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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 les peintures antisalissures —

Partie 1: Méthode générale d'extraction des biocides

Reference number
ISO 15181-1:2007(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

This second edition cancels and replaces the first edition (ISO 15181-1:2000), which has been technically revised, in particular to extend the use of the general extraction method to the later parts of ISO 15181.

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*
- *Part 3: Calculation of the zinc ethylene-bis(dithiocarbamate) (zineb) release rate by determination of the concentration of ethylenethiourea in the extract*
- *Part 4: Determination of pyridine-triphenylborane (PTPB) concentration in the extract and calculation of the release rate*
- *Part 5: Calculation of the tolylfluanid and dichlofluanid release rate by determination of the concentration of dimethyltolylsulfamide (DMST) and dimethylphenylsulfamide (DMSA) in the extract*

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 under the specified laboratory conditions can be determined using the method given in this part of ISO 15181, which can be used for quality assurance and material selection purposes. The actual release rate of biocides from antifouling paints on ships' hulls into the environment will, however, depend on many factors, such as ship operating schedules, length of service, berthing conditions, paint condition, as well as the temperature, salinity, pH, pollutants and biological community in a particular area.

The results of this test do not reflect environmental biocide release rates for antifouling products and are not suitable for direct use in the process of generating environmental-risk assessments, producing environmental-loading estimates or for establishing release rate limits for regulatory purposes. In comparison with copper and organotin release rates obtained either by direct or indirect measurements of the copper release rate from ships' hulls and from measurements made on panels exposed in harbours, all available data indicate that the results obtained using this generic test method significantly overestimate the release rates of biocides under in-service conditions. Published results demonstrate that the results of this test method are generally higher than direct *in situ* measurements of copper and organotin release rates from in-service ship hulls by a factor of about 10 or more for several commercial antifouling coatings [1, 2]. A similar relationship is expected to be found for other biocides. Realistic estimates of the biocide release rate from a ship's hull under in-service conditions can only be obtained from this test method if this difference is taken into account.

Where the results of this test method are used in the process of generating environmental-risk assessments, producing environmental-loading estimates or for regulatory purposes, it is most strongly recommended that the relationship between laboratory release rates and actual environmental inputs be taken into account to allow a more accurate estimate of the biocide release rate from antifouling coatings under real-life conditions to be obtained. This can be accomplished through the application of appropriate correction factors [2].

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 specifies a general method for extracting biocides from antifouling paint films into artificial seawater under specified laboratory conditions. It is used in conjunction with the other parts of ISO 15181 to determine the amounts of specific biocides in the extract, for example copper and/or certain organic biocides, and to enable the release rate of those biocides from the paint film under the specified laboratory conditions to be calculated.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 2808, *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 15181-3, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 3: Calculation of the zinc ethylene-bis(dithiocarbamate) (zineb) release rate by determination of the concentration of ethylenethiourea in the extract*

ISO 15181-4, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 4: Determination of pyridine-triphenylborane (PTPB) concentration in the extract and calculation of the release rate*

ISO 15181-5, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 5: Calculation of the tolylfluanid and dichlofluanid release rate by determination of the concentration of dimethyltolylsulfamide (DMST) and dimethylphenylsulfamide (DMSA) in the extract*

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

ASTM D 1141-98(2003), *Standard Practice for the Preparation of Substitute Ocean Water*

3 Principle

Test cylinders painted with antifouling paint are immersed, together with reference cylinders, 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 is then determined. This operation is repeated at defined time intervals and hence the release rate of the biocide under the specified laboratory conditions can be calculated.

4 Required supplementary information

For each application, the items of supplementary information listed in Annex A shall be supplied as appropriate to enable the test method given in this part of ISO 15181 to be carried out.

5 Apparatus

NOTE Some biocides have a strong tendency to adsorb onto certain glass or plastic substrates.

