
**Paints and varnishes — Determination of
release rate of biocides from antifouling
paints —**

Part 1:

General method for extraction of biocides

*Peintures et vernis — Détermination du taux de lixiviation des biocides
contenus dans la peinture antisalissure —*

Partie 1: Méthode générale d'extraction des biocides



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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 15181 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15181-1 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

ISO 15181 consists of the following parts, under the general title *Paints and varnishes — Determination of release rate of biocides from antifouling paints*:

- *Part 1: General method for extraction of biocides*
- *Part 2: Determination of copper-ion concentration in the extract and calculation of the release rate*

Annex A forms a normative part of this part of ISO 15181.

Introduction

By using standard conditions of temperature, salinity and pH at low biocide concentrations in the surrounding artificial seawater, a repeatable value of the release rate can be determined which can be used for quality assurance, material selection, environmental regulations or paint comparison purposes. However the actual release rate of biocides from antifouling paints on ships hulls into the environment will depend on many factors, such as ship operating schedules, length of service, berthing conditions, paint condition, as well as temperature, salinity, pH, pollutants and bacterial content.

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Paints and varnishes — Determination of release rate of biocides from antifouling paints —

Part 1:

General method for extraction of biocides

1 Scope

This part of ISO 15181 is one of a series of standards dealing with the sampling and testing of paints, varnishes and related products.

This part of ISO 15181 specifies a general method for extracting biocides from paint films of antifouling paints into a specified artificial seawater under specified conditions. It is used in conjunction with ISO 15181-2 to determine the amount of copper biocides in the extract and allow the calculation of the release rate of the biocide from the paint film.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 15181. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 15181 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1513, *Paints and varnishes — Examination and preparation of samples for testing.*

ISO 2808:1997, *Paints and varnishes — Determination of film thickness.*

ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

ISO 15181-2, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 2: Determination of copper-ion concentration in the extract and calculation of the release rate.*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling.*

ASTM D 1141:1998, *Standard specification for substitute ocean water.*

3 Principle

Test cylinders painted with antifouling paint and reference cylinders are immersed in flowing artificial seawater in a holding tank. At specified time intervals the cylinders are removed and exposed for a defined period in individual release rate measuring containers containing the same artificial seawater before being replaced in the holding tank. The concentration of the biocide released into the water of the individual release rate measuring containers can then be determined. This operation is repeated at defined time intervals and hence the release rate of the biocide can be calculated.

4 Required supplementary information

For any particular application, the test method specified in this part of ISO 15181 needs to be completed by supplementary information. The items of supplementary information are given in annex A.

