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AMERICAN SOCIETY FOR TESTING AND MATERIALS  
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## Standard Test Method for Organotin Release Rates of Antifouling Coating Systems in Sea Water<sup>1</sup>

This standard is issued under the fixed designation D 5108; 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 ( $\epsilon$ ) 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 organotin expressed as tributyltin (TBT) is released from an antifouling (AF) coating in synthetic sea water using graphite furnace atomic absorption spectrophotometry (GF-AAS). This does not exclude the use of other analytical methodology for measurement of organotin in sea water such as gas chromatography.

1.2 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses 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.* For specific hazard statements, see Section 7.

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 1141 Specification for Substitute Ocean Water<sup>2</sup>

D 1212 Test Methods for Measurement of Wet Film Thickness of Organic Coatings<sup>3</sup>

D 4138 Test Method for Measurement of Dry Film Thickness of Protective Coatings by Destructive Means<sup>4</sup>

### 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 sea water where the tin levels are kept low by circulating the sea water through a carbon filter. At specified intervals, each specimen is placed in 1500 mL of unused sea water and is rotated for 1 h. The rate of tributyltin release from the paint is determined by measuring tributyltin concentrations in the sea water.

3.2 Analysis of sea water for tributyltin is conducted by

extracting the organotin with toluene, washing with sodium hydroxide, and measuring for total tin 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 solvent soluble tin (tributyl- and triphenyltin) that occur during a period of immersion under specified conditions of constant temperature, pH, salinity, and low heavy-metal concentrations in the surrounding sea water. Quantitative measurement of the release rate is necessary to help in selection of materials, in providing quality assurance, and in understanding the performance mechanism.

4.2 This test method serves only as a guide for organotin release rates in service. Organotin release rates of antifouling (AF) 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 necessarily reflect actual tributyltin release rates that will occur in service, but provide reliable comparisons of the release rate characteristics of different antifouling formulations.

4.3 This test method will serve to characterize the early release rate pattern, as well as estimate the steady state release, of tributyltin from both self-polishing copolymer and free-association antifouling paints.

### 5. Apparatus

5.1 *Release-Rate Measuring Container*—A 2-L (nominal ½ gal) polycarbonate container,<sup>5</sup> approximately 13.5 cm (5.5 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 water with the test cylinder during rotation. The rods will be secured to the container walls using acetone or methylene chloride.

5.2 *Constant Temperature Bath*—A temperature controlled

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.45 on Marine Coatings.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 06.02.

<sup>5</sup> A Nalgene Container, available from Cole-Palmer, 7425 N. Oak Ave., Chicago, IL 60648, catalog number R-6761-20, or equivalent, has been found satisfactory for this purpose.

water bath capable of maintaining a temperature of  $25 \pm 2^\circ\text{C}$  into which one or more release rate measuring test containers can be placed.<sup>6</sup>

**5.3 Holding Tank**—A container of such dimensions so as to permit immersion of four or more test cylinders; must be equipped with a system to continuously circulate synthetic sea water in the tank through a carbon filter. The rate of water flow and the size of the carbon filter should be selected to maintain tributyltin concentrations below  $100 \mu\text{g/L}$ . Flow rates should generally be set to obtain 2 to 8 turnovers per h. 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 synthetic sea water past all test cylinders in the tank. Maintain the pH of the synthetic sea water between 7.8 and 8.2, and the salinity between 30 and 35 parts per thousand (ppt). The tank shall be provided with heaters to maintain the temperature between  $21$  and  $27^\circ\text{C}$  ( $70$  and  $81^\circ\text{F}$ ).

**5.4 Test Cylinders**—Approximately  $6.4 \text{ cm}$  (nominal  $2 \frac{1}{2}$  in.) outside diameter polycarbonate pipe coated with a  $10\text{-cm}$  band of AF paint around the exterior circumference of the test cylinder to provide  $200 \text{ cm}^2$  of paint film that can be immersed and freely rotated in the release rate measuring container. 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 bottom  $1$  to  $2 \text{ cm}$  of the test cylinder. The test cylinder shall be of such height so that a rotating device can be attached to rotate the cylinder and the upper open end of the cylinder is above the level of the test container immersion liquid to prevent entry of the immersion liquid into the test cylinder.

**5.5 Test Cylinder Rotating Device**—The device shall be capable of rotating the test cylinder in the release rate measuring container at  $60 \pm 5 \text{ r/min}$ . No part of the device shall be immersed in sea water.<sup>7</sup>

**5.6 Centrifuge Tubes**,  $50\text{-mL}$  capacity, with screw closures<sup>8</sup> (or disposable bottles, culture tubes, separatory funnels, etc.) made of polycarbonate, TFE fluorocarbon, or borosilicate glass.

