INTERNATIONAL STANDARD

ISO 15181-6

First edition
2012-07-15

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

Part 6: Determination of tralopyril release rate by quantitation of its degradation product in the extract

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

Partie 6: Calcul du taux de lixiviation du tralopyril par quantitation de son produit de dégradation dans l'extrait

Reference number
ISO 15181-6:2012(en)

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Published in Switzerland

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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 15181-6 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*

— *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*

— *Part 6: Determination of triclopyril release rate by quantitation of its degradation product 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 depends, however, on many factors, such as ship operating schedules, length of service, berthing conditions, paint condition, as well as temperature, salinity, pH, pollutants, and biological community.

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 rate measurements 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 of this generic test method significantly overestimate the release rate of biocide 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 rate from the hulls of harboured ships 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 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 environment 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 6: Determination of tralopyril release rate by quantitation of its degradation product in the extract

1 Scope

This part of ISO 15181 specifies a method for determining the amount of tralopyril that has been released from an antifouling paint into artificial seawater in accordance with the procedure given in ISO 15181-1.

Tralopyril is unstable in water and degrades hydrolytically to form 3-bromo-5-(4-chlorophenyl)-4-cyano-1H-pyrrole-2-carboxylic acid (BCCPCA). This part of ISO 15181 specifies a method for accelerating the conversion of the released tralopyril into this degradation product by heat treatment and quantifying the concentration of the BCCPCA degradation product in the artificial seawater extract, and gives the final calculation for the release rate of tralopyril under the specified laboratory conditions.

This part of ISO 15181 is designed to allow the concurrent determination of tralopyril and other biocides that can be released by a given antifouling paint (for example, zineb) through the analysis of separate sub-samples of an artificial seawater extract generated in accordance with ISO 15181-1.

When used in conjunction with ISO 15181-1, the practical limits for quantifying release rates by this method are from 0,36 µg cm^{-2} d^{-1} to 270 µg cm^{-2} d^{-1}. The quantitation of release rates lower than this range requires the use of an analytical method with a limit of quantitation for tralopyril in artificial seawater of less than 2 µg/l.

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 D6442-06, *Standard test method for determination of copper release rate from antifouling coatings in substitute ocean water*

3 Principle

The quantity of tralopyril released into artificial seawater by the method given in ISO 15181-1 is determined by accelerating the hydrolytic degradation of the tralopyril in the leachate by heat treatment under controlled conditions and subsequently quantifying the concentration of the degradation product, 3-bromo-5-(4-chlorophenyl)-4-cyano-1H-pyrrole-2-carboxylic acid (BCCPCA) by high-performance liquid chromatography (HPLC) or by an alternative method, provided that it demonstrates a limit of quantitation for tralopyril in artificial seawater of 2 µg/l or less. The release rate of the biocide under the specified laboratory conditions is then calculated as tralopyril.

NOTE Additional information on tralopyril and BCCPCA is given in Annex B.

4 Supplementary information

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

5 Apparatus

5.1 High-performance liquid chromatograph (HPLC), or **other suitable instrument**, which demonstrates a limit of quantitation for tralopyril in artificial seawater by the analytical method of 2 µg/l or less. The limit of quantitation shall be determined by the general procedure given in ASTM D6442-06, Annex 2 (determination of the LOQ for copper in substitute ocean water for the analytical method), suitably modified for tralopyril. If HPLC is used, the system shall, where possible, include the components specified in 5.1.1 to 5.1.6.

5.1.1 Isocratic pump, capable of achieving a pressure of 150 bar (15 MPa) and a flow-rate of 1,5 ml/min.

5.1.2 Ultraviolet detector, capable of monitoring at 280 nm.

5.1.3 Autosampler, capable of making 200 µl injections.

5.1.4 Chromatography column: a reverse-phase column with an internal diameter of 4,0 mm and a length of 100 mm, packed with a microparticulate octadecylsilane (C-18, end-capped) stationary phase (mean particle size 3,0 µm) or equivalent.

