# INTERNATIONAL STANDARD

# ISO 15181-5

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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*

Reference number
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# Contents

# 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 tolylfuanid 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, $C_\mathrm{S}$, in µg/l, in each calibration standard from certified purity of the standard and the subsequent dilution using the equation

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

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, $C_{\text{ST}}$, in µg/l, in each treated conversion check standard from the certified purity of the standard and the subsequent dilution using the equation

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

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).

## 10 Procedure

### 10.1 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 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 (6.7).

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

Ensure that all treated test samples, calibration standards, and recovery and conversion check standards are at equilibrium at room temperature prior to analysis.

### 10.2 Sample treatment

Into a 25 ml volumetric flask, pipette 20 ml of antifouling paint extract generated as described in ISO 15181-1, add 2 ml of 0,1 mol/l sodium hydroxide solution. Seal the flask, mix well, and allow to stand for 20 min. Acidify to pH 2 to 3 with concentrated hydrochloric acid, fill to the mark with water and mix well. Using a syringe, transfer about 2 ml of this solution into a vial and seal the vial.

The treated sample should not be filtered before transfer to the vial as this has been shown to affect the results.

The solution can then be stored at a temperature between 2 °C to 4 °C for up to 7 days before analysis.

### 10.3 Chromatography eluent

A programmed solvent gradient comprising a 0,05 % by mass solution of formic acid in water (component A) and acetonitrile (component B), as shown in Table 1, is recommended.

**Table 1 — HPLC programmed solvent gradient**

| **Time** min | **A** % | **B** % |
|---|---|---|
| 0 | 60 | 40 |
| 7 | 60 | 40 |
| 17 | 30 | 70 |
| 25 | 30 | 70 |
| 28 | 15 | 85 |
| 30 | 15 | 85 |

### 10.4 Instrument calibration

At the beginning of each instrument run, determine the concentration of DMST, DMSA, or both (as appropriate) in an artificial seawater blank and the calibration standards using the HPLC system. Generate a calibration curve by plotting peak area as ordinate against 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.

### 10.5 Conversion and recovery determination

Using the HPLC system, determine the concentration of DMST, DMSA, or both (as appropriate), $C_{\mathrm{SD}}$, in µg/l, in each conversion check standard and calculate the conversion and recovery, $\alpha$, using the equation

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

where

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

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

If the conversion and recovery for any sample is $< 80$ % or $> 120$ %, repeat the method.

### 10.6 Sample determination

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

Using the specified chromatographic equipment and conditions, the retention times for DMST and DMSA are generally about 6,5 min to 7,0 min for DMST and 4,5 min to 5,0 min for DMSA (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 injector volume, column dimensions and stationary phase may be varied if necessary to improve chromatographic resolution.

The parent biocide, dichlofluanid or tolylfluanid, should not be seen in the chromatogram.

If the determined concentration of DMST, DMSA, or both (as appropriate) in the treated extract is outside of 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

