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

Part 3:

**Calculation of the zinc
ethylene-bis(dithiocarbamate) (zineb)
release rate by determination of the
concentration of ethylenethiourea in the
extract**

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

*Partie 3: Calcul du taux de lixiviation de l'éthylène-bis(dithiocarbamate)
de zinc (zineb) par détermination de la concentration
d'éthylenethiourée dans l'extrait*



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Contents

Page

Foreword.....	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Principle	2
4 Supplementary information required for the zineb extraction procedure	2
5 Apparatus	2
6 Reagents and materials	3
7 Test samples	3
8 Procedure	3
9 Calculation and expression of results.....	5
10 Validation of the method.....	8
11 Test report	8
Annex A (normative) Supplementary information required for the zineb extraction procedure	10
Annex B (informative) Additional information on zineb and ETU	11
Bibliography	12

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 15181-3 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*

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].

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

Part 3: Calculation of the zinc ethylene-bis(dithiocarbamate) (zineb) release rate by determination of the concentration of ethylenethiourea in the extract

1 Scope

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

Zineb is released from antifouling paints in the form of ionic ethylene-bis(dithiocarbamate) which is unstable in the marine environment. This part of ISO 15181 describes a method for converting the released species into a stable degradation product, ethylenethiourea, and determining its concentration in the treated artificial seawater samples, and gives the final calculation for the release rate of zineb under the specified laboratory conditions.

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This part of ISO 15181 is designed to generally allow the concurrent determination of zineb 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 the procedure given in ISO 15181-1.

When used in conjunction with ISO 15181-1, the practical limits on the quantitative measurement of release rates by this method are from $2,9 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ 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 ethylenethiourea 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 amount of polymeric ethylene-bis(dithiocarbamate) (zineb) released from a test cylinder into artificial seawater in accordance with the procedure given in ISO 15181-1 is determined by degrading the ethylene-bis(dithiocarbamate) species in the leachate under controlled conditions and determining the concentration of the degradation product, ethylenethiourea (ETU), by high-performance liquid chromatography (HPLC) or by an alternative analytical method, provided that it demonstrates a limit of quantitation for ETU in artificial seawater of 6 µg/l or less. The release rate of the biocide under the specified laboratory conditions is then calculated as zineb.

Additional information on zineb and ETU is given in Annex B.

4 Supplementary information required for the zineb extraction procedure

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

5 Apparatus

5.1 High-performance liquid chromatograph, or other suitable instrument, which has a limit of quantitation for ETU in artificial seawater of 6 µg/l or less. The limit of quantitation shall be determined by the 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 ETU. 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 and a flow-rate of 1,0 ml/min.

5.1.2 Ultraviolet detector, capable of monitoring at 233 nm.

5.1.3 Autosampler, capable of making 25 µl injections.

5.1.4 Chromatography column: A reverse-phase column with an internal diameter of 4,6 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.

5.1.5 Column oven, providing a constant column temperature within the range 20 °C to 40 °C.

5.1.6 Electronic data-processing system, capable of controlling the HPLC system, acquiring data and automatically integrating peak areas.

5.2 Reflux apparatus, consisting of the components specified in 5.2.1 to 5.2.3.

5.2.1 Borosilicate glass flask, volume 50 ml.

5.2.2 Reflux condenser.

5.2.3 Heating device, for example a heating mantle or hotplate, capable of refluxing seawater.

5.3 Dispensers, automatic or repeating, for reagents.

5.4 Pipettes, with disposable tips.

5.5 Volumetric flasks, volume 100 ml, 200 ml and 500 ml.

5.6 Syringes, glass or disposable, volume 5 ml.

5.7 Syringe filters, disposable, PVDF membrane, pore size 0,45 µm.

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 Ethylenethiourea (ETU), with a certified mass fraction of ETU of at least 99,0 %.

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

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

6.5 Methanol, HPLC grade.

6.6 Sodium dihydrogen phosphate monohydrate.

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

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

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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 in triplicate using the following method.

Clean all non-disposable or re-used apparatus by immersion in 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 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 at equilibrium at room temperature prior to analysis.

8.2 Sample treatment

Into a 50 ml round-bottom flask, pipette 10 ml of antifouling paint extract generated as described in ISO 15181-1, add 1 ml of 0,1 mol/l sodium hydroxide solution and heat to reflux for 30 min. Cool the flask, add 100 µl of orthophosphoric acid and mix well. Quantitatively transfer the contents into a 25 ml volumetric flask, make up to the mark with water and mix well. Using a syringe, transfer about 2 ml of this solution into a vial via a 0,45 µm PVDF filter unit, and seal the vial.

