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Water quality — Determination of pH

Qualité de l'eau — Détermination du pH
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Reference number
ISO 10523:1994(E)

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.

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.

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

Annexes A, B, C, D and E of this International Standard are for information only.

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. It is the most essential parameter used 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.

Various methods of determination, ranging from simple methods using indicator paper to sophisticated methods using a pH-meter are used. The determination of pH may be broadly classified into two classes, colorimetric and electrometric methods (see [1] and [2] in annex E).

Colorimetric methods employ indicators which develop a range of colours at different pH. Their accuracy is restricted and they are only satisfactory for use in a field test.

The electrometric method is based on measuring the electromotive force of an electrochemical cell, consisting of the sample, a glass electrode and a reference electrode. A standard deviation of $\Delta\text{pH} = 0,05$ or less can be obtained using this method. If the sample is low in ionic strength, i.e. less than 5 mS/m electrolytic conductivity, special analytical equipment and procedures are necessary (see 7.3).

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Water quality — Determination of pH

1 Scope

1.1 Field of application

This method is applicable to all types of water and waste water samples in the range from pH 3 to pH 10.

1.2 Interferences

The temperature, some gases and organic materials interfere with the pH-measurement. Suspended materials in the sample may cause significant errors (suspension effect). Wait for sedimentation and only insert the electrodes in the clear fraction. Alternatively, an ultrafiltrate can be taken. When measuring sewage and some surface waters, there is a particularly high risk of smearing the electrodes or contaminating the membranes and diaphragms with oil, grease or other contaminants.

In the case of reference electrodes, this can be prevented (see 5.4, note 2). If precipitation takes place in the diaphragm, for example silver sulfide or protein flocs, it will be necessary to form an electrolyte bridge between the sample and the reference electrode with inert electrolytes, e.g. $c(\text{KNO}_3) = 1 \text{ mol/l}$.

Regular cleaning of the electrodes is necessary (see 9.2).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most re-

cent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-3:—¹⁾, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 pH: The negative decadic logarithm of the numerical value of hydrogen ion activity expressed in moles per litre. Because of ion interactions, the activity of the hydrogen ions is somewhat lower than their concentration.

The practical pH-scale is specified in terms of the pH of a series of primary standard reference solutions (see annex B).

4 Reagents

4.1 Water which is free from carbon dioxide

Prepare this water from distilled or deionized water by boiling or by equilibration with nitrogen. This water is required to dilute the buffer solutions for the double calibration (see 9.1).

4.2 Standard buffer solutions

Use solutions B, C, D, F and I, which are given in annex B, or commercially available primary buffer solutions that are not affected by the growth of microorganisms. If the solutions are not sterilized, they are stable for about 6 weeks. Carbon dioxide

1) To be published. (Revision of ISO 5667-3:1985)

from the atmosphere affects buffers with pH-values of more than 4.

Buffer solutions which are of greater ionic strength than the buffer solutions in annex B are not suitable for measurements in water with a low salt concentration (see [9] in annex E).

NOTES

1 Commercially available buffer solutions containing mercury salts as a preservative should be avoided.

2 For other buffer solutions, see [6], [10] and [11] in annex E.

4.3 Reference electrolyte

Electrolyte solution to refill the reference electrode according to the instructions of the manufacturer, e.g. potassium chloride solutions with the following concentrations:

I: $c(\text{KCl}) = 3,5 \text{ mol/l}$ [$\rho(\text{KCl}) = 261 \text{ g/l}$]

II: $c(\text{KCl}) = 3,0 \text{ mol/l}$ [$\rho(\text{KCl}) = 224 \text{ g/l}$]

III: $c(\text{KCl}) = 1,0 \text{ mol/l}$ [$\rho(\text{KCl}) = 74,6 \text{ g/l}$]

Dissolve the specified mass of potassium chloride in water and dilute to 1 litre. If saturation with silver chloride is recommended, add a few millilitres of silver nitrate solution [$c(\text{AgNO}_3) \approx 1 \text{ mol/l}$].

