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COVER NOTE

From:	Secretary-General of the European Commission, signed by Ms Martine DEPREZ, Director
To:	Mr Jeppe TRANHOLM-MIKKELSEN, Secretary-General of the Council of the European Union
No. Cion doc.:	SWD(2020) 328 final
Subject:	COMMISSION STAFF WORKING DOCUMENT Union submission to the 8th session of the Sub-Committee for Pollution Prevention and Response (PPR 8) of the International Maritime Organization (IMO), scheduled to take place virtually from 22 to 26 March 2021, proposing to revise the Guidelines for brief sampling of anti-fouling systems on ships to include controls on cybutryne

Delegations will find attached document SWD(2020) 328 final.

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COMMISSION STAFF WORKING DOCUMENT

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Union submission to the 8th session of the Sub-Committee for Pollution Prevention and Response (PPR 8) of the International Maritime Organization (IMO), scheduled to take place virtually from 22 to 26 March 2021, proposing to revise the Guidelines for brief sampling of anti-fouling systems on ships to include controls on cybutryne

Purpose

The Staff Working Document is presented in order to establish the position of the Union on a Union submission to the 8th session of the Sub-Committee on Pollution Prevention and Response (PPR 8) of the IMO with a view to its submission to the IMO prior to the required deadline, 18 December 2020[1]. The submission invites the Sub-Committee to consider the information relating to revision of the Guidelines for brief sampling of anti-fouling systems on ships to include controls on cybutryne. The draft Union submission contains two Annexes: Annex 1 detailing the suggested changes to the guidelines and Annex 2, with appendix, highlighting the editions to the existing guidelines.

At its 71st session, the IMO's Marine Environment Protection Committee (MEPC) approved a new output to amend Annex 1 to the AFS Convention to include controls on cybutryne. These amendments are yet to be adopted. However, should controls on cybutryne be introduced, three different sets of guidelines will also have to be revised, one of which being the Guidelines for brief sampling of antifouling systems on ships (resolution MEPC.104(49))[2]. PPR7 therefore invited interested delegations to submit proposals to PPR 8 on amendments to the Guidelines for brief sampling, survey and certification, and inspection of anti-fouling systems on ships, due to the introduction of controls on cybutryne, taking into account the issues raised by the Group at PPR 6.The draft Union submission therefore suggests modifications to the Guidelines for brief sampling of antifouling systems on ships. Its aim is to set up a framework of sampling activities with the objective of verifying compliance with the AFS Convention with respect to anti-fouling systems containing cybutryne.

Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products[3] establishes a harmonised system in the EU concerning the placing on the market and use of biocidal active substances and biocidal products. In particular, it aims at establishing at Union level a list of active substances which may be used in biocidal products. Pursuant to Article 9 of Regulation

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[1] The submission of proposals or information papers to the IMO, on issues falling under external exclusive EU competence, are acts of external representation. Such submissions are to be made by an EU actor who can represent the Union externally under the Treaty, which for non-CFSP (Common Foreign and Security Policy) issues is the Commission or the EU Delegation in accordance with Article 17(1) TEU and Article 221 TFEU. IMO internal rules make such an arrangement absolutely possible as regards existing agenda and work programme items. This way of proceeding is in line with the General Arrangements for EU statements in multilateral organisations endorsed by COREPER on 24 October 2011.

[2] The other two being the 2010 Guidelines for survey and certification of anti-fouling systems on ships (resolution MEPC.195(61)) and the 2011 Guidelines for inspection of anti-fouling systems on ships (resolution MEPC.208(62)).

3 OJ L 167, 27.6.2012, p. 1.

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(EU) No 528/2012, decisions to approve or not an active substance are adopted at EU level by the Commission.

By Commission Implementing Decision (EU) 2016/107 of 27 January 2016[4] cybutryne was not approved as an active substance for use in biocidal products for product-type 21 [for use in antifouling paints].The adoption of a non-approval decision triggered legal periods for the withdrawal from the market and the end of use of biocidal products containing that substance. Pursuant to Article 89(2) of Regulation 528/2012, Member States could have allowed the making available on the market up to 12 month after the date of decision, and the use up to 18 months after the date of the decision. To be noted that these deadlines have since expired.

The draft Union submission therefore covers matters that fall under EU exclusive competence[5]

4 OJ L 21, 28.1.2016, p. 81.

5 A formal EU position under Article 218(9) TFEU is to be established in due time should the IMO Maritime Safety Committee eventually be called upon to adopt an act having legal effects as regards the subject matter of the said draft Union submission. The concept of '*acts having legal effects*' includes acts that have legal effects by virtue of the rules of international law governing the body in question. It also includes instruments that do not have a binding effect under international law, but that are '*capable of decisively influencing the content of the legislation adopted by the EU legislature*' (Case C-399/12 Germany v Council (OIV), ECLI:EU:C:2014:2258, paragraphs 61-64).

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SUB-COMMITTEE ON POLLUTION PREVENTION AND RESPONSE
8th session
Agenda item X

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REVISION OF THE GUIDELINES FOR BRIEF SAMPLING OF ANTI-FOULING SYSTEMS ON SHIPS TO INCLUDE CONTROLS ON CYBUTRYNE

Proposal to revise the Guidelines for brief sampling of anti-fouling systems on ships to include controls on cybutryne

Submitted by the European Commission on behalf of the European Union

SUMMARY

Executive summary:	This document provides information on suggested modifications to the *Guidelines for brief sampling of anti-fouling systems on ships* (Resolution MEPC.104(49)) in order to include controls on cybutryne.
Strategic direction, if applicable:	2
Output:	2.19
Action to be taken:	Paragraph 3
Related documents:	Resolution A.895(21), Resolution MEPC.104(49), PPR 6/INF.7 and PPR 7/6/1

Background

1 The Sub-Committee on Pollution Preparedness and Response (PPR) 7, agreed with the draft amendments to Annex 1 to the AFS Convention, as prepared by the Technical Group and set out in the final report of the Sub-Committee PPR 7-WP.4. The draft amendments are pending to be considered at the 75th session of the Maritime Environment Protection Committee (MEPC 75) with a view to subsequent adoption by MEPC 76.

2 In view of this future introduction of controls on cybutryne, three different guidelines will have to be revised: Guidelines for brief sampling of antifouling systems on ships (resolution MEPC.104(49)); 2010 Guidelines for survey and certification of antifouling systems on ships (resolution MEPC.195(61)); 2011 Guidelines for inspection of antifouling systems on ships (resolution MEPC.208(62)). This document concerns only the Guidelines for brief sampling of antifouling systems on ships.

Action requested to the sub-committee

3 The Sub-Committee on Pollution Preparedness and Response is invited to consider the information provided in ANNEX 1 and ANNEX 2 to this document. ANNEX 1 explains and

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justifies modifications to the guidelines. ANNEX 2 highlights suggested textual edits to the existing guidelines.

ANNEX 1
Modifications to the Guidelines for brief sampling of anti-fouling systems on ships to include controls on cybutryne

1. Introduction

The proposed amendment to Annex 1 of the AFS Convention, will ban the use of cybutryne in anti-fouling systems of ships. For existing ships bearing an anti-fouling system that contains cybutryne in the external coating layer of their hulls or external parts or surfaces, a sealant can be used to prevent the release of cybutryne to the marine environment or the anti-fouling system must be removed. Ships may, in any port, shipyard, or offshore terminal of a Party, be inspected by officers to determine whether the ship is in compliance with the convention. Such inspection is based on verification, when required, of an on-board International Anti-fouling System Certificate or a Declaration on Anti-fouling System and/or based on a brief sampling of the ship's anti fouling system.

The above amendments to Annex 1 of the AFS Convention will necessitate a revision of the *Guidelines for brief sampling of anti-fouling systems on ships* (Resolution MEPC.104(49) that presently cover only organotin compounds with a view to setting up a framework of sampling activities with the objective of verifying compliance with the AFS Convention with respect to anti-fouling systems containing cybutryne. The users of these guidelines are the national administrations and recognized organizations, port state control authorities, companies, shipbuilders, and manufacturers of anti-fouling systems.

The existing Guidelines for brief sampling of anti-fouling systems on ships should not be modified substantially. Rather, the aim should be to test and apply the existing guidelines to cybutryne and make modifications only where needed. This will minimise additional training needs for the users of these guidelines and provide a cost-efficient solution for testing procedures.

Compliance with Annex 1 of the Convention is assumed if the antifouling system contains cybutryne at a level that does not provide a biocidal effect, using the same principle of compliance mentioned in the existing guidelines for organotin compounds.

A technical study is currently being conducted by the RISE Research Institutes of Sweden to gather data and complete experimental work, which could be used for the purposes of the possible modifications to these guidelines.