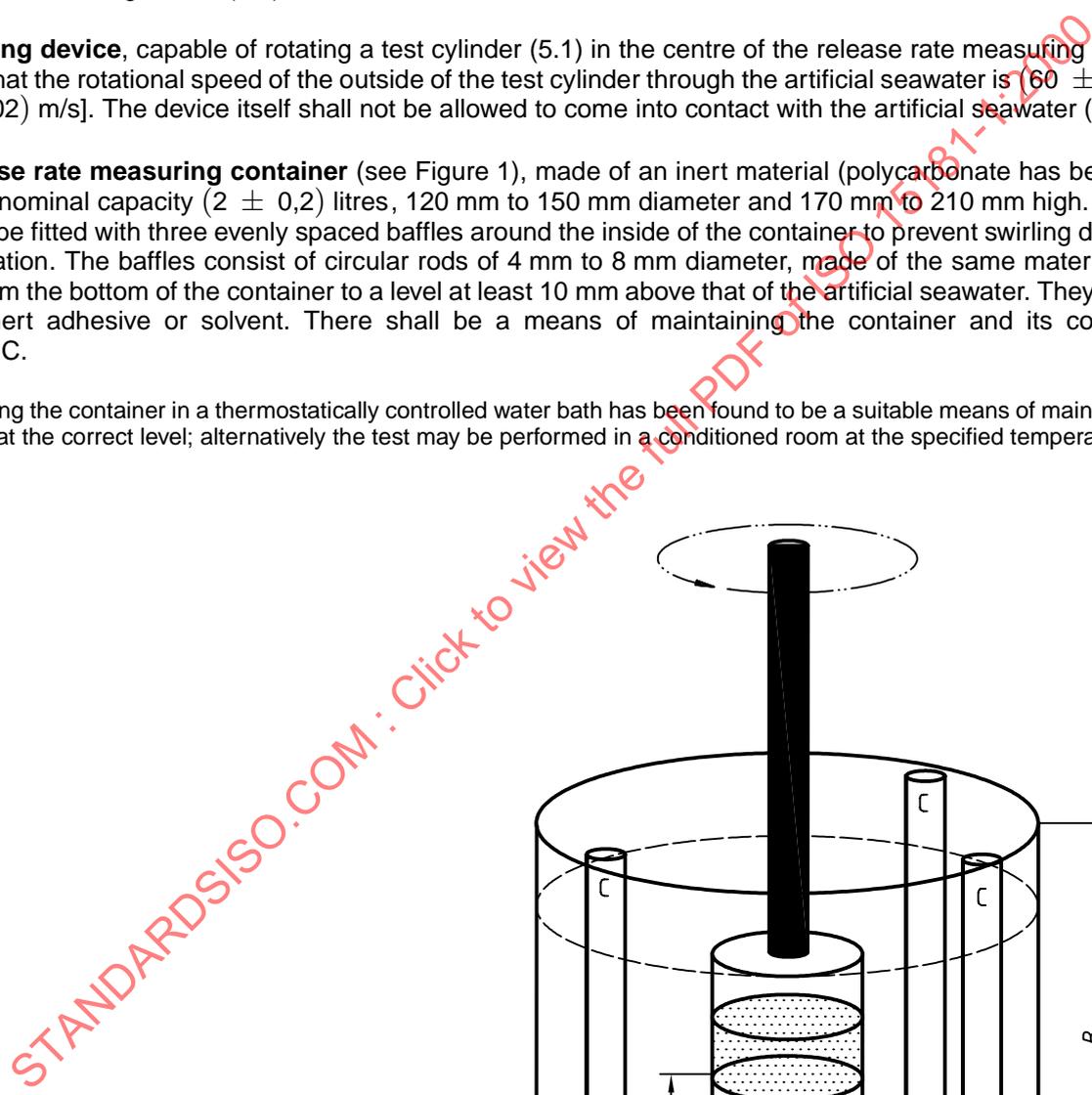
5 Apparatus, equipment and reagents

5.1 Test cylinder, made of an inert material (polycarbonate has been found suitable) of diameter (65 ± 5) mm, watertight-closed at both ends, of sufficient length to allow the application of the antifouling paint (7.3) and allow attachment to the rotating device (5.2).

5.2 Rotating device, capable of rotating a test cylinder (5.1) in the centre of the release rate measuring container (5.3) such that the rotational speed of the outside of the test cylinder through the artificial seawater is (60 ± 5) r/min $[(0,2 \pm 0,02)$ m/s]. The device itself shall not be allowed to come into contact with the artificial seawater (5.6).

5.3 Release rate measuring container (see Figure 1), made of an inert material (polycarbonate has been found suitable) of nominal capacity $(2 \pm 0,2)$ litres, 120 mm to 150 mm diameter and 170 mm to 210 mm high. The container shall be fitted with three evenly spaced baffles around the inside of the container to prevent swirling during test cylinder rotation. The baffles consist of circular rods of 4 mm to 8 mm diameter, made of the same material, which shall run from the bottom of the container to a level at least 10 mm above that of the artificial seawater. They are fixed using an inert adhesive or solvent. There shall be a means of maintaining the container and its contents at (25 ± 1) °C.

NOTE Placing the container in a thermostatically controlled water bath has been found to be a suitable means of maintaining the temperature at the correct level; alternatively the test may be performed in a conditioned room at the specified temperature.



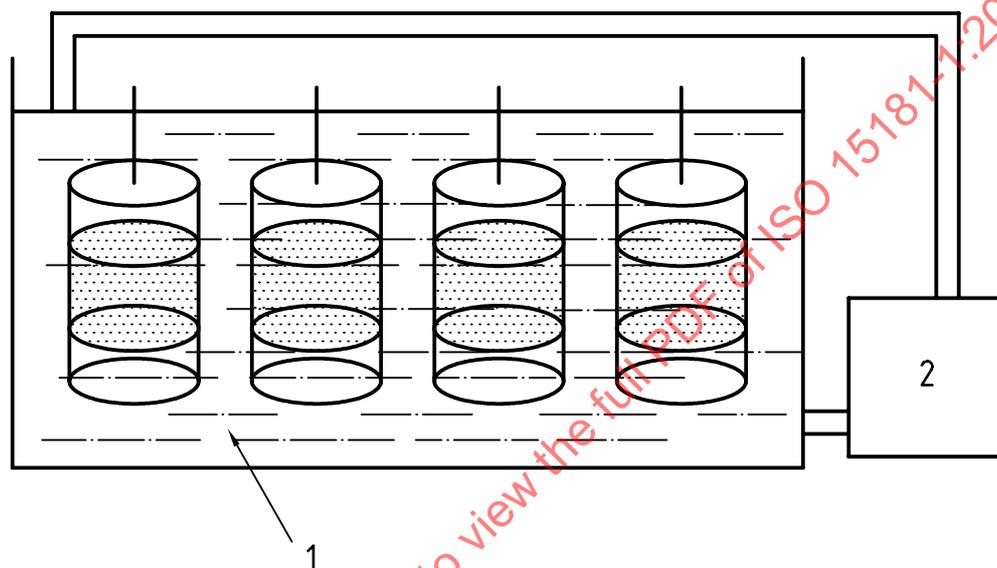
Release rate measuring container
 capacity: 1,8 litres to 2,2 litres
 diameter (A): 120 mm to 150 mm
 height (B): 170 mm to 210 mm
 baffles (C): three circular cross section rods of 4 mm to 8 mm diameter