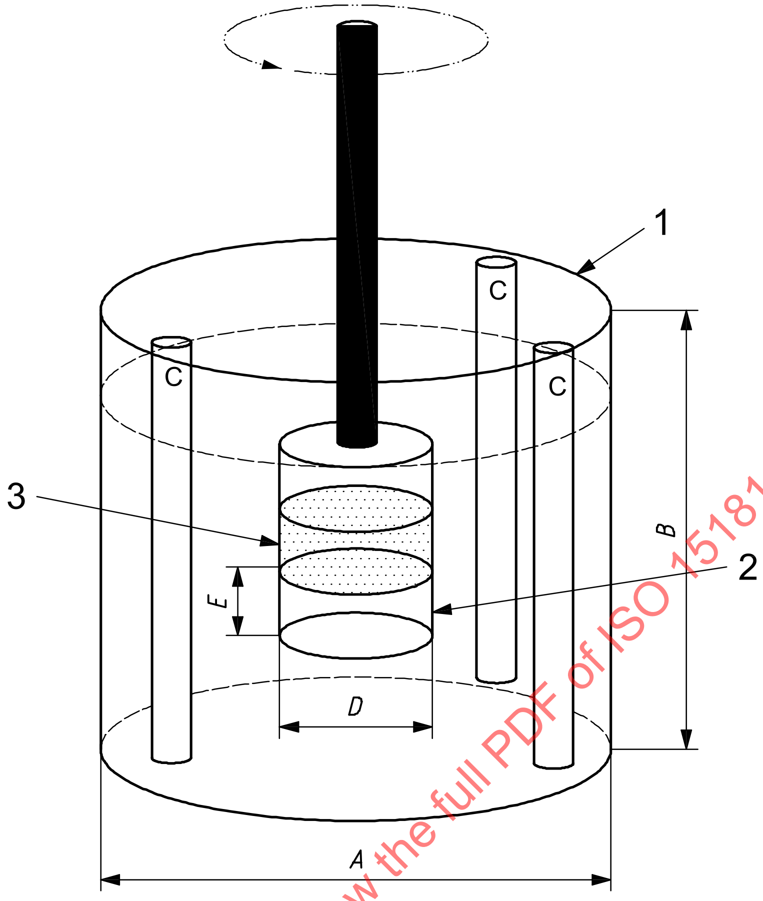
5.1 Test cylinder, made of an inert material [see Annex A, item A.2 a)], having a diameter of (64 ± 5) mm and length of (178 ± 15) mm, and closed at both ends so that it is watertight.

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 ± 0,02) m/s]. The device itself shall not be allowed to come into contact with the artificial seawater.

5.3 Release rate measuring container (see Figure 1), made of an inert material [see Annex A, item A.2 b)], of nominal capacity (2 ± 0,2) litres, 120 mm to 150 mm in 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 shall consist of circular rods of diameter 5 mm to 7 mm running from the bottom of the container to a level at least above that of the artificial seawater. They shall be fixed in place 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.

If the release rate of a highly photosensitive biocide is being determined, then the container shall be protected from natural and artificial visible-light sources. Details of this requirement to protect the container from light are indicated in the part of this standard relating to determination of the release rate of that biocide.



Key

1 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 diameter 5 mm to 7 mm

2 test cylinder
 diameter (D): 59 mm to 69 mm
 paint-free zone (E): 10 mm to 20 mm