2. Suggested amendments

1.1. Definition of compliance

The proposed draft amendments to Annex 1 to the AFS Convention, will ban cybutryne from anti-fouling systems. Cybutryne (contrary to organotin compounds) is only used as biocide in the anti-fouling system. Therefore, by definition, the detection of cybutryne in the anti-fouling system should trigger non-compliance. However, the principle of compliance as it stands in the existing guidelines, will allow the presence of cybutryne in the anti-fouling system up to a level which does not provide a biocidal effect. This implies that cybutryne may be present on the ship's hull (e.g. inner layer of an old anti-fouling system) up to a certain amount.

In order to accurately determine if a ship complies or not with the AFS Convention it is fundamental to have a reference value that can be used for comparison purposes to determine if the ship complies with the AFS Convention or not. This value must be in line

with the suggested test method and it must ensure that the release of cybutryne to the marine environment is at a level that it does no cause a negative impact to the environment.

An initial approach to define a threshold value would be to find a correlation between the amount of cybutryne in antifouling systems in mg/kg dry paint and the release of cybutryne to the marine environment and its amount in water. However, there is no direct correlation between the two concentrations: amount of cybutryne in the hull and amount of cybutryne released to water. Ideally, this correlation could be obtained by running a full range of laboratory tests using anti-fouling paints in different formulations and with different concentrations of cybutryne using the ISO 15181-1[6] test method. This method measures the release rate at steady state with the application of a correction factor for the expected overestimation. This would be an adequate approach to derive an experimental correlation. However, this would be costly and time consuming and more importantly, not based on real market formulations.

Instead, this paper presents a compliance reference value by looking at the amount of cybutryne left at the end of life cycle of the antifouling systems and by estimating its predicted effect concentration (PEC) considering the different marine scenarios. The scenarios below do not take into consideration the expected emissions from the application and removal of anti-fouling systems containing cybutryne as the ban assumes that antifouling systems containing cybutryne will no longer be applied.

1.1.1. Original concentration of cybutryne in anti-fouling systems

In some cases, the exact original concentration of an active substance in an AFS is difficult to obtain as these values are covered by industrial secrets and are normally made available to public authorities for biocide testing and not to the general public. The information in the Safety Data Sheets usually present a range of cybutryne concentration (from – to) in % (w/w).

The table below from a Swedish report in 2007 (Woldegiorgis et al., 2007) presents a list of antifouling products containing cybutryne (commercial name Irgarol 1051). It contains the list of antifouling products approved by the Swedish Chemicals Agency.

	Conc. cybutryne (% w/w)	Cat.		Conc. cybutryne (% w/w)	Cat.
Cruiser	2.41	cat. 3	Antifouling Sargasso AL KNM	2	cat.2
Cruiser White	1.89	cat. 3	Hempel's Antifouling Combic ALU 71800	1.1	cat.2
Micron WQ	2.2	cat. 3	Interspeed Extra BWO 500 Röd	2	cat.2
Micron WQ White	1.97	cat. 3	Interspeed Premium Antifouling Black	2.3	cat.2
Mille White SE	3.5	cat. 3	*Average*	*1.85*	
Trilux	2.18	cat. 3			
Trilux Prop-o-Drev	0.87	cat. 3			
Trilux White	1.87	cat. 3			

[6] Paints and varnishes – Modelling of biocide release rate from antifouling paints by mass-balance calculation (ISO 10890:2010)

VC 17 New Technology	0.6	cat. 3			
Average	*1.94*				

Table 1 - Antifouling products containing Cybutryne approved in Sweden: pleasure boats <12m length (cat. 3); professional ships >12m length (cat.2); adapted from (Woldegiorgis et al., 2007).

From the table above, it is possible to calculate an average concentration of cybutryne (% w/w) for "cat. 2" products 1.8% (w/w) and for "cat. 3" products 1.94% (w/w). Although the list above is far from being representative of all anti-fouling products containing cybutryne on the market, it was used as the starting point for defining compliance with the AFS convention.

A conservative 2% (w/w) was taken as a starting concentration of cybutryne for globally market available products i.e. 20 000 mg/kg of cybutryne per kg of dry paint.

1.1.2. End-of-life of the anti-fouling system and expected impact to the marine environment

It is expected that the distribution of the remaining anti-fouling paint in the hull surface would not be homogenous. Due to hull design and consequent action of the sea water during the service life of the paint, the paint will not have homogenously eroded, some parts in the hull will still have some paint, other parts will not have any paint left. Thus, there may be cases where cybutryne is not acting as a biocide in technical terms however is still present on some parts of the hull.

Also, it is possible that old paint systems containing cybutryne may have been covered with other paint systems or by application of sealant or other products. During the sampling procedure the inner layers containing old cybutryne may be exposed and collected due to the action of abrasive pads.

The PPR 6/INF.7 proposes a maximum of 2 ng/L (PNEC, Predicted No Effect Concentration) of maximum allowed concentration of cybutryne in water. Any concentration above this threshold in water, would cause significant adverse effects in certain marine species and consequently to the marine ecosystem and corresponding food chains.

The MAMPEC model 3.1.0.5 was used to estimate the Predicted Effect Concentration (PEC) of cybutryne in water associated to the amount of cybutryne left at the end of life of the antifouling system.

The MAMPEC model integrates a 2D hydrodynamical and chemical fate model, based on the Delft3D-WAQ and Silthar model. It is used by regulatory authorities and applicants for exposure assessment of antifoulants in harbours, rivers, estuaries and open water. The MAMPEC model has built-in a set of agreed OECD-EU emission scenarios that the user can choose. These scenarios are based on the Emission Scenario Document (OECD, 2005), that recommends and describes the emission scenarios for anti-fouling products in OECD countries. These scenarios are intended to be used for general risk assessment and not for site specific risk assessment. The calculations are based on the initial local concentration in the primary receiving environment. The scenarios take into consideration the shipping characteristics (hull area, ships moving, ships at berth), leaching rate and the application factor i.e. fraction of ships painted with the specific product.

Assuming that at the end of the life of the anti-fouling systems only a fraction of the original concentration of cybutryne is left, in a simplified manner we can correlate this with a decrease in the hull area in contact with water. The leaching rate used was 1.9µg/cm^2/day as explained in PPR 6/INF.7.

The release of cybutryne to the marine environment was estimated considering different amounts of cybutryne left at the “end of life” of the anti-fouling system. The reference point was 10 % of the original concentration (2 000 mg/kg of dry paint), as the ISO 10890:2010[1] refers that it is normally assumed that 90 % of the biocide is released over the lifetime of the paint in the anti-fouling system. Additionally, a value of 5% (1000 mg/kg of dry paint) and 1% (200 mg/kg of dry paint) of cybutryne left were used to have a range of values to support the selection of the threshold value.

Three scenarios built-in in MAMPEC based on the Emissions Scenarios Document (OECD, 2005) were used to depict the expected emissions from a ship and the receiving environment: shipping lane, commercial harbour and marina. The PEC values in a marina will always be higher than in a commercial harbour, which in turn will be higher than in a shipping lane. This is due to the number of ships per m^3 due to the size and to low water exchange rates expected in a marina.

For the OECD-EU marina scenario two different sub scenarios were used: the default scenario that defines 500 ships at berth and a modified scenario with 276 boats at berth. This sub-scenario was agreed to be more realistic, see table footnote.

The table below summarises the results:

	End of life of the anti-fouling system (ng/L)								
	2 000 mg/kg 10 %			1 000 mg/kg 5 %			200 mg/kg 1 %		
Application factor	0.5	0.2	0.1	0.5	0.2	0.1	0.5	0.2	0.1
OECD-EU shipping lane	9.9 E-04	4.0 E-04	2.0 E-4	5.0 E-04	2.0 E-04	9.9 E-5	9.9 E-05	4.0 E-05	2.0 E-05
OECD-EU commercial harbour	1.9	0.8	0.4	1.0	0.4	0.2	0.2	0.08	0.04
OECD-EU Marina (default)	18	7.4	3.7	9.2	3.7	1.8	1.8	0.7	0.4
OECD-EU Marina (modified)*	10	4.1	2.0	5.1	2.0	1.0	1.0	0.4	0.2

** In MAMPEC the OECD-Marina scenario has the following note: The number of boats in the ESD marina scenario, Table 0.6, should be reduced to 276 to reflect a more realistic boat density of 1.38 boats / 100 m2, [Source: Final minutes of TM V 2007].*

Table 2 – Average values for different scenarios PEC values for water (nanograms per litre)

With the cybutryne ban, anti-fouling systems containing cybutryne will no longer be applied on ship’s hulls. For ships that have an anti-fouling system with cybutryne they can keep the anti-fouling system until next dry-docking period (or up to 5 years since the application of an anti-fouling systems containing cybutryne). At the next dry-dock, these ships will have to remove the anti-fouling system that contains cybutryne or apply a sealant to prevent the release of cybutryne to the marine environment.

The proposed ban scheme will result in a gradual reduction of number of ships bearing an anti-fouling system with cybutryne in the external coating layer of their hulls. This means that the market share of ships with cybutryne will be reduced significantly. Five years after the ban, emissions of cybutryne to water related to anti-fouling systems of ships should be zero. This can be transposed to the MAMPEC estimations by changing the application factor (i.e. percentage of ships with cybutryne).

