
**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**

*Peintures et vernis — Détermination du taux de lixiviation des biocides
contenus dans les peintures antisalissures —*

*Partie 2: Détermination de la concentration ionique du cuivre dans
l'extrait et calcul du taux de lixiviation*



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Contents

Page

Foreword.....	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Principle	1
4 Supplementary information required for the copper extraction procedure	2
5 Apparatus	2
6 Reagents and materials	2
7 Test samples	2
8 Procedure	3
9 Calculation and expression of results.....	4
10 Precision.....	7
11 Test report	7
Annex A (normative) Supplementary information required for the copper extraction procedure	9
Bibliography	10

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 15181-2 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 15181-2:2000), which has been technically revised.

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 2: Determination of copper-ion concentration in the extract and calculation of the release rate

1 Scope

This part of ISO 15181 specifies the apparatus and analytical method for determining the amount of copper (based) biocide that has been released from an antifouling paint into artificial seawater in accordance with the procedure given in ISO 15181-1.

It determines the copper-ion concentration and gives the final calculation for the release rate of copper under the specified laboratory conditions. This part of ISO 15181 is designed to generally allow the concurrent determination of copper ions and other biocides that might be released by a given antifouling paint through the analysis of separate sub-samples of an artificial seawater extract generated in accordance with the procedure given in ISO 15181-1, and analysed in accordance with the procedures given in other parts of this International Standard.

When used in conjunction with ISO 15181-1, the practical limits on the quantitative measurement of release rates by this method are from $1,8 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ to $500 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$. The quantitative measurement of release rates below this range will require the use of an analytical method with a lower limit of quantitation for copper in artificial seawater than the limit specified in 5.1.

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

ISO 15181-1:2007, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 1: General method for extraction of biocides*

ASTM D 6442-06, *Standard Test Method for Determination of Copper Release Rate from Antifouling Coatings in Substitute Ocean Water*

3 Principle

The concentration of the copper ions released into artificial seawater in accordance with the procedure given in ISO 15181-1 is determined by the use of an atomic absorption spectrometer or by an alternative analytical method, provided that it demonstrates a limit of quantitation for copper in artificial seawater of $10 \mu\text{g/l}$ or less. The release rate of the biocide is then calculated as copper metal.

4 Supplementary information required for the copper extraction procedure

The items of supplementary information required to be able to use the general extraction procedure, described in ISO 15181-1, for copper-based biocides are given in Annex A.

5 Apparatus

5.1 Atomic absorption spectrometer, preferably with autosampler, or **other suitable instrument**, which has a limit of quantitation for copper in artificial seawater of 10 µg/l or less. The limit of quantitation shall be determined by the procedure given in Annex 2 (Determination of the LOQ for Copper in Substitute Ocean Water for the Analytical Method) of ASTM D 6442-06.

5.2 Mechanical shaker, with appropriate holders.

5.3 Dispensers, automatic or repeating, for reagents.

5.4 Pipettes, of appropriate volume, with disposable tips.

5.5 Volumetric flasks, of appropriate volume.

5.6 Sample tubes, of appropriate capacity, with screw closures, made of an inert material.

NOTE Polypropylene, polycarbonate and borosilicate glass have been found to be suitable.

6 Reagents and materials

Suppliers' material safety data sheets should be consulted for details of any hazards associated with the reagents listed below, and the risks associated with their use should be assessed. Appropriate protective clothing and equipment should be utilized.

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 Nitric acid, concentrated (ρ approximately 1,42 g/ml).

6.3 Artificial seawater, as defined in ISO 15181-1.

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

7 Test samples

Use extracts taken from the release rate measuring containers as described in ISO 15181-1.

8 Procedure

8.1 General

Carry out all determinations on the extract using the following method. An alternative method of analysis is allowed providing it has a limit of quantitation for copper ions in artificial seawater of 10 µg/l or less, determined by the procedure given in Annex 2 (Determination of the LOQ for Copper in Substitute Ocean Water for the Analytical Method) of ASTM D 6442-06, a recovery of (100 ± 10) % for artificial seawater recovery check standards containing copper ions at concentrations of 50 µg/l and 200 µg/l, and a recovery of (100 ± 15) % for an artificial seawater recovery check standard containing copper ions at a concentration of 10 µg/l.