5 Apparatus

5.1 Sample bottle, of minimum capacity 500 ml, flat bottomed and made of low alkaline glass, e.g. borosilicate glass. Plastics bottles shall be impermeable to gases.

5.2 Thermometer, with a 0,5 °C scale.

5.3 pH-meter, with an input impedance greater than $10^{12} \Omega$, and with temperature compensation facilities and slope correction in millivolts per pH-value. The pH-meter shall be capable of being read to a discrimination of a pH of 0,01 or better.

5.4 Glass electrode and reference electrode. The glass electrode measuring system shall have a zero voltage between pH = 6,5 and pH = 7,5, using a reference electrode similar to the reference electrode inside the glass membrane (symmetrical electrode system) (see [12] and [13] in annex E). The membrane resistance of the glass electrode shall be $R_m < 10^9 \Omega$.

The cell can also be a commercially available combination electrode (i.e. a mono-rod measuring chain).

NOTES

3 Calomel electrodes contain mercury and its salts. In the event of a breakage, the heavy toxic contents enter the medium, therefore in general and especially in water used for drinking or swimming, a silver/silver chloride reference electrode should be used. To prevent clogging the diaphragm with silver chloride, a reference electrolyte of $c(\text{KCl}) = 1,0 \text{ mol/l}$ is recommended.

4 Reference electrodes with a flowrate of 0,1 ml to 2 ml per day are recommended. All new electrodes should be tested before use and then at regular intervals (see 9.1). To prevent contamination of the diaphragm, an excess hydrostatic pressure in the reference electrolyte, equivalent to a difference in water level of 2 cm or more, is necessary.

5 Glass electrode for water with a low conductivity (see 7.3.1).

6 Test procedures of electronic units and electrodes (see [8] in annex E).

6 Sampling and samples

The pH-value may change rapidly as a result of chemical, physical or biological processes in the water sample. For this reason, measure the pH as quickly as possible but not later than 6 h after sampling (see ISO 5667-3). If, in particular cases, this is not possible or not necessary, pass a flexible tube from the sampling tap to the bottom of a sampling bottle and fill the bottle to overflowing. Alternatively, rinse the bottle with the water sample and immerse it in the sample. Fill the bottle, avoiding turbulence if possible. Remove all air bubbles from the sample by gentle shaking and stopper the bottle. Analyse as soon as possible, but not later than 24 h after sampling. Avoid changes in temperature and gas exchange with the atmosphere.

7 Procedure

7.1 Preparation

Measure the temperature of the buffer solutions (see [14] in annex E). Set the temperature control on the pH-meter. In accordance with the instruction of the manufacturer, consider the isopotential point. If possible, buffers and samples should have the same temperature.

7.2 Calibrating and direct measurement

Measure the temperature of the sample (see [14] in annex E) and reset the temperature control on the

pH-meter in accordance with the manufacturer's instructions.

Wash the electrode with water and with sample and immerse it in the sample. Swirl the solution and read the pH-value without stirring.

Rinse the electrode with water and immerse it in water to remove traces of sample or buffer solution.

Wash the electrode with water and immerse it in buffer D (see 4.2). Swirl the solution gently about the electrode and allow the solution to come to rest (reading without stirring). Set the zero point of the instrument at the pH-reading of buffer D. The zero point compensation shall be $\Delta\text{pH} \leq 0,5$ (see clause 5). If this is not the case, then one of the electrodes is defective. Rinse the electrode with water and immerse in buffer C or F (see 4.2). Swirl the solution and take the pH-reading without stirring. Adjust the slope factor control until the reading that matches the buffer value at the measured temperature is obtained. (For the permissible range of slope factors, see table A.1).

Repeat both steps of the calibration until no further improvements are obtained.

NOTE 7 Buffer B, C, F or I should be chosen so that the expected pH of the sample lies within the range of the buffers used.