From the table above, it is possible to conclude that a threshold of 2 000 mg/kg (corresponding to 10% of cybutryne left at the end of life of the AFS) might still lead to a negative impact if the receiving environment is a marina (the most sensitive scenario) as the PEC/PNEC >1 despite using a low application factor (i.e. percentage of ships with cybutryne).

Reducing the threshold to 1 000 mg/kg (corresponding to 5% of cybutryne left at the end of life of the anti-fouling system) and using an application factor of 0.10, the MAMPEC results show that for all scenarios the PEC/PNEC<1. This means that if there are 10 ships berthed at a marina and there is one ship that has 5 % left of the anti-fouling systems containing cybutryne, no negative impact to the marine environment is expected.

The results from the table above must be interpreted with caution. The scenarios used are generic and therefore the results should be read as indicative. The aim is to understand at which level the presence of any remaining cybutryne in the hull will not create a negative impact to the environment.

Assuming that the cybutryne ban scheme will lead to a gradual reduction of emissions of cybutryne to water related to anti-fouling systems of ships, we can conclude that a compliance value of 1 000 mg/kg of cybutryne per kg of dry paint should be set as threshold value. Below this value emissions of cybutryne from the ship hull to the marine environment are expected not to create a negative impact to the environment.

1.2. Sampling and testing methodologies to determine cybutryne

The starting point is to test if the sampling and testing methodologies described in the guidelines were adequate or appropriate for cybutryne. If required, modifications can then be proposed having in mind the cost efficiency of the testing methodologies and minimisation of training needs of the guidelines' users.

The suggested modifications are applicable to both Method 1 and Method 2 described in the existing *Guidelines for brief sampling of anti-fouling systems on ships*.

1.2.1. First-stage and second-stage analysis

The first approach was to replicate the step-wise approach in the existing guidelines (both in method 1 and method 2): a STEP 1 to check the presence of total cybutryne and then a STEP 2 only applied when STEP 1 produces positives results. The STEP 2 analysis is done at an ISO 17025 laboratory using the GC/MS (Gas Chromatography/Mass Spectrometry) analytical technique. The STEP 2 analysis is more costly and time consuming than STEP 1 analysis.

Unfortunately, not having a metal to detect with ICP/MS (inductively coupled plasma/mass spectrometry) and XRF (X-ray fluorescence analysis) methods (as for organotin compounds), prevented the development of a quick reaction test method to detect cybutryne. The methodologies tested were not feasible as they gave too many false positives and were very expensive.

Therefore, it is suggested to add to the existing guidelines a STEP 3 to be carried out at a laboratory using GC/MS analytical method to determine the amount of cybutryne present in the sample. This STEP 3 for cybutryne is described in ANNEX 2.

Proposal to simplify the existing guidelines

Depending on the Port Sate Control officer's intention to do a brief sampling analysis to look for one substance only (organotin or cybutryne) or two substances simultaneously there is some potential to simplify the existing guidelines.

This new need of a STEP 3 for cybutryne will make the step-wise strategy used for organotin compounds less obvious and less beneficial in economic terms, as the samples will still have to go to a laboratory for cybutryne determination. Considering the suggested modifications and associated costs, it may be advantageous to send the samples directly to a laboratory for CG/MS analysis to determine both the cybutryne and organotin compounds.

The table below presents the approximate costs for STEP 1, STEP 2, STEP 3 and the single step for the cybutryne analysis:

	Method name	Approx. Cost
STEP 1 (only for organotin)	ICP or XRF for total tin	150 Euro
STEP 2 (only for organotin)	GC/MS for organotin	350 Euro
STEP 3 (only for cybutryne)	GC/MS for cybutryne	350 Euro
Single STEP (for organotin and cybutryne)	GC/MS for both cybutryne and organotin *(still to be validated)*	450 Euro

Table 3 – Approximate costs for determining organotin and cybutryne (according to RISE Research Institutes of Sweden)

From the table above, it is possible to roughly calculate the costs for checking compliance with the AFS Convention for both organotin and cybutryne assuming a STEP 1 non-compliance for organotin. The total costs will be the sum of STEP 1 (150 EUR), plus STEP 2 (350 EUR), and finally the cost for the single STEP cybutryne (350 EUR) giving a total for a compliance test of 850 EUR.

The strategy to skip STEP 1 and go directly for GC/MS for both compounds will reduce the cost of sample collection and sample preparation at laboratory to 450 instead of the 850 EUR calculated above. Ideally the same sample preparation with the right solvent could be used to detect both organotin and cybutryne in just one GC/MS analysis. This possibility of a joint GC/MS analysis using similar extraction and sample preparation work, will be validated at laboratory at a later stage in the project.

1.2.2. Sampling strategy

The guidelines define that triplicate specimens of paint at each sampling point should be taken in close proximity to each other on the hull (e.g. within 10 cm of each other).

Method 1 mentions a minimum number of eight independent samples to be collected. For each sample point three specimens: 'specimen A' for STEP 1 analysis, Specimen B for STEP 2 analysis and a third specimen for storage/back-up. It is suggested to collect a fourth 'Specimen C' for cybutryne analysis. This gives a new total of 32 fibre glass pads to be collected with the introduction of cybutryne analysis.

The description of Method 2 is not as detailed as of method 1. It refers "at each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least six specimens". It is suggested to collect another specimen in each sampling point for the

cybutryne analysis, giving a total of a minimum of nine abrasive paper pads. It should be noted that the first stage analysis for organotin analysis does not destroy the sample. The sample can be re-used for the second stage analysis as the STEP 1 is non-destructive.

These two suggested modifications are described in ANNEX 2.

Proposal to simplify the existing guidelines

If the single STEP GC/MS analysis for organotin compounds and cybutryne proofs to be feasible, then the number of samples can be reduced to 16 samples. This would enable some costs saving in terms of sample collection and analysis.

Another possibility is to keep the same number of samples as the current version of the guidelines and split the sample that will go to GC/MS analysis in two (STEP 2): one half is used in the organotin analysis and the other half is used in the cybutryne analysis. An additional weighing of the half abrasive pads must be introduced to determine the amount of paint on each half pad after splitting. This will be confirmed at a later stage.

1.2.3. Extraction

To quantify the amount of cybutryne present in the sample pad, cybutryne needs to be extracted from the paint in the pad to a solvent. It is suggested that the sample is extracted with 10 ml of ethyl acetate using an internal standard (see below justification for solvent and internal standard choice).

1.2.4. Internal standard

The optimal internal standard for Mass Spectometry detection is isotopically (deuterium) labelled cybutryne. This substance is available on the market, but at a very high price. Therefore, another trizine with the same secondary amines and sulphur chemistries as cybutryne is proposed, ametryn (CAS No. 834-12-8). This substance is readily available at a reasonable price and is chemically very similar.

1.2.5. Solvent

The solubility of both ametryn and cybutryne was determined to be above 20 mg/ml in acetone for ethylacetate, dichloromethane and toluene. Based on safety, health and environmental (SHE) aspects, use ethyl acetate could be used as solvent.

1.2.6. Separation and detection with CG/MS method

It is suggested to use the CG/MS analytical method to quantify the amount of cybutryne[7]. The calibration and maintenance of the GC/MS system should be performed according to ISO 17025 laboratory practices.

[7] It is suggested to do a splitless injection of 1 µl etylacetate extract at 300 °C using a spitless time of 30 seconds. The separating column should be a 30 meter; 0,25 mm wide, 25 µm thick 5% phenyl 95 % methyl phase operated with helium or hydrogen as the carrier gas. For the separation a typical temperature program of 35 °C for 5 min, ramp to 325 C at 10 °C/min should be used. It is suggested to do the detection of the baseline between the analyte and the internal standard using the following conditions: MS operating in Selected Ion Mode (SIM) using the m/z 253, 238 and 183 ions for Cybutryne and m/z 227, 212 and 185 ions for Ametryn.

1.2.7. Calculation and reporting

It is suggested to calculate the concentration of cybutryne in the paint sample using the internal standard approach. The results should be reported individually and as an average value.

1.2.8. Limit of quantification

In order to determine the limit of quantification for the above test method for cybutryne quantification, duplicate samples of two dried paints (Boero Magellan 630 Extra (SPC mechanism)) and Akzo Nobel International Interspeed 5617 Red (ablative mechanism)) containing 0,02 weight % cybutryne (wet basis) were tested. The samples were collected with an abrasive pad, extracted and analysed with GC/MS analysis according to the method described above and in ANNEX 2. The RMS signal (s/n) to noise was 200. This means that it is possible to perform analytical work at least one order of magnitude below, at 0,002 %, giving a limit of quantification of 20 mg/kg.

