INTERNATIONAL STANDARD

ISO 15181-2

First edition
2000-11-15

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 la peinture antisalissure —

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

Reference number
ISO 15181-2:2000(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

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 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 15181-2 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*

Annexes A and B form 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.

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 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 the apparatus and analysis technique for determining copper (based) biocides in artificial seawater which have been extracted from antifouling paints in accordance with ISO 15181-1. It determines the copper-ion concentration and gives the final calculation for the release rate of copper. It has been proven that small changes in certain parameters of the test method can greatly affect the leaching rate of certain biocides, therefore, the release rates are compared against a well-documented reference standard as a means of establishing that test conditions are within normal operating parameters.

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 1524, *Paints, varnishes and printing inks — Determination of fineness of grind*.

ISO 2811-1, *Paints and varnishes — Determination of density — Part 1: Pyknometer method*.

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

ISO 15181-1:2000, *Paints and varnishes — Determination of release rate of biocides from antifouling paints — Part 1: General method for extraction of biocides*.

3 Principle

The concentration of the copper ions released into artificial seawater by the method defined in ISO 15181-1 is determined by the use of an atomic absorption spectrometer or by another agreed instrument which has been shown to have equivalent or better precision. The release rate of the biocide is then calculated as copper metal.

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 Atomic absorption spectrometer, preferably with autosampler, or **other agreed instrument** which has been shown to have a quantification limit for the analytical method of 10 μg/l or less.

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 Centrifuge tubes, of appropriate capacity, with screw closures, made of an inert material, or disposable tubes have been found suitable.

5.7 Cleaning reagents, for cleaning all 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.

5.8 Analysis reagents, all of analytical grade or equivalent.

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

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

5.8.3 Standard copper in artificial seawater solutions.

Prepare a suitable number of standards of a copper salt in the artificial seawater at concentrations between 0 μg/l and 400 μg/l, which contain nitric acid (5.8.1) at a concentration of 1,0 % by volume. Appropriate copper concentrations shall be made dependent upon expected results.

5.8.4 Standard calibration check solution.

Prepare a standard of a suitable copper salt as a calibration check sample at a suitable concentration dependent upon expected results, containing nitric acid (5.8.1) at a concentration of 1,0 % by volume.

6 Procedure

6.1 General

Carry out all determinations on the extract in triplicate using the following method. An alternative method of analysis is allowed providing it has as good as or better detection limits, repeatability and reproducibility.

Clean all non-disposable or reused 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. Rinse thoroughly with water of grade 2 quality in accordance with ISO 3696.

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 (5.1) in accordance with the manufacturer's instructions.

6.2 Instrument calibration

At the beginning of each instrument run, determine the copper-ion concentrations of a blank (5.8.2), the standards (5.8.3) and the calibration check sample (5.8.4). Plot separate calibration curves for each analysis of the standards (absorbance versus copper-ion concentration).

6.3 Sample determination

Analyse for copper content with the atomic absorption spectrometer (5.1). If any result differs by more than 10 % from the mean, discard that result and reanalyse another sample of the extract.

6.4 Calculation

6.4.1 Calculate (see clause 7) the average copper release rate, in μg/cm^2 per day. If the difference between triplicate test cylinders is more than 20 % then examine the results and the trend from the results at measurements on days on either side. If these indicate that the measurement of one of the cylinders may be erroneous, then that cylinder shall be ignored.

6.4.2 If the results of the release rate of the reference paint (annex B) are outside the range of 12 μg/cm^2 per day to 36 μg/cm^2 per day, then the reasons shall be investigated and the method repeated.

6.4.3 Calculate (see clause 7) the average copper release rate, in μg/cm^2 per day, the total release rate, in μg/cm^2 per day and the cumulative total release rate for 45 days (or 73 days, if specified), in μg/cm^2.

7 Expression of results

7.1 Calculate the concentration of the released copper in the artificial sea water in the measuring container as follows:

$$C_{\text{Cu}} = (C_{\text{v}} \times F) - C_{\text{B}}$$

where

C_{Cu} is the concentration of released copper, in μg/l;

C_{v} is the concentration of copper in the volumetric flask, in μg/l;

C_{B} is the concentration of copper in the artificial seawater blank;

F is a correction factor for the amount of sample in the volumetric flask $(= 1{,}01)$ (this factor is obtained from the extract treatment as described in annex A).