7.3 Measurement in water with a low conductivity

pH-measurements in water with low ionic strength (conductivity less than 5 mS/m) and low buffer capacity need special care. Examples of such waters are deionized condensate and rainwater.

7.3.1 Equipment

Use a commercially available glass electrode with a glass membrane of low solubility, i.e. a high alkali electrode. These electrodes are recommended for all measurements in waters. It is necessary to take a reference electrode with a sleeve ground joint and a reference electrolyte with $c(\text{KCl}) = 1 \text{ mol/l}$. Avoid the influence of potassium chloride on the glass electrode by slowly stirring the solution. To avoid the influence of air, allow part of the sample to flow through the measuring cell. To eliminate electrostatic effects, the sample shall be shielded by a Faraday cage and grounded by a metallic electrode in the sample.

7.3.2 Calibration

Check the calibration using one of the standard solutions of low buffer capacity given in annex C.

8 Calculation of pH for various temperatures

The pH shall be referred at 25 °C. If the value is measured at another temperature, this shall be stated. If required, express the pH for a temperature other than that measured, referring to figure 1 and using the following calculation:

$$\text{pH}_{25} = \text{pH}_{\text{tm}} + \Delta\text{pH}_{\text{tm}}$$

where

pH_{25} is the pH at 25 °C;

pH_{tm} is the pH at the measured temperature;

$\Delta\text{pH}_{\text{tm}}$ is the pH-deviation with reference to 25 °C for the measured temperature (see figure 1).

NOTE 8 The calculation is valid for waters with a buffer capacity mainly due to hydrogen carbonate ions.

9 Checking of the accuracy and maintenance of the equipment

9.1 Checking the equipment

Use the following test for screening the reference and glass electrodes for unsatisfactory performance. It shall be applied to new electrodes, to electrodes that have not been used for 2 weeks or more, and to electrodes in regular use at intervals of 1 or 2 weeks.

Calibrate the electrodes using one of the primary standard solutions in table B.1. This value is $\text{pH}(\text{S})$. Then dilute the same buffer with CO_2 -free water to double the volume. The observed deviation ΔpH , which exceeds the dilution effect $\Delta\text{pH}_{1/2}$ given in table B.1, is the liquid junction error ΔpH_j (double calibration):

$$\Delta\text{pH}_j = \Delta\text{pH} - \Delta\text{pH}_{1/2}$$

where

$\Delta\text{pH}_{1/2}$ is the pH of the diluted standard solution.

Stir the solution gently and, while still stirring, note the new stable pH_s . The shift on stirring, ΔpH_s , is calculated as follows:

$$\Delta\text{pH}_s = \text{pH}_s - \text{pH}(\text{S}) - \Delta\text{pH}_j$$

where $\text{pH}(\text{S})$ is the pH of the primary standard solution.

If the signal fluctuates, estimate the difference, ΔpH_n , between the maximum and minimum readings. Use the list in table 1 for assessing the performance of the electrode.

Table 1

Performance characteristic	Good range	Acceptable range
Liquid junction error ΔpH_j	$\leq 0,03$	$\leq 0,05$
Shift on stirring ΔpH_s	$\leq 0,005$	$\leq 0,02$
Noise ΔpH_n	$\leq 0,005$	$\leq 0,02$

9.2 Maintenance of the electrodes

After an extensive series of measurements, it is necessary to clean the electrode system (measuring cell) when the pH of a standard solution requires a longer equilibrium period. Clean the electrodes regularly (daily or weekly) by wiping carefully with cellulose tissues, or, if the samples contained organic impurities, with ethanol (70 %), acetone or warm detergent solution. Remove calcite with dilute hydrochloric acid. Use organic solvents for a short time only, because they decrease the sensitivity of glass electrodes by dehydrating the leached layer of the glass membrane. If organic solvents are used, the electrode shall be recharged by standing in water for several hours. Recalibration is essential.

