



## Water quality - Determination of pH

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## Water quality — Determination of pH

*Qualité de l'eau — Détermination du pH*

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 10523 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 10523:1994), which has been technically revised.

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## Introduction

The measurement of the pH value of water is of great importance for many types of sample. High and low pH values are toxic for aquatic organisms, either directly or indirectly. The pH value is the most useful parameter in assessing the corrosive properties of an aquatic environment. Also, it is important for the effective operation of water treatment processes and their control (e.g. flocculation and chlorine disinfection), control of plumbosolvency of drinking waters and biological treatment of sewage and sewage discharges.

The electrometric methods addressed in this International Standard are based on measuring the potential difference of an electrochemical cell where one of the two half-cells is a measuring electrode and the other is a reference electrode. The potential of the measuring electrode is a function of the hydrogen ion activity of the measuring solution (Reference [5]).

In view of its great practical importance, universality and exactitude, only measuring using the pH glass electrode is described in this International Standard.

In the reference electrode, electrolytes applied can be in liquid, polymer or gel form.

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# Water quality — Determination of pH

**WARNING** — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address any safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

**IMPORTANT** — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

## 1 Scope

This International Standard specifies a method for determining the pH value in rain, drinking and mineral waters, bathing waters, surface and ground waters, as well as municipal and industrial waste waters, and liquid sludge, within the range pH 2 to pH 12 with an ionic strength below  $I = 0,3 \text{ mol/kg}$  (conductivity:  $\gamma_{25}^{\circ\text{C}} < 2\,000 \text{ mS/m}$ ) solvent and in the temperature range  $0^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ .

## 2 Normative references

The following referenced documents are indispensable for the application 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.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4796-2, *Laboratory glassware — Bottles — Part 2: Conical neck bottles*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

## 3 Terms and definitions

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

### 3.1

#### pH

measure of the activity of hydrogen ions in solution

NOTE 1 Adapted from ISO 80000-9 [1].

NOTE 2 Whether a reaction is acid or alkaline is determined by the activity of the hydrogen ions present.

### 3.2

#### pH value

logarithm to the base 10 of the ratio of the molar hydrogen-ion activity ( $a_{\text{H}}$ ) multiplied by  $-1$

$$\text{pH} = -\lg a_{\text{H}} = -\lg(m_{\text{H}} \gamma_{\text{H}} / m^{\circ}) \quad (1)$$

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where

$a_{\text{H}}$  is the relative (molality basis) activity of the hydrogen ions;

$\gamma_{\text{H}}$  is the molal activity coefficient of hydrogen ions at  $m_{\text{H}}$ ;

$m_{\text{H}}$  is the molality, in moles per kilogram, of the hydrogen ions;

$m^{\circ}$  is the standard molality

NOTE 1 Adapted from ISO 80000-9 [1].

NOTE 2 pH value is an absolute measure characteristic.

NOTE 3 The pH(PS) (PS = primary standard) as a measure of single ion activity is not measurable. Therefore, the pH(PS) of solutions of primary reference materials is established, in order to calculate it as closely as possible and enable it to be traced back. This is achieved by using an electrochemical measuring procedure that rests upon the stringent thermodynamic dependency of the potential of the platinum/hydrogen electrode of the activity of the hydrogen ions and excludes diffusion current by using cells without transfer.

## 4 Principle

The determination of the pH value is based on measuring the potential difference of an electrochemical cell using a suitable pH meter.

The pH of a sample also depends on the temperature because of dissociation equilibrium. Therefore, the temperature of the sample is always stated together with the pH measurement.

## 5 Interferences

Deviations in the measurements are caused by additional voltages in the pH electrode, especially in the membrane, the diaphragm, and the measuring solution, and result in incorrect measurements. These deviations are lowest if both calibration/adjustment and measurement are carried out under similar conditions (e.g. temperature, flow characteristics, ionic strength).

Ageing and sedimentations (coatings) on the membrane (e.g. calcium carbonate, hydroxides of metals, oil, grease) of the measuring electrode induce an apparent decrease of the slope of the pH electrode, long response times or the occurrence of cross-sensibilities against anions and cations.

