}$ = the mean release rate (µgCu cm^{-2}d^{-1}) between Day 21 and the last day of sampling,
$\bar{R}_{i,j}$ = the mean release rate (µgCu cm^{-2}d^{-1}) between consecutive sampling days i and j for all data points from Day 21 through to the last day of sampling,
i and j = time elapsed (days) since the start of the trial for each pair of consecutive data points, specifically Days 21 and 24, 24 and 28, 28 and 31, etc., respectively, and
R_i and R_j = the mean release rates (µgCu cm^{-2}d^{-1}) for each set of triplicate test cylinders for each pair of consecutive data points from Day 21 through to the last day of sampling, specifically Days 21 and 24, Days 24 and 28, Days 28 and 31, etc., respectively.

NOTE 6—Eq 4 calculates the weighted mean release rate, taking into account any differences in time between data points, and is a more valid treatment of the data than calculation of the simple arithmetic mean of the data.[6] The calculation may be conveniently done using a suitable computer-generated spreadsheet.

10.4.2 Eq 4 may be modified to calculate the mean release rate over other periods if required.

10.5 If the coating exhibits a pseudo-steady state, calculate the pseudo-steady state copper release rate as follows:

$$\bar{R}_{PSS} = \frac{\sum \bar{R}_{i,j}(j-i)}{\sum (j-i)} = \frac{\sum \frac{(R_i+R_j)}{2}(j-i)}{\sum (j-i)} \qquad (5)$$

where:

$\bar{R}_{PSS}$ = the mean copper release rate (µgCu cm^{-2}d^{-1}) over the pseudo-steady state period, Day x to Day y,
$\bar{R}_{i,j}$ = the mean release rate (µgCu cm^{-2}d^{-1}) between consecutive sampling days i and j for all data points from Day x through to Day y,
i and j = time elapsed (days) since the start of the trial for each pair of consecutive data points, for example, Days 21 and 24, 24 and 28, 28 and 31, etc., respectively, and

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1132. The Statistical Evaluation of the Revised Data Treatment Adopted for Test Method D6442.

R_i *and* R_j = the mean release rates (µgCu $cm^{-2}d^{-1}$), for each set of triplicate test cylinders for each pair of consecutive data points, for example Days 21 and 24, Days 24 and 28, Days 28 and 31, etc., respectively.

For the purposes of this standard, a "pseudo-steady state" is defined as being a period of at least 24 days and containing 4 or more data points, where the arithmetic mean of the release rate values for each set of triplicate test cylinders at each data point differs from the weighted mean release rate over the calculation period by no more than 15 %, and the final day of the pseudo-steady state is the final day of the trial.

NOTE 7—Not all coatings will exhibit a pseudo-steady state. Where a coating does exhibit a pseudo-steady state, the determined pseudo-steady state copper release rate of the coating should not be assumed to necessarily reflect a true steady state release rate under the conditions of the test as the release rate of the coating may continue to change beyond the test period.

11. Report

11.1 Report the following information:

11.1.1 Report the concentration in µg L^{-1} of copper in the substitute ocean water of the holding tank and the measuring tank and the rate of copper release (µg $cm^{-2}d^{-1}$) for each sampling point (give values for individual replicates as well as the mean). Plot the rate of copper release as a function of time (use linear axes).

11.1.2 Report the cumulative release from the start of the trial through to Day 45 (10.3.1), and report the mean release rate for Days 21 through the end of the study (10.4.1). Also, where calculated, report the cumulative release over other periods (10.3.2), the mean release rate over other periods (10.4.2), and the pseudo-steady state release rate (10.5).

11.1.3 Report samples where the concentration of copper exceeded 200 µg L^{-1} in the individual measuring containers, and samples where the period of rotation was less than 1 h.

11.1.4 Report the limit of quantitation for copper in substitute ocean water, determined by the laboratory performing the test method in accordance with Annex A2.

11.1.5 Report coating application method and initial and final coating dry film thicknesses from 9.4 and 9.5.

11.1.6 Report the pH, temperature, and salinity in the holding tank at each monitoring point (9.7).

11.1.7 Report any deviations from this method or the requirements of this method.

11.1.8 Report the analytical method used for copper assays.

12. Precision and Bias

12.1 *Bias*—No information can be presented on bias of the procedure in Test Method D6442 for measuring copper release rate from antifouling coatings because no material having an accepted reference value is available.

