testo

Field Manual

Guide to pH Measurement Engineering

pH

°C

2nd Edition

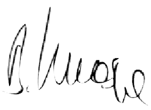
Foreword

This “Guide to pH Measurement Engineering” was written in response to requests by several of our customers.

Testo has organised the Guide to provide the committed beginner with an overview of the full spectrum of pH measurement, whilst for experienced pH professionals the Guide remains a valuable reference work, full of handy tips - from the field, for the field.

We would be grateful for any suggestions, which we will be glad to work into a new edition. Please do not hesitate to write to us.

Management Board:



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1. General

1.1 What is the pH value?

1.1.1 Introduction

In addition to temperature, the pH value is one of the most important parameters in the chemical, pharmaceuticals and environmental engineering sectors. The pH value has an important indicator function in many chemical and biochemical reactions. Due to advances in measurement engineering, new probe technology and a more compact design, pH measurement has gone from being a complicated procedure for specialists to being a standard measurement in daily working life.

– Example: Food

The pH value of raw materials and foodstuffs is of major significance for the quality of the finished product. This applies to meat deliveries as well as to the maturing of meat and sausage meat and to the pickles, fruit juice or delicatessen sector.

– Example: Electroplating/Hardening

Setting the correct pH value in galvanic baths is critical to the quality of the final metal coating. Also, when cleaning the contamination from electroplating and hardening plants, optimal efficiency is usually achieved within a very narrow pH range.

– Example: Environmental protection (drinking water and waste water)

The pH value has long been an indispensable guiding parameter in environmental protection. When monitoring the quality of surface water, ground water, rainwater and waste water, the pH value indicates the aggressivity and therefore, for example, the biological compatibility of the water.

– Example: fishing waters

The pH value indicates, for example, whether a watercourse is suitable for fish. This indication can be represented in the ammonium/ammoniac balance, which is heavily dependent on pH.

Ammoniac (NH3) is highly toxic to fish. By contrast, ammonium (NH4+) is relatively harmless. At pH 6, practically only ammonium is present with no hazardous ammoniac, whilst at pH 9, the ammoniac concentration is already 25%.

1.1.2 Definition of the pH value

pH is the abbreviation for the Latin expression "pondus hydrogenii" (pondus = pressure, hydrogenium = hydrogen). It is a measure of the concentration of hydrogen ions in a medium. This concentration is directly related to the medium's acidic, neutral or basic character.

Table (1) shows that with an increasing concentration of hydrogen ions (rising up the scale), the pH value falls and therefore the medium becomes more acidic.

Range	pH	H+ concentration (mol/l)	
	0	10^{-0}	1
	1	10^{-1}	0.1
	2	10^{-2}	0.01
acidic	3	10^{-3}	0.001
	4	10^{-4}	0.0001
	5	10^{-5}	0.00001
	6	10^{-6}	0.000001
neutral	7	10^{-7}	0.0000001
	8	10^{-8}	0.00000001
	9	10^{-9}	0.000000001
	10	10^{-10}	0.0000000001
alkaline	11	10^{-11}	0.00000000001
	12	10^{-12}	0.000000000001
	13	10^{-13}	0.0000000000001
	14	10^{-14}	0.00000000000001

Table 1: pH scale

To make the variable of "concentration" easier to handle, Sørensen in 1909 proposed the introduction of a "hydrogen exponent" as the logarithm, to the base 10, of the reciprocal of the hydrogen ion concentration (i.e. the negative logarithm of the hydrogen ion concentration) [1]:

$$pH = -\log c\,H^{+} . \qquad (1) \qquad c = \text{concentration}$$

The negative exponent in Table 1 therefore corresponds to the pH value.

Example: *H^{+} concentration = 10^{-4} mol/l -> pH value = 4*

The (practical) pH scale is today determined by a series of standardised buffer solutions [1-4]. Buffer solutions are solutions with a precisely defined pH value, which can theoretically be calculated from the composition of the solution.