7.2 Calculate the release rate as follows:

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

where

R is the release rate, in μg/cm^2 per day;

D is the number of hours per day $(= 24)$;

V is the volume, in litres, of seawater in the measuring container $(= 1{,}5)$ (this is the volume of seawater specified in ISO 15181-1:2000, 9.2);

t is the time the cylinder is immersed in the measuring container, in hours (see annex A, A.2);

A is the surface area, in cm^2, of the paint film [= 100 (or 200)] (see annex A, A.2).

This formula can be simplified if the above standard volumes, times and sizes are used:

$$R = \frac{C_{Cu} \times 1{,}5 \times 24}{t \times 100}$$

$$R = \frac{C_{Cu} \times 0{,}36}{t}$$

7.3 Calculate the 14-day cumulative release of copper as follows:

$$R = R_1 + 2R_3 + 4R_7 + 3R_{10} + 4R_{14} + 2\,\frac{(R_1 - R_3)}{2} + 4\,\frac{(R_3 - R_7)}{2} + 3\,\frac{(R_7 - R_{10})}{2} + 4\,\frac{(R_{10} - R_{14})}{2}$$

$$R = R_1 + 2\,\frac{(R_1 + R_3)}{2} + 4\,\frac{(R_3 + R_7)}{2} + 3\,\frac{(R_7 + R_{10})}{2} + 4\,\frac{(R_{10} + R_{14})}{2}$$

$$R = 2R_1 + 3R_3 + \frac{7}{2}R_7 + \frac{7}{2}R_{10} + 2R_{14}$$

where

R is the 14-day cumulative release, in $\mu g/cm^2$;

R_1 is the release rate for sampling day 1, in $\mu g/cm^2$ per day;

R_3 is the release rate for sampling day 3, in $\mu g/cm^2$ per day;

R_7 is the release rate for sampling day 7, in $\mu g/cm^2$ per day;

R_{10} is the release rate for sampling day 10, in $\mu g/cm^2$ per day;

R_{14} is the release rate for sampling day 14, in $\mu g/cm^2$ per day.

7.4 Calculate the 45-day cumulative release of copper as follows:

$$R = 2R_1 + 3R_3 + \frac{7}{2}R_7 + \frac{7}{2}R_{10} + \frac{11}{2}R_{14} + 5R_{21} + \frac{7}{2}R_{24} + \frac{7}{2}R_{28} + \frac{7}{2}R_{31} +$$
$$+ \frac{7}{2}R_{35} + \frac{7}{2}R_{38} + \frac{7}{2}R_{42} + \frac{3}{2}R_{45}$$

where

R is the 45-day cumulative release, in $\mu g/cm^2$;

R_1 is the release rate for sampling day 1, in $\mu g/cm^2$ per day;ISO 15181-1ISO 15181-1ISO 15181-1

R_3 is the release rate for sampling day 3, in $\mu g/cm^2$ per day;

R_7 is the release rate for sampling day 7, in $\mu g/cm^2$ per day;

R_{10} is the release rate for sampling day 10, in $\mu g/cm^2$ per day;

R_{14} is the release rate for sampling day 14, in $\mu g/cm^2$ per day;

R_{21} is the release rate for sampling day 21, in μg/cm^2 per day;

R_{24} is the release rate for sampling day 24, in μg/cm^2 per day;

R_{28} is the release rate for sampling day 28, in μg/cm^2 per day;

R_{31} is the release rate for sampling day 31, in μg/cm^2 per day;

R_{35} is the release rate for sampling day 35, in μg/cm^2 per day;

R_{38} is the release rate for sampling day 38, in μg/cm^2 per day;

R_{42} is the release rate for sampling day 42, in μg/cm^2 per day;

R_{45} is the release rate for sampling day 45, in μg/cm^2 per day.

NOTE A simplified version of this equation is given in ASTM D6442-99 [1].

