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Secretariat: ANSI

**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](http://www.iso.org/directives)).

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## 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<sup>[1]</sup>. 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*<sup>[2]</sup> (G9 Procedure of the Convention) 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<sub>2</sub>) 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<sub>2</sub> 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<sup>[5]</sup>. 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.

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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

## 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. ~~This~~These requirements and guidance ~~is~~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*

~~IEC 61000-4-3, *Electromagnetic compatibility (EMC) — Part 4-3: Testing and measurement techniques — Radiated, radio frequency, electromagnetic field immunity test*~~

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 60068-1, *Environmental testing — Part 1: General and guidance*~~

~~IEC 60092-504, *Electrical installation in ships — Part 504: Control and Instrumentation*~~

~~IEC 60533, *Electrical and electronic installations in ships — Electromagnetic compatibility (EMC) — Ships with a metallic hull*~~

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

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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

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 ~~69~~, *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 *TRO* 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 ~~15039~~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 *TRO* 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

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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<sub>2</sub>), ozone (O<sub>3</sub>), or chemicals that are quickly converted to sodium hypochlorite

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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 BWMS 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 (DBPs) 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)

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3.12

**TRO sensor unit**

**TSU**

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

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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

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#### 4 Determination of details 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.

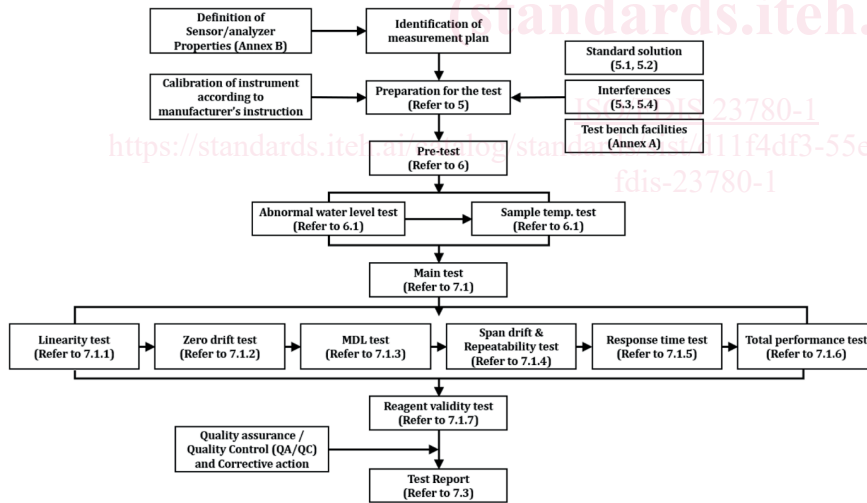
The manufacturer shall check the general requirements of the TRO sensor unit (TSU) in accordance with Annex A and. The manufacturer shall also provide the information to the testing agency as specified in Annex B, to conduct the performance evaluation of the TSU in the laboratory. The test bench facilities (see Annex A) may 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 5.34 and 5.45), 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.



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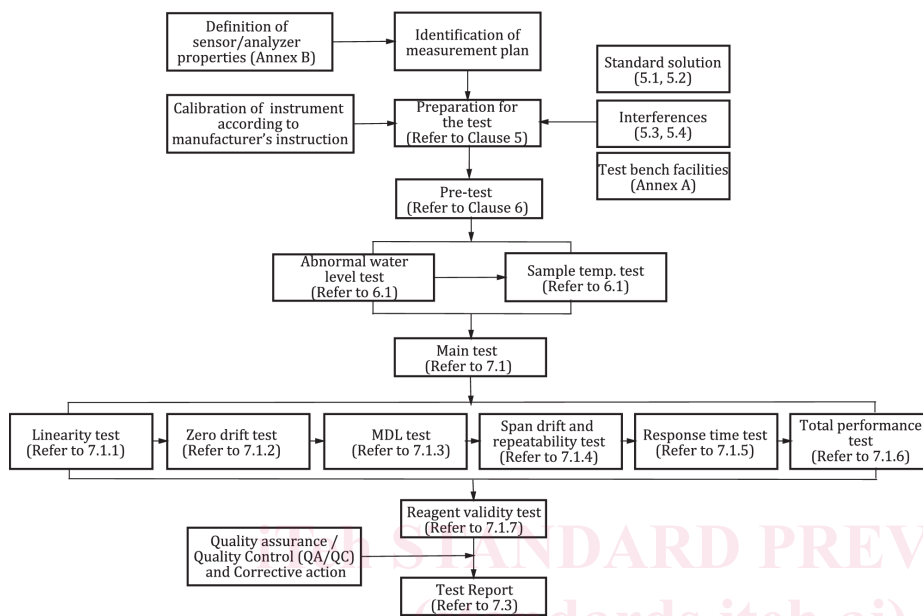


Figure 1 — Schematic of the test procedure

## 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 ~~according to~~ **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 5.2.13 or quantified liquid reagent and fill distilled water to 1-000 ml.
- b) Pour 100 ~~mL~~ ml of the standard stock solution (calcium hypochlorite) into the measured 9,9 ~~ml~~ ml 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.

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