1.2.9. Measurement uncertainty and tolerance range

In order to test the uncertainty of the test method, dry paint (with 2% cybutryne) was sampled and analysed in duplicate but reported as single sample determinations. Several paints were used. The precision was calculated as the relative standard deviation of the repeatability (rsd r) and the trueness is based on the recovery. The relative standard deviation of the repeatability was determined to be 14% and the Bias to be 3%.

The expanded measurement uncertainty (U) was calculated as two times (k=2) the measurement uncertainty (u), corresponding to 95% a confidence interval, and resulted in 25%. This corresponds to a tolerance range of 0,025% (250 mg/kg) for the method.

For the suggested analytical method, the range of uncertainty to be considered on the measured value is 25%. This means that compliance should be achieved at measured concentration lower than the threshold plus the tolerance range) i.e. 1 000 plus 250 mg cybutryne / kg dry paint.

1.2.10. Compliance criteria

It is suggested to use the average concentration of all paint samples as the best value to represent the content of cybutryne in the hull surface. As mentioned before, the distribution of any remaining anti-fouling paint in the hull surface is not homogenous. Therefore, it is suggested that the average value of all samples is below the threshold plus the tolerance range, i.e. 1 250 mg of cybutryne per kg of dry paint.

3. References

Woldegiorgis et al., 2007, Results from the Swedish screening programme 2006, sub-report 3: zinc pyrithiione and Irgarol 1051, IVL Swedish Environemtnal Research Institute Ltd., IVL Report B1764, url https://www.ivl.se/webdav/files/Rapporter/B1764.pdf.

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ANNEX 2
Text editions to the guidelines for brief sampling of anti-fouling systems on ships

[Note: suggested new text is inside square brackets, formatted in red and italics]
** to be inserted once the threshold is fixed.*

GUIDELINES FOR BRIEF SAMPLING OF ANTI-FOULING SYSTEMS ON SHIPS

Table of contents

APPENDIX

POSSIBLE METHODS FOR BRIEF SAMPLING AND ANALYSIS OF ANTI-FOULING SYSTEMS ON SHIPS

1 General

Purpose

1.1 Article 11 of the International Convention on the Control of Harmful Anti-fouling Systems on Ships, 2001, hereinafter referred to as "the Convention", and resolution MEPC.102(48) Guidelines for Survey and Certification of Anti-Fouling Systems on Ships refer to sampling as a method of verification of compliance of a ships anti fouling system with the Convention for inspection and survey.

1.2 The "Guidelines for Brief Sampling of Anti-Fouling Systems on Ships", hereinafter referred to as "the Guidelines", provide procedures for sampling to support the effectiveness of survey and inspection to ensure that a ship's anti-fouling system complies with the Convention and thus assists:

.1 Administrations and recognized organizations (ROs) in the uniform application of the provisions of the Convention;

.2 port State control officers with guidance on methods and handling of brief sampling in accordance with Article 11 (1)(b) of the Convention; and

.3 companies, shipbuilders, manufacturers of anti-fouling systems, as well as any other interested parties in understanding the process of sampling as required in terms of the Convention.

1.3 However, inspections or surveys do not necessarily always need to include sampling of anti-fouling system.

1.4 These Guidelines apply to surveys and inspections of ships subject to the Convention.

1.5 The sole purpose of the sampling activities described in the Guidelines is to verify compliance with the provisions of the Convention. Consequently, such activities do not relate to any aspect not regulated by the Convention, (even if such aspects relate to the performance of an anti-fouling system on the hull of a ship, including the quality of workmanship).

Structure of these Guidelines

1.6 These Guidelines contain:

.1 a main body covering aspects of general nature common to "sampling" procedures related to the regulation of anti-fouling systems controlled by the Convention; and

.2 appendices describing the unique procedures associated with the sampling and analysis of anti-fouling systems controlled by the Convention. These appendices only serve as examples of sampling and analytical methods and other sampling

methods not described in an appendix may be used subject to the satisfaction of the Administration or the port State, as appropriate.

1.7 For reasons including the event of other anti-fouling systems becoming controlled under the Convention, or in the light of new experience acquired, these Guidelines may need to be reviewed or amended in the future.

2 Definitions

For the purposes of these Guidelines:

2.1 "Administration" means the Government of the State under whose authority the ship is operating. With respect to a ship entitled to fly a flag of a State, the Administration is the Government of that State. With respect to fixed or floating platforms engaged in exploration and exploitation of the sea-bed and subsoil thereof adjacent to the coast over which the coastal State exercises sovereign rights for the purposes of exploration and exploitation of their natural resources, the Administration is the Government of the coastal State concerned.

2.2 "Anti-fouling system" means a coating, paint, surface treatment, surface or device that is used on a ship in order to control or prevent attachment of unwanted organisms.

2.3 "Threshold value" means the concentration limit of the chemical under investigation below which compliance with the relevant provisions of the Convention may be assumed.

2.4 "Company" means the owner of the ship or any other organization or person such as the manager or the bareboat charterer, who has assumed the responsibility for the operation of the ship from the owner of the ship and who, on assuming such responsibility, has agreed to take over all duties and responsibilities imposed by the International Safety Management (ISM) Code.

2.5 "Length" means the length as defined in the International Convention on Load Lines, 1966, as modified by the Protocol of 1988 relating thereto, or any successor Convention.

2.6 "Tolerance range" means the numerical range added to the threshold value indicating the range where detected concentrations above the threshold value are acceptable due to recognised analytical inaccuracy and thus do not compromise the assumption of compliance.

3 Personnel safety when sampling

Health

3.1 Persons carrying out sampling should be aware that solvents or other materials used for sampling may be harmful. Wet paint which is sampled may also be harmful. In these cases the material safety data sheet (MSDS) for the solvent or paint should be read and appropriate precautions should be taken. This will normally include the wearing of long sleeve solvent resistant gloves of suitable impervious material -e.g. nitrile rubber.

3.2 Quantities of dry anti-fouling paint removed during sampling from ships' hulls will normally be too small to cause significant health effects.

Safety

3.3 Access to ships to carry out sampling safely may be difficult. If a ship is moored alongside persons carrying out sampling must ensure they have safe access to reach the hull from e.g. platforms, crane baskets, cherry-pickers, gangways. They must ensure that they are protected by railings or a climbing harness or take other precautions so that they cannot fall into the water between the quay and the ship. If in doubt a lifejacket and possibly a safety line, should be worn when sampling.

3.4 Access to ships in dry-dock should be made by secure means. Scaffolding should be securely constructed and cherry-pickers or dock-arms should be properly constructed and maintained if they are to be used to gain access. There should be a system to record the presence of the inspector in the dock area, and he should preferably be accompanied. Safety harnesses should be worn in cherry-picker baskets, if used.

4 Sampling and Analysis

Sampling methods

4.1 During sampling, care should be taken not to affect the integrity or operation of the anti-fouling system.

4.2 Sampling where the anti-fouling coating is visibly damaged[8] or on block mark areas on the flat bottom of the ship (where the intact anti-fouling system is not applied) should be avoided. Sampling adjacent to or below areas where the anti-fouling system is damaged should also be avoided. When a sample point on the hull has been selected, any fouling present should be removed with water and a soft sponge/cloth before taking a specimen of the anti-fouling system (to avoid contamination of sample). Where possible, if carried out in dry-dock, sampling should be carried out after the hull has been water-washed.

4.3 The materials required for brief sampling methodologies should ideally be inexpensive, widely available and therefore readily accessible, irrespective of sampling conditions and/or location.

4.4 The sampling procedure should ideally be easily and reliably undertaken. Persons conducting sampling should receive appropriate training in sampling methods.

Technical aspects

4.5 The sampling method should take into account the type of anti-fouling system used on the ship.

4.6 Specimens of paint for analysis during survey and certification can be taken either as wet paint[9] from product containers, or dry paint film sampled from the hull.

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[8] During in-service periods, anti-fouling coatings on ships' hulls often become damaged. The extent of damage varies between ships and damaged areas can be visually recognised. Typically damage can be restricted to localised areas e.g. anchor chain damage (bow region), fender damage (vertical sides of hull), 'rust through areas' (underlying rust causing coating failure) or in some cases be in smaller areas scattered over larger areas of the hull (usually older ships where over-coating of original system has taken place many times).

[9] In order to prevent contamination, wet paint samples should be taken from a newly opened container. Paint should be stirred to ensure even consistency before sampling and all equipment used should be cleaned prior to use. Liquid paint samples should be stored in appropriate sealed packaging which will not react with or contaminate the sample. In the case of multi-component coatings (where on-site mixing of several components

Sampling strategy and number of samples

4.7 The sampling strategy is dependent on the precision of the sampling method, the analytical requirements, costs and required time and the purpose of the sampling. The number of paint specimens taken of each sample should allow for a retention quantity for back-up/storage in the event of a dispute. For dry samples, ~~triplicate~~ *[quadruplicate]* specimens of paint at each sampling point should be taken in close proximity to each other on the hull (e.g. within 10 cm of each other).