In highly concentrated acids or lyes, it is quite possible to find pH values below 0 and above 14. In other words, the H^+ concentrations in these cases are greater than 1 mol/l (pH <0) or less than 10^{-14} mol/l (pH value >14).

Figure (1) shows various examples of the pH values of common everyday substances.

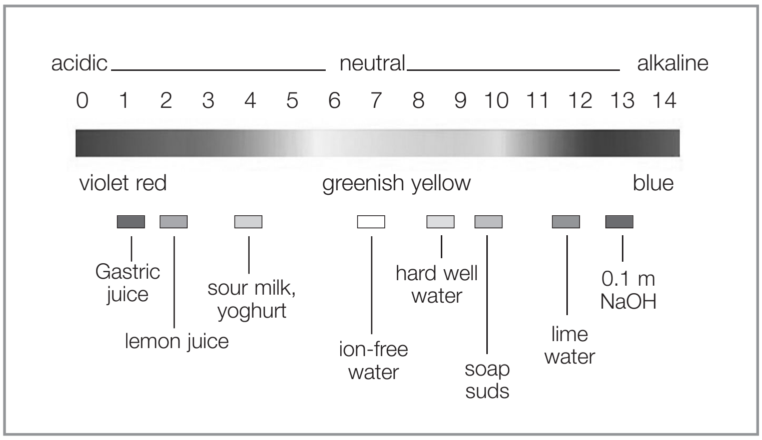

Figure 1: pH scale with typical examples

1.2 Methods of determining pH

1.2.1 Estimating pH

The oldest method of determining acidity is the sense of taste. When taste samples are taken of substances of different pH, the nerve endings in the mouth experience different stimuli that we describe as "acidic" or "soapy". However, this method of determining acidity is very imprecise and, more seriously, involves considerable dangers to health: imagine, for example, having to identify hydrochloric acid by taste. Other methods have therefore been developed to determine pH precisely and safely.

In colour indicators (pH strips), use is made of the fact that several chemical reactions are influenced by pH [1]. The special compounds in these indicators are able to release or absorb hydrogen ions - protons - and therefore change colour. The intensity and type of colour change can be determined, for example, with a comparative scale. The colour change defines the pH of the measured medium. Although this method is an easy way to measure pH, it can only provide a rough approximation of the actual pH of the medium. Accuracy is limited to a few tenths of a pH unit. Measurements must generally be carried out at room temperature, with a general conductivity greater than about 100 µS/cm.

Photometers also operate on the principle of recognising a colour change. They convert current intensity into pH on the basis of a calibration from a previous series of standard measurements. Solutions of known pH (-> buffer solutions) serve as reference. As with pH paper, the achievable accuracy is not very high, and the measuring range is very limited. Scientists have therefore progressed to potentiometric pH measurement.

1.2.2 Potentiometric measurement (for example Testo pH electrodes)

Measurement by pH glass electrode is at present the most widely used method of determining pH. The glass electrode transmits a voltage which is proportional to the pH value. Since the electrode can only transmit a very low voltage (the expert calls it a very high electrical inner resistance) reference is made to a potentiometric measurement with an electrochemical sensor.

Electrochemical sensors transmit a voltage that varies directly with the concentration of hydgrogen ions in the medium. Depending on the sensor type and the quality of calibration, accuracy levels better than ± 0.03 units can be attained.

The pH glass electrode has a broad measuring range and is highly precise and easy to use. It is also extremely versatile. Other electrodes include the hydrogen, quinhydrone, antimony and bismuth electrodes. pH sensors using semiconductor technology (ISFETs) also exist [5], but the signals from these sensors cannot be analysed by standard pH meters.

2. pH measurement engineering in detail

2.1 Measuring system configuration

Different types of pH meters can be used, depending on the job. In the mobile sector, there is a choice between compact pocket meters (for example testo 206) in which the probe and measurement electronics are combined in one housing (Figure 2) and instruments with replaceable pH probes such as testo 230 and testo 206 pH-3.