3 painted zone

Figure 1 — Release rate measuring container and test cylinder

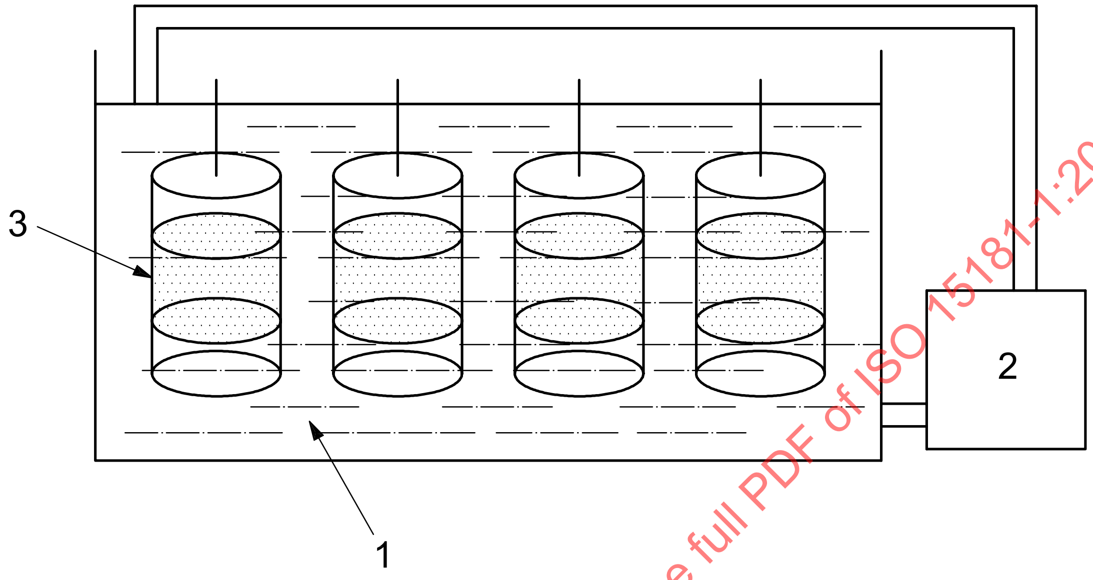
5.4 Holding tank, made of an inert material (polycarbonate has been found suitable) of such dimensions as to permit the immersion of at least four test cylinders.

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 c)] so that the concentration of the biocide remains below the specified limit [see Annex A, item A.2 d)] for the duration of the test [see Annex A, item A.2 e)]. To achieve the required flow rates and maintain a low biocide level in the holding tank, it might be necessary to have more than one pump/filter unit. It is recommended that the capacity of the filter units be selected so that they require regeneration or replacement no more frequently than once every 30 days.

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 should be between two and eight changes of artificial seawater per hour.

There shall be a means of maintaining the holding tank and its contents at (25 ± 1) °C (see Note to 5.3).

A typical holding tank set-up is shown in Figure 2.



Key

1	seawater
2	filter unit
3	painted zone

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, polypropylene and borosilicate glass have been found suitable), either new single-use disposable or cleaned glass (see 9.1), of appropriate capacity.

6 Reagents and materials

Unless otherwise specified, use only reagents of recognized analytical grade.

6.1 Cleaning reagents.

Use one of the following reagents for cleaning all the equipment:

6.1.1 Hydrochloric acid, concentrated aqueous solution, 37 % by mass.

6.1.2 Hydrochloric acid, aqueous solution, 10 % by volume.

6.2 Artificial seawater, conforming to the requirements of Section 6 of ASTM D 1141-98(2003).

The pH of the artificial seawater shall be in the range 7,9 to 8,1 and 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.

NOTE 1 The term “substitute ocean water” used in ASTM D 1141 is synonymous with the term “artificial seawater” used in this part of ISO 15181.

NOTE 2 Proprietary sea salt mixtures which conform to the requirements of 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 c)].

NOTE 3 This is because the chemicals used to prepare the artificial seawater could contain high concentrations of the biocide metal being determined even though they are of analytical grade.

6.3 **Sodium hydroxide**, aqueous solution, 1,0 mol/l.

6.4 **Hydrochloric acid**, aqueous solution, mass fraction 10 %.

6.5 **Sodium chloride**, aqueous solution, 5 mol/l.

6.6 **Water**, conforming to the requirements of grade 2 of ISO 3696.

7 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.

8 Preparation of test cylinders

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

8.2 Clean the test cylinders and rinse thoroughly with water. The surface area to be painted shall be lightly abraded with 200 grit paper to promote adhesion. Wipe the abraded area to remove any dust before coating.

