SVENSK STANDARD
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Färg och lack – Bestämning av urlakningshastighet av biocider från påväxtförhindrande färg – Del 6: Bestämning av urlakningshastighet av tralopyril genom kvantifiering av dess nedbrytningsprodukt i extrakt (ISO 15181-6:2012)

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 (ISO 15181-6:2012)

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Europastandarden EN ISO 15181-6:2014 gäller som svensk standard. Detta dokument innehåller den officiella engelska versionen av EN ISO 15181-6:2014.

The European Standard EN ISO 15181-6:2014 has the status of a Swedish Standard. This document contains the official version of EN ISO 15181-6:2014.

Förhållandet till övriga delar under samma huvudtitel - Utdrag ur Förord i ISO 15181-6:2012/ Relations to other parts under the same general title - Extract from the Foreword of ISO 15181-6:2012

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 tralopyril release rate by quantitation of its degradation product in the extract*

Upplysningar om sakinnehållet i standarden lämnas av SIS, Swedish Standards Institute, telefon 08-555 520 00. Standarder kan beställas hos SIS Förlag AB som även lämnar allmänna upplysningar om svensk och utländsk standard.

Information about the content of the standard is available from the Swedish Standards Institute (SIS), telephone +46 8 555 520 00. Standards may be ordered from SIS Förlag AB, who can also provide general information about Swedish and foreign standards.

Denna standard är framtagen av kommittén för Färg och lack, SIS/TK 433.

Har du synpunkter på innehållet i den här standarden, vill du delta i ett kommande revideringsarbete eller vara med och ta fram andra standarder inom området? Gå in på www.sis.se - där hittar du mer information.

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN ISO 15181-6

June 2014

ICS 87.040

English Version

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 (ISO 15181-6:2012)

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 détermination de la concentration de son produit de dégradation dans l'extrait (ISO 15181-6:2012)

Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 6: Bestimmung der Auswaschrate von Tralopyril durch Quantifizierung seiner Abbauprodukte im Extrakt (ISO 15181-6:2012)

This European Standard was approved by CEN on 8 May 2014.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
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CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

The text of ISO 15181-6:2012 has been prepared by Technical Committee ISO/TC 35 “Paints and varnishes” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 15181-6:2014 by Technical Committee CEN/TC 139 “Paints and varnishes” the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by December 2014, and conflicting national standards shall be withdrawn at the latest by December 2014.

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Endorsement notice

The text of ISO 15181-6:2012 has been approved by CEN as EN ISO 15181-6:2014 without any modification.

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.