Figure 2: Compact pocket meters to measure the pH value and temperature (testo 206-pH1, testo 206-pH2).

In the case of compact pocket meters, the probe is permanently attached to the instrument making a cable connection between probe and instrument unnecessary. These instruments are usually used for measurements which are repeated over and over again and for measurements where it is important that the instrument can be easily transported. As an alternative, there are measurement systems in which the measurement instrument and probes are separated.

Figure 3: Example of a pH measurement system with separate measurement probes (testo 230 with pH probe and stainless steel temperature probe and testo 206-pH3).

Instruments with replaceable probes have the advantage that the probes can be adapted to a wide range of applications. These instruments are used mostly in laboratories and for changing measurement tasks in production, environmental sector etc.

2.2 pH electrode

Measuring pH means converting the concentration of hydrogen ions to an electric voltage. In order to do this, experiments with polished platinum sheets and an electrolytic bridge (saline solution) had already been carried out in the 19th century. Since the electrolyte is used up and the readings have to refer to a reference to achieve stable results, the two electrode system was introduced.

pH measurement engineering in detail

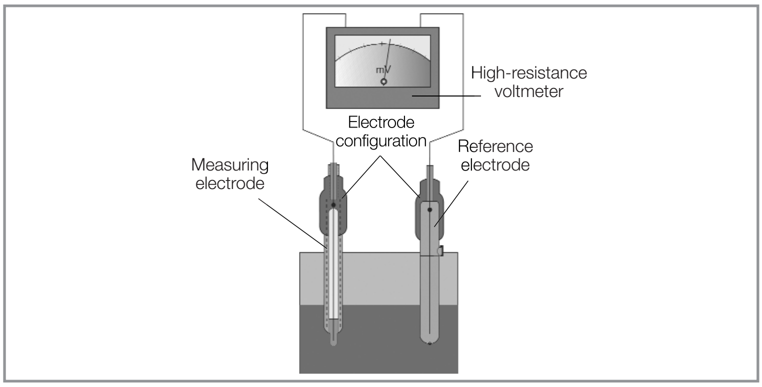

Figure 4: pH measurement system consisting of measurement electrode and reference electrode.

The reference electrode transmits voltage which is proportional to the pH value. The reference electrode shows the system's voltage reference. The pH value is the differential voltage between the measurement electrode and the reference electrode.

Thanks to technical progress, it is now easier to handle two probes (laboratory application) by integrating both measurement chains in one single electrode known as the combined electrode. Nowadays, only pH combined electrodes are used.

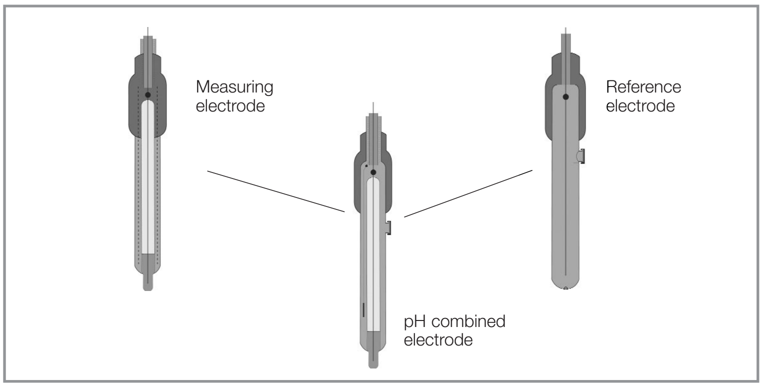

Figure 5: A pH combined electrode consists of a pH measuring electrode and a reference electrode

An electric voltage can be measured between two measuring points. Each measuring point in this case has a particular electric potential. The measured voltage therefore corresponds to the potential difference between the two potentials.

pH measurement by measuring electrode and reference electrode can be understood in exactly the same way. A potential is generated at the measuring electrode as a function of the hydrogen ion concentration (pH value) in the measured medium. The reference electrode must have a known potential.

Summary: the output voltage of a combined electrode measured by the pH measuring unit therefore results from the potential difference between the measuring electrode and the reference electrode.

