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Ships and marine technology — Procedure for testing the performance of continuous monitoring TRO sensors used in ships —

Part 1:
DPD sensors

Navires et technologie maritime — Méthode de contrôle des performances des capteurs de TRO de surveillance continue utilisés à bord des navires —

Partie 1: Capteurs à la DPD

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 8, *Ships and marine technology*.

A list of all parts in the ISO 23780 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The International Maritime Organization (IMO) adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention) in 2004[1]. The Convention entered into force in September 2017 and requires that ballast water management systems (BWMS) be installed on board vessels according to an implementation schedule in the ensuing years. The Convention requires that the use of active substances by BWMS be evaluated using the *Procedure for approval of ballast water management systems that make use of active substances* (G9 Procedure of the Convention) [2] to ensure that the use of the BWMS does not pose any unacceptable risk to the environment, human health, property or resources. Oxidants are an important active substance associated with certain treatment systems. Total residual oxidant (TRO) is a critical process control parameter during both uptake and discharge of oxidant treatment technologies. TRO sensors are also used for compliance monitoring (maximum allowable discharge concentration) of ship discharges.

Sensors that monitor TRO are used in oxidant-based ballast water treatment to control both oxidant dose at ballast uptake and oxidant neutralization at ballast discharge. On uptake, the TRO sensor is used to monitor and control the addition of oxidant. This will vary depending upon the oxidant demand (due to organic matter) in the water being treated. On discharge, the TRO sensor monitors and controls the neutralization of any residual oxidant prior to overboard discharge, consistent with the approval by the IMO Marine Environment Protection Committee (MEPC). Consequently, the TRO sensor is expected to provide reliable, real-time monitoring.

N,N-Diethyl-*p*-phenylenediamine (DPD) is used in total and free chlorine (Cl_2) colorimetric analysis because it reacts with hypochlorous acid and hypochlorite ions. Most conventional TRO analysis methods apply to drinking water and low-saline water treatment in land-based facilities. Using these methods, most of the TRO measurements are made under stable environmental conditions, for example in terms of continuous flow and water properties. By contrast, the BWMS TRO measurements must consider varying conditions. Several factors interfere with TRO measurements. For example, the salts and other ions in seawater can affect the development of a specific colour that is quantitatively related to the TRO concentration in water. The pH and water temperature may affect the oxidation potential of Cl_2 in water, interfering with the TRO measurement. The production of a relatively weak colour may be due to shadow effects from particles or organic matter in water.

The testing of the performance of TRO sensors in water is currently per ISO 7393-3. This method is appropriate for drinking water and other waters where additional halogens like bromine, iodine, and other oxidizing agents are present in almost negligible amounts. Seawater and waters containing bromides and iodides comprise a group for which special procedures are to be carried out. TRO sensors are now being used on ships, which are often in marine waters, and a method for evaluating the potential substances that may interfere with both shipboard and marine waters is currently not available.

Ships and marine technology — Procedure for testing the performance of continuous monitoring TRO sensors used in ships —

Part 1: DPD sensors

1 Scope

This document provides a method to ensure the performance of continuous monitoring TRO sensors, which can be installed in a BWMS or elsewhere in a ship, taking into consideration environmental factors associated with shipboard conditions, such as high salinity, vibration, variation in humidity and temperature, and predictable sea conditions. This document is intended for use by BWMS manufacturers, sensor manufacturers, testing agencies, and ship owners to verify the performance of a TRO sensor unit.

This document is intended to provide requirements and guidance for TRO sensors that use the N, N-diethyl-1,4-phenylene diamine (DPD) method. These requirements and guidance are applicable to testing of sensor units in a laboratory prior to installation. This document identifies:

— performance characteristics to be defined by manufacturers of TRO sensors used in the shipboard treatment environment (e.g. salinity range);

— pre-qualification and performance procedures to document instrument capabilities;

— performance test procedures to be used in different environmental conditions.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

IACS UR E10, *Test specification for type approval*

ISO 7393-2, *Water quality — Determination of free chlorine and total chlorine — Part 2: Colorimetric method using N,N-dialkyl-1,4-phenylenediamine, for routine control purposes*

IEC 60529, *Degrees of protection provided by enclosures (IP Code)*

IEC 60079 (all parts), *Explosive atmospheres*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
abnormal water level
minimum water level that can be measured in measurement cell

3.2
active substance
AS
substance or organism, including a virus or fungus that has a general or specific action on or against harmful aquatic organisms and pathogens

[SOURCE: IMO, Resolution MEPC.169(57):2008, 2.1]

3.3
calibration solution
solution containing a substance or mixture of substances giving a defined value of the *determinand* (3.4) and used for calibration of the *total residual oxidant sensor* (3.11) instrument

3.4
determinand
property or substance that is required to be measured and reflected by, or present in, a *calibration solution* (3.3)

[SOURCE: ISO 15839:2003, 3.13]

3.5
reagent validity test
stability test of buffer and indicator reagent solution required for *total residual oxidant* (3.10) measurement

3.6
response time
time interval between the instant when the *total residual oxidant sensor* (3.11) is subjected to a *zero solution* (3.14) in *determinand* (3.4) value and the instant when the readings cross a band defined by 90 % of *span solution* (3.8)

3.7
span drift
variation of the indicated value for the span of the measuring device for a certain period of time

3.8
span solution
solution with a certain percentage of analyte concentration within the measuring range specified for the instrument

3.9
standard solution
set of simple or synthetic reference solutions having different analyte concentrations

Note 1 to entry: The zero solution is, in principle, the solution having zero concentration of the analyte.

3.10
total residual oxidant
TRO
complete amount of oxidising compounds in water, including biocidal compounds added via chemical injection, electrolysis, or ozonation, such as chlorine gas, chlorine dioxide (ClO_2), ozone (O_3), or chemicals that are quickly converted to sodium hypochlorite

Note 1 to entry: TROs also include compounds derived from reactions with primary oxidants, such as hypohalites, hypohalous acids, chloramines, bromamines, and N-Cl linked compounds.

Note 2 to entry: Active substances (AS) should be defined by the ballast water management system (BWMS) manufacturer, which should be controlled as intended through the risk assessment of the BWMS. Then a BWMS with an AS defined by the manufacturer would be evaluated with equivalent oxidation potential of TRO. Therefore, the concept of TRO in this application of BWMS is rather conceptual. Even some potential substances in treated water such as chlorine gas, chloramines and other disinfection by-products are not considered and proposed as the AS or TRO by the manufacturer.

3.11
total residual oxidant sensor
TRO sensor
sensor which measures the concentration of *total residual oxidant* (3.10)

3.12
TRO sensor unit
TSU
device designed for processes that require continuous in-line monitoring of *total residual oxidant (TRO)* (3.10) levels

Note 1 to entry: It monitors the concentration levels of TRO during ballasting and de-ballasting.

Note 2 to entry: It should be composed of buffer solution, indicator and sample measurement cell separately.

3.13
zero drift
variation of the indicated value for the zero of the measuring device for a certain period of time

3.14
zero solution
solution having no residual oxidant, such as purified water, which can be used for zero-point solution

4 Determination of the measurement procedure

The laboratory test is designed to demonstrate the performance characteristics of the TRO sensor that will be installed in the ballast water management systems.

The manufacturer shall check the general requirements of the TRO sensor unit (TSU) in accordance with Annex A. The manufacturer shall also provide the information to the testing agency as specified in Annex B, to conduct the performance evaluation of the TSU in the laboratory. The test bench facilities (see Annex A) can be slightly different for each test environment. However, the following conditions shall be applied in all instruments.

The test bench facilities shall match the requirements specified for the instruments by the manufacturer. The facilities shall include the ability to record (manually or automatically) readings of the sensor equipment in analogue or digital form.

Where appropriate, it shall be possible to change the calibration solution determinand value measured by the instrument within less than 10 % of the response time declared by the manufacturer. Typical examples where this is not appropriate are the determination of turbidity and electrical conductivity. The facilities shall include laboratory instruments for analysis of the required determinand(s). The methods used and test results shall be reported (see 7.3).

After confirming the performance of the interferences of the TRO sensor (see 5.4 and 5.5), the manufacturer should present it to the test agency, which should then verify the performance provided by the manufacturer.

A schematic of the test procedure is shown in Figure 1.

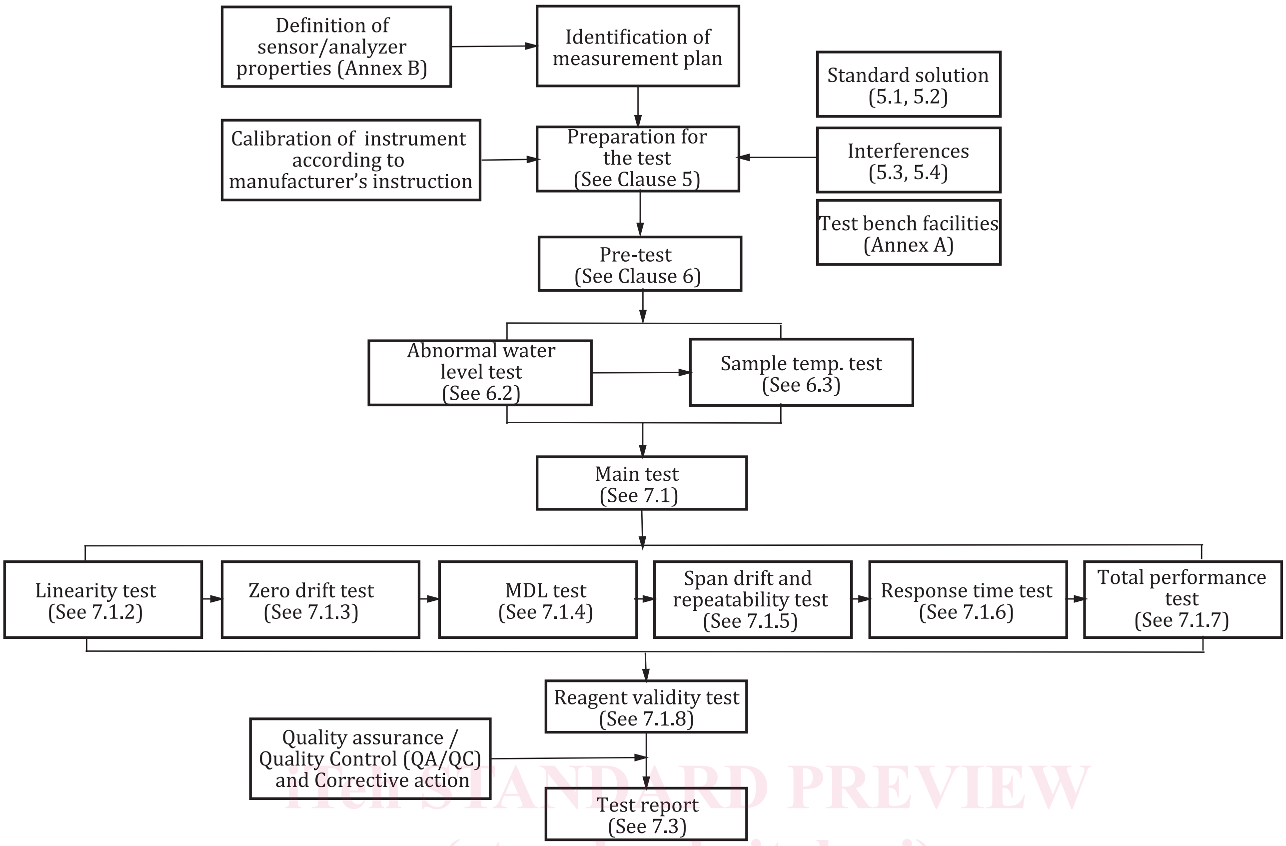

Figure 1 — Schematic of the test procedure

5 Preparation for the test

5.1 Confirmation of effective chlorine concentration

There are two ways to make a chlorine standard solution: solid and liquid. When using solid or liquid standard matter, determine the effective chlorine concentration before preparing the standard solution. Steps for determining the effective concentration of chlorine shall be in accordance with Annex C.

5.2 Preparation for chlorine standard solution

The standard solution shall be prepared at the time of testing and verified in accordance with ISO 7393-2, using the following procedure.

a) Standard stock solution (1 000 mg/l): Dissolve the amount obtained in 5.3 or quantified liquid reagent and fill distilled water to 1 000 ml.

b) Pour 100 ml of the standard stock solution (calcium hypochlorite) into the measured 9,9 l distilled water in container (= 10 mg/l).

c) As an analysis result, the sample should be diluted and analysed again if the measurement value gets out of specification of the instrument.

5.3 Verification of standard solution

a) Verify the standard solution is not expired by measuring values of the 50 % sea water span solution two times directly after making the solution and passing a certain time period.

b) Fresh liquid standard solution shall be prepared from solid calcium hypochlorite immediately prior to each test and directly discarded after the test is complete.

5.4 Interferences

5.4.1 General

Potential sources of interferences to the measurement are identified in this clause. In this test, an interference measurement procedure is presented to consider the effect of interferences.

The N, N-diethyl-1,4-phenylene diamine (DPD) method detects oxidants used as disinfectants: chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), bromine (Br_2), and disinfection by-products such as chlorite, chlorate, bromite and bromate.

Based on the TRO sensor equipment and test environment conditions, the testing organization shall prepare the test bench, check the general equipment items, and test them in accordance with Annexes A and B.

The calibration test of the TRO sensor shall be performed taking into account turbidity, salinity and temperature.

5.4.2 Salinity

Halogen ions in saline-containing solutions can cause a relatively low colour reaction, interfering with TRO measurements in sea water.

5.4.3 Manganese compounds

Manganese can exist in oxidation states of +2 through +7. The higher oxidation states, typically +3 to +7, will interfere with the DPD method. Free chlorine reacts to oxidize soluble manganese compounds.

5.4.4 Colour and turbidity

One critical problem when applying colorimetric procedures to samples is interference from turbidity and colour in the water. For certain parameters, a preliminary filtration can be performed to remove particulate matter from the sample without any modification of oxidant's potential, nor time delay to measuring. The residual sample colour is "zeroed" at the measuring wavelength.

5.4.5 Dissolved oxygen

The indicator reagent will be oxidized by dissolved oxygen at higher pH. The reagent should always be maintained in a buffer with pH between 6 and 8.

5.4.6 Temperature

Higher temperatures increase the oxidation reaction rates of free chlorine with various organic and inorganic compounds.

5.5 Procedures for determining the impact on interferences

5.5.1 General

There are several factors that interfere with TRO, but this document presents a test procedure to confirm the effects of salinity, temperature, and turbidity, which are the major interferences. These tests shall be performed within the range agreed upon by the manufacturer and the testing agency. The testing institute should check this course is in line with the items suggested by the manufacturer before this test, particularly in terms of sensor performance. The purpose of interference testing is to assess the particles suspended in fluid that scatter and absorb light at the TRO measurement wavelengths.