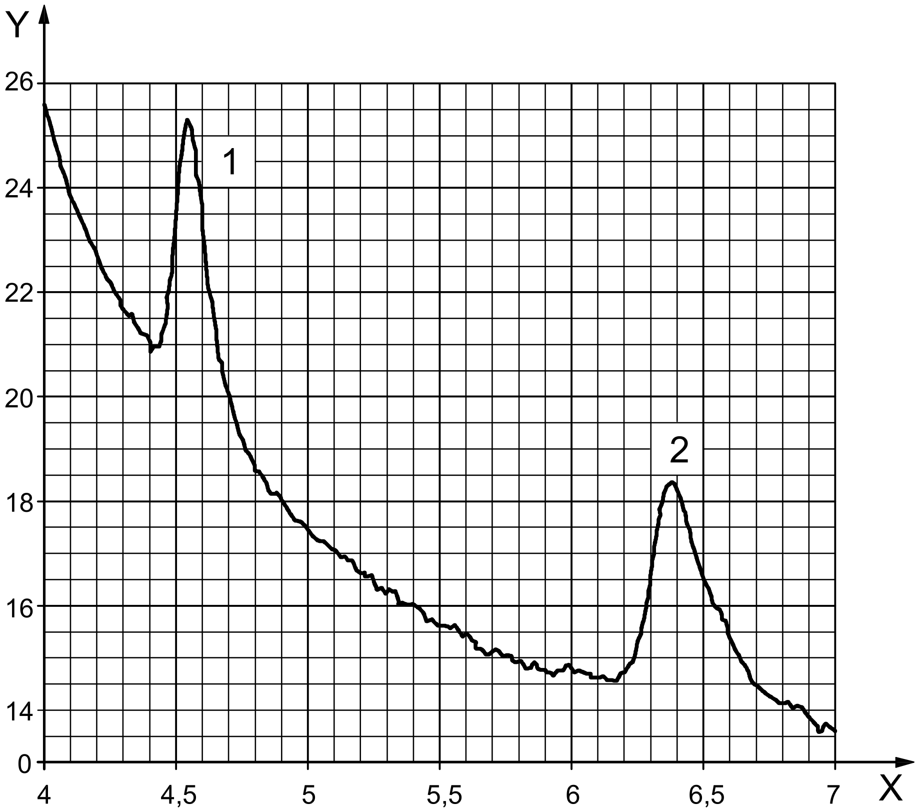
### 11.1 Calculation of the tolylfluanid and/or dichlofluanid concentration

Calculate the concentration of the tolylfluanid, $C_{\mathrm{tolyl}}$, in µg/l, or dichlofluanid, $C_{\mathrm{dichlo}}$, in µg/l, or both (as appropriate), released into the artificial seawater in the measuring container using the following two equations

$$C_{\mathrm{tolyl}} = \frac{\left(C_{\mathrm{DMST}} - C_{\mathrm{Blank}}\right) \times F \times 347{,}3}{214{,}3}$$

or

$$C_{\mathrm{dichlo}} = \frac{\left(C_{\mathrm{DMSA}} - C_{\mathrm{Blank}}\right) \times F \times 333{,}2}{200{,}3}$$



**Key**

X retention time, in minutes

Y instrument response, in milliabsorbance units (mAU)

1 DMSA 13 µg/l

2 DMST 14 µg/l

Figure 1 — Representative chromatogram for DMST/DMSA analysis by HPLC

where

| | |
|---|---|
| $C_{\text{DMST}}$ | is the concentration of DMST in the treated test sample, derived from the calibration curve, in µg/l; |
| $C_{\text{Blank}}$ | is the concentration of DMST or DMSA in the artificial seawater blank, derived from the calibration curve, in µg/l; |
| $F$ | is a correction factor for the dilution of the sample during the sample treatment (= 1,25); |
| 347,3 | is the molecular mass of tolylfluanid, in g/mol; |
| 214,3 | is the molecular mass of DMST, in g/mol; |
| $C_{\text{DMSA}}$ | is the concentration of DMSA in the treated test sample, derived from the calibration curve, in µg/l; |
| 333,2 | is the molecular mass of dichlofluanid, in g/mol; |
| 200,3 | is the molecular mass of DMSA, in g/mol. |

## 11.2 Release rate for each test cylinder

Calculate the release rate of tolylfluanid and/or dichlofluanid $R$, in µg·cm$^{-2}$·d$^{-1}$, for each test cylinder at each measurement point, according to either one of the following equations (as appropriate)

$$R = \frac{C_{\text{tolyl}} \times V \times 24}{t \times A}$$

or

$$R = \frac{C_{\text{dichlo}} \times V \times 24}{t \times A}$$

where

$C_{\text{tolyl}}$ is the concentration of released tolylfluanid, in µg/l (see 11.1);

$C_{\text{dichlo}}$ is the concentration of released dichlofluanid, in µg/l (see 11.1);

24 is the number of hours per day;

1,5 is the volume, in litres, 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 Annex A, Table A.1, item 6);

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

These equations can be simplified if the above standard volumes, times and sizes are used:

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

or

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

## 11.3 Mean release rate for each set of three cylinders

Calculate the mean tolylfluanid and/or dichlofluanid release rate (as appropriate), in µg·cm$^{-2}$·d$^{-1}$, for each set of three test cylinders at each test day (see 11.2).

