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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.

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.

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 $I = 0,3$ mol/kg (conductivity: $\gamma_{25\ °\mathrm{C}} < 2\ 000$ mS/m) solvent and in the temperature range 0 °C to 50 °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_H) multiplied by −1

$$\mathrm{pH} = -\mathrm{lg}\, a_\mathrm{H} = -\mathrm{lg}\left(m_\mathrm{H}\ \gamma_\mathrm{H} / m^\circ\right) \qquad (1)$$

where

a_H is the relative (molality basis) activity of the hydrogen ions;

γ_H is the molal activity coefficient of hydrogen ions at m_H;

m_H is the molality, in moles per kilogram, of the hydrogen ions;

$m°$ 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, $c(KNO_3)$ = 0,1 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, $c(\mathrm{KCl}) = 3$ 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:

a) zero point of the pH electrode (or offset voltage);

b) slope of the pH electrode;

c) temperature of the pH electrode;

d) 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.

The resolution of the pH value reading on the pH meter shall be 0,01 or better.

Whether the pH meter is provided with a manual or an automatic routine calibration is not a limiting characteristic within the scope of this International Standard.

NOTE The temperature compensation carried out by commercially available pH meters is based on the Nernst equation; i.e. it is dependent on temperature, and the corresponding theoretical slope of the electrodes is taken into account in the indication of the pH value. This does not, however, compensate for the temperature dependence on the pH value of the measuring solution.

7.4 Glass electrode and reference electrode. The chain zero-point of glass electrodes should not deviate by more than Δ pH = 0,5 (manufacturer's declared value) from the nominal pH electrode value. The value of the practical slope shall be at least 95 % of the theoretical slope.

Use electrodes with electrolyte solutions and a flow rate of 0,1 ml/day to 2 ml/day as reference electrodes.

For reference electrodes with an electrolyte solution, ensure that an excess hydrostatic pressure is generated by setting the filling level of the electrolyte in the reference electrode to be higher than that of the buffer solution or the measuring solution, as appropriate. It is also possible to use pressurized reference electrodes.

In limited applications, reference electrodes with a solidified electrolyte (electrolyte gel or a polymerizate of an electrolyte) may also be used.

Store the electrodes according to the manufacturer's instructions.

For samples with low conductivity, electrodes with high electrolyte discharge should be used. If the conductivity is $>$ 30 mS/m, it is also possible to use an electrolyte gel or polymerizate in the reference electrodes. In general, ensure that for electrolyte gels or polymerizates, the exchange within the diaphragm is not be caused by the discharge of the electrolyte, but by diffusion of the ions involved.

7.5 Stirrer or **agitator**, operating with a minimum exchange of gas between the test portion and air.

8 Sampling

The pH value may change rapidly as a result of chemical, physical or biological processes in the water sample. For this reason, whenever applicable, it is advisable to measure the pH value immediately at the sampling point.

If this is not possible, take a water sample in a sampling bottle (7.1).

When filling the sampling bottle, avoid gas exchange, e.g. release of carbon dioxide, between the sample and the ambient air.

Fill the bottle completely and stopper it, bubble-free, e.g. with a solid stopper.

Samples should be kept cool (2 °C to 8 °C) and in the dark during transport and storage (ISO 5667-3).

The sampling bottle is preferably filled by flushing to overflowing from a water sampler via a flexible tube extending to the bottom of the bottle.

In the laboratory, measure the pH value as soon as possible. When the samples are measured in the laboratory, check possible influences of transport and storage on the pH value of the samples to be analysed.

Pay special attention to sampling strategies for certain types of water matrices (see ISO 5667-3).

Usually, sampling and transport are the major factors of uncertainty when measuring the pH value in the laboratory. Therefore, the results of on-site measurements often show lower measurement uncertainty.

9 Procedure

9.1 Preparation

Follow the manufacturer's instructions when operating the pH electrode. Ensure the functionality of the pH electrode by periodic maintenance and testing (9.2).

Prepare the calibration buffer solutions. For devices with automatic buffer identification, follow the manufacturer's calibration instructions.

Choose the buffer solutions so that the expected measurement of the sample lies between the values of the two buffers.

When using a pH electrode without an internal temperature sensor, immerse a temperature sensor in the test solution.

