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

*Navires et technologie maritime — Protection de l'environnement
marin — Méthode de surveillance continue du pH à bord*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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.

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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 $\pm 0,1$ 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 $\pm 0,1$ 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 $\pm 0,1$ 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 $\pm 0,1$ 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 $\pm 0,1$ 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.

7 Requirements for pH meters for continuous on-board monitoring

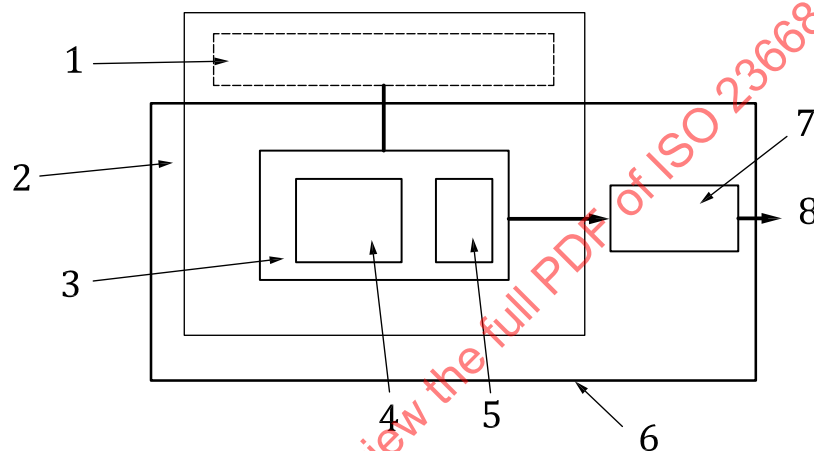
7.1 General

The manufacturer shall state the specification and the operating condition of the pH meter and shall provide an instruction manual for specific procedures regarding the calibration, maintenance and use of the pH meter.

7.2 Apparatus

7.2.1 General

See [Figure 1](#) for an illustration of a pH meter for continuous on-board monitoring.



Key

- 1 cleaning device for the pH combination electrode (optional component)
- 2 electrode mounting
- 3 pH combination electrode
- 4 glass electrode/reference electrode
- 5 temperature sensor
- 6 pH meter
- 7 transmitter
- 8 output

NOTE The temperature sensor can be separate from the pH combination electrode.

Figure 1 — Example of the outline of a pH meter for continuous on-board monitoring

7.2.2 pH combination electrode

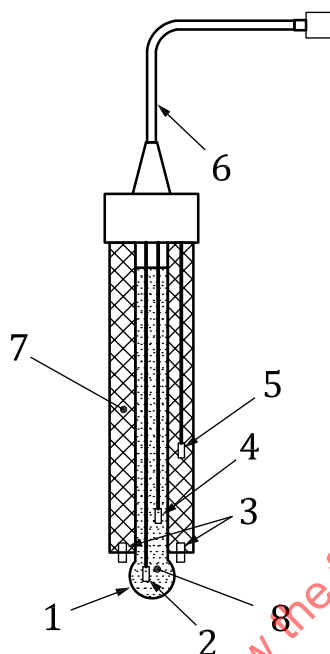
A pH combination electrode illustrated in [Figure 2](#) holds a glass electrode, a reference electrode, and a temperature sensor in a single unit, and uses a gel reference electrolyte.

The pH value is temperature-compensated by the transmitter using temperature measured by the temperature sensor. The temperature sensor may be incorporated into the combination electrode or may be a separate probe. The position of the temperature sensor shall be designed in a way that it measures the temperature of the sample as close to the combination electrode as possible. The temperature compensation shall be as specified in ASTM D6569-14, 6.4 and 6.5.

The maintenance of the pH combination electrode is specified in [Clause 9](#). For oil, grease, or suspended solids-bearing samples, an automatic cleaning device should be installed. When without the device,

the liquid junction with a relatively large surface area, typically greater than 15 mm², can reduce the chances of becoming completely blocked.

NOTE The gel electrolyte can supersaturate the electrolyte with KCl so as to be 4 mol/l or more, which can reduce the interference of Na ions and K ions in seawater. The gel electrolyte type electrode can also reduce the frequency of refilling the electrolyte. These characteristics have an advantage in use for open-loop scrubbers in particular.



Key

- | | | | |
|---|---------------------|---|-----------------------------|
| 1 | thin glass membrane | 5 | reference electrode |
| 2 | temperature sensor | 6 | cable |
| 3 | liquid junction | 7 | gel reference electrolyte |
| 4 | glass electrode | 8 | glass electrode electrolyte |

Figure 2 — Example of combination electrode with a built-in temperature sensor (gel electrolyte type)

7.2.3 Transmitter

7.2.3.1 General

The transmitter shall provide an output of temperature-compensated pH values derived from the electromotive force of the pH combination electrode, the temperature measured by the temperature sensor, and the state signal.

7.2.3.2 Impedance

The transmitter shall have a high impedance to measure the potential of the pH combination electrode. Therefore, an input impedance of the transmitter shall be at least 10⁵ MΩ, which corresponds to 1 000 times the impedance compared to that of the glass electrode.