5.1.5 Column oven, facilitating a constant column temperature of 35 °C.

5.1.6 Electronic data-processing system, capable of controlling the HPLC system, acquiring data and enabling automated integration of peak areas.

5.2 Pipettes, with disposable tips.

5.3 Volumetric flasks, glass.

5.4 Thermostatically controlled cabinet, capable of maintaining a temperature of (50 ± 5) °C.

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.

6.1.1 Hydrochloric acid, concentrated aqueous solution, 37 % by mass; or 6.1.2.

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

6.2 Acetonitrile, HPLC grade.

6.3 Orthophosphoric acid, aqueous solution, 85 % by mass.

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

6.5 **Calibration stock solution solvent**.

6.5.1 **Methanol**, HPLC grade; or 6.5.2.

6.5.2 **Tetrahydrofuran**, HPLC grade.

6.6 **Artificial seawater**, as defined in ISO 15181-1.

6.7 **Tralopyril**, analytical standard with a certified mass fraction of tralopyril.

6.8 **BCCPCA**, analytical standard with a certified mass faction of BCCPCA.

7 Test samples

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

8 Preparation of calibration standards

8.1 General

Stock solutions of a certified BCCPCA reference standard shall be prepared at approximately 500 mg/l and 100 mg/l in the calibration stock solution solvent, as described in 8.2 and 8.3. These stock solutions shall then be used to prepare calibration standards by dilution with artificial seawater. A minimum of five calibration standards shall be prepared at concentrations appropriate to the samples being analysed and to define the working range for the determination of BCCPCA. Fresh stock solutions and calibration standards shall be prepared every 14 days or more frequently if required.

Methanol or tetrahydrofuran shall be used as the calibration stock solution solvent.

8.2 Stock solution A

Weigh, to the nearest 0,1 mg, about 50 mg (M) of BCCPCA into a 100 ml (V_1) volumetric flask, add 25 ml of the calibration stock solution solvent and mix to dissolve. Make up to the mark with the calibration stock solution solvent and mix well to give a homogenous solution (dilution factor, f_i = 1).

NOTE The mixture of BCCPCA and the calibration stock solution solvent can be sonicated to aid dissolution.

8.3 Stock solution B

Pipette 20 ml of stock solution A into a 100 ml volumetric flask, make up to the mark with the calibration stock solution solvent and mix well to give a homogenous solution (dilution factor, f_i = 0,2).

8.4 Preparation of calibration standards from stock solutions

Select a minimum of five suitable target concentrations for calibration standards, appropriate to the expected concentrations of BCCPCA in the test samples and in order to define the working range of the method. Calculate the volume of stock solution required to achieve each target concentration by dilution to 100 ml.

EXAMPLE 1 A calibration standard of nominal concentration 10 µg/l can be prepared by dilution of 10 µl of stock solution B to 100 ml.

EXAMPLE 2 A calibration standard of nominal concentration 100 µg/l can be prepared by dilution of 20 µl of stock solution A to 100 ml.

For each calibration standard, add about 97 ml of seawater to a 100 ml (V_2) volumetric flask. Using a microlitre syringe, add the required volume (V_i) of stock solution A or stock solution B by injection below the surface of the seawater, and immediately mix well. Make up to the mark with artificial seawater, and mix well to give homogenous calibration standard solutions.

Calculate the actual concentrations of standard, C_S, in µg/l, in each calibration standard from the certified purity of the standard and the subsequent dilution using the equation

$$C_S = \frac{V_i \times M \times P \times f_i \times 10^3}{V_1 \times V_2 \times 100}$$

where

V_i is the pipetted volume of stock solution A or B, in µl;

M is the mass of certified standard, in mg;

P is the purity of certified standard, in % by mass;

f_i is the stock solution dilution factor;

V_1 is the volume of stock solution A prepared, in ml (= 100 ml);

V_2 is the volume of calibration standard prepared, in ml (= 100 ml).