4.8 In cases where it is recognized that more than one type of anti-fouling system is present on the hull, where access can be gained, samples should be taken from each type of system:

.1 for survey purposes or for more thorough inspections pursuant to article 11 (2) of the Convention, in order to verify the compliance of an anti-fouling system, the number of sample points should reflect representative areas of the ship's hull; and

.2 for inspection purposes pursuant to article 11(1) of the Convention sample points on the hull should be selected covering representative areas where the anti-fouling system is intact. Depending on the size of the vessel and accessibility to the hull, at least four sample points should be equally spaced down the length of the hull. If sampling is undertaken in dry-dock, flat bottom areas of the hull should be sampled in addition to vertical sides as different anti-fouling systems can be present on these different areas.

Analysis

4.9 The analysis of the anti-fouling system should ideally involve minimal analytical effort and economic cost.

4.10 The analysis should be conducted by a recognized laboratory meeting the ISO 17025 standard or another appropriate facility at the discretion of the Administration or the port State.

4.11 The analytical process should be expeditious, such that results are rapidly communicated to the officers authorized to enforce the Convention.

4.12 The analysis should produce unambiguous results expressed in units consistent with the Convention and its associated Guidelines. For example, for organotin, results should be expressed as: mg tin (Sn) per kg of dry paint *[and mg of cybutryne respectively]*.

NOTE: Compound-specific sampling and analytical methodologies are described in the appendices to these Guidelines.

5 Thresholds and tolerance limits

is required prior to application), samples of each component should be taken and the required mixing ratio recorded. When a sample of wet paint is taken from a container, details of the paint should be recorded e.g. details required for the IAFS Certificate along with a batch number for the product.

Thresholds

5.1 The analysis should be quantitative to the point of being able to accurately verify the threshold limits within the given tolerance.

5.2 In cases where compliance with acceptable limits, or lack thereof, is unclear, additional sampling or other methodologies for sampling should be considered.

Tolerance range

5.3 Statistical reliability for each (compound-specific) brief sampling procedure should be documented. The analysis should be quantitative to the point of being able to accurately verify the threshold limits within the given tolerance. On the basis of these data a compound-specific tolerance range should be derived and stated compound-specific in the method description. In general, the tolerance range should not be higher than the standard deviation under typical conditions for testing and should under no circumstances go beyond 30 %.

6 Definition of compliance

6.1 Compliance with Annex 1 of the Convention is assumed if the anti-fouling system contains organotin *[and/or cybutryne]* at a level which does not provide a biocidal effect. In practice organotin compounds should not be present above 2,500 mg organotin (measured as Sn) per kg of dry paint. *[Cybutryne should not be present above x,xxx* mg of cybutryne per kg of dry paint].*

6.2 Compliance is largely dependent on the results of sampling and subsequent analysis. As every method of sampling and analysis has its specific accuracy, a compound-specific tolerance level may be applied in borderline cases with concentrations very close to the threshold level.

6.3 In general, compliance is assumed when the samples yield results below the threshold value.

7 Documentation and recording of information

7.1 The results of the sampling procedure should be fully documented on a method-specific record sheet. Examples are provided in the appendices to these Guidelines.

7.2 Such record sheets should be completed by the sampler and should be submitted to the competent authority of the Port State or Administration.

APPENDIX
Possible methods for brief sampling and analysis of anti-fouling systems on ships

- ORGANOTIN *[AND CYBUTRUNE]* -

METHOD 1

1 Purpose of this method concerning brief sampling and analysis of anti-fouling systems

1.1 This method has been developed in order to describe a rapid methodology appropriate for the identification of anti-fouling systems on ship hulls containing organotin compounds *[and/or cybutryne]* acting as biocide. This method has been designed such that sealers should not be affected, and any underlying anti-fouling agent (or primer) is not taken up in the sampling procedure. The method is not recommended for silicon-based anti-fouling systems.

1.2 ~~This~~ *[The]* method *[for organotin compounds]* is based on a two-step analysis. The first step detects total tin as an indicator for organotin; the second step, detecting specific organotin compounds, is only necessary in the case of the first step proving positive. *[The method for cybutryne is based on a one step analysis].*

2 Sampling device and materials

2.1 The sampling device is constructed in a way that only the upper layer of paint is removed, thereby and should leave any underlying paint (sealer, primer etc.) intact. This result is achieved through the use of a moving disk, (eccentric rotation) which is covered by an abrasive material like quartz or glass fibre fabric. This abrasive material has to be suitable for its use as a supporting material for the removed paint.

2.2 The device fulfils the following requirements:

.1 the device has to work independently from any stationary power supply. The device may be driven by an electrical motor (battery-driven) or may be mechanically driven by a clockwork-like spring, provided it is able to sustain the movement over the required time period;

.2 the applied force has to be constant during the operation, and the area for paint removal has to be defined;

.3 the abrasive material has to be inert against chemical solvents and acids and must not contain more than trace amounts of tin or tin compounds *[and/or cybutryne]*; and

.4 the amount of paint removed after a regular operation of the device has to be shown to exceed 20 mg per sample.

2.3 The device as described in the following section has been shown to be suitable for the brief sampling procedure. Any other device may be used however, provided such a device has proven to meet all the above-mentioned requirements.

2.4 The sampling device described here consists of a polyethylene disk, on which fibre glass fabric can be mounted by the use of an O-ring. The disk is moved on an eccentrically rotating axis.

3 Sampling procedure

3.1 The sampling procedure should be performed in the following manner:

.1 control samples should be taken through the entire sampling and analytical process to account for possible contamination;

.2 the mass of the fibre glass pads is weighed with a precision of at least 1 mg. The weight should be documented for each sample;

.3 the fabric should be moistened thoroughly with isopropanol (0.7ml per sample) immediately before sampling;

.4 when a sample point on the hull has been selected, any fouling present should be removed with water and a soft sponge/cloth before taking a specimen of the anti-fouling system (to avoid contamination of sample). Where possible, if carried out in dry-dock, sampling should be carried out after the hull has been water-washed;

.5 the sampling device is then held against the surface to be sampled for a period of 5 seconds, prior to the sampling device being switched on;

.6 the sampling device is switched on, thereby removing paint by the circular motion of the fibre glass fabric against the surface of the ship;

.7 the sampling device should be applied to the surface of the hull for a suitable period of time, such that at least 20 mg of paint is taken up by the pad. As a general rule, if the pad colour after sampling matches the colour of the hull coating a sufficient sample has been taken;

.8 the two-step analysis procedure *[for organotin compounds]* requires that every sample should be taken in triplicate. Two of the specimens should be labelled Specimen 'A' and Specimen 'B'. In addition a third specimen for storage/back-up should be taken. These specimens should be taken as close to each other as possible, but without overlap;

[.x A fourth ‘specimen C’ for the one step analysis for cybutryne should be taken as close to each other as possible, but without overlap].

.9 upon completion of the sampling, the fibre glass fabric pads should be left to dry, and re-weighed.

3.2 Samples should be stored in appropriate sealed packaging, which will not react with or contaminate the sample.

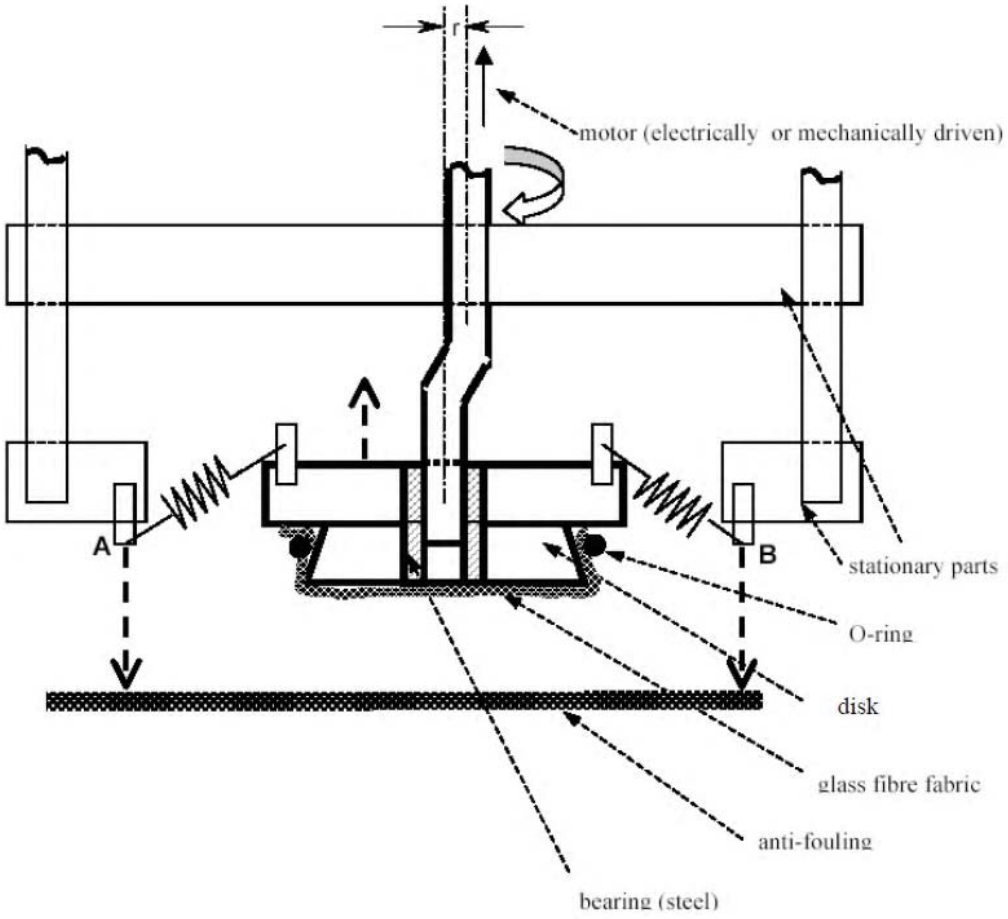

DIAGRAM A: Schematic cross section of the sampling device

The indicated points A and B are to be pressed against the surface. The polyethylene disk, covered with the glass fibre fabric, is moved with an amplitude of 2 r (r = 1,0 cm) on the surface.