7.2.3.3 Function check

For a function check of the transmitter, a pH/mV calibrator can be used to simulate a signal from a pH combination electrode. The test procedures shall be in accordance with IEC 60746-2:2003, 6.2.

7.2.4 Electrode mounting

The electrode mounting shall have a robust structure that prevents damage of the pH meter by vibration and shaking caused from engines and ship motions. In relation to compliance purposes, the robustness of the pH meter shall be followed by the requirement of the authorities and the classification societies. The structure shall allow easy calibration and maintenance work.

7.2.5 Cleaning device

The cleaning device is an optional equipment and its accessories, that automatically cleans the pH combination electrode, are given in detail in [9.3](#).

7.3 Placement

When enclosing the sensing portion of the pH combination electrode directly in process piping, it should be placed as far as possible from the nearest bends, elbows, pumps, valves, etc., to ensure it is in an area with a uniform flow profile, as far as possible. The sensor should also be placed close to the pipe wall to minimize damage.

The flow speed range should be 0,5 m/s to 3 m/s. The pH combination electrode should be designed to prevent damage when there is a possibility of a flow rate of more than 3 m/s.

7.4 Report

The pH meter for continuous on-board monitoring shall have the function of outputting the pH value, temperature, and status signal to an external recording device installed outside of the pH meter.

8 Calibration

The pH meter for continuous on-board monitoring shall be calibrated with practical-use pH buffer solutions to keep the sensor normal. This shall be done especially at the initial operation of the pH meter, at returning after stopping of the pH meter for longer than the manufacturer's recommended period, and after exchanging the pH combination electrode.

Before the calibration, clean the pH combination electrode in accordance with the instruction manual supplied by the manufacturer. Refer to [9.2](#) for information on manual cleaning. Further, the pH sensor should be returned to the sample solution for a few minutes to reach a steady-state before calibration.

NOTE After chemical or physical cleaning, the equilibrium of the liquid junction between the glass electrode and the reference electrode can be temporarily disturbed. It is expected to take a few minutes to re-establish equilibrium before calibration.

The pH combination electrode shall be calibrated for at least two points using the practical-use pH buffer solutions. The calibration shall be conducted in the anticipated measurement range in accordance with the manufacturer's instruction of the pH meter.

Calibration shall be repeated for each practical-use pH buffer solution until the difference between the designated pH value of practical-use pH buffer and the measured value is within $\pm 0,1$ pH. After measuring each practical-use pH buffer solution, wash the pH combination electrode with clean water and remove water droplets.

If the pH meter is used for compliance or control purposes, it is recommended that the transmitter signals be put on hold during calibration to avoid recording extraordinary values because of process upset.

9 Maintenance

9.1 General

Maintenance of the pH combination electrode shall be carried out in accordance with the instruction supplied by the manufacturer. Further, in relation to compliance purposes, performance of the pH meter shall be checked regularly with the practical-use pH buffer solution, and if the deviation is more than $\pm\text{pH } 0,2$, it shall be calibrated in accordance with [Clause 8](#).

The frequency of calibration should be determined by experience since it is highly application dependent. Regarding compliance or control purposes, if the stable pH measurement cannot be carried out during continuous measurement even in the same operating conditions of all the connected systems and the provided water over 15 minutes, the pH combination electrode probably should be calibrated. Experience with process control applications has suggested typical continuous pH measurement errors can be on the order of 0,2 pH to 0,5 pH according to ASTM D6569-14.

NOTE For example, the pH of the washwater used for open-loop scrubbers is affected by the operation conditions of systems consisting of engines, scrubbers, and the property of inlet water.

If the pH combination electrode is dried up, it shall be reconditioned in accordance with the manufacturer's instructions before calibration.

With regard to compliance purposes, if stable measurement cannot be carried out during continuous measurement (approximately $\pm\text{pH } 0,5$ in stable operation condition), the pH combination electrode probably should be calibrated.

Manufacturer's recommendation for the environment of usage and the replacement timing of the pH combination electrode shall be followed.

The pH combination electrode shall not be exposed to shock.

If the pH meter is used for compliance or control purposes, the transmitter signals shall be put on hold during the cleaning process to avoid recording extraordinary values because of process upset.

9.2 Manual cleaning

When fluctuation or drift of the measured pH value is observed, and when stable measurement cannot be achieved despite the automatic cleaning if applied, manual cleaning should be conducted according to the manufacturer's instructions. If there are no manufacturer's instructions for manual cleaning, the following procedure should be used depending on the fouling on the pH combination electrode:

- a) wash the pH combination electrode with clean water and wipe off fouling with a soft cloth;
- b) if the fouling is not fully removed after (a), wipe the pH combination electrode off with a soft cloth soaked with neutral detergent and rinse it with clean water;
- c) if the fouling is not well removed after (b), soak the pH combination electrode in diluted hydrochloric acid (about 1 mol/l) for 10 min to 30 min and rinse it with clean water. Hereafter, immerse the pH combination electrode in clean water for 5 min or the time recommended by the manufacturer.

Adequate safety precautions shall be taken when handling substances such as hydrochloric acid for cleaning.

NOTE Undiluted hydrochloric acid can damage the pH combination electrodes.