2.2.1 Measuring electrode

Of all possible sensors (cf. Chapter 1.2.3), the glass electrode (Figure 6) has by far the best technical measurement properties. In addition to ease of use, it offers maximum accuracy. It is also universally applicable and is highly resistant to influencing factors in the solutions, such as colour, viscosity and chemical composition.

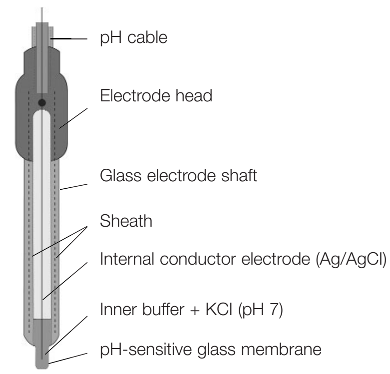

Figure 6: Construction of a measurement electrode

The core of this measuring electrode is a very thin glass membrane (pH membrane) made of special pH-selective glass. This glass has the ability to react with moisture or water, so that a very thin, invisible watery “swell layer” is formed on the surface of the glass. This gelling or swelling layer acts as a selective barrier, which practically only exchanges H+ ions with the solution being measured. The exchange of other ions is blocked.

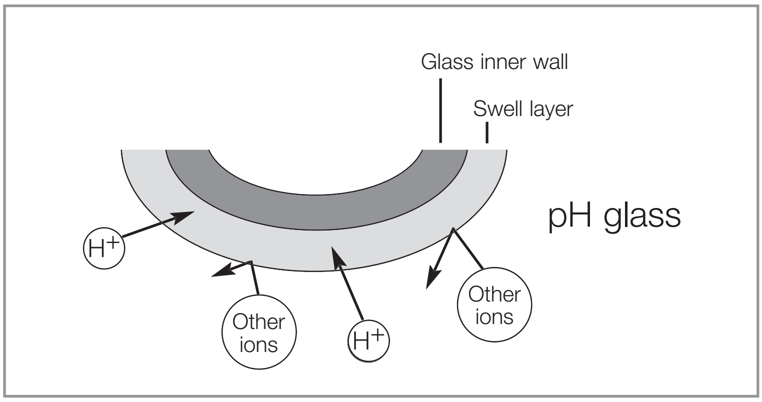

Figure 7: Schematic construction of a pH membrane

Example: During measurement in an acid sample with several H^+ ions, positively charged particles diffuse into the swell layer. The electric charge - i.e. potential - of the pH membrane increases. The pH membrane delivers a positive voltage. This voltage is analysed by the pH meter and is displayed as a pH value.

2.2.2 Reference electrode

The reference electrode is the second electrode needed. Its potential is not affected by the measurement solution. Since earth potential is not constant enough, the task of the reference electrode is to supply a constant reference potential.

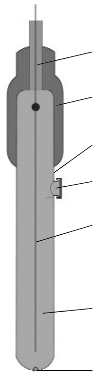

Figure 8: Construction of a reference electrode

Each reference electrode consists of a reference element in a defined electrolyte solution. This electrolyte must be in contact with the measured medium. In the case of standard commercially available reference electrodes, this connection is made by means of a "diaphragm". This configuration guarantees the flow of electric current.

The potential of the reference system is defined by the reference electrolyte and the reference element. Usually, a 3 molar potassium chloride solution (KCl) is used as reference electrolyte. In this case, the reference element will usually consist of chlorinated silver wire. For electrochemical balance, silver chloride (AgCl) must also be dissolved in the reference electrolyte.

Since, in several measuring solutions, the AgCl can lead to clogging of the (ceramic) diaphragm, more modern pH electrodes have been supplied with a "cartridge" in the reference system to retain the AgCl. In this case, the top-up reference electrolyte must be free of AgCl.

There are several types of diaphragm, such as a piece of wood, a porous ceramic pin, a small hole, ground glass, a gap or a bundle of fibres, to name but a few examples (see Chapter 3.2.3).