Specific data:

Force applied on the paint surface:	25N (Newton)
Effective diameter of the disk:	5cm
Frequency of rotation:	6 rotations/s
Solvent used	isopropanol (0.8ml per sample).

4 Sampling strategy

4.1 Sampling should be conducted in accordance with paragraph 4 of the Guidelines.

4.2 For inspection purposes in most cases accessibility to all parts of the hull will not be given. A minimum number of eight independent samples should be taken from different accessible parts of the hull.

5 Analytical procedure

5.1 The two components comprising the analytical procedure *[for organotin compounds]* are illustrated in the flow diagram B. The two components, or steps, are as follows:

.1 (STEP I) - An analysis of 'Specimen A 'for the presence of total tin; and

.2 (STEP 2) - A more cost- and time-consuming analysis of 'Specimen B', that is applied only when Step 1 produces positive results. This test involves organotin analysis by gas chromatography/mass spectrophotometry (GC/MS) after derivatisation and provides specific data on the respective organotin species.

[.* For cybutryne a one-step analysis:*

.3 STEP 3 – An analysis of 'Specimen C' for determining the amount of cybutryne, using gas chromatography/mass spectrophotometry (GC/MS)]

Step 1: Investigation of total tin content in Specimen 'A'

Analysis of Specimen 'A'

5.2 Specimen 'A' is analysed for mass of total tin per kilogram of dry paint (or mass of tin per sample) by applying inductively coupled plasma/mass spectrometry (ICP/MS), once the material had been solubilized by digestion using aqua regia. It should be noted that any other scientifically recognized procedure for tin analysis (such as AAS, XRF and ICP-OES) is acceptable.

Step 2: Characterization of organotin in Specimen 'B'

Analysis of Specimen 'B'

5.3 Should Specimen 'A' produce positive results, organotin compounds should be identified and quantified in Specimen 'B'. Specimen 'B' may be analysed using the following procedure:

.1 solvent extraction of Specimen 'B' as supported by sonication in an ultrasonic bath;

.2 derivatisation with ethylmagnesium bromide;

.3 clean-up of the extract;

.4 analysis using high resolution gas chromatography/mass spectrophotrometry (GC/MS); and

.5 quantifications using tripropyltin as a standard.

5.4 Any equally reliable method for the chemical identification and quantification of organotin compounds is acceptable.

[step 3: Characterisation of cybutryne in 'Specimen C'

Analysis of 'Specimen C'

x.x 'Specimen C' should be analysed using the following procedure:

.1 Sample extraction using ethylacetate with added internal standard (ametryn) using an ultrasonic bath for 15 minutes;

.2 Centrifugation of the samples at 600 rcf for 5 minutes;

.3 Analysis of the supernatant using high resolution capillary GC/MS, with the MS operating in SIM mode;

.4 Quantification using reference cybutryne solutions and an internal standard normalization procedure;

.5 Modified GC/MS methods resulting in an expanded measurement uncertainty (k=2; 95% confidence) of 25% are acceptable.]

6 Threshold and tolerance range

6.1 The threshold value *[for organotin compounds]* for the brief sampling method as described here is:

"2,500mg tin (Sn) per kg of dry paint."

[x.x The threshold value for cybutryne for the brief sampling method as described here is:

"x xxx mg of cybutryne per kg of dry paint.]*

Tolerance range

6.2 The tolerance range is 500mg Sn / kg of dry paint (20%) in addition to the threshold value.

[x.x The tolerance range is xxx mg cybutryne / kg of dry paint (xx%*) in addition to the threshold value.]*

Organotin containing compounds acting as biocides or catalysts

6.3 As stated in the appendix of resolution MEPC.102(48), for the purposes of defining compliance with annex 1 of the Convention, it should be noted that small quantities of organotin compounds, acting as chemical catalysts (such as mono- and di-substituted organotin compounds) are allowed, provided they are not acting as a biocide.

6.4 Inorganic impurities in the constituents of the paints should be considered.

6.5 At present neither organotin catalysts nor inorganic impurities are found at concentrations which will be close to the threshold level (2,500mg Sn/kg of dry paint) or higher. However, organotin-containing compounds, when present in paint in order to act as a biocide, were found in concentrations up to 50,000mg Sn/kg of dry paint. Thus the discrimination between anti-fouling systems containing organotin compounds acting as a

biocide and anti-fouling systems not containing these compounds or not containing these compounds at concentrations where they act as a biocide, is reliably possible.

7 Definition of compliance

Two-step procedure

7.1 The analytical verification of the compliance with the Convention *[for organotin compounds]* is performed in a two-step procedure according to the flow-diagram (diagram B).

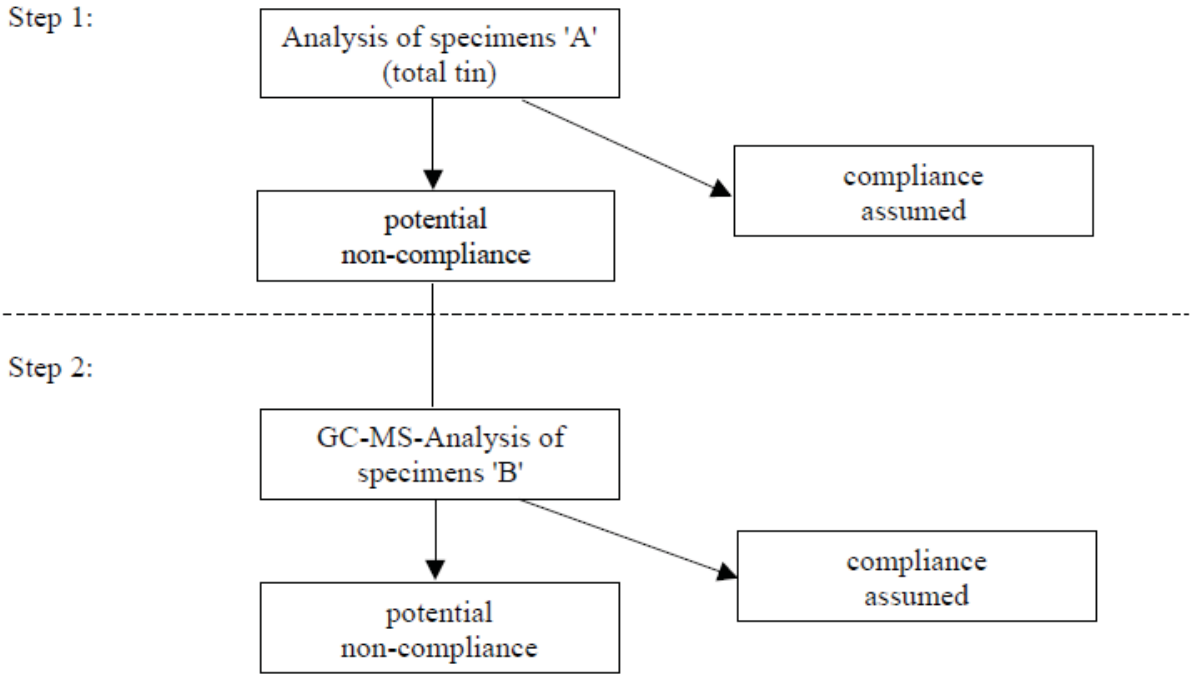

DIAGRAM B: Flow diagram illustrating the two-step analysis procedure *[for organotin compounds]*

Compliance with the criteria at the 'Step 1-level'

7.2 Compliance with the Convention is assumed when the results from the specimens 'A', analysed in step 1, meet the following:

.1 no more than 25% of the total number of samples yield results above 2,500 milligrams total tin per kilogram dry paint (2,500 mg Sn/kg of dry paint); and

.2 no sample of the total number of at least eight samples shows a concentration of total tin higher than the sum of threshold value plus the tolerance range, i.e. no sample must exceed the concentration 3,000 mg Sn/kg of dry paint.