For measurement, prepare the glass and either the reference electrode or the mono-rod pH electrode, following the manufacturer's instructions.

Turn on the measuring device; for devices with automatic buffer identification, activate the stored data of the buffer solutions prepared for calibration.

Measure the temperature of the buffer and of the sample solutions.

If possible, buffer and sample should have the same temperature.

If there is no temperature sensor, adjust the device to the measuring temperature.

Take the pH values of the buffer solutions from the respective certificates, depending on the existing temperature (for examples of buffers, see Annex A) or use automatic buffer recognition.

9.2 Calibration and adjustment of the measuring equipment

Calibrate the pH electrode at two points using buffer solutions of the expected range of pH values (two-point calibration), following the manufacturer's instructions. Afterwards, adjust the devices manually, based on the data determined. For automatic measuring devices, ensure that the prepared buffer solutions correspond to the data of the buffer solutions stored in the software of the measuring device.

Immerse the pH electrode and the temperature sensor in the first buffer, usually the one at pH 7, which is used for adjusting the zero point. Subsequently stir to avoid the enrichment of potassium chloride caused by leaking reference electrolytes near the glass electrode.

Turn off the stirrer and start the calibration procedure on the measuring device.

Automatic devices independently identify the stability of the measurement, store this value and adjust the zero point.

When using devices with manual adjustment, initially adjust the zero point at pH 7, unless otherwise specified in the manufacturer's instructions.

Thoroughly rinse the pH electrode and the temperature sensor before, between, and after the measurements using water (6.1).

Immerse the pH electrode in the second buffer solution and stir. Turn off the stirrer and start the calibration procedure for the second buffer on the measuring device. Automatic devices independently identify the stability of the measurement, store this value, and adjust the slope. For devices with manual adjustment, adjust the slope so that the pH value of the second buffer is reached.

Check the result of the adjustment of the pH electrode on two new samples of the buffer solutions used.

The calibration should be checked by measuring an independent calibration checking solution buffer instead of the buffer solutions used.

The measurements shall not deviate by more than 0,03 from the relevant set point. Otherwise, repeat the procedure, and replace the pH electrode if necessary.

As a result of the calibration, record the zero point and the slope of the pH electrode together with the measuring temperature.

If information is required either on the condition of the pH electrode for a broad pH range or on the quality of the buffer solutions, calibrate the pH electrode at more than two points, usually at five points (multi-point calibration, see Reference [8]).

9.3 Measurement of the samples

Whenever possible, measure the samples under the same conditions as during calibration. Preferably, determine the pH value in the sampling bottle (7.1).

When changing solutions, rinse the pH electrode and the measuring vessel with distilled or deionized water (6.1) and then, if possible, with the next solution to be measured.

Repeat the procedure with other subsamples, if appropriate.

The special features of pH measurements as operative measurements in flow systems, of measurements of waters with low ionic strength, of on-site measurements and of measurements of waters under increased pressure (sea water; surface water and industrial water) are described in Annexes B, C, and D.

The mass concentrations of solids in liquid sludge should be < 5 %.

10 Expression of results

In general, the value for the quantity pH is expressed to one decimal place. Only if the composition of the unknown solution is similar to the composition of the buffer solutions and the quality of calibration justifies it, is it reasonable to report a second decimal place. If the second decimal place is required although the conditions mentioned are not met, the reasons for taking this decision should be stated in the test report.

Report also the measuring temperature.

EXAMPLE pH value 9,8

Measuring temperature $\theta = 16,4$ °C

11 Test report

The test report shall contain at least the following information:

a) all the information required for the complete identification of the sample;

b) the sampling method used (see Clause 8);

c) the test method used, together with reference to this International Standard;

d) all operating details not specified in this International Standard, or regarded as optional, together with details of any incident that may have influenced the result(s);

e) the measuring conditions;

f) the test result(s) (see Clause 10) obtained.