Test cylinder
 diameter (D): 60 mm to 70 mm
 paint-free zone (E): 10 mm to 20 mm

Figure 1 — Release rate measuring container

5.4 Holding tank, made of an inert material (polycarbonate has been found suitable) of such dimensions as to permit the immersion of at least four test cylinders. The tank shall be equipped with a system to circulate the artificial seawater continuously through a filter/pump unit [see annex A, item A.2 g)] (see note) so that the concentration of the biocide remains below the specified limit [see annex A, item A.2 l)]. The size and positioning of the inlet and outlet ports shall be such as to obtain a slow and relatively uniform flow of artificial seawater past all the immersed cylinders. In general there shall be between six to eight changes of artificial seawater per hour. There shall be a means of maintaining the holding tank and its contents at $(25 \pm 1) ^\circ\text{C}$ (see note in 5.3). A typical holding tank set-up is shown in Figure 2.

NOTE To achieve the required flow rates and maintain a low biocide level in the holding tank, it may be necessary to have more than one pump/filter unit.



Key

- 1 Sea water
- 2 Filter unit

Figure 2 — Example of a holding tank

5.5 Sample bottles, for sampling the water at the end of each release rate period, which are sealable and of an inert material (polycarbonate has been found suitable), either new single-use disposable or cleaned glass (see 9.1) of appropriate capacity.

5.6 Artificial seawater, complying with ASTM D 1141.

The pH of the artificial seawater shall be in the range 7,9 to 8,1. Any necessary corrections shall be made by additions of solutions of 0,1 mol/l hydrochloric acid or 0,1 mol/l sodium hydrogen carbonate of analytical grade. If large corrections are to be made, then stronger solutions may be employed.

The salinity (including all dissolved salts) shall be in the range 33 to 34 parts per thousand practical salinity units (psu) when measured using a suitably calibrated conductivity probe apparatus or other method of equivalent accuracy, and adjusted by means of additions of water to grade 2 as defined in ISO 3696 or 5 mol/l sodium chloride solution.

NOTE 1 Proprietary sea salt mixtures which comply with ASTM D 1141 may be used. Their use will considerably decrease the preparation time and amount of solution storage required.

Before use, the artificial seawater shall be passed through a filter [see annex A, item A.2 g) and ISO 15181-2] until the concentration of the biocide is below the specified limit [see annex A, item A.2 m) and ISO 15181-2].

NOTE 2 This is because the chemicals used to prepare the artificial seawater might contain high concentrations of the biocide metal being determined even though they are of analytical grade.

5.7 Cleaning reagents, for cleaning all the equipment.

One of the following analytical-grade quality reagents will be required.

5.7.1 Hydrochloric acid, concentrated (ρ approximately 1,18 g/ml).

5.7.2 Hydrochloric acid, 10 % aqueous solution by volume, or **nitric acid**, 10 % aqueous solution by volume.

6 Sampling

Take a representative sample of the product to be tested (or of each product in the case of a multicoat system), as specified in ISO 15528.

Examine and prepare each sample for testing, as specified in ISO 1513.

7 Preparation of test cylinders

7.1 Perform testing on three cylinders for each antifouling paint system.

7.2 Clean the test cylinders (5.1) by immersing them in the concentrated hydrochloric acid (5.7.1) for at least 30 min, or one of the dilute acids (5.7.2) for at least 6 h to remove all traces of the biocide. Rinse thoroughly with water of at least grade 2 quality as defined in ISO 3696. The surface area to be painted may be lightly abraded with 200 grit paper to promote adhesion. Wipe the abraded area to remove any dust before coating.

NOTE Some biocides have a strong tendency to adsorb on certain glass or plastic surfaces which necessitates the above precautions.

7.3 Using masking tape, prepare an unmasked band on the exterior of the cylinder to the required area (see annex A, item A.2 j)), which will leave at least 10 mm to 20 mm height of unpainted area at the bottom once the tape has been removed.