**5.7 Mechanical Shaker**, with appropriate holders.

**5.8 Dispensers**, automatic or repeating, for reagents.

**5.9 Pipets**, with disposable polypropylene tips.

**5.10 Graphite Furnace**, atomic absorption spectrophotometer (GF-AAS) with automatic sampler.

**5.11 pH Meter**, with a mercury/mercurous chloride ( $\text{Hg}/\text{Hg}_2\text{Cl}_2$ ) electrode.

**5.12 Appropriate Volumetric Flasks.**

## 6. Reagents and Materials

**6.1 Synthetic Sea Water**—Substitute ocean water in accordance with Section 6 of Specification D 1141 or a proprietary

equivalent with a salinity of 30 to 35 ppt.

**6.2 Extraction Solvent**—Toluene, spectrograde or equivalent.

**6.3 Tributyltin Standards**—Prepare standards using a stock solution of tributyltin chloride (reagent grade, minimum 96 % pure) in methanol (suggested concentration of approximately  $10 \text{ mg/L}$ ). The standards are acidified with acetic acid (less than pH 4) to obtain a stable solution.

**6.4 Hydrochloric Acid** (HCl) ( $10 \%$  aqueous solution).

**6.5 Hydrochloric Acid** (HCl) ( $0.1\text{N}$ ).

**6.6 Nitric Acid** ( $\text{HNO}_3$ ) ( $10 \%$  aqueous solution) can be used in place of HCl to clean labware.

**6.7 Sodium Hydroxide** (NaOH) ( $3 \%$  aqueous solution).

**6.8 Sodium Hydroxide** (NaOH) ( $0.1\text{N}$ ).

**6.9** All reagents and cleaning agents used must be tin-free.

## 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. 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. Do not flush spills, overspray, and unused material down the drain, but should be disposed of as hazardous waste.

**7.2** See antifouling paint supplier's Material Safety Data Sheet.

## 8. Calibration and Standardization

**8.1** Prepare three standards throughout the range of the quantification limit to  $100 \mu\text{g}$  of tin per litre by dilution in toluene of a stock solution of tributyltin chloride ( $96 \%$  pure) in methanol. Include one standard with a concentration of approximately  $50 \mu\text{g}$  of tin per litre. An alternate range of concentrations may be used when appropriate.

**8.2** Prepare synthetic sea water spiked with three concentrations of TBT in the range of  $10$  to  $50 \mu\text{g}$  of tin per litre by spiking with stock solution of tributyltin chloride in methanol. When the concentration of tin extracted in toluene exceeds  $100 \mu\text{g/L}$  appropriate dilution should be employed to keep it within the limits of the calibration curve ( $0$  to  $100 \mu\text{g/L}$ ).

**8.3** Operate the graphite furnace in accordance with manufacturer's instructions. Optional conditions are described in Appendix X1.

**8.4** Analyze the following:

**8.4.1** At the beginning of each instrument run, perform analysis of the toluene blank and standards in toluene in order to establish that the response of the instrument is linear. Plot separate calibration curves for each analysis of the standards (peak height absorbance versus tin concentration), and calculate the slope, intercept, and coefficient of determination for each curve using least squares regression or another appropriate procedure.

**8.4.2 Sea Water Blank**—Extract and analyze as specified for test samples to establish baseline.

**8.4.3 Spiked Sea Water Samples**—Extract and analyze as specified for test samples to determine extraction efficiency. Recovery must be  $90$  to  $110 \%$ .

<sup>6</sup> Boekel Water Baths, Models 148003 and 148004 available from Boekel Industries Inc., 509-T Vine St., Philadelphia, PA 19106, or equivalent, have been found satisfactory for this purpose.

<sup>7</sup> A six-paddle stirrer, Model 300, manufactured by Whitaker Medical Mfg. Co., Phipps and Bird Div., 8741 Landmark Rd., Richmond, VA 23228, or equivalent, has been found satisfactory for this purpose.

<sup>8</sup> Oak Ridge Tubes, available from Cole-Parmer, or equivalent, have been found satisfactory for this purpose.

8.4.4 If changing the graphite tube during a run is necessary, analyze the blank and standards in toluene to ensure proper response and linearity before continuing the sample analysis.

8.5 Determine the tin concentration of individual test samples with reference to the 50 µg/L calibrating standard analyzed immediately after those test samples.

## 9. Procedure

9.1 Organotins have a strong tendency to adsorb on certain glass or plastic surfaces. Therefore, all labware (glass or polycarbonate) used for organotin release measurements must be treated as follows: clean thoroughly by soaking in 10 % HCl or HNO<sub>3</sub> for a minimum of 6 h. Rinse labware thoroughly with distilled water and allow to dry. Cleaning can also be accomplished by soaking in concentrated HCl for ½ h. Prepare all samples, blanks, and standards in labware treated in this manner. Disposable materials (pipet tips, centrifuge tubes, etc.) do not have to be acid-washed before use.