The solution may then be stored at a temperature between 2 °C to 4 °C for up to 7 days or at – 5 °C for up to 1 month before analysis.

8.3 Preparation of ETU calibration standards

Weigh, to the nearest 0,1 mg, about 50 mg of the certified ETU standard into a 100 ml volumetric flask, add 75 ml of water, and mix to dissolve. Make up to the mark with water and mix well. Pipette 2 ml of this solution into a 500 ml volumetric flask, make up to the mark with artificial seawater and mix well. Successively pipette 1 ml, 2 ml, 4 ml, 10 ml, 20 ml and 100 ml portions of this solution into separate 200 ml volumetric flasks, make each up to the mark with artificial seawater and mix well.

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

$$C_S = \frac{V \times M \times P}{500}$$

where

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V is the pipetted volume, in ml;

M is the mass of ETU standard taken, in mg;

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P is the purity of the ETU standard, in % ETU by mass.

8.4 Preparation of chromatography eluent

Dissolve 1 g of sodium dihydrogen phosphate in 960 ml of water, adjust the pH of the resulting solution to 5,0 by the addition of 0,1 M sodium hydroxide solution, add 40 ml of methanol and mix well.

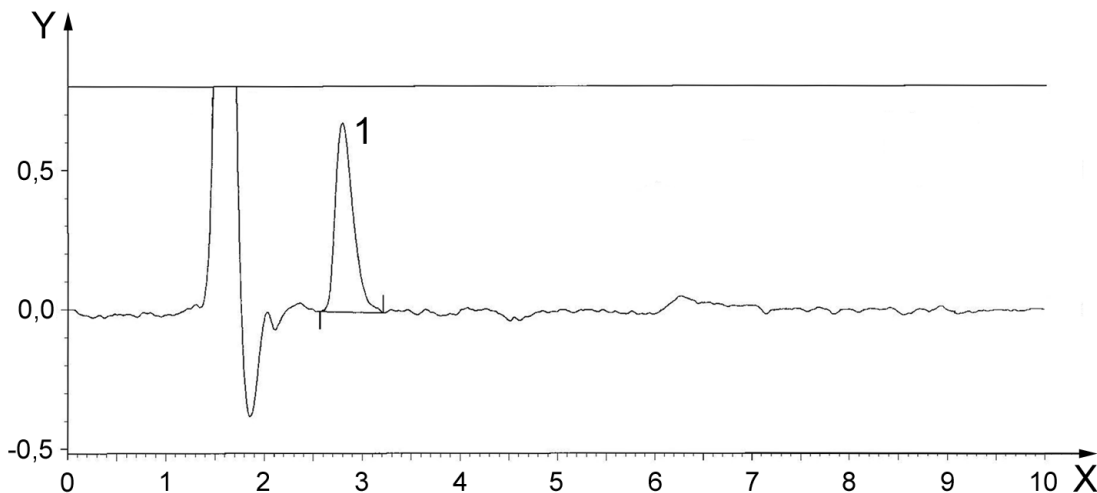
8.5 Instrument calibration

At the beginning of each instrument run, determine the ETU concentration in an artificial seawater blank and in the ETU calibration standards using the HPLC system, or another suitable instrument (see 5.1). In the case of HPLC, generate a calibration curve by plotting peak area as ordinate against ETU 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 re-calibrate.

8.6 Sample determination

Using the HPLC system, or another suitable instrument (see 5.1), determine the concentration of ETU in the treated test sample for each test cylinder and the 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 re-analyse another sample of the extract.

The retention time for ETU using the chromatographic equipment and conditions specified in Clause 5 is generally about 2,5 min to 3,5 min (see Figure 1 for 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 injection volume, the column dimensions and the stationary phase may be varied, if necessary, to improve the chromatographic resolution.



Key

X time (min)

Y detector response (mAU)

1 ETU peak (retention time 2,79 min)

Sample details: concentration of ETU solution 42,1 µg/l, injection volume 25 µl.

Figure 1 — Representative chromatogram for ETU analysis by HPLC

9 Calculation and expression of results

9.1 Calculation of zineb concentration

Calculate the concentration of zineb released into the artificial seawater in the measuring container, C_{Zineb} , in µg/l, using the equation

$$C_{\text{Zineb}} = \frac{(C_{\text{ETU}} - C_{\text{Blank}}) \times 2,5 \times 275,7}{102,16}$$

where

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

C_{Blank} is the concentration of ETU in the artificial seawater blank, in µg/l;

2,5 is a correction factor for the dilution of the sample during the sample treatment described in 8.2;

275,7 is the molecular mass of zineb, in g/mol;

102,16 is the molecular mass of ETU, in g/mol.