The type used depends on the required measurement conditions and also often on the in-house philosophy of the electrode manufacturer. The widely used ceramic diaphragm can cause problems in critical measuring media due its porous, sponge-like structure. It is liable to clogging, with the result that the measured value can become unstable. Consequently, for special requirements in ultra-pure water, pH electrodes with ground-glass diaphragms are used.

However, for most measuring requirements, the “user-friendly” ceramic diaphragm is used for everyday applications while a particle-resistant hole diaphragm is used for electrolyes with gel electrolyte.

Testo electrode type	Diaphragm type	Application
Type 01, 02, 04	Ceramic	Samples with low particle levels, when using AgCl-saturated reference electrolytes, not in samples containing S_2, Br, J in standard electrodes
Type 05	Pore/ capillary	Samples with very high particle levels, sewage, emulsions, suspensions, waters with low ion concentration, concentrates
Type 03	Hole	In combination with solid electrolytes in penetration electrodes, for measurements in solids such as meat, cheese and pastes
Special electrode	Ground glass	Water with low ion concentration, depending on the type of reference electrode in partially aqueous/non-acqueous solutions, sewage, emulsions, concentrates, precision meas.
–	Wooden pin	Specially for sewage
–	Fibre bundle	Similar to ceramic diaphragm
–	Metal wires	Not in strong oxidising and reducing solutions

Table 2: Diaphragm types and corresponding applications

2.2.3 Combined electrode

Separate measuring and reference electrodes only make sense if they have widely differing life spans. In practice, the combined electrode has now largely taken the place of separate electrodes, because it is easier to use than the separate configuration.

In a combined electrode, the measuring electrode and reference electrode are combined in a single unit (Figure 9).

In conjunction with an additional built-in temperature sensor, only a single measuring sensor is therefore now needed for pH measurement.

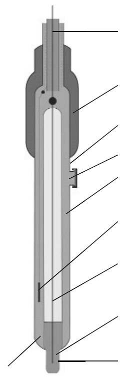

Figure 9: Construction of a combined electrode

The reference electrode 3 molar potassium chloride solution (KCl) is available in liquid form in this electrode design. This liquid can be refilled through the refill opening. These types of probes have a long service life with the disadvantage that the reference electrolyte solution has to be refilled on a regular basis. If this reference electrolyte is replaced by a gel, it is then referred to as a gel electrolyte.

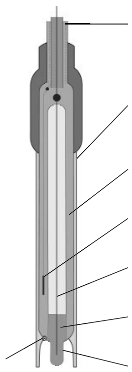

Figure 10: Construction of a combined electrolyte with gel electrolyte

2.2.4 Testo pH electrodes with polymer electrolyte

Patented Testo pH electrodes have combined electrodes with integrated temperature probe. In this way, simultaneous temperature measurement as well as determination of the pH value is possible when penetration electrodes are used. A polymer gel is used as the electrolyte. Due to the large space inside (filling volume), the electrode has a longer service life than other comparable electrodes. The problem of glass breaking, particularly in food applications, was counteracted by almost completely surrounding the measurement glass electrode with a plastic casing. Only the probe tip juts several millimetres out of the plastic casing so that the swell layer has contact with the object being measured. By positioning the small glass pipe in a certain way, a certain level of flexibility is achieved when placed on hard materials resulting in a longer service life even if used for tough applications.

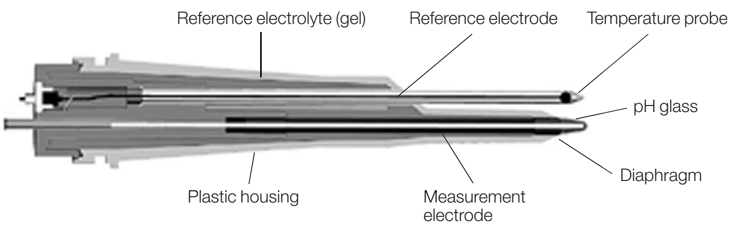

Figure 11: Cross-section through the patented Testo gel electrode.