12.2 *Precision:*

12.2.1 *Repeatability*—The repeatability of the procedure in Test Method D6442 for measuring copper release rate from antifouling coatings can be summarized as follows. Data from one laboratory (6 paints) have been analyzed. The analysis shows that variation in release rate measured among replicate cylinders, but within a laboratory, differs among coatings and depends to some extent on when the release rate is quantified. Based on results from 6 paints, the mean standard deviation, across all sampling dates, ranged from 1.1 to 9.2 µg $cm^{-1}d^{-1}$. As a percentage of the mean release rate, variation in daily release rate ranged from 0 to 49 %, while the mean deviation across sampling dates ranged from 6 to 11 % of the mean release rate over all sampling dates. Release rates measured during the first week of exposure tended to be more variable than later measurements. See Appendix X1 for repeatability statement for GF-AAS.

12.2.2 *Reproducibility*—The reproducibility of the procedure in Test Method D6442 for measuring copper release rate from antifouling coatings is being determined and will be available on or before December 2011. When the standard on organic biocide release rate method has been published, laboratories will participate in a combined round robin effort on both Test Method D6442 and the new test method. By doing this, participating laboratories will benefit from economy of effort, and the joint round robin will result in reproducibility data for multiple methods.

13. Keywords

13.1 antifouling coating; copper; release rate

ANNEXES

(Mandatory Information)

A1. DESCRIPTION OF PROPOSED TESTING APPARATUS

A1.1 A 200-cm^2 antifouling paint film of specified thickness is applied to the outer curved surface of a polycarbonate cylinder closed at one end. This cylinder is suspended with its closed end immersed within and concentric with a larger polycarbonate cylinder holding substitute ocean water. The coated internal cylinder is rotated about its axis at 60 ± 5 rpm in order to produce a peripheral speed of about 0.2 $m \cdot s^{-1}$ (about 0.4 knots). In practice, the commercially available polycarbonate "multipurpose jars" described in this test method will hold 1500 mL of substitute ocean water, and provide ample volume for test cylinder volume displacement (see Fig. A1.1).

Test Container Dimensions:

Capacity, liter	2
Inside Diameter, cm	12.7
Outside Diameter, cm	13.5
Height (without cover), cm	19

Rotating Test Cylinder Dimensions:

D = Approximately 6.4 cm (nominal 2-1/2")
H = 12 cm minimum, immersion depth
L = 10 cm coated section
X = 1 cm uncoated band

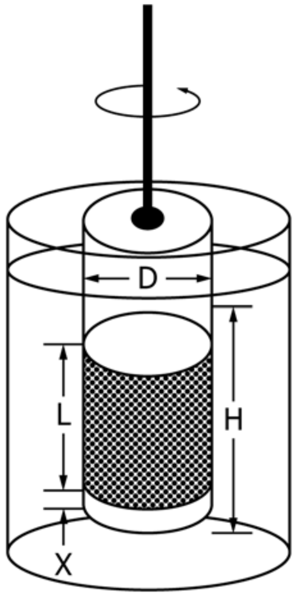

FIG. A1.1 Polycarbonate Cylinder in Measurement Chamber (required baffles not shown)

A2. DETERMINATION OF THE LOQ FOR COPPER IN SUBSTITUTE OCEAN WATER FOR THE ANALYTICAL METHOD

A2.1 Scope

A2.1.1 This procedure is based on the U.S. Environmental Protection Agency Method Detection Limit (MDL) procedure found in Title 40 Code of Federal Regulations Part 136 (40 CFR 136, Appendix B, revision 1.11).

A2.1.2 This procedure was designed for applicability to a broad variety of physical and chemical methods and is device or instrument independent. The procedure should be applicable to any analytical method used to assay copper in substitute ocean water.

A2.1.3 The procedure requires a complete, specific, and well defined analytical method.

A2.1.4 It is essential that all sample processing steps of the analytical method be included in the determination of the LOQ.

A2.1.5 This procedure shall be performed before copper release rate measurements are started in a laboratory, whenever changes are made to the instrumentation or analytical method, and repeated at least annually.

A2.2 Procedure

A2.2.1 Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in substitute ocean water.

(c) That region of the standard curve where there is a significant change in sensitivity, that is, a break in the slope of the standard curve.

(d) Instrumental limitations.

A2.2.2 Prepare substitute ocean water that is as free of copper as possible.

A2.2.3 Prepare a spike in substitute ocean water at a concentration between one and five times the estimated detection limit.

A2.2.4 Take a minimum of seven aliquots of the spike and process each through the entire analytical method, that is, each aliquot shall be acidified by the addition of 0.10 mL of high purity nitric acid per 100 mL of aliquot and then subjected to all specified intermediate sample preparation and processing steps prior to analysis.