Annex A
(informative)

pH values of primary standard reference solutions

A.1 Temperature dependence of the pH values of the primary standard reference solutions

Table A.1 — Examples of pH values of primary standard reference solutions in accordance with Reference [5]

Temperature °C	B Saturated potassium hydrogen tartrate	C Potassium hydrogen phthalate 0,05 mol/kg	D Phosphate 0,025 mol/kg	F Borax 0,01 mol/kg	I Sodium carbonate/sodium hydrogen carbonate 0,025 mol/kg
0	— [a]	4,000	6,984	9,464	10,317
5	— [a]	3,998	6,951	9,395	10,245
10	— [a]	3,997	6,923	9,332	10,179
15	— [a]	3,998	6,900	9,276	10,118
20	— [a]	4,000	6,881	9,225	10,062
25	3,557	4,005	6,865	9,180	10,012
30	3,552	4,011	6,853	9,139	9,966
35	3,549	4,018	6,844	9,102	9,926
37	3,548	4,022	6,841	9,088	9,910
40	3,547	4,027	6,838	9,068	9,889
50	3,549	4,050	6,833	9,011	9,828

[a] Cannot be used below 25 °C.

A.2 Extended uncertainties u[pH(S)] of standard reference solutions

In addition to the internationally agreed primary buffer solutions (see DIN 19266[3]) there are secondary, technical and ready-to-use buffer solutions. Table A.2 lists the desired uncertainties for these buffers.

Table A.2 — Extended uncertainties u[pH(S)] of standard reference solutions (Reference [7])

Type of buffer	Desired extended uncertainty k [a] $= 2$
Primary	0,003 to 0,006
Secondary (same composition as primary ones)	0,003 to 0,006
Ready-to-use buffers, technical buffers (if applicable, different composition from primary ones)	$\leqslant$ 0,01

[a] Coverage factor.

Annex B
(informative)

Operative measurements in flow systems

B.1 Direct calibration and adjustment

Measuring chains that can be removed from the process are adjusted in accordance with 9.2.

B.2 Indirect calibration and adjustment of measuring chains

This method can be used if it is impossible or requires great effort to remove the measuring chains from the medium of which the pH value is to be determined. It is necessary to use a second pH meter and a second pH electrode. The uncertainty of this method is correspondingly higher compared to that of direct adjustment.

Demonstrate and document the functionality of the process measuring equipment used by adjusting it in accordance with 9.2 at the time of commissioning.

Take a sample of the process water to be measured, if possible, in the vicinity of the process series of measurements. Record the value measured by the process pH electrode at that moment.

Measure the sample using an adjusted pH meter.

Compare the pH value determined with the one valid at the time of sampling and obtained on the process series of measurements, and balance the two by manually setting the zero point of the pH electrode or the offset voltage (see manufacturer's information concerning the pH meter).

As this is a one point calibration, the practical slope of the process measuring chains is not determined. Therefore, only a limited range of pH values can be measured. Take the change in the slope of the process measuring chains into consideration.

B.3 Measurement

As continuous routine measurement is carried out in a mobile, generally flowing, medium, additional measures concerning the equipment may be necessary. If the measurements are performed under increased pressure and/or in a flowing medium, changes in the boundary layers and in the diffusion processes are possible, accompanied by resulting changes of the potential. Therefore, the measurements are performed under conditions that are as uniform as possible. In this case, the statement of the pH value should necessarily include information concerning the measuring conditions for which the stated value is valid.

Especially for waters with a conductivity of < 10 mS/m, it makes sense to use a measuring chamber, in which the flow rate is preset and can be controlled. Moreover, such flow equipment minimizes the accumulation of particles and contamination and should be easy to clean.

The data are collected by the user of the process as required.

In reference electrodes, an electrolyte gel or polymerizate can also be used if the conductivity is > 30 mS/m. As it diminishes the influence of stirring effects or of the flow, a symmetrical arrangement of the points of electrolyte discharge improves the accuracy of the measurement; this is not, however, imperative.

In general, ensure that for electrolyte gels or polymerizates, the exchange within the diaphragm is not due to the discharge of the electrolyte, but to diffusion of the ions involved. When changing between media of different composition (e.g. continuous measurement of water with a conductivity of < 5 mS/m and buffer solution), additional interfering potentials can be generated. In these cases, it may be preferable to apply indirect adjustment.

To ensure a continuously high electrolyte concentration, it is possible to use reference electrodes with salt reservoirs.

For estimating contributions to the uncertainty, values derived from control cards for the target value, the range or the mean values may be used.