Clean all non-disposable or re-used apparatus by immersion in concentrated hydrochloric acid (6.1.1) for at least 30 min, or dilute acid (6.1.2) for at least 6 h, to remove all traces of biocide. Rinse thoroughly with grade 2 water (6.4).

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

Operate the spectrometer or other apparatus in accordance with the manufacturer's instructions.

8.2 Sample treatment

Immediately acidify the test samples by the addition of 0,10 ml of concentrated nitric acid (6.2) per 100 ml of test sample, agitate for at least 10 min, and then filter through a 0,45 µm filter. The solution may then be stored at a temperature between 2 °C to 6 °C for up to 14 days before analysis. Solutions shall be allowed to come to equilibrium at room temperature before analysis.

8.3 Preparation of standard calibration solutions

Prepare five calibration standards of a copper salt in artificial seawater, which has been acidified by the addition of 0,10 ml of concentrated nitric acid per 100 ml of artificial seawater, to define the working range of the method. Select the copper concentrations as a function of the results expected.

If an instrument other than an atomic absorption spectrometer is used (see 5.1), calibration standards may be prepared in a medium appropriate to the instrument used.

8.4 Preparation of recovery check standards

Prepare standards of a suitable copper salt as recovery check standards at concentrations of 10 µg/l, 50 µg/l and 200 µg/l in artificial seawater and treat as specified in 8.2. Additional check samples may be prepared at copper concentrations appropriate to the samples being analysed.

8.5 Instrument calibration

At the beginning of each instrument run, analyse the calibration standards and calculate the slope, intercept and correlation coefficient for each calibration curve using the least squares fit or another appropriate technique. Plot separate calibration curves for each analysis of the calibration standards (instrument response versus copper-ion concentration). Analyse an artificial seawater blank that has been treated as specified in 8.2. Analyse the recovery check standards and determine the recovery. If the recovery of any check standard is outside the range (100 ± 10) % for recovery check standards containing copper ions at a concentration of 50 µg/l and 200 µg/l, or (100 ± 15) % for recovery check standards containing copper ions at a concentration of 10 µg/l, then prepare fresh calibration and recovery check standards and recalibrate.

The acceptable limits for the recovery of additional check standards, if used, are (100 ± 15) % for recovery check standards with copper concentrations below 50 µg/l, and (100 ± 10) % for recovery check standards with copper concentrations greater than 50 µg/l.

If an instrument other than an atomic absorption spectrometer is used (see 5.1), it is important that the artificial seawater blank and recovery check standards are processed exactly as specified for test samples.

8.6 Sample determination

Using the atomic absorption spectrometer or other suitable instrument (see 5.1), determine the concentration of copper in the treated test samples for each test cylinder and uncoated reference blank (see 8.1 and 8.7 of ISO 15181-1:2007).

9 Calculation and expression of results

9.1 Calculation of copper concentration

Calculate the concentration of the copper released into the artificial seawater, C_{Cu} , in $\mu\text{g/l}$, for each individual measuring container on each test day using the equation

$$C_{Cu} = (C_V \times F) - C_B$$

where

C_V is the concentration of copper in the treated test sample, in $\mu\text{g/l}$;

C_B is the concentration of copper in the artificial seawater blank, in $\mu\text{g/l}$;

F is a correction factor for the amount of sample in the volumetric flask (= 1,001) (this correction factor is made necessary by the way the extract is treated — see 8.2).

9.2 Release rate for each test cylinder

Calculate the release rate, R , in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, for each test cylinder on each test day using the equation

$$R = \frac{C_{Cu} \times V \times 24}{t \times A}$$

where

C_{Cu} is the concentration of the copper released into the measuring container, in $\mu\text{g/l}$ (see 9.1);

24 is the number of hours in a day;

V is the volume, in litres, of seawater in the measuring container (= 1,5), as specified in 10.1 of ISO 15181-1:2007;

t is the length of time, in hours, the cylinder was immersed and rotated in the measuring container (see Annex A, Table A.1, item 5);

A is the surface area, in cm^2 , of the paint film (= 200) (see Annex A, Table A.1, item 6).