## 11.4 Cumulative tolylfluanid and/or dichlofluanid release

Calculate the 14-day cumulative release of tolylfluanid and/or dichlofluanid (as appropriate), $R_{0,14}$, in µg·cm$^{-2}$ using the equation

$$R_{0,14} = \sum \overline{R}_{i,j}(j - i) = \sum \frac{(R_i + R_j)}{2}(j - i)$$

where

| | |
|---|---|
| $\overline{R}_{i,j}$ | is the mean tolylfluanid or dichlofluanid release rate (as appropriate), 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 times, in days, from the start of the trial for each pair of consecutive test days, specifically 0 and 1 days, 1 and 3 days, 3 and 7 days, etc. (see ISO 15181-1:2007, 9.6 and 9.7); |
| $R_i$ and $R_j$ | are the mean tolylfluanid or dichlofluanid release rates (as appropriate) 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., and where the release rate on day 0 ($R_0$) is taken as 0 µg·cm$^{-2}$·d$^{-1}$. |

NOTE The cumulative release of tolylfluanid or dichlofluanid for other periods of time can be calculated if specified, using the equation

$$R_{x,y} = \sum \overline{R}_{i,j}(j-i) = \sum \frac{(R_i + R_j)}{2}(j-i)$$

where

| | |
|---|---|
| $R_{x,y}$ | is the cumulative release of tolylfluanid or dichlofluanid (as appropriate), in µg·cm$^{-2}$, from day $x$ to day $y$; |
| $\overline{R}_{i,j}$ | is the mean tolylfluanid or dichlofluanid release rate (as appropriate), in µg·cm$^{-2}$·d$^{-1}$, between consecutive test days $i$ and $j$ for all data points 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 days, 1 and 3 days, 3 and 7 days, etc., and where day 0 is included, the release rate on day 0 ($R_0$) is taken as 0 µg·cm$^{-2}$·d$^{-1}$; |
| $R_i$ and $R_j$ | are the mean tolylfluanid or dichlofluanid release rates (as appropriate) for each set of three test cylinders, in µg·cm$^{-2}$·d$^{-1}$ (see 11.3), for 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., and where day 0 is included, the release rate on day 0 ($R_0$) is taken as 0 µg·cm$^{-2}$·d$^{-1}$. |

## 11.5 Mean tolylfluanid and/or dichlofluanid release rate

Calculate the weighted mean tolylfluanid or dichlofluanid release rate (as appropriate) from day 21 to the final test day, $\overline{R}_{21,\text{end}}$, in µg·cm$^{-2}$·d$^{-1}$, using the equation

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

where

| | |
|---|---|
| $\overline{R}_{i,j}$ | is the mean tolylfluanid or dichlofluanid release rate (as appropriate), 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, which have elapsed since the start of the trial for each pair of consecutive test days, specifically 21 and 24 days, 24 and 28 days, 28 and 31 days, etc. (see ISO 15181-1:2007, 9.6 and 9.7); |
| $R_i$ and $R_j$ | are the mean tolylfluanid or dichlofluanid release rates (as appropriate) for each set of three test cylinders, in µg·cm$^{-2}$·d$^{-1}$ (see 11.3), for 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. |

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 calculating the simple arithmetic mean. The calculation can be conveniently done using a suitable computer-generated spreadsheet.