Sedimentations (coatings) or precipitations on or in the diaphragm (e.g. silver chloride, silver sulfide and proteins) interfere with the electrical contact to the measuring solution. Defects in the diaphragm can be identified by measuring the dilution effect of the measuring solutions.

If reactions between the electrolyte and the measuring solution result in precipitations in the diaphragm, establish an internal electrolyte bridge (e.g. KCl/KCl + AgCl) or an electrolyte bridge with inert electrolytes (e.g. potassium nitrate,  $c(\text{KNO}_3) = 0,1 \text{ mol/l}$ ) between the sample solution and the reference electrolyte.

Especially in waters with low conductivity, high diffusion voltages may occur. Stirring effects and memory effects (back-diffusion of the measuring solution into the reference electrode) can cause deviations in the measurements. Special pH electrodes (e.g. with a ground diaphragm or with an internal bridge with an AgCl-free solution of reference electrolytes) shall then be used.

In waters with low buffering capacity, the pH value may change very easily (e.g. by introduction or loss of carbon dioxide from the air or absorption of alkaline substances from glass vessels). In these cases, it is recommended to use suitable materials and to carry out the measurements in a closed flow system.

The release of gases in the vicinity of the pH electrode can cause additional interferences and, thus, a change of the pH value.

In suspensions, deviations in the measurements may occur. In this case, let the sample settle in a completely filled and closed vessel and subsequently measure in the clear supernatant.

Deviations in the measurements may occur when measuring ground waters or mineral waters rich in carbon dioxide. In these cases saturation with carbon dioxide under high pressure and degassing may occur during the measurement and cause changes of the original pH value. The pH value in anaerobic water containing Fe(II) and/or sulfide also changes in contact with air.

For the influence of temperature on the pH value of aqueous solutions, see 7.2, 7.3 and Clause 9.

## 6 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

**6.1 Distilled or deionized water**, e.g. deionized water as specified in ISO 3696, grade 2, conductivity < 0,1 mS/m.

**6.2 Buffer solutions**, preferably certified buffers with stated measurement inaccuracy for calibrating pH meters. Follow the manufacturer's instructions regarding storage and stability.

If certified buffers are not available and it is necessary to prepare buffer solutions in-house, see Annex A. The in-house preparation of buffer solutions should be the exception.

Atmospheric carbon dioxide influences buffer solutions, especially those of alkaline pH. Purging the gas in the headspace with protective gas improves stability. For all buffer solutions, avoid frequent opening and closing of the vessels and removal of small amounts. Mark the time of the first opening on the reagent bottle.

**6.3 Electrolytes for liquid-filled reference electrodes**. Use the electrolyte solutions recommended by the manufacturer.

**6.4 Potassium chloride solution**,  $c(\text{KCl}) = 3 \text{ mol/l}$ . To prepare the KCl solution as electrolyte for reference electrodes, use a suitable amount of solid potassium chloride and dissolve it in water (6.1).

## 7 Apparatus

**7.1 Sampling bottle**, sealable, flat-bottomed, made of polyethylene or glass, e.g. laboratory bottle as specified in ISO 4796-2, designation 100 WS. The type of stopper used shall allow the exclusion of all air from the sample bottle.

**7.2 Temperature measurement device**, capable of measurement with a total uncertainty not greater than 0,5 °C. The temperature sensor (7.2.2) is preferred.

**7.2.1 Thermometer with a 0,5 °C scale**.

**7.2.2 Temperature sensor**, separate or integrated into the pH electrode, e.g. Pt 100, Pt 1 000 or negative temperature coefficient.

Temperature measurement deviations due to the device shall be corrected against a calibrated thermometer.

**7.3 pH meter**, providing the following means for adjustment:

- zero point of the pH electrode (or offset voltage);
- slope of the pH electrode;
- temperature of the pH electrode;
- input resistance >  $10^{12} \Omega$ .

Moreover, it shall be possible to change the display of the pH meter to give readings of either the pH value or the voltage.