Annex C
(informative)

Field measurement (on-site measurement)

C.1 Calibration and adjustment

Calibrate and adjust the pH electrodes and the pH meters in accordance with 9.2.

C.2 Measurement

Before carrying out measurements on the water sample, clean the pH electrode with deionized or distilled water (6.1).

Whenever possible, insert the electrodes in the water to be determined. Avoid strong water flows, but move the electrodes slowly during the measurement in standing water. Otherwise, transfer a representative sample into the measuring vessel, preferably filled by flushing to overflowing from a water sampler via a flexible tube extending to the bottom of the bottle. Immerse the pH electrode.

When measuring directly in surface water, immerse the pH electrode as deeply as possible below the water surface.

It may be necessary to homogenize prior to immersion of the pH electrode.

Avoid vigorous stirring which could cause the release of gases from the sample or their absorption from the air.

Stop stirring and read the measurement of the sample after the display has stabilized. When using measuring devices with automatic drift control, wait for the displayed value to stabilize. If necessary, repeat the measurement with other identical subsamples. For samples with higher conductivity, the reproducibility of the measurement should be 0,1 of a pH unit or better.

Following the measurement, thoroughly rinse the pH electrode with deionized or distilled water. When measuring samples of waste water or leachates, use at least tap water. For the removal of sedimentations on the glass membrane or on the diaphragm, follow the cleaning instructions of the electrode manufacturer.

For samples with low conductivity, electrodes with high electrolyte discharge should be used (see 7.4).

Annex D
(informative)

Measurements of the pH value in water with low ionic strength

D.1 Calibration and adjustment

Calibrate and adjust the pH electrodes and the pH meters in accordance with 9.2.

If the calibration requires checking with a standard solution of low buffer capacity, dilute either buffer solution C or D (see Table A.1).

D.2 Measurement

Measurements of the pH value in water with low ionic strength (conductivity < 5 mS/m) and low buffering capacity require special measuring conditions.

In samples with low ion content ($< 10^{-3}$ mol/l), the ion content can be raised above 0,01 (10^{-2}) mol/l by adding KCl (1 mol/l).

To measure the pH value, special pH electrodes are necessary. It is useful to apply reference electrodes with diaphragms (e.g. ground diaphragms) ensuring an increased discharge of the electrolyte from the reference electrode.

The distance between the measuring electrode and the reference electrode should be small to minimize the resistance of the measuring solution and, thus, the influence of scattering fields.

If possible, no electrolyte from the reference electrode should reach the measuring electrode. This can be achieved e.g. by a continuous flow of fresh measuring solution through the measuring vessel and by arranging the reference electrode behind the measuring electrode, in the direction of flow.

In samples with low ion content, the response intervals of the pH meter can be significantly longer. Follow the manufacturer's instructions.

Gases affecting the pH value such as carbon dioxide can be released or dissolved in the sample; therefore minimize contact with air.

Annex E
(informative)

Performance data

The statistical data in Table E.1 were obtained by an interlaboratory trial carried out in March 2006.

Table E.1 — Performance data

Sample	Matrix	No. laboratories after outlier rejection	No. analytical results after outlier rejection	No. outliers	Overall mean (without outliers)	Standard deviation of repeatability	Coefficient of variation of repeatability	Standard deviation of reproducibility	Coefficient of variation of reproducibility	pH range [a]
		n_L	n	n_{AP} %	$\bar{x}$	s_r	CV(r) %	s_R	CV(R) %	
1	Drinking water	15	45	16,7	7,97	0,030	0,37	0,076	0,95	7,86 to 8,12
2	Drinking water	17	51	5,6	6,40	0,011	0,18	0,032	0,50	6,35 to 6,46
3	River water	17	51	5,6	7,61	0,038	0,50	0,138	1,8	7,32 to 7,83
4	River water	18	54	0,0	6,36	0,019	0,29	0,053	0,83	6,28 to 6,44
5	Waste water	17	51	5,6	7,92	0,029	0,37	0,085	1,1	7,78 to 8,09
6	Waste water	18	54	0,0	5,45	0,043	0,78	0,181	3,3	5,06 to 5,75

[a] Range from lowest to highest laboratory mean, without outliers.

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