NOTE 2 The mean tolylfluanid or dichlofluanid release rate (as appropriate) 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 tolylfluanid or dichlofluanid release rate

If the coating exhibits a pseudo-steady state, calculate the pseudo-steady-state tolylfluanid or dichlofluanid release rate (as appropriate), $\bar{R}_{\mathrm{PSS}}$ in μg·cm$^{-2}$·d$^{-1}$, using the equation

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

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 tolylfluanid or dichlofluanid release rate for the set of three test cylinders at 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 will 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 quantifying tolylfluanid and dichlofluanid in artificial seawater by degradation to DMST and DMSA, respectively, gave the following results.

a) For solutions of tolylfluanid at concentrations of 10 μg/l, 30 μg/l and 140 μg/l in artificial seawater, the respective mean recoveries (as DMST) were 102,3 %, 98,7 %, and 93,4 % with precisions (relative standard deviations) of 2,3 %, 3,6 %, and 1,1 % when a calibration standards covering the concentration range of 3 μg/l to 150 μg/l were used.

b) For solutions of dichlofluanid at concentrations of 10 μg/l, 30 μg/l and 140 μg/l in artificial seawater, the respective mean recoveries (as DMSA) were 92,8 %, 95,0 % and 100,2 % with precisions (relative standard deviations) of 1,7 %, 1,4 % and 1,1 % when a calibration standards covering the concentration range of 3 μg/l to 130 μg/l were used.

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 15181-5:2008);

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

- the type of analytical equipment used, the manufacturer of the equipment and the method of analysis employed;
- all details as given in ISO 15181-1:2007;
- 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:

- the limit of quantitation for tolylfluanid and/or dichlofluanid as appropriate in artificial seawater by the analytical method, determined by the laboratory performing the test method (see 5.1);
- the concentration of tolylfluanid and/or dichlofluanid in the artificial seawater, in μg/l, for each test cylinder on each test day (see 11.1);
- the rate of tolylfluanid and/or dichlofluanid release into the artificial seawater, in $\mu g \cdot cm^{-2} \cdot d^{-1}$, for each test cylinder on each test day (see 11.2), and the mean rate of tolylfluanid and/or dichlofluanid release, in $\mu g \cdot cm^{-2} \cdot d^{-1}$, for each set of three test cylinders on each test day (see 11.3);
- a graph showing the rate of tolylfluanid and/or dichlofluanid 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 length of time the cylinders were rotated to extract the biocide on each test day (see Annex A, Table A.1, item 6);

e) any deviations 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 tolylfluanid and/or dichlofluanid from the antifouling paint by the method given in ISO 15181-1.

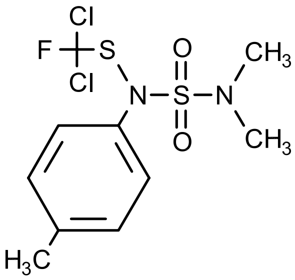
**Table A.1 — Information for the extraction of the biocide**

| | | |
|---|---|---|
| 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.<br>NOTE Combining an activated-charcoal filter with an ion-exchange resin might reduce the overall size of the required filter unit. |
| 4 | Maximum initial water biocide limit | The maximum initial water biocide limit shall be 10 µg/l, expressed as tolylfluanid and/or dichlofluanid (as appropriate). |
| 5 | Maximum holding tank biocide limit | The maximum holding tank biocide limit shall be 100 µg/l, expressed as tolylfluanid and/or dichlofluanid (as appropriate). |
| 6 | Rotation period | The length of time the cylinders are rotated shall be 1,0 h, except that if the biocide concentration, expressed as tolylfluanid and/or dichlofluanid (as appropriate), determined in a particular release rate measuring container exceeds 200 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 200 µg/l. If the next measurement also exceeds 200 µg/l, then the rotation period shall be further reduced for the subsequent measurement. Once the rotation period has been reduced sufficiently for the biocide concentration, expressed as tolylfluanid and/or dichlofluanid (as appropriate), to no longer exceed 200 µg/l, then the rotation period shall subsequently be incrementally increased to 1 h at the earliest practical subsequent point in testing without the concentration of biocide, expressed as tolylfluanid and/or dichlofluanid (as appropriate), exceeding 200 µg/l.<br>If the biocide concentration or the biocide concentration, expressed as tolylfluanid and/or dichlofluanid (as appropriate), is greater than 200 µg/l for any measurement, record this in the final report. If the rotation period was less than 1 h for any measurement, report this fact also. |
| 7 | Sample area | The sample area shall be 200 cm$^2$.<br>NOTE Alternative sample areas may 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$^2$ may be used to avoid exceeding biocide concentrations of 200 µg/l in the measuring container. |

