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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

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

Partie 5: Calcul du taux de lixiviation du tolylfluanide et du dichlofluanide par détermination de la concentration du diméthyl-tolylsulfamide (DMST) et du diméthyl-phénylsulfamide (DMSA) dans l'extrait

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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 15181-5 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*

The following part is under preparation:

— *Part 6: Determination of tralopyril release rate by quantification of its degradation product 3-bromo-5-(4-chlorophenyl)-4-cyano-1H-pyrrole-2-carboxylic acid (BCCPCA) 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 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 by a factor of about 10 or more for several commercial antifouling coatings than direct *in situ* measurements of copper and organotin release rates from in-service ship hulls [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 5:
Calculation of the tolylfluanid and dichlofluanid release rate by determination of the concentration of dimethyltolylsulfamide (DMST) and dimethylphenylsulfamide (DMSA) in the extract

1 Scope

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

Tolylfluanid and dichlofluanid are unstable in the marine environment and degrade to form dimethyltolylsulfamide (DMST) and dimethylphenylsulfamide (DMSA), respectively. This part of ISO 15181 specifies a method for converting the released species into these degradation products, quantifying their concentration in the treated artificial seawater samples, and gives the final calculation for the release rate of tolylfluanid and dichlofluanid under the specified laboratory conditions.

This part of ISO 15181 is designed to allow the concurrent determination of tolylfluanid, dichlofluanid and other biocides that can be released by a given antifouling paint (for example, copper) 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 1,3 $\mu g \cdot cm^{-2} \cdot d^{-1}$ to 500 $\mu g \cdot cm^{-2} \cdot d^{-1}$. The quantitation of release rates lower than this range will require the use of an analytical method with a lower limit of quantitation for tolylfluanid, dichlofluanid, or both (as appropriate) in artificial seawater than that specified in Clause 3 and 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 amount of tolylfluanid released from a test cylinder into artificial seawater by the method given in ISO 15181-1 is determined by promoting the degradation of the tolylfluanid in the leachate under controlled conditions and subsequently quantifying the concentration of the degradation product, dimethyltolylsulfamide (DMST), by a high-performance liquid chromatography (HPLC) method or by an alternative analytical method, provided that it has a limit of quantitation for tolylfluanid in artificial seawater of 7 µg/l or less. The release rate of the biocide under the specified laboratory conditions is then calculated as tolylfluanid.

The amount of dichlofluanid released from a test cylinder into artificial seawater by the method given in ISO 15181-1 is determined by promoting the controlled degradation of the dichlofluanid in the leachate, and quantifying the concentration of the degradation product, dimethylphenylsulfamide (DMSA), by a similar HPLC method or by an alternative analytical method, provided that it demonstrates a limit of quantitation for dichlofluanid in artificial seawater of 7 µg/l or less. The release rate of the biocide under the specified laboratory conditions is then calculated as dichlofluanid.

Additional information on tolylfluanid, dichlofluanid, DMST and DMSA 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 dichlofluanid and tolylfluanid are given in Annex A.

5 Apparatus

5.1 High-performance liquid chromatograph (HPLC), or **other suitable instrument**, which has a limit of quantitation for tolylfluanid, dichlofluanid, or both (as appropriate) in artificial seawater of 7 µg/l or less. The limit of quantitation shall be determined by the general procedure given in Annex 2 of ASTM D 6442-06 (Determination of the LOQ for Copper in Substitute Ocean Water for the Analytical Method), suitably modified for tolylfluanid, dichlofluanid, or both (as appropriate). If HPLC is used, the system shall, where possible, include the components specified in 5.1.1 to 5.1.6.

5.1.1 Gradient-programmed pump, capable of achieving a pressure of 150 bar and a flow-rate of 0,5 ml/min.

5.1.2 Ultraviolet detector, capable of monitoring at 195 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 2,0 mm and a length of 150 mm, packed with a microparticulate octadecylsilane (C-18, end-capped) stationary phase (mean particle size 5,0 µm) or equivalent, and equipped with a reverse-phase pre-column with an internal diameter of 4,6 mm and a length of 30 mm, packed with a microparticulate octadecylsilane (C-18, end-capped) stationary phase (mean particle size 5,0 µm) or equivalent.