This equation can be simplified if the standard volume, time and area, as given above, are used:

$$R = \frac{C_{Cu} \times 0,18}{t}$$

9.3 Mean release rate for each set of three cylinders

Calculate the mean copper release rate, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, for each set of three test cylinders on each test day (see 9.2).

9.4 Cumulative copper release

Calculate the 14-day cumulative release of copper, $R_{0,14}$, in $\mu\text{g}\cdot\text{cm}^{-2}$, using the equation

$$R_{0,14} = \sum \bar{R}_{i,j}(j-i) = \sum \frac{(R_i + R_j)}{2}(j-i)$$

where

$\bar{R}_{i,j}$ is the mean copper release rate, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, between consecutive test days i and j for all test days up to day 14;

i and j are the times, in days, from the start of the trial for each pair of consecutive test days, specifically 0 and 1 days, 1 and 3 days, 3 and 7 days, etc. (see 9.6 and 9.7 of ISO 15181-1:2007);

R_i and R_j are the mean copper release rates for each set of three test cylinders, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ (see 9.3), for each pair of consecutive test days from the start of the trial up to day 14, specifically days 0 and 1, days 1 and 3, days 3 and 7, etc., and where the release rate on day 0 (R_0) is taken as $0 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$.

NOTE The cumulative release of copper for other periods of time may be calculated, if specified, using the equation

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

where

$R_{x,y}$ is the cumulative release of copper, in $\mu\text{g}\cdot\text{cm}^{-2}$, from day x to day y ;

$\bar{R}_{i,j}$ is the mean copper release rate, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, between consecutive test days i and j for all test days from day x to day y ;

i and j are the times, in days, from the start of the trial for each pair of consecutive test days, for example 0 and 1 days, 1 and 3 days, 3 and 7 days, etc., and, where day 0 is included, the release rate on day 0 (R_0) is taken as $0 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$;

R_i and R_j are the mean copper release rates for each set of three test cylinders, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ (see 9.3), for each pair of consecutive test days from day x to day y , for example days 0 and 1, days 1 and 3, days 3 and 7, etc., and, where day 0 is included, the release rate on day 0 (R_0) is taken as $0 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$.

9.5 Mean copper release rate

Calculate the weighted mean copper release rate from day 21 to the final test day, $\bar{R}_{21,end}$, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, using the equation

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

where

$\bar{R}_{i,j}$ is the mean copper release rate, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, between consecutive test days i and j for all test days from day 21 through to the final test day;

i and j are the times, in days, which have elapsed since the start of the trial for each pair of consecutive test days, specifically 21 and 24 days, 24 and 28 days, 28 and 31 days, etc. (see 9.6 and 9.7 of ISO 15181-1:2007);

R_i and R_j are the mean copper release rates for each set of three test cylinders, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ (see 9.3), for each pair of consecutive test days from day 21 up to the final test day, specifically days 21 and 24, days 24 and 28, days 28 and 31, etc.

NOTE 1 This equation calculates the weighted mean release rate, taking into account any differences in time between test days, and is a more valid treatment of the data than calculating the simple arithmetic mean. The calculation may be conveniently done using a suitable computer-generated spreadsheet.

NOTE 2 The mean copper release rate over other periods of time may be calculated, if specified, by modifying this equation to account for the different test days used.

9.6 Pseudo-steady-state mean copper release rate

If the coating exhibits a pseudo-steady state, calculate the pseudo-steady-state copper release rate, \bar{R}_{PSS} , in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, using the equation

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

where $\bar{R}_{i,j}$, j , i , R_i and R_j are as defined in the Note to 9.4.

For the purposes of this part of ISO 15181, a “pseudo-steady state” is defined as being a period of at least 24 days and including four or more test days, where the mean copper release rate for the set of three test cylinders on each test day (see 9.3) 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 Not all coatings will exhibit a pseudo-steady state. Where a coating does exhibit a pseudo-steady state, the determined pseudo-steady-state biocide release rate 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 can continue to change beyond the test period.

10 Precision

10.1 Repeatability

To be determined.

10.2 Reproducibility

The value below which the relative difference between two single test results, each the mean of duplicates, obtained from identical material (an organotin copolymer reference paint containing cuprous oxide) by operators in different laboratories using the standardized test method may be expected to lie, with a 95 % probability, is:

14-day cumulative: 10 %;

45-day cumulative: 14 %;

21- to 45-day average: 23 %.