9 Recovery and conversion check standards

9.1 General

Stock solutions of certified tralopyril reference standards shall be prepared at approximately 500 mg/l and 100 mg/l in acetonitrile, as described in 9.2 and 9.3. These stock solutions shall then be diluted with artificial seawater to prepare conversion check standards that shall then be treated in accordance with 10.2. The conversion check standards shall have approximate concentrations of 5 µg/l, 50 µg/l, and 100 µg/l tralopyril. Additional conversion check standards may be prepared at appropriate concentrations to cover the working range for the determination of BCCPCA. Fresh stock solutions and conversion check standards shall be prepared every 14 days or more frequently if required.

NOTE Stock solutions of alternative concentrations can be prepared if more convenient for the selected conversion check standards.

9.2 Stock solution C

Weigh, to the nearest 0,1 mg, approximately 50 mg (M) of tralopyril into a 100 ml (V_3) volumetric flask, add 25 ml of acetonitrile, and mix to dissolve. Make up to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, f_j = 1).

9.3 Stock solution D

Pipette 20 ml of stock solution C into a 100 ml volumetric flask, make up to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, f_j = 0,2).

9.4 Preparation of recovery and conversion check standards

Pipette 10 ml of artificial seawater into an appropriate number of 100 ml (V_4) volumetric flasks. Using a microlitre syringe, add 5 µl and 50 µl (V_j) of stock solution D and 20 µl of stock solution C to separate, prefilled volumetric flasks. Make up to the mark with artificial seawater and mix well. Prepare additional conversion check standards if required by dilution of an appropriate volume of stock solution C or stock solution D. Each conversion check standard shall then be treated as described in 10.2.

Calculate the theoretical concentrations of BCCPCA as appropriate, C_{ST}, in µg/l, in each treated conversion check standard from the certified purity of the standard and the subsequent dilution using the equation:

$$C_{ST} = \frac{V_j \times M \times F \times P \times f_j \times 10^3}{V_3 \times V_4 \times 100}$$

where

V_j is the pipetted volume of stock solution C or D, in µl;

M is the mass of certified standard, in mg;

F is the ratio of the relative molar mass of BCCPCA analyte to the relative molar mass of parent tralopyril (= 0,931);

P is the purity of certified standard, in % by mass;

f_j is the stock solution dilution factor;

V_3 is the volume of stock solution C prepared, in ml (= 100 ml);

V_4 is the volume of conversion check standard prepared, in ml (= 100 ml).

10 Procedure

10.1 General

Carry out all determinations on the extract in triplicate using the following method.

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

Operate the chromatograph or other suitable instrument in accordance with the manufacturer's instructions.

Ensure that all treated test samples and calibration standards are equilibrated at room temperature prior to analysis.

10.2 Sample treatment

Pipette 20 ml of antifouling paint extract generated as described in ISO 15181-1 into a 25 ml glass vial, and close the vial hermetically. Place the vial in a thermostatically controlled cabinet, at a temperature of (50 ± 5) °C, for a minimum of 4 h and a maximum of 24 h.

The treated samples may then be stored at a temperature of −5 °C for up to 3 months before analysis.

The samples can be stored in the dark at 4 °C for up to 1 day before treatment.

10.3 Preparation of chromatography eluent

Prepare a mixture comprising acetonitrile, water, and the orthophosphoric acid solution at a ratio of 50 + 49,95 + 0,05 parts by volume for use as the chromatography eluent.

10.4 Instrument calibration

At the beginning of each instrument run, determine the BCCPCA concentration in an artificial seawater blank and the BCCPCA calibration standards using the HPLC system. Generate a calibration curve by plotting peak area as ordinate against BCCPCA concentration (C_S) as abscissa, perform linear regression

analysis and calculate the slope, intercept, and correlation coefficient. If the correlation coefficient for the linear regression analysis is <0,999, then prepare fresh calibration standards and recalibrate.

10.5 Conversion and recovery determination

Using the HPLC system, determine the concentration of BCCPCA, C_{SD}, in µg/l, in each conversion check standard and calculate the conversion and recovery, α, using the equation:

$$\alpha = \frac{C_{SD}}{C_{ST}}$$

where

C_{SD} is the determined concentration of degradate in each treated conversion check standard, in µg/l;

C_{ST} is the theoretical concentration of degradate in each treated conversion check standard, in µg/l.