8.3 Using masking tape, prepare an unmasked band of the required area on the exterior of the cylinder (see Annex A, item A.2 f)], which will leave a 10 mm to 20 mm high unpainted area at the bottom once the tape has been removed.

8.4 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 g)], 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, unless otherwise specified. If, during the test, the film thickness will be expected to fall below 50 µm, then apply a greater thickness of paint, unless otherwise specified. Identify each cylinder with a coating sample code or designation. Paints used shall have been manufactured at least 7 days prior to testing, shall be within the manufacturer's recommended shelf life and shall have been stored as specified by the manufacturer.

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

8.6 Dry and condition the cylinders at a temperature of (25 ± 2) °C and relative humidity of (55 ± 25) % for (7 ± 1) days unless otherwise recommended by the paint manufacturer.

8.7 Prepare one uncoated cylinder (i.e. a cylinder without any paint) as specified in 8.2 as a reference blank.

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

9 Procedure

9.1 Clean all glass apparatus by immersion in concentrated hydrochloric acid (6.1.1) for at least 30 min, or in dilute acid (6.1.2) for at least 6 h, to remove all traces of biocide. If the holding tank, release rate measuring container and associated equipment has not been cleaned previously, then it shall also be cleaned. Rinse thoroughly with grade 2 water (6.6). Pass grade 2 water through the filter until the water is clear.

9.2 Set up the holding tank, fill with artificial seawater and adjust so that the temperature is within the range (25 ± 1) °C, the salinity is within the range 33 to 34 parts per thousand practical salinity units (psu), and the pH is within the range 7,9 to 8,1. Adjust the salinity as necessary using water or sodium chloride solution, and adjust the pH as necessary using hydrochloric acid (6.4) or sodium hydroxide solution (6.3) until the conditions are stable.

NOTE Alternative concentrations of these solutions may be used to adjust the salinity and pH of the artificial seawater where appropriate to the magnitude of the required correction.

9.3 Place the painted and reference blank cylinders (see Clause 8) in the holding tank and arrange them so that the painted surfaces are completely submerged, the cylinders are stationary, and the artificial seawater can flow unimpeded around them.

9.4 Maintain the artificial seawater in the holding tank under the conditions specified in 9.2 for the duration of the test [see Annex A, item A.2 e)]. Monitor the conditions at least every third day and adjust as required to maintain them as specified in 9.2.

NOTE More frequent monitoring of the pH and salinity might be required to maintain the artificial seawater in the holding tank within the prescribed ranges, particularly during the early stages of a study while the system equilibrates.

9.5 Maintain the concentration of the biocide in the holding tank below the specified limit [see Annex A, item A.2 d)] for the duration of the test [see Annex A, item A.2 e)]. On each test day (see 9.6 and 9.7), sample the water and determine the concentration of biocide [see Annex A, item A.2 j)]. When the concentration of the biocide approaches the specified limit [see Annex A, item A.2 l)], then change the filter.

9.6 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 10).

9.7 If testing beyond 45 days is specified, then perform the extraction method (see Clause 10) at least once every 7 days until the maximum time has elapsed.

10 Extraction method

10.1 Set up individual release rate measuring containers containing 1 500 ml of fresh artificial seawater at a temperature of (25 ± 1) °C. Before use, pass the artificial seawater through a filter [see Annex A, item A.2 c)].

10.2 Remove each cylinder (including the references) from the holding tank, 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, ensuring that the paint film is fully submerged. Immediately start the rotation of the device.

10.3 After the defined period [see Annex A, item A.2 k)], 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.

10.4 Place an appropriate amount of water from the individual release rate measuring containers into sample bottles. If required, treat the extract, then store it and analyse the water to determine the biocide concentration as specified [see Annex A, item A.2 j)].

10.5 At the conclusion of the test, allow the cylinders to dry for a minimum of 12 h under ambient conditions and re-measure the dry-film thickness of the coating on the test cylinders (see 8.4).