7.4 Apply the antifouling paint system to the exterior circumferential surface of the test cylinders following the manufacturer's instructions for mixing and application [see annex A, item A.2 a)] to produce a smooth intact coating film (if applied by brush, the film shall not show brush marks) to give a 100 μm to 200 μm dry film thickness as measured by one of the non-destructive methods given in ISO 2808:1997 (e.g. method 1), unless otherwise specified. If during the test, the film thickness will be expected to fall below 50 μm , then a greater thickness of paint should be applied, unless otherwise specified. Identify each cylinder with a coating sample code or designation. Paints used shall be within the manufacturer's recommended shelf life and shall have been stored as specified by the manufacturer.

7.5 Carefully remove the masking tape without damaging the wet paint as soon as is practical.

7.6 Dry and condition the cylinders at a temperature of $(25 \pm 2) ^\circ\text{C}$ and relative humidity $(50 \pm 10) \%$ for at least 7 days unless otherwise recommended by the paint manufacturer. The painted cylinders shall not be stored beyond the manufacturer's recommended storage period prior to testing.

7.7 Prepare one cylinder painted with the reference paint [see annex A, item A.2 i)] as specified in 7.1 to 7.6.

NOTE Due to a proposed ban on the application of triorganotin antifouling paints from 2003-01-01, the specified reference paint for legislative purposes may not be readily available after this date. In such cases, another well-characterized composition may be substituted.

7.8 Prepare one uncoated (no paint) cylinder as a reference blank as specified in 7.2.

7.9 If several paints are evaluated in the same series, at the same time and in the same holding tank, then only one reference blank and one reference paint need to be used.

8 Procedure

8.1 Clean all the apparatus by immersion in the concentrated hydrochloric acid (5.7.1) for at least 30 min, or one of the dilute acids (5.7.2) for at least 6 h to remove all traces of the biocide. If the holding tank and associated equipment has not been cleaned previously, then it shall also be cleaned. Rinse thoroughly with water of grade 2 quality as defined in ISO 3696. Pass water of grade 2 quality as defined in ISO 3696 through the filter until the water is clear.

8.2 Set up the holding tank (5.4), fill with the artificial seawater (5.6) and adjust to meet the conditions specified in 5.4. Adjust the artificial seawater using the procedures defined in 5.6 until the conditions are stable.

8.3 Place the painted and reference cylinders (clause 7) into the holding tank (5.4) and arrange them so that the painted surfaces are completely submerged and that the artificial seawater can flow unimpeded around them.

8.4 At daily intervals, monitor the temperature and pH of the water, adjust using 0,1 mol/l hydrochloric acid or 0,1 mol/l sodium hydrogen carbonate as necessary (see 5.6).

8.5 Every 7 days, monitor the salinity, and adjust as required (see 5.6).

8.6 On each test day (see 8.7 and 8.8), sample the water and determine the concentration of biocide [see annex A, item A.2 f) and ISO 15181-2]. If the concentration of the biocide exceeds the specified limit [see annex A, item A.2 l) and ISO 15181-2], then change the filter.

8.7 After 1 day, 3 days, 7 days, 10 days, 14 days, 21 days, 24 days, 28 days, 31 days, 35 days, 38 days, 42 days and 45 days, perform the extraction method (see clause 9).

8.8 If testing beyond 45 days is specified, then perform the extraction method (see clause 9) at least once every 7 days until the maximum time has elapsed.

9 Extraction method

9.1 Prior to use, clean the release rate measuring containers (5.3) and any previously used or non-disposable sample bottles (5.5) by immersing them in the concentrated hydrochloric acid (5.7.1) for at least 30 min, or one of the dilute acids (5.7.2) for at least 6 h to remove all traces of the biocide. Rinse thoroughly with water of grade 2 quality as defined in ISO 3696.

9.2 Set up individual release rate measuring containers containing 1 500 ml of fresh artificial seawater (5.6) at a temperature of (25 ± 1) °C.

9.3 Remove each cylinder (including the references) from the holding tank and allow to drain for approximately 10 s. Dip in a cleaned beaker containing at least 500 ml of artificial seawater (5.6) for approximately 10 s, remove and allow to drain for approximately 10 s and transfer immediately to the release rate measuring containers. Do not allow the paint surface to dry. Attach to the rotating device (5.4) ensuring that the paint film is fully submerged. Immediately start the rotation of the device.

9.4 After the defined period [see annex A, item A.2 h)], remove the rotating device and transfer the cylinders back to the holding tank. When transferring the cylinders, do not touch the surfaces or in any way damage the paint coating, and do not allow the surface to dry.

9.5 Place an appropriate amount of water from the individual release rate measuring containers into the sample bottles (5.5). If required, treat the extract, store and analyse the water for biocide concentration as specified [see annex A, item A.2 k)].