If the conversion and recovery for any sample is <70 % or >110 %, repeat the method.

10.6 Sample determination

Using the HPLC system or other suitable instrument (see 5.1), determine the concentration of BCCPCA in the treated test sample for each test cylinder, and uncoated reference blank (see ISO 15181-1:2007, 8.1 and 8.7). For each set of triplicate analyses, if any result differs by more than 10 % from the mean, discard that result and reanalyse another sample of the extract.

NOTE 1 The retention time for BCCPCA using the chromatographic equipment and conditions specified in Clause 5 is generally about 1,5 min to 2,5 min (Figure 1 shows a representative chromatogram). The specified equipment and conditions are typical starting points for the analysis and the composition of the mobile phase; the mobile phase flow-rate, the injector volume, column dimensions and stationary phase can be varied if necessary to improve chromatographic resolution.

NOTE 2 A peak for the parent biocide, tralopyril, is not seen in the chromatogram (the retention time for tralopyril is generally about 7,5 to 8,1 min under the aforementioned conditions).

If the determined concentration of BCCPCA in the treated extract is outside the working range for the method defined by the calibration standards, then prepare fresh calibration standards to redefine an appropriate working range for the method and reanalyse.

11 Calculation and expression of results

11.1 Calculation of the tralopyril concentration

Calculate the concentration of the released tralopyril, $C_{tralopyril}$, in µg/l, in the artificial seawater in each individual measuring container using the equation:

$$C_{tralopyril} = \frac{(C_{BCCPCA} - C_{Blank}) \times 349{,}54}{325{,}55}$$

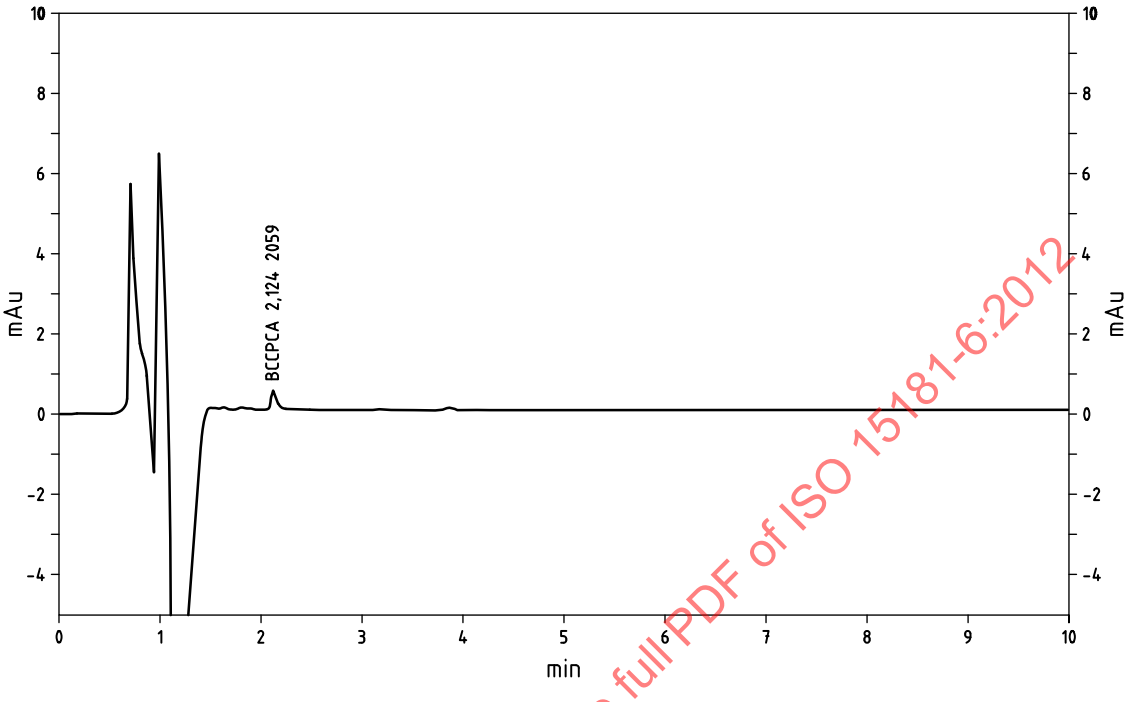
where

C_{BCCPCA} is the concentration of BCCPCA in the treated test sample, derived from the calibration curve, in µg/l;

C_{Blank} is the concentration of BCCPCA in the artificial seawater blank, derived from the calibration curve, in µg/l;

349,54 is the molecular mass of tralopyril, in g/mol;

325,55 is the molecular mass of BCCPCA, in g/mol.



Key

1 BCCPCA peak (retention time 2,14 min)

Figure 1 — Representative chromatogram for BCCPCA analysis by HPLC

11.2 Release rate for each test cylinder

Calculate the release rate of tralopyril, R, in µg cm^{-2} d^{-1}, for each test cylinder at each measurement point using the equation

$$R = \frac{C_{\text{tralopyril}} \times 1{,}5 \times 24}{t \times A}$$

where

$C_{\text{tralopyril}}$ is the concentration of tralopyril released into the measuring container, in µg/l (see 9.1);

24 is the number of hours per day;

1,5 is the volume, in l, of seawater in the measuring container, as specified in ISO 15181-1:2007, 10.1;

t is the time the test cylinder is immersed and rotated in the measuring container, in hours (see Table A.1, item 6);

A is the surface area, in cm^2, of the paint film [= 200] (see Table A.1, item 7).

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

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

11.3 Mean release rate for each set of three cylinders

Calculate the mean tralopyril release rate, in µg cm^{-2} d^{-1}, for each set of three test cylinders at each test day (see 11.2).

11.4 Cumulative tralopyril release

Calculate the 14-day cumulative release of tralopyril, $R_{0,14}$, in µg 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 tralopyril release rate, in µg cm^{-2} d^{-1}, between consecutive test days i and j for all test days up to day 14;

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

R_i and R_j are the mean tralopyril release rates for each set of three test cylinders, in µg cm^{-2} d^{-1} (see 11.3), at each pair of consecutive test days from the start of the trial through to day 14, specifically days 0 and 1, days 1 and 3, days 3 and 7, etc. respectively, and where the release rate on day 0 (R_0) is taken as 0 µg cm^{-2} d^{-1}.

NOTE The cumulative release of tralopyril for other periods of time can 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 tralopyril, in µg cm^{-2}, from day x to day y;

$\bar{R}_{i,j}$ is the mean tralopyril release rate, in µg cm^{-2} 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, 1 and 3, 3 and 7 days, etc. respectively, and where day 0 is included, the release rate on day 0 (R_0) shall be taken as 0 µg cm^{-2} d^{-1};

R_i and R_j are the mean tralopyril release rates for each set of three test cylinders, in µg cm^{-2} d^{-1} (see 11.3), at 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., respectively, and where day 0 is included, the release rate on day 0 (R_0) shall be taken as 0 µg cm^{-2} d^{-1}.

11.5 Mean tralopyril release rate

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

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

where

$\bar{R}_{i,j}$ is the mean tralopyril release rate in, µg cm^{-2} 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, elapsed since the start of the trial for each pair of consecutive test days, specifically 21 and 24, 24 and 28, 28 and 31 days etc., respectively;

R_i and R_j are the mean tralopyril release rates for each set of three test cylinders, in µg cm^{-2} d^{-1} (see 11.3), at each pair of consecutive test days from day 21 through to the final test day, specifically days 21 and 24, days 24 and 28, days 28 and 31, etc., respectively.

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 calculation of the simple arithmetic average of the data. The calculation can be conveniently done using a suitable computer-generated spreadsheet.