7.3 If the results in specimen 'A' indicate that no organotin acting as biocide is present, then performing step 2 is not necessary.

Non-compliance with the criteria at the 'Step 1-level'

7.4 A positive result (non-compliance) is indicated if provisions of paragraph 7.2 are not met.

7.5 A positive result at step 1 (specimen 'A') would indicate that step 2 should be undertaken, and those samples labelled specimen 'B' should be analysed in order to determine and characterize the organotin present (see diagram B).

Compliance with the criteria at the 'Step 2-level'

7.6 Compliance with the Convention is assumed when the results from the specimens 'B', analysed in step 2, meet the following requirements at the same time:

.1 no more than 25% of the total number of samples yield results above 2,500 milligrams total tin per kilogram dry paint (2,500 mg Sn/kg of dry paint); and

.2 no sample of the total number of at least eight samples shows a concentration of total tin higher than the sum of threshold value plus the tolerance range, i.e., no sample must exceed the concentration 3,000 mg Sn/kg of dry paint.

Non-compliance at 'step 2-level'

7.7 A positive result in step 2 indicates non-compliance if the provisions of paragraph 7 .6 are not met. Such results should be interpreted to mean that organotin compounds are present in the anti-fouling system at a level at which it would act as a biocide.

[Compliance with the criteria for the Step 3 for cybutryne

x.x Compliance with the Convention is assumed when the results from specimen 'C', analysed in a STEP 3 for cybutryne, meet the following requirement:

***.1** The average value of the total number of specimens shows a concentration below the threshold plus the tolerance range i.e. x,xxx* mg of cybutryne per kg of dry paint.]*

Non-compliance at the Step 3 for cybutryne

x.x Non-compliance with the Convention is assumed when the average value of the total number of specimens shows a concentration above the threshold plus the tolerance range i.e. x,xxx mg of cybutryne per kg of dry paint. Such results should be interpreted to mean that cybutryne is present in the anti-fouling system at a level at which it would act as a biocide.]*

APPENDIX TO METHOD 1

RECORD SHEET FOR THE BRIEF SAMPLING PROCEDURE FOR COMPLIANCE WITH THE CONVENTION IN TERMS OF THE PRESENCE OF ORGANOTIN ACTING AS A BIOCIDE IN ANTI-FOULING SYSTEMS ON SHIP HULLS

RECORD SHEET : **GUIDELINES FOR BRIEF SAMPLING OF ANTI-FOULING SYSTEMS ON SHIPS - ORGANOTIN -**		***RECORD NUMBER:***
SECTION A: Administration		
1. Country	**2. Name of port**	**3. Date**
4. Reason for sampling: ☐ Port State control ☐ Survey & Certification ☐ Other flag State compliance inspection		
5. Company details: 1. Name of ship: 2. Distinctive number or letters: 3. Port of registry: 4. Gross tonnage: 5. IMO number:	**6. Inspecting official's details** 1. Name: 2. Comments:	
SECTION B: Sampling		
1. Time sampling procedure initiated:		
2. Description of location from where samples were taken (frame number and distance from boot topping, refer to paragraph 3.2):		
3. Number of samples taken (three specimens per sample): 4. Photographs taken of the sample points prior to sampling? ☐ Yes ☐ No		
5. Time sampling procedure completed:		
6. Additional comments concerning sampling procedure:		

SECTION C: Analysis and results

1. Step 1 total tin analysis:

Company name: ……..

Analyst responsible:…… Date :……

2. Specimen 'A' results: _____ total number of specimens 'A' analysed: _____

No.	mg Sn / kg	No.	mg Sn / kg	No.	mg Sn / kg	No.	mg Sn / kg
1		5		9		13	
2		6		10		14	
3		7		11		15	
4		8		12		16	

Number of specimens exceeding 2,500 mg/kg: _____

1 or more specimens exceeding 3,000 mg/kg: yes ☐ no ☐

Conclusion: Step 2 required ☐

Compliance, Further analysis unnecessary: ☐

3. Additional comments concerning analysis of results from Specimen 'A':

4. Organotin analysis undertaken by:

Company name: ……

Analyst responsible:…… Date :……

5. Specimen 'B' results: _____ total number of specimens 'B' analyzed: _____

No.	organotin (mg / kg) as Sn	No.	organotin (mg / kg) as Sn	No.	organotin (mg / kg) a Sn	No.	organotin (mg / kg) as Sn
1		5		9		13	
2		6		10		14	
3		7		11		15	
4		8		12		16	

Number of specimens exceeding 2,500 mg/kg: _____

1 or more specimens exceeding 3,000 mg/kg: yes ☐ no ☐

Conclusion: Non-compliance assumed ☐

Compliance assumed ☐

6. Additional comments concerning analysis of results from Specimens 'B':

7. Summarized conclusion:

Compliance assumed ☐

Non-compliance assumed ☐

THIS IS TO CERTIFY that this Record is correct in all respects.

Issued at .....
(Place of issue of Record)

.....
(Date of issue) (Printed name and signature of authorized official issuing the Record)

(Seal or stamp of the authority /organization)

METHOD 2

1 Purpose of this method

1.1 This method provides sampling and analysis procedures to identify the presence of organotin compounds *[and/or cybutryne]* in the anti-fouling systems on ships. The method is designed such that the sampling and the first stage analysis could be carried out by ship surveyors or port State control officers (PSCOs) on the survey/inspection site, e.g. at a dry dock.

1.2 This~~s~~ *[e]* method *[for organotin compounds]* is based on a two-stage analysis. The first stage detects total tin as an indicator for the presence of organotin and the second stage is necessary only in the case that the first stage analysis providing a positive result to detect specific organotin compounds.

[x.x The method for cybutryne analysis is based on a single step analysis based on the gas chromatography/mass spectrophotometry analytical method (GC/MS).]

2 Sampling

2.1 The sampling is carried out by using abrasive paper rubbing on the surface of the anti-fouling system. This results in collection of paint fragment of the anti-fouling system from thin area, less than several micrometer in depth from the surface, which do not affect the coatings lying underneath such as sealers.

2.2 Abrasive paper is pasted on a disc of approximately 10 mm in diameter. Rubbing the surface of the anti-fouling system with the disc collects several milligrams of the sample on to the abrasive paper.

2.3 The sampling device consists of an electric motor, two (or three) rotating rods on each of which a disc is attached, and a battery for electric power supply. The discs are pressed on to the surface of ship's hull by spring coils. The disks rotate counter-clockwise while the rods tum clockwise around the centre of the device. Schematic diagram is illustrated in figure 1.

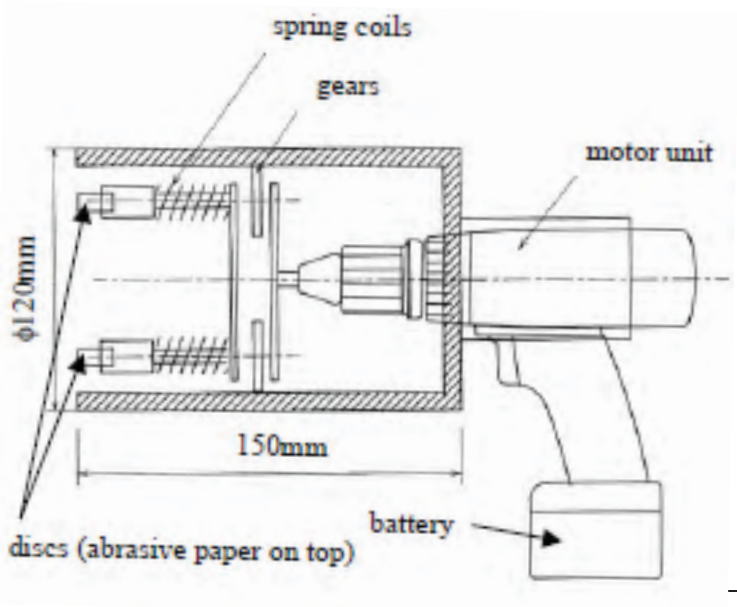

Figure 1. Schematic diagram of sampling device

2.4 Sampling point is selected such that the anti-fouling system is intact over an area of approximately 50 cm x 50 cm or more. At each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least ~~six~~ *[nine]* specimens.

2.5 The device is pressed on the ship's hull where it is appropriate to be sampled and held by hand. The electric motor is switched on to slide along the painted surface to lightly scrape off the fragments of the paint onto the abrasive paper. After the sample collection, each disc is removed from the device and stored in an inert container.

2.6 Sampling should normally be carried out with the sampling device. However, in the case that accessibility to the sampling point is poor, it is acceptable to collect samples with the discs by hand if necessary.