A2.2.5 If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each spike aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

A2.3 Calculations

A2.3.1 Calculate the standard deviation (S) of the replicate measurements as follows:

$$S = \sqrt{\frac{1}{n-1}\left[\left[\sum x_i^{2} - \frac{\left(\sum x_i\right)^{2}}{n}\right]\right]} \quad (A2.1)$$

A2.3.2 Calculate the LOQ as follows:

TABLE A2.1 Table of Student's t-Values at the 99 Percent Confidence Level

Number of Replicates	Degrees of Freedom (n – 1)	$t_{(n-1,\ 1-\alpha=0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
∞	∞	2.326

$$LOQ = 10 \times S \quad (A2.2)$$

A2.3.3 Calculate the limit of detection (LOD) as follows:

$$LOD = t_{(n-1,\ 1-\alpha=0.99)} \times S \quad (A2.3)$$

where:

$t_{(n-1,\ 1-\alpha=0.99)} \times S$ = the Student's t-value appropriate for a 99 % confidence level and a standard deviation estimate with n – 1 degrees of freedom. See Table A2.1.

A2.3.4 If the level of copper in the spike used was below the determined LOD or exceeds 10 times the LOD, do not use the calculated LOD or LOQ. The procedure must be repeated with a suitable concentration.

A2.3.5 This procedure shall be repeated whenever any changes are made to the instrumentation or analytical method that may affect the performance of the method. If no changes are made to the instrumentation or the analytical method, this procedure shall be repeated at least annually.

APPENDIX

(Nonmandatory Information)

X1. ANALYSIS FOR COPPER IN SUBSTITUTE OCEAN WATER USING SOLID PHASE EXTRACTION AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (GF-AAS)

X1.1 Scope

X1.1.1 This procedure is written to include necessary steps to isolate the copper from substitute ocean water, thereby increasing sensitivity and eliminating salts that interfere with the use of graphite furnace technique.

X1.2 Apparatus

X1.2.1 *Vortex Mixer, or Ultrasonic Bath.*

X1.2.2 *GF-AAS,* with appropriate background correction and optional automatic sampler.

X1.2.3 *Column Processing System.*

X1.2.4 *Vacuum Pump.*

X1.3 Reagents and Materials

X1.3.1 *Extraction Media,* chelating ion-exchange resin, iminodiacetic (imminodiacetic) acid exchange resin on a styrene support, nominal particle size range approximately 0.038 to 0.075 mm (200 to 400 mesh).

X1.3.2 *Nitric Acid (HNO_3),* Concentrated, high purity grade.

X1.3.3 *Nitric Acid (HNO_3),* 10 % v/v, aqueous solution.

X1.3.4 *Sodium Hydroxide (NaOH),* 1 *N*, aqueous solution.

X1.3.5 *Magnesium Nitrate Hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$)* , 99.999 %.

X1.3.6 *AA Modifier Solution (1 % Pd).*

X1.4 Calibration and Standardization

X1.4.1 Pipette 5 mL of 1000 mg L^{-1} copper standard into a 100–mL volumetric flask, add 3 to 4 mL of nitric acid and dilute to volume with deionized water (50 mg L^{-1}). Pipette 2 mL of this solution into another 100–mL volumetric flask and dilute to volume with 10 % HNO_3 (1000 µg L^{-1}). Pipette 1, 3, 5, 8 and 10 mL of this solution into separate 100–mL volumetric flasks and dilute to volume with 10 % HNO_3 (10, 30, 50, 80 and 100 µg L^{-1}).

X1.4.2 Prepare spikes in substitute ocean water at 10, 50 and 200 µg L^{-1}.

X1.4.3 Operate the graphite furnace in accordance with the manufacturer's instructions. Modifications may be needed with respect to drying, pre-ash, ashing, atomization time cycles, and matrix modifiers to achieve optimum results.

X1.4.4 At the beginning of each instrument run, analyze the 10 % HNO_3 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.

X1.4.5 Analyze the following:

X1.4.5.1 *Substitute Ocean Water Blank*—Acidify, extract and analyze as specified (see 9.10 and 9.11) for the test samples, to establish baseline.

X1.4.5.2 *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 % ± 10 % for the 50 µg L^{-1} spike and spikes of higher concentration. Recovery must be 100 % ± 15 % for spikes with a concentration below 50 µg L^{-1}.

X1.4.5.3 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.

X1.4.6 Determine the copper concentration of individual test samples with reference to the 50 µg L^{-1} calibration standard, analyzed immediately before those test samples.