These reproducibility values were obtained from a mixed biocide reference system that showed good reproducibility in a round-robin test^[3]. However, some materials do exhibit poor reproducibility, and it has been found that some systems have a reproducibility which can be expected, with a 95 % probability, to be, typically:

14-day cumulative: 22 %;

45-day cumulative: 33 %;

21- to 45-day average: 56 %.

NOTE These last three reproducibility values were obtained in a round robin conducted for 42 days (see Reference [3]).

11 Test report

The test report shall contain at least the following information:

- a) all information necessary for identification of the sample tested;
- b) a reference to this part of ISO 15181 (ISO 15181-2:2007);
- c) all details necessary to describe the method used:
 - the type of analytical equipment used, the manufacturer of the equipment and the method of analysis employed,
 - all details required by ISO 15181-1;
- d) the results of the test, including the results of the individual determinations and their mean, calculated as specified in Clause 9, including:
 - the limit of quantitation for copper in artificial seawater for the analytical method, determined by the laboratory performing the test method (see 5.1);
 - the concentration of copper in the artificial seawater, in µg/l, for each test cylinder on each test day (see 9.1);

- the rate of copper release into the artificial seawater, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, for each test cylinder on each test day (see 9.2) and the mean copper release rate, in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, for each set of three test cylinders on each test day (see 9.3);
 - a graph showing the rate of copper release as a function of time;
 - the 14-day cumulative copper release and the cumulative copper release for other periods, if specified (see 9.4);
 - the mean release rate from day 21 to the end of the trial, and the mean release rate for other periods, if specified (see 9.5);
 - the pseudo-steady-state release rate, if calculated (see 9.6);
 - the length of time the cylinders were rotated to extract the biocide on each test day (see Annex A, Table A.1, item 5);
- e) any deviations from the test procedure specified;
- f) any unusual features (anomalies) observed during the test;
- g) the name of the test laboratory;
- h) the dates of the test.

Annex A (normative)

Supplementary information required for the copper extraction procedure

The items of supplementary information listed in Table A.1 shall be used when extracting the copper from the antifouling paint by the method given in ISO 15181-1.

Table A.1 — Information concerning the copper extraction procedure

1	Test cylinder	The test cylinder shall be made of polycarbonate.
2	Release rate measuring container	The release rate measuring container and baffles shall be made of polycarbonate.
3	Holding tank filter type	An activated charcoal filter, optionally combined with a styrene-supported iminodiacetic acid chelating ion-exchange resin with a typical particle-size range of about 0,300 mm to 0,850 mm, which is capable of removing transition metals from seawater. NOTE Combining an activated-charcoal filter with an ion-exchange resin might reduce the overall size of the required filter unit.
4	Maximum holding tank biocide limit	The maximum holding tank biocide limit shall be 100 µg/l.
5	Length of time the cylinders are rotated to extract the biocide	The length of time the cylinders are rotated shall be 1,0 h except that, if, when a measurement is made, the copper-ion concentration determined in a particular release rate measuring container exceeds 200 µg/l, then the rotation period for the next measurement shall be reduced. The amount by which the rotation period is reduced shall be selected based on familiarity with the coating being evaluated and experience with the test method, and shall take into account the extent by which the measurement exceeds 200 µg/l. If the next measurement also exceeds 200 µg/l, then the rotation period shall be further reduced. Once the rotation period has been reduced sufficiently for the copper-ion concentration to no longer exceed 200 µg/l, then the rotation period shall subsequently be incrementally increased to 1 h at the earliest possible opportunity without the copper-ion concentration exceeding 200 µg/l. If the copper-ion concentration exceeds 200 µg/l for any measurement, record this in the test report. If the rotation period was less than 1 h for any measurement, report this fact also.
6	Area of cylinder coated	The area of the cylinder surface coated shall be 200 cm ² . NOTE Alternative sample areas may be used when 200 cm ² is not appropriate; for example, where a coating is expected to show a high release rate, a sample area of 100 cm ² may be used to avoid exceeding copper concentrations of 200 µg/l in the measuring container.

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