NOTE 2 The mean tralopyril release rate over other periods of time can be calculated if specified by modifying this equation to account for sampling on different days.

11.6 Pseudo-steady-state mean tralopyril release rate

If the coating exhibits a pseudo-steady state, calculate the pseudo-steady-state tralopyril release rate, $\bar{R}_{PSS}$, in µg cm^{-2} 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 11.4.

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 containing four or more test days, where the mean tralopyril release rate for the set of three test cylinders on each test day (see 11.3) 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 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.

12 Validation of the method

A validation study on the HPLC analytical method for determining tralopyril in seawater gave the following results.

a) The limit of quantitation for BCCPCA in artificial seawater using the HPLC method has been assessed at 1,87 µg/l with a precision (coefficient of variation) of 2,6 % when calibrated against the average instrument response for a known concentration of BCCPCA in seawater.

b) The respective mean recoveries (as BCCPCA) for solutions of tralopyril at concentrations of 10 µg/l, 50 µg/l, 75 µg/l, and 100 µg/l in artificial seawater were 109,4 %, 99,3 %, 96,8 % and 98,1 % with precisions (coefficients of variation) of 10,4 %, 7,2 %, 8,5 %, and 8,1 %.

Repeatability and reproducibility of the method have yet to be determined.

13 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 15181-6:2012);

c) all details necessary to describe the method used including:

— the type and manufacturer of analytical equipment and methodology employed,

— all details as given in ISO 15181-1,

— the items of supplementary information referred to in Annex A;

d) the results of the test, including the results of the individual determinations and their mean, calculated as specified in Clause 11, including as necessary:

— the limit of quantitation for tralopyril in artificial seawater by the analytical method determined by the laboratory performing the test method (see 5.1),

— the concentration of tralopyril in the artificial seawater, in µg/l, for each test cylinder on each test day (see 11.1),

— the rate of tralopyril release into the artificial seawater, in µg cm^{-2} d^{-1}, for each test cylinder on each test day (see 11.2), and the mean rate of tralopyril release, in µg cm^{-2} d^{-1}, for each set of three test cylinders on each test day (see 11.3),

— a graph showing the rate of tralopyril release as a function of time,

— the 14-day cumulative release and the cumulative release for other periods, if specified (see 11.4),

— the mean release rate from day 21 to the end of the trial, and the mean release rate for other periods, if specified (see 11.5),

— the pseudo-steady-state release rate, if calculated (see 11.6),

— the immersion and rotation period on each test day (see Table A.1, item 6);

e) any deviation 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

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

Table A.1 — Information for the extraction of the biocide

1	Test cylinder	The test cylinder shall be made of polycarbonate or glass.
2	Release rate measuring container	The release rate measuring container and baffles shall be made of polycarbonate or glass.
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 The combination of an activated charcoal filter with an ion-exchange resin can reduce the overall size of the required filter unit.
	Maximum initial water biocide limit	The maximum initial water biocide limit shall be 1 µg/l (expressed as tralopyril).
5	Maximum holding tank biocide limit	The maximum holding tank biocide limit shall be 100 µg/l (expressed as tralopyril).
6	Rotation period	The rotation period for the initial measurement shall be 1,0 h, except that if the biocide concentration, expressed as tralopyril, in the individual release rate measuring container exceeds 100 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 of the test method, and shall take into account the extent by which the measurement exceeds 100 µg/l. If the next measurement also exceeds 100 µg/l, then the rotation period shall be further reduced for the subsequent measurement. Once a measurement has been taken where the biocide concentration, expressed as tralopyril, no longer exceeds 100 µg/l, then the rotation period shall be incrementally extended to 1 h at the earliest practical subsequent point in testing without the concentration of biocide, expressed as tralopyril, exceeding 100 µg/l. If the biocide concentration, expressed as tralopyril, is greater than 100 µg/l for any measurement, record this fact in the test report.
7	Sample area	The sample area shall be 200 cm^2. NOTE Alternative sample areas can 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 can be used to avoid exceeding biocide concentrations of 100 µg/l in the measuring container.