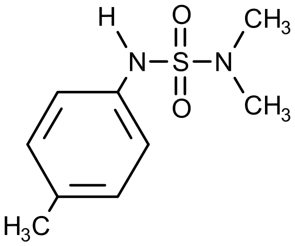
# Annex B
(informative)

# Additional information on tolylfluanid, DMST, dichlofluanid and DMSA

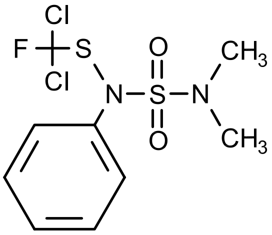
## B.1 Tolylfluanid

| | |
|---|---|
| **Common names** | Tolylfluanid |
| **Structural formula** |  |
| **Chemical names** | |
| **(IUPAC)** | *N*-{[dichloro(fluoro)methyl]sulfanyl}-*N′*,*N′*-dimethyl-*N*-(4-methylphenyl)sulfamide |
| **(CAS)** | Methanesulfenamide, 1,1-dichloro-N-[(dimethylamino) sulfonyl]-1-fluoro-N-(4-methylphenyl)- |
| **Empirical formula** | $C_{10}H_{13}Cl_2FN_2O_2S_2$ |
| **Relative molecular mass** | 347,3 g/mol |
| **CAS No.** | [731-27-1] |

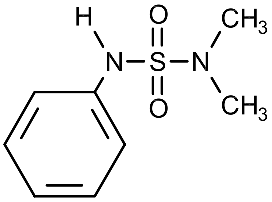
## B.2 DMST

| | |
|---|---|
| **Common names** | Dimethyltolylsulfamide, DMST |
| **Structural formula** |  |
| **Chemical names** | |
| **(IUPAC)** | *N*,*N*-dimethyl-*N′*-(4-methylphenyl)sulfamide |
| **(CAS)** | Sulfamide, N,N-dimethyl-N′-(4-methylphenyl)- |
| **Empirical formula** | $C_9H_{14}N_2O_2S$ |
| **Relative molecular mass** | 214,3 g/mol |
| **CAS No.** | [66840-71-9] |

## B.3 Dichlofluanid

| | |
|---|---|
| **Common names** | Dichlofluanid |
| **Structural formula** |  |
| **Chemical names** | |
| **(IUPAC)** | *N*-{[dichloro(fluoro)methyl]sulfanyl}-*N′*,*N′*-dimethyl-*N*-phenylsulfamide |
| **(CAS)** | Methanesulfenamide, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenyl- |
| **Empirical formula** | $C_9H_{11}Cl_2FN_2O_2S_2$ |
| **Relative molecular mass** | 333,2 g/mol |
| **CAS No.** | [1085-98-9] |

## B.4 DMSA

| | |
|---|---|
| **Common names** | Dimethylphenylsulfamide, DMSA |
| **Structural formula** |  |
| **Chemical names** | |
| **(IUPAC)** | *N*,*N*-dimethyl-*N′*-phenylsulfamide |
| **(CAS)** | Sulfamide, N,N-dimethyl-N′-phenyl- |
| **Empirical formula** | $C_8H_{12}N_2O_2S$ |
| **Relative molecular mass** | 200,3 g/mol |
| **CAS No.** | [4710-17-2] |

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[1] VALKIRS, A.O., SELIGMAN, P.F., HASLBECK, E., and CASO, J.S. Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: implications for loading estimation to marine bodies. *Marine Pollution Bulletin*, **46**, 2003, pp. 763-779

[2] FINNIE, A.A., Improved estimates of environmental copper release rates from antifouling products. *Biofouling*, **22,** 2006, pp. 279-291

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