9.2 Prepare the exposure surfaces (200 cm<sup>2</sup>) of three replicate test cylinders to provide a suitable surface for adhesion of the paint system to be applied. Mask the surfaces to remain uncoated (including the bottom 1 to 2 cm of the exterior circumferential surface of the test cylinder).

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 one or more coats of antifouling paint to the exterior circumferential surface of a test cylinder to produce a band of AF paint with an exposure surface of 200 cm<sup>2</sup> and a minimum dry film thickness of 100 µm (4 mils). Follow manufacturer's instructions with respect to mixing and drying. At a minimum, mechanically shake until the paint appears homogeneous. Apply using a sponge 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 days at 23 to 27°C.

9.5 Estimate the initial dry film thickness using a suitable nondestructive method such as Test Methods D 1212. If the leaching tests exceed 6 months measure the film thickness at the conclusion of the test. Methodology for the final measurement can be either that used for the initial measurement of Test Method D 4138. If a nonstandard method is used, make several film thickness measurements for each cylinder and estimate the variability of the determination. Film thickness should remain greater than 50 µm throughout the test. For tests of long duration, the initial thickness may need to be greater than 100 µm to maintain a thickness greater than 50 µm throughout the test.

9.6 Place all cylinders in a single batch in a holding tank after the 7-day drying period. A batch consists of one or more sets of three replicate cylinders coated with a test paint and one control (unpainted) cylinder. The painted surface on the cylinders must be completely submerged. Cylinders must be stationary and positioned so that sea water moving through the tank will flow around each cylinder.

9.7 Monitor the pH (using a pH meter with a calomel electrode) and the temperature of the synthetic sea water in the

holding tank daily. Adjust the pH if necessary using either 0.1 N NaOH or 0.1 N HCl. Quantitate salinity every 14 days and adjust if necessary. Determine TBT concentrations weekly. When TBT levels increase, change the carbon filter before the TBT concentration exceeds 100 µg/L. More frequent monitoring of synthetic sea water may be necessary in some instances to maintain the specified environmental conditions.

9.8 After 1, 3, 7, 10, 14, 21, 24, 28, 31, 35, 38, 42, and 45 days, transfer all cylinders in given batch into individual measuring containers containing 1500 mL of fresh synthetic sea water. Randomly assign cylinders (control and painted) to measuring containers at each leaching. When transferring cylinders, lift the cylinder out of the holding tank, allow sea water to drain off, install the cylinder into the rotating device, and submerge the painted area into the sea water. Immediately start rotation of the cylinder at 60 ± 5 r/min, and continue rotation for 60 min. When transferring the cylinders, do not touch or in any way damage the paint film, and do not allow the paint surface to dry. Complete the transfer as quickly as possible (generally, in less than 5 min).

9.9 If testing beyond the minimum (45 days) length requirement is desired, the study may be extended to 73 days. During the extended test, remove the cylinders from the holding tank every 3 to 4 days to make a measurement of the leach rate.

9.10 At the completion of the cylinder rotation, immediately remove the cylinder from the measuring tank and return it to the holding tank. Pipet a 25-mL subsample of the sea water into a 50-mL centrifuge tube containing sufficient 10 % HCl to reduce the pH to ≤4.0. If the number of samples from the leach measuring steps exceeds the daily analysis capacity, the samples may be refrigerated and stored in the acidified state in a sealed container for up to 14 days. Clean the measuring containers using appropriate procedures (distilled water or acid wash) before reuse.

9.11 Partition acidified sea water samples with 10 mL of toluene (15 min shaking on a mechanical shaker). Remove most of the toluene and wash it with 5 mL of a 3 % aqueous NaOH solution (10 min shaking). Pipet off (or separate using a separatory funnel) the organic phase and analyze for total tin content by GF-AAS. The toluene extract can be stored sealed in the dark at 4°C for up to 24 h before analysis.

## 10. Calculation

10.1 Calculate the concentration of the TBT cation in the sea water of the measuring container as follows:

$$C_{\text{TBT}} = (C \times E \times F) / S$$

where:

$C_{\text{TBT}}$  = concentration of TBT cation (µg/L),

$C$  = concentration of tin in the toluene extraction (µg/L),

$E$  = volume of toluene = 10 mL,

$F$  = correction factor to convert tin to TBT = 2.5, and

$S$  = aliquot of sea water analyzed = 25 mL.

This equation can be simplified as follows if the prescribed volume of sea water and toluene are used:

$$\begin{aligned} C_{\text{TBT}} &= (C_{\text{Sn}} \times 10 \times 2.5) / 25 \\ &= C_{\text{Sn}} \end{aligned}$$