Observe the manufacturer's instructions regarding storage and maintenance. Reference electrodes and combined electrodes should be stored in the solutions which are also used as the reference electrolyte. Glass electrodes should be stored in water.

Electrodes used for low conductivity water shall not be used for other samples, e.g. sewage.

10 Expression of results

Report the pH to two decimal figures.

Report the temperature at which the measurement is carried out to the nearest degree.

EXAMPLES

pH 8,45, measured at 10,2 °C.

pH 7,62, measured at 16,4 °C in the laboratory 2 h after sampling.

11 Standard deviation

The standard deviation of the repeatability obtained from 10 replicate measurements with drinking water, performed in two laboratories, is $\Delta\text{pH} = 0,01$.

Systematic deviations up to $\Delta\text{pH} = 0,05$ may be caused by unavoidable interferences, e.g. in low conductivity water.

A collaborative test with synthetic samples of low conductivity (C) shows that a standard deviation of $\Delta\text{pH} = 0,05$ or less is achievable. The laboratories met the target of $\Delta\text{pH} = 0,2$ total error.

NOTE 9 The relative error is: $\pm \Delta C/C = 10^{\mp \Delta\text{pH}} - 1$. A deviation of $\Delta\text{pH} = 0,05$ means a factor of 1,12 and an error of 12 % in estimating the hydrogen ion activity.

12 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- precise identification of the sample, source locality, time, sampling procedure and time elapsed between sampling and measurement;
- expression of the results according to clause 10;
- any deviation from this method and a description of any circumstances which may have influenced the results;
- in addition, for rainwater: duration of sample collection.

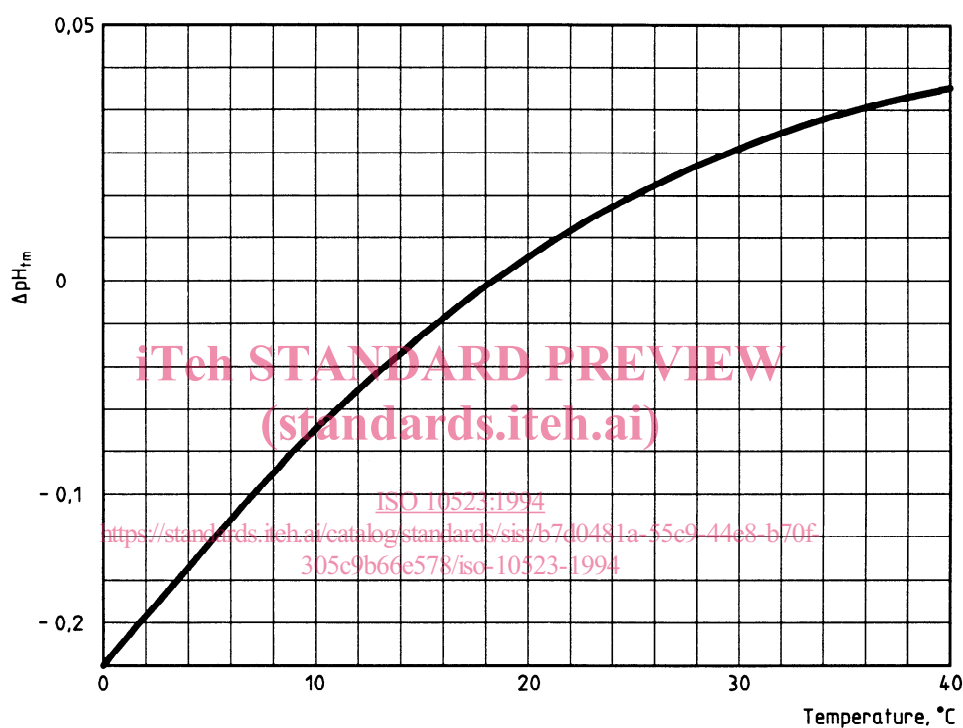


Figure 1 — Graphic temperature correction