5.1.5 Column oven, providing a constant column temperature of 40 °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 Glass vials, volume 30 ml, screw-topped.

5.3 Dispensers, automatic or repeating, for reagents.

5.4 Pipettes, with disposable tips.

5.5 Volumetric flasks, volume 25 ml and 100 ml.

5.6 Microlitre syringe, capable of accurately dispensing volumes of between 1 µl and 100 µl.

5.7 Syringe, glass or disposable, capable of dispensing 2 ml.

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 Tolylfluanid, analytical standard with a certified mass fraction of tolylfluanid of at least 99,0 %, for use in determining the tolylfluanid release rate. See also Clause 9.

6.3 Dichlofluanid, analytical standard with a certified mass fraction of at least 99,0 %, for use in determining the dichlofluanid release rate. See also Clause 9.

6.4 Dimethyltolylsulfamide (DMST), analytical standard with a certified mass fraction of at least 99,0 %, for use in preparing the calibration standard for determination of the tolylfluanid release rate. See also Clause 8.

6.5 Dimethylphenylsulfamide (DMSA), analytical standard with a certified mass fraction of at least 99,0 % for use in preparing the calibration standard for determination of the dichlofluanid release rate. See also Clause 8.

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

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

6.8 Acetonitrile, HPLC grade.

6.9 Formic acid, minimum 98 % by mass.

NOTE Formic acid may be substituted by acetic acid.

6.10 Sodium hydroxide, aqueous solution 0,1 mol/l.

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 certified reference standards shall be prepared at approximately 1 000 mg/l and 100 mg/l in acetonitrile, as described in 8.2 and 8.3. These stock solutions shall then be used to prepare calibration standards by dilution with artificial seawater acidified to pH 2 to 3 with concentrated hydrochloric acid. A minimum of 5 calibration standards shall be prepared at concentrations appropriate to the samples being analysed and to define the working range for the determination of DMST and DMSA.

Where tolylfluanid and dichlofluanid release rates are being concurrently determined, both DMST and DMSA calibration standards shall be prepared.

8.2 Stock solution A

Weigh, to the nearest 0,1 mg, about 100 mg (M) of DMST or DMSA into a 100 ml (V_1) volumetric flask, add 50 ml of acetonitrile, and mix to dissolve. Make up to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, $f_i = 1$).

8.3 Stock solution B

Pipette 10 ml of stock solution A into a 100 ml volumetric flask, make up to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, $f_i = 0{,}1$).

8.4 Preparation of calibration standards from stock solutions

Select a minimum of 5 suitable target concentrations for calibration standards, appropriate to the expected concentrations of analyte in the test samples and in order to define the working range of the method. Calculate the volume of stock solution A or stock solution B required to achieve each target concentration by dilution to 100 ml.

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

EXAMPLE 2 A calibration standard of nominal concentration 300 µg/l may be prepared by dilution of 30 µl of stock solution A to 100 ml.

For each calibration standard, to a 100 ml (V_2) volumetric flask add about 97 ml of seawater acidified to pH 2 to 3 with concentrated hydrochloric acid. 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 acidified seawater, and immediately mix well. Fill to the mark with artificial seawater acidified to pH 2 to 3 with concentrated hydrochloric acid 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 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 reference standards shall be prepared at approximately 1 000 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 20 µg/l, 50 µg/l, and 200 µg/l dichlofluanid or tolylfluanid. Additional conversion check standards may be prepared at appropriate concentrations to cover the working range for the determination of DMST and DMSA.

9.2 Stock solution C

Weigh to the nearest 0,1 mg about 100 mg (M) of tolylfluanid or dichlofluanid into a 100 ml (V_3) volumetric flask, add 50 ml of acetonitrile, and mix to dissolve. Fill to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, f_j = 1).

9.3 Stock solution D

Pipette 10 ml of stock solution C into a 100 ml volumetric flask, fill to the mark with acetonitrile and mix well to give a homogenous solution (dilution factor, f_j = 0,1).

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 20 µl and 50 µl (V_j) of stock solution D and 20 µl of stock solution C to separate, pre-filled volumetric flasks. Fill to below 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 DMSA or DMST 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 analyte to the relative molar mass of parent biocide (= 0,617 for DMST/tolylfluanid, = 0,601 for DMSA/dichlofluanid);

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).