One other asset of these electrodes is the special diaphragm. A small connection hole between the electrolyte and the measurement medium is sufficient on account of the gel character of the reference (not liquid). The **hole diaphragm** has two small holes in the Testo probes which make it possible to exchange electrons. The main advantage of the hole diaphragm is that almost no blockage occurs. This is of particular significance for fatty solutions, and for the food and sewage sectors.

2.3 Preparation and backgrounds of a measurement

2.3.1 Calibration

At this point, three terms should be differentiated. In metrology, the distinction is drawn between:

- **Calibration**
- **Adjustment**
- **Inspection.**

"Calibration" means the process of observing and documenting any deviation. The measured value is compared to a set value, and the deviation is noted. However, the instrument continues to display the "incorrect" value, although its deviation from the set value is now known.

"Adjustment" is the process of setting the measuring instrument to the deviation observed on calibration. The instrument now displays the "correct" value.

"Inspection" is the official verification conducted by the relevant national or regional Calibration Authority to make sure that the instruments remain within the limits of error laid down in legal metrology.

Strictly speaking, therefore, the term "calibration" does not include the process of setting (adjusting) the instrument. However, the combination of calibration and adjustment under the single term "calibration" has become part of everyday language, and so in this document we will use the word "calibration" to cover both the calibration and adjusting processes.

Why is calibration necessary?

The internal construction of a pH electrode is designed to make the electrode deliver an electric voltage of 0 mV at pH 7.00. This point is described as the zero point of a combined electrode. However, in practice, the real zero point of a combined electrode deviates from this ideal zero. The electrode therefore delivers a voltage that deviates slightly from 0 mV at pH 7.0 (e.g. +5 mV).

The reasons for this deviation are e.g. different production batches and the ageing of the pH electrode. Consequently, during calibration, a "zero offset" is performed to correct the zero point. The zero point voltage (neutral voltage) of a pH electrode is often also termed its asymmetry potential, although this term is not quite electrochemically correct.

However, another aspect has to be considered. As described in section 2.2, a pH electrodes delivers a voltage in mV. At 25°C, this pH-dependent voltage is about 59 mV/pH (millivolts per pH unit). So, for example, if the pH of a measured substance is changed from pH 4.00 to pH 5.00, the voltage delivered by the electrode will also change by about 59 mV. This relationship is described by the Nernst equation [1].

The amount of voltage change when the pH changes by one unit is expressed as the slope of the pH electrode. This slope also depends on the condition of the pH electrode (age, stress etc.).

Since its zero point and slope can be altered by external measuring conditions and by the natural ageing process, a pH electrode must be regularly calibrated.

Summary: During calibration, the neutral voltage and the slope of a pH electrode are determined and stored in the measuring unit. Only after calibration can each measured voltage be accurately assigned to a pH value.

Why is calibration necessary?

The following description is based on modern microprocessor-controlled pH meters. With these measuring units, unlike pH meters with rotary potentiometers etc., the sequence of buffer solutions used is of no importance.

The calibration process, as described above, should define the function between the voltage output of the electrode and the corresponding pH value. In a 2-point calibration, a linear relationship is assumed between the voltage and pH value. The voltage/pH relation is therefore represented as a straight line.

To determine the zero point and slope of the electrode, it is necessary to measure the electrode voltage at two measuring points, i.e. at 2 known pH values - hence the term "2-point calibration".

To define the line equation, the value pairs (pH_1/mV_1) and (pH_2/mV_2) are required. The two values pH_1 and pH_2 are defined by using buffer solutions of known pH, such as pH 4.00 and pH 7.00. By dipping the pH electrode into the two buffer solutions, the measuring unit successively measures the corresponding voltage U_1 and U_2.