3 The first-stage analysis

3.1 The first-stage analysis is assumed to be carried out on the spot of the survey or inspection, e.g. dry docks and sea ports. In order to accomplish the on-site analysis, X-ray fluorescence analysis (XRF) is used in this method to detect total tin content.

3.2 Analytical characteristics, such as detection limit and accuracy, are highly dependent on the type of the instrument, i.e. type of X-ray tube, spectrometer, optical arrangement (filters or collimators), etc. Among several types of the XRF instruments, an energy-dispersive spectrometer with a silicon drift detector (SDD), which is compact in size and be able to be operated without liquid nitrogen, is preferable to the present analytical system for a field use, whereas wave-length dispersion system or solid-state detector are also available if the analysis carried out at laboratories.

3.3 Software customized for the tin analysis is prepared to assist the operator, who is assumed to be a ship surveyor or PSCO, to detect total tin in the specimens.

3.4 The customized software may in advance need a calibration curve of the characteristic X-ray intensity of tin in relation to the tin content particularly in the range of 0.1 to 0.5%.

3.5 After the preparation including the warming-up of the XRF instrument and starting-up of the computer, a specimen (sampling disc) is placed on the sample stage of the instrument. Afterwards, analysis is executed by the customized software. A single batch of analysis for one specimen normally takes 5 minutes and the result is shown on a display automatically.

3.6 Since the XRF analysis does not affect any properties of the specimens, all of the collected specimens (~~six to~~ nine *[to twelve]* specimens), including those for the second analysis and storage, are able to be used for this analysis.

4 Interpretation of the result at the first-stage analysis

4.1 Following the procedures above, XRF data of ~~six, or~~ nine *[or twelve]*, specimens are obtained for each sampling point. Omitting the maximum and minimum values from the data, an average of the tin content is calculated from the intermediate values for the representing value of the sampling point.

4.2 Compliance with the Convention is assumed when none of the tin contents (average values) from the samples do not exceed the sum of the threshold (2,500 mg per kg) and a tolerance (500 mg per kg).

4.3 When one or more average values of samples from different sampling points do not meet the above criteria, the samples should be sent to a laboratory for the second stage analysis. Regardless of the results, it is also possible to undergo the second stage analysis when the surveyor or PSCO considers that it is necessary to do so.

5 Second-stage analysis

5.1 Since the second-stage analysis provides the final and definitive results of the samples, the method should be thoroughly reviewed by experts based on scientific evidence. The following is a brief summary of a tentative methodology for the second stage analysis.

5.2 The collected paint specimens are removed from the abrasive paper and total mass is measured with an electronic balance to an order of 0.1 mg. The specimens are hydrolysed with sodium hydroxide aqueous solution, extracted with organic solvent, and then derivatised with propylmagnesium bromide. After cleaning up the extract, analysis using high resolution gas chromatography/mass spectrometry (GC/MS) is carried out. For quantification analysis, tetrabutyl tin d36 is added as the internal standard.

5.3 These analyses provide the data of chemical species and their content (mg per kg of the specimens). The content of organotin is obtained in a unit of mg per kg of dry paint.

[x STEP 3 for cybutryne

The collected paint specimens are removed from the abrasive paper and total mass is measured with an electronic balance to an order of 0.1 mg. The following procedure is proposed for determining the concentration of cybutryne:

.1 Sample extraction using ethylacetate with added internal standard (ametryn) using an ultrasonic bath for 15 minutes;

.2 Centrifugation of the samples at 600 rcf for 5 minutes;

.3 Analysis of the supernatant using high resolution capillary GC/MS, with the MS operating in SIM mode;

.4 Quantification using reference cybutryne solutions and an internal standard normalization procedure;

.5 Modified GC/MS methods resulting in an expanded measurement uncertainty (k=2; 95% confidence) of 25% are acceptable.]

6 Compliance with the Convention

6.1 Compliance with the Convention *[for organotin compounds]* is assumed when the results from the second-stage analysis meet the following requirements at the same time:

.1 no more than 25% of the total number of samples yield results above 2,500 milligrams tin as organic form per kilogram dry paint (2,500 mg Sn/kg of dry paint); and

.2 no sample of the total number of specimens shows a concentration of tin as organic form higher than the sum of the threshold value plus the tolerance range, i.e., no sample must exceed the concentration 3,000 mg Sn/kg dry paint.

6.2 When the result does not meet the above criteria, it is interpreted to mean that organotin compounds are present in the anti-fouling system at a level where they would act as a biocide.

[x.x Compliance with the Convention for cybutryne is assumed when the results from the step 3 for cybutryne meets the following criteria:

.1 The average value of the total number of specimens shows a concentration below the threshold plus the tolerance range i.e. x,xxx mg of cybutryne per kg of dry paint.*

x.x When the result does not meet the above criteria, it is interpreted to mean that cybutryne is present in the anti-fouling system at a level where they would act as a biocide.]

APPENDIX TO METHOD 2

Record Sheet for the Sampling and Analysis of Anti-Fouling Systems on Ship Hulls - Organotin Compounds

		Record Number
Section A: Administration		
1. Country		2. Location
3. Date		
4. Reason for Survey/Inspection		
5. Details of the Ship		
	5.1 Name of Ship	
	5.2 Distinctive Number or Letters	
	5.3 Gross Tonnage	5.4 Year of Built
	5.5 Owner or Operator of Ship	
	5.6 Flag State	5.7 Class of Ship
	5.8 Authority of AFS Certificate	
	5.9 Date of Issue	
	5.10 Date of Last Endorsement	
	5.11 IMO Number	
	5.12 Name of Shipmaster	
	5.13 Product Name of Anti-Fouling System	
	5.14 Name of Manufacturer	
	5.15 Name of Shipyard where applied	
	5.16 Comments	
6. Inspecting Official's Details		
	6.1 Name	
	6.2 Comments	

Record Number

Section C: Stage II Analysis (Gas Chromatograph Mass Spectrometry)

Date

Instrument I.D.

Comments on the Method

Sample I.D.	Specimen Used	Content of Tin (XRF analysis) (mg/kg)	Content of Tin (as organotin) (mg/kg)	Compliance
A				□>2,500mg/kg □>3,000mg/kg
B				□>2,500mg/kg □>3,000mg/kg
C				□>2,500mg/kg □>3,000mg/kg
D				□>2,500mg/kg □>3,000mg/kg

4. Conclusion

☐Not Compliant ____ samples out of __ are above 2,500mg(Sn)/kg(dry paint).
Sample(s) ___ is (are) above 3,000mg(Sn)/kg(dry paint).

☐Compliant

5. Additional Comments

6. Laboratory Name

7. Analyzed by | 8. Signature

Section D: Final Conclusion

1. Conclusion

☐Anti-fouling system is compliant with the AFS Convention 2001.

☐Anti-fouling system is NOT compliant with the AFS Convention 2001.

2. Comments

3. Processed Official

3.1 Name _____ 3.2 Date _____

3.3 Signature

4. Authorized Administrator

4.1 Name _____ 4.2 Date _____

4.3 Signature

Record Number	
Section B: Sampling and Stage I Analysis (X-ray Fluorescence Analysis)	
Date	Instrument I.D.

Sample/Location	Specimen I.D.	Sampling Disc	Content of Tin (mg/kg)	max	min	Average
A	A1	□abrasives		□	□	
	A2	□metal		□	□	
	A3	□others		□	□	Average
	A4	□abrasives		□	□	
	A5	□metal		□	□	_____ mg/kg
	A6	□others		□	□	□>2,500mg/kg
	A7	□abrasives		□	□	□>3,000mg/kg
	A8	□metal		□	□	
	A9	□others		□	□	
B	B1	□abrasives		□	□	
	B2	□metal		□	□	
	B3	□others		□	□	Average
	B4	□abrasives		□	□	
	B5	□metal		□	□	_____ mg/kg
	B6	□others		□	□	□>2,500mg/kg
	B7	□abrasives		□	□	□>3,000mg/kg
	B8	□metal		□	□	
	B9	□others		□	□	
C	C1	□abrasives		□	□	
	C2	□metal		□	□	
	C3	□others		□	□	Average
	C4	□abrasives		□	□	
	C5	□metal		□	□	_____ mg/kg
	C6	□others		□	□	□>2,500mg/kg
	C7	□abrasives		□	□	□>3,000mg/kg
	C8	□metal		□	□	
	C9	□others		□	□	
D	D1	□abrasives		□	□	
	D2	□metal		□	□	
	D3	□others		□	□	Average
	D4	□abrasives		□	□	
	D5	□metal		□	□	_____ mg/kg
	D6	□others		□	□	□>2,500mg/kg
	D7	□abrasives		□	□	□>3,000mg/kg
	D8	□metal		□	□	
	D9	□others		□	□	

□Stage II required	☐ ___ samples out of ___ are above 2,500mg/kg ☐ Sample ___ is above 3,000mg/kg	□Compliant
Sampled by	Analyzed by	
Signature	Signature	