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Ships and marine technology — Marine environment protection — Continuous on-board pH monitoring method

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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).

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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*, Subcommittee SC 2, *Marine environment protection*.

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 pH of water is an important indicator of water quality. Continuous pH monitoring of water served in marine equipment/systems installed on-board ships for various applications, such as exhaust gas cleaning systems (scrubbers) and boilers, is essential. “Continuous” describes a monitoring situation. The pH meter for continuous monitoring is situated in a fixed position on-board to monitor a stream, as opposed to batched-based deployment in a laboratory. This situation imparts some challenges that should be addressed. For installation of systems such as scrubbers to remove sulfur oxide from the exhaust gas by using seawater or freshwater, pH monitoring of the processed water is important not only for the process control of the systems but also for ensuring compliance with regulations when discharging the processed water [see IMO Resolution MEPC. 340(77)]. It is expected that reliable pH meters are robust over time, and suitable for processed water that can contain sea salts and/or oily substances or can exhibit a wide range of pH.

Ships and marine technology — Marine environment protection — Continuous on-board pH monitoring method

1 Scope

This document specifies the performance requirements and the test procedures for a pH meter used for continuous on-board monitoring using combination electrodes. The pH meter applies to measuring the pH of the following water for on-board consumption and research purposes:

a) natural seawater and freshwater,

b) freshwater produced from freshwater generators,

c) the used process water for running machinery on-board ships.

This document also specifies the method for evaluating performance, calibration, and maintenance of a pH meter used for continuous on-board monitoring.

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.

ASTM D6569-14, *Standard Test Method for On-Line Measurement of pH*

IEC 60746-2:2003, *Expression of Performance of Electrochemical Analyzers — Part 2 — pH value*

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
pH value
value derived from the potential difference between the *glass electrode* (3.5) and the *reference electrode* (3.6) and compensated using temperature measured with the *temperature sensor* (3.7)

Note 1 to entry: This is based on a measure of the relative hydrogen ion activity in an aqueous solution given in IEC 60746-2:2003, 3.1

3.2
continuous monitoring
measurement using fixed equipment that continually and automatically takes a reading at a predetermined interval and then returns a result

3.3
pH meter for continuous on-board monitoring
on-board equipment composed of a *pH combination electrode* (3.4), a *transmitter* (3.9), and an *electrode mounting* (3.10), which automatically and continuously measures pH and contains a *cleaning device* (3.11), if needed

3.4
pH combination electrode
electrode holding a *glass electrode* (3.5) and a *reference electrode* (3.6) in a single unit

3.5
glass electrode
electrode measuring the electromotive force that corresponds to hydrogen ion concentration

3.6
reference electrode
electrode measuring reference potential to determine the electromotive force of the *glass electrode* (3.5)

3.7
temperature sensor
sensor that measures the actual temperature of a sample solution to compensate for changes in the *slope force* (3.8) of the *glass electrode* (3.5) due to temperature variations

3.8
slope force
electromotive force per a unit pH of the *glass electrode* (3.5)

Note 1 to entry: Theoretical Nernstian slope, which is temperature dependent, is 59,16 mV at 25 °C. The temperature dependency of theoretical Nernstian slope is specified in IEC 60746-2:2003, Table A.1.

3.9
transmitter
device capable of outputting the potential difference as *pH value* (3.1), temperature, and state signal

3.10
electrode mounting
equipment to hold in place the *pH combination electrode* (3.4) when used for *continuous monitoring* (3.2), which may contain a *cleaning device* (3.11), if needed

3.11
cleaning device
optional equipment and accessories that automatically clean the *pH combination electrode* (3.4)

4 pH buffer solution

4.1 General

There are two types of pH buffer solutions: the certified pH buffer solution and the practical-use pH buffer solution. The pH value of the pH buffer solution and its accuracy shall be guaranteed by the manufacturer. Depending on the intended measurement range, at least two buffer solutions should be used, from pH 4 (phthalate buffer solution), pH 7 (phosphate buffer solution), and pH 9 (borax buffer solution). The temperature dependence of the pH values of the buffer solutions provided by the manufacturer shall be considered.

The buffer solutions shall be stored in appropriate conditions and used within the period in accordance with the manufacturer's instruction.

4.2 Certified pH buffer solution

A certified pH buffer solution shall be used when pH meter manufacturers verify the performance of the pH combination electrode. The certified pH buffer solution shall be traceable to an international or a national pH standard.

4.3 Practical-use pH buffer solution

A practical-use buffer solution should be used when calibrating the pH meter on-board ships.

NOTE The practical-use pH buffer solution is commercially available from pH meter manufacturers or reagent manufacturers.

5 Performance requirements for the combination electrode

5.1 General

The manufacturer shall state the specification of the combination electrode for the users to choose the appropriate pH combination electrode suitable for the process conditions: repeatability, linearity, and the range of pH and operating temperature.

5.2 Slope force

5.2.1 Requirement

The slope force shall be confirmed to be 56,20 mV or more at 25 °C.

5.2.2 Verification

Measure the certified pH buffer solutions of pH 4 and pH 7 alternately three times by the pH combination electrode. The slope force derived from the average of the difference in the electromotive force of pH 4 and pH 7 shall be 56,20 mV or more at 25 °C.

NOTE A slope force of 56,20 mV at 25 °C is equivalent to 95 % of the theoretical Nernstian slope of 59,16 mV at 25 °C.

5.3 Repeatability

5.3.1 Requirement

The repeatability of the measured pH values of the certified pH buffer solutions shall be confirmed to be within ±0,1 pH at both pH 4 and pH 7.

5.3.2 Verification

Measure the certified pH buffer solutions of pH 4 and pH 7 respectively three times by the pH combination electrode. The repeatability of the measured pH values shall be confirmed to be within ±0,1 pH at both pH 4 and pH 7.

5.4 Linearity

5.4.1 Requirement

The pH combination electrode shall be calibrated for at least two points using two certified pH buffer solutions. After the calibration, the measured value of a third certified pH buffer solution shall be confirmed to be within ±0,1 pH of the designated pH value of the third certified pH buffer solution.

The certified pH buffer solutions shall include pH 4, pH 7 and another certified pH buffer solution encompassing or in close proximity to the anticipated pH measurement range. The manufacturer shall guarantee the pH meter has a repeatable response within ±0,1 pH over the whole measurement range of the pH meter.

5.4.2 Verification

After the pH combination electrode is calibrated with the two certified pH buffer solutions, measure the third certified pH buffer solution three times, and every measured value shall be confirmed to be within ±0,1 pH of the designated pH value of the pH buffer solution.

6 Interferences

6.1 General

Continuous monitoring of pH is affected by factors such as conductivity, electrode fouling, electrical noise, and air bubbles. To keep the accurate on-board monitoring as long as possible, the pH meter shall be designed to minimize these interferences.

6.2 Sample conductivity

The combination electrode shall be targeted for a sample solution with a conductivity of 0,1 S/m or more. In principle, the pH value cannot be determined for a sample solution with a low conductivity such as pure water.

Alternatively, the pH measurement in high ionic strength samples, such as seawater, leads to deviations in measured pH values from the designated ones due to the generation of liquid junction potential.

NOTE It is possible to reduce the effect of seawater with high conductivity by using a gel-like inner liquid for the reference electrode as described in 7.2.2.

6.3 Electrode fouling

When the electrode or liquid junction becomes fouled, it leads to an error in pH values or causes pH values to become unstable. Therefore, the cleaning of the electrode is important for accurate measurement. Cleaning methods for the electrode for different types of fouling are specified in Clause 9.

6.4 Electrical noise

The electrical noise generated from the cable connecting the pH combination electrode and the transmitter can cause error in the measured value (see Figure 2). The cable shall be independent of AC power supply and switching circuit wiring. In case of measurement error due to interference of the earth circuit, the pH meter shall have an isolation output.

6.5 Air bubbles

Fluctuation and error of the measured pH value increase when air bubbles adhere to the glass membrane and liquid junction of the pH combination electrode (see Figure 2). For stable measurements during continuous on-board monitoring, the bubbles shall be reduced before the pH measurement.