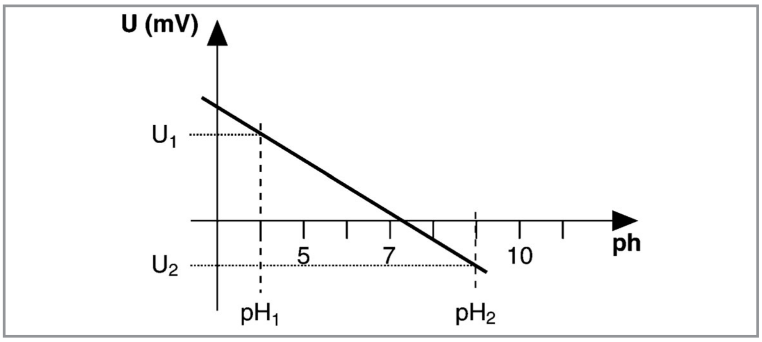

Figure 12: 2-point calibration of a pH electrode

The measuring unit calculates the associated calibration curve from the two value pairs (pH_1/U_1) and (pH_2/U_2). By this method, both the zero offset (Figure 13) and electrode slope S (Figure 14) can be defined.

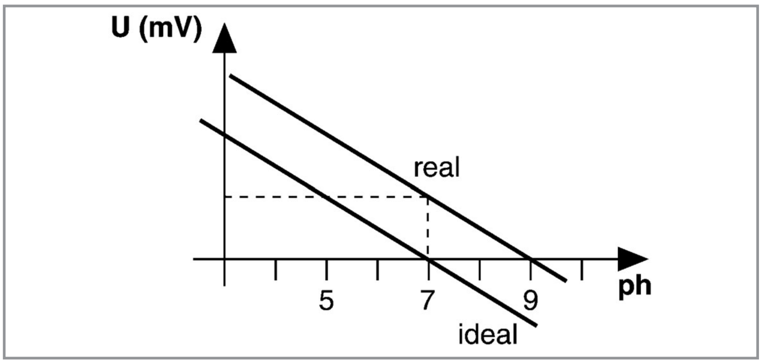

Figure 13: Determination of the zero offset of a pH electrode

Temperature also has an essential influence on the pH value. pH varies with temperature (see Chapter 2.3.3), because the activity of the ions and extent of dissociation (dissociation constant) of the ingredients of an aqueous liquid vary with temperature. This fact naturally also applies to the pH buffer solutions used in calibration.

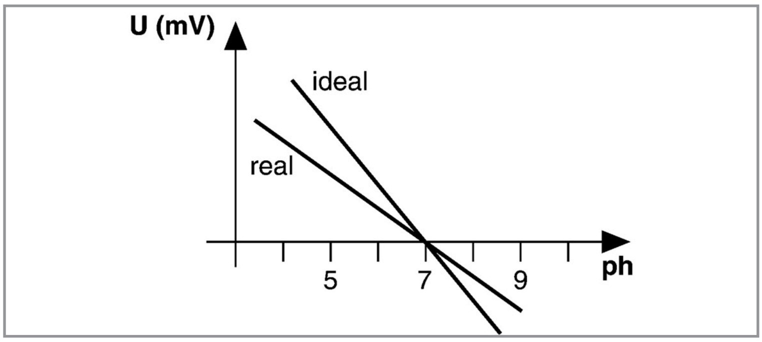

Figure 14: Determination of the slope S of a pH electrode

It is therefore essential that the precise temperature response of the pH buffers used must be known and stored in the measuring unit. Also, the measuring unit must be informed of the current temperature. This information can be entered either automatically by temperature sensor or manually via the keyboard. With manual input, the temperature must be known or estimated.

When should calibration take place?

Calibration must be repeated as soon as checking with a pH standard shows that the measurement value displayed by the measuring unit no longer coincides with the value printed on the buffer solution. The required accuracy of measurement must be taken into account during calibration.

2.3.2 Buffer solutions

Buffer solutions are required to verify and calibrate a pH measuring system. They are termed pH buffer solutions, because they can maintain the pH value very stable, i.e. they can "buffer" it very efficiently against change.