If specified (see 7.5), the 73-day release R_L is calculated as follows:

$$R_L = 2R_1 + 3R_3 + \frac{7}{2}R_7 + \frac{7}{2}R_{10} + \frac{11}{2}R_{14} + 5R_{21} + \frac{7}{2}R_{24} + \frac{7}{2}R_{28} + \frac{7}{2}R_{31} + \frac{7}{2}R_{35} + \\ + \frac{7}{2}R_{38} + \frac{7}{2}R_{42} + 5R_{45} + 7R_{52} + 7R_{59} + 7R_{66} + \frac{7}{2}R_{73}$$

where

R_L is the 73-day cumulative release, in μg/cm^2;

R_{52}, R_{59}, R_{66} and R_{73} are the release rates for sampling days 52, 59, 66 and 73, respectively.

If sampling beyond day 45 takes place more often than every 7 days (see ISO 15181-1:2000, 8.8), this equation may be modified to take account of the additional data points.

7.5 Calculate the average release rate, in μg/cm^2 per day, by averaging individual release rate measurements taken from day 21 through to day 45 (or up to day 73 if specified). If the values at day 21 are high and it is suspected that the release has not reached pseudo-steady-state conditions, then compare the release rate at day 21 to the mean for all release rates from day 21 through to the termination of testing at day 45 (or up to day 73 if specified). If the release rate exceeds the mean by two or more standard deviations, then the release rate may be excluded from the average. If the day 21 rate is excluded, the day 24 release rate may be evaluated by the same procedure.

8 Precision

8.1 Repeatability

To be determined.

8.2 Reproducibility

The value below which the absolute difference between two single test results, each the mean of duplicates, on identical material (B.2), obtained 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 %

This reproducibility was based on the mixed biocide reference system that showed good reproducibility in the ring test. However, some materials do exhibit poor reproducibility and it has been found that typically some systems have a reproducibility expected to lie within a 95 % probability of:

14-day cumulative 22 %

45-day cumulative 33 %

21- to 45-day average 56 %

NOTE The expected reproducibility is based on a round robin conducted for 42 days; see reference [2].

9 Test report

The test report shall contain at least the following information:

a) all details as given in ISO 15181-1;

b) a reference to this part of ISO 15181 (i.e. ISO 15181-2);

c) the items of supplementary information referred to in annex A;

d) the results of the test, in terms of the stated requirements;

e) the concentration of copper ions in the artificial seawater, in μg/l, for each sampling time;

f) the rate of copper release into the artificial seawater, in $\mu g/cm^2$ per day, for each sampling time;

g) a graph showing the rate of copper ions release as a function of time;

h) the 14-day cumulative release rate;

i) the 45-day cumulative release rate (or 73-day if specified);

j) the average release rate;

k) the leach duration for each time period;

l) the type and manufacturer of analysis equipment and methodology employed;

m) any deviation from the test procedure specified;

n) the dates of the test.

Annex A
(normative)

Required supplementary information

A.1 The items of supplementary information listed in this annex shall be supplied as appropriate to enable the method to be carried out.

A.2 The information required should preferably be agreed between the interested parties and may be derived, in part or totally, from an international or national standard or other document related to the product under test.

a) Any deviations from the defined method of analysis to be used.

b) The following information to allow the extraction of the biocide by the method of ISO 15181-1.

1	Holding tank filter type	A chelating ion exchange resin, which will remove transition metals from seawater and an activated charcoal filter.
2	Initial water biocide limit	10 μg/l maximum
3	Holding tank biocide limit	100 μg/l maximum
4	Rotation period	The rotation period for the initial measurement shall be 1,0 h. The rotation period for subsequent measurements shall be adjusted so that the copper-ion concentration in the release rate measuring container remains in the range 100 μg/l to 200 μg/l based on the previous measurement and the anticipated behaviour of the paint. If the copper-ion concentration is outside this range for any measurement, record this in the final report.
5	Reference paint	For legislative purposes the reference paint shall be: French Navy M150 standard formulation, an “acrylic self-polishing antifouling topcoat, red” (see annex B). For batch-to-batch or product development purposes, the reference paint may be of any suitable well-characterized composition.
6	Sample area	100 cm^2 NOTE A sample area of 200 cm^2 can also be used in special cases (e.g. for organotin-based paints where the copper leaching is normally medium to low).
7	Extract treatment	Immediately acidify with nitric acid (5.8.1) to give a 1 % by volume solution and then filter through a 0,45 μm filter. The solution may then be stored at a temperature between 2 °C to 4 °C for up to 7 days before analysis. Solutions shall be allowed to equilibrate to room temperature before analysis.