X1.5 Procedure

X1.5.1 *Column Preparation*—Place a retaining frit in the bottom of an empty 6 mL solid phase extraction (SPE) column. Transfer 1.0 g of ion-exchange resin (nominal particle size range approximately 0.038 to 0.075 mm (200 to 400 mesh)) into a test tube with a small amount of deionized water. Vortex mix or sonicate for 30 s to disperse the resin, pour the slurry into the extraction column, then draw off the water.

X1.5.1.1 Place the second frit on top of the resin bed and rinse bed with 5 mL of deionized water. Draw 5 mL of 10 % HNO_3 through the column which will cause the resin bed to shrink. Rinse with 5 mL of deionized water, gently press the top frit down to the shrunken resin bed. Rinse again with 5 mL of deionized water and slowly draw 5 mL of 1 *N* NaOH through the column. Rinse with 5 mL of deionized water; the resin will swell at this point. Seal the columns at top and bottom for storage until used.

X1.5.2 *Sample Extraction:*

X1.5.2.1 Prepare a spike sample with each batch of extractions. Place the desired number of columns onto the SPE manifold, and then rinse each with 5 mL of deionized water.

X1.5.2.2 Add 10 mL or less of an appropriate volume of sample to produce a final concentration of copper between 0 and 100 µg L^{-1}. The dilution factor = (10 mL)/(sample volume).

X1.5.2.3 Wash at least two times with 5 mL deionized water. Place a 10 mL volumetric flask into each desired position of the rack. Remove the manifold cover, dry needles with a tissue, and place the rack inside the manifold. Replace cover, with columns attached, on the manifold.

X1.5.2.4 Elute with two aliquots of approximately 4.5 mL of 10 % HNO_3 solutions. Note that the resin bed will shrink and the vacuum required will be less after the first few seconds. Remove volumetric flasks after collection of the 10 % HNO_3, dilute to volume with 10 % HNO_3, mix well.

X1.5.2.5 Rinse each used column with 5 mL deionized water, gently press the top frit down and rinse again with 5 mL. Slowly draw 5 mL of 1 *N* NaOH through each column, draw 5 mL of deionized water through the column (resin bed will swell). Use columns again for additional extractions or seal columns for storage and future use.

X1.5.2.6 The above procedure may require modification, for example where copper concentrations are low (at or below 10 µg L^{-1}). Modifications such as the use of sample volumes larger than 10 mL or a reduction in the level of acid added to the substitute ocean water sample may be needed to avoid low recovery. When a modified procedure is used, the recovery at anticipated levels must be checked. See X1.4.5.

X1.5.2.7 Report any modifications to the procedure (X1.5.1 and X1.5.2). Report the recoveries obtained for the 10, 50, and 200 µg L^{-1} substitute ocean water spikes.

X1.5.3 *Sample Analysis Order*—Run a blank and standards to establish linearity. Then run a blank, a 50 µg L^{-1} standard, and three samples. Repeat blank and standard for each set of three samples. Set instrument conditions to analyze individual blank, standard and sample aliquots in triplicate.

X1.6 Calculation

X1.6.1 Calculate the copper concentration as follows:

$$\text{Copper concentration } (\mu g\ L^{-1}) = \frac{(\text{Sample Area} - \text{Blank Area}) \times \text{Concentration of Std} \times \text{Dilution Factor}}{(\text{Standard Area} - \text{Blank Area})} \quad (X1.1)$$

X1.6.2 The LOQ for copper in substitute ocean water using this method has been determined in two laboratories using the procedure described in Annex A2. The determined LOQs were 5.3 µg L^{-1} and 6.4 µg L^{-1} respectively.[7]

X1.7 Precision and Bias

X1.7.1 The mean extraction recovery for copper was determined by two laboratories. One laboratory reported 95.4 %, extraction recovery with a precision of ± 5.5 %, based on 9 substitute ocean water spiked samples having a concentration of 10 µg L^{-1} analyzed on a single day. The second laboratory reported 102.7 %, extraction recovery with a precision of ± 7.3 %, based on 17 substitute ocean water spiked samples having a concentration of 10 µg L^{-1} analyzed on two separate days.[7]

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D01 – 1131, Intralaboratory Study for the Analysis for Copper in Substitute Ocean Water Using Solid Phase Extraction and GF-AAS.

SUMMARY OF CHANGES

Committee D01 has identified the location of selected changes to this standard since the last issue (D6442 - 05) that may impact the use of this standard. (Approved June 1, 2006.)

(1) Revised 1.1 and 1.4 in the Scope.
(2) Added new Note 1 in the Scope.
(3) Revised 4.1 – 4.4 in Significance and Use.
(4) Added new footnotes 3 and 4 in 4.3 and 4.4.

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