In general, the following three types of buffer solution are identified:

– DIN buffer solutions according to DIN 19266
– Technical buffer solutions
– Special buffer solutions

DIN buffer solutions conforming to DIN 19266

DIN 19266 recommends standard solutions that are suitable calibration standards for precision measurements [6]. The "standard" buffer solutions were selected by the National Bureau of Standards (NBS, now NIST, USA) because they are easy to manufacture and because of their durability, good buffering characteristics and reproducibility. The specified uncertainty of the pH values of the "standard" buffer solutions is max. 0.005 pH units in the temperature range from 0 °C to 60 °C and max. 0.008 pH units in the range from 60 °C to 95 °C.

The high accuracies achievable also demand careful working procedures during calibration. This requirement applies both to maintenance of the measuring system and to the calibration process itself. Relevant information is provided in Chapter 2.3.1.

Technical buffer solutions

Unlike buffer solutions conforming to DIN 19266, technical buffer solutions, which include Testo buffer solutions, are designed more for daily use. There are a variety of recipes for their production [1].

The accuracy requirements for these buffer solutions are more adapted to everyday use; tolerances normally lie between 0.01 and 0.05 pH units.

Because of their slightly lower accuracy, these buffers can be sold at a cheaper price than DIN 19266 buffers. Moreover, technical buffers often have a higher buffer capacity, i.e. their pH remains stable for longer [1]. To prevent users confusing different buffers, these buffers are often also supplied in different colours.

Another variant of the technical buffers is provided by technical buffer solutions conforming to DIN 19267 [7].

	DIN buffer solutions					Testo buffer solutions		
°C	1.685	4.006	6.865	9.180	2.00	4.00	7.00	10.00
10	1.670	4.000	6.923	9.332	2.00	4.00	7.07	10.18
15	1.672	3.999	6.900	9.276	2.00	4.00	7.04	10.14
20	1.675	4.001	6.881	9.225	2.00	4.00	7.02	10.06
25	1.679	4.006	6.865	9.180	2.00	4.00	7.00	10.00
30	1.683	4.012	6.853	9.139	1.98	4.01	6.99	9.95
35	1.688	4.021	6.844	9.102	1.99	4.02	6.98	9.91
38	1.691	4.027	6.840	9.081				
40	1.694	4.031	6.838	9.068	2.00	4.03	6.97	9.85
45	1.700	4.043	6.834	9.038				
50	1.707	4.057	6.833	9.011	1.99	4.05	6.96	9.78
55	1.715	4.071	6.834	8.985				
60	1.723	4.087	6.836	8.962	1.99	4.08	6.96	9.75

Table 3: Comparison between DIN buffers and Testo buffers

Table 3 shows the temperature responses of different DIN [6] and Testo buffer solutions. It should be noted that a buffer solution only corresponds to its printed label value at a specific temperature. For example, a pH 7.00 buffer only has a pH value of 7.00 at exactly 25 °C. At 15 °C, for example, the same solution has a pH of 7.04.

Special buffer solutions

For special applications, in theory, any solution of known pH at a specific temperature can be used as a calibration solution. In addition, in biology for example, several special buffer solutions are available. The most well-known are the TRIS solutions. Here, it is naturally an advantage if the user has the facility to enter the pH values of these buffers in the measuring unit, since otherwise calibration is impossible.

Other background information and tips for handling pH buffer solutions

Basic buffer solutions are less stable in air than acid buffer solutions, because their pH is lowered by acidic effect of reaction with carbon dioxide. Consequently, the pH buffer bottles must be tightly sealed after use.

Buffer solutions must only be used once. Never pour buffer solution back into the bottle, since otherwise accuracy of measurement will be impaired.

2.3.3 Temperature influence

Temperature is one of the most important parameters that has to be taken into account when measuring pH. All chemical processes are temperature-dependent equilibrium reactions. Therefore, both the pH of the measured solution and the signal response of the pH measuring system are temperature-dependent.

The temperature response of the pH buffer solutions has already been discussed in the previous section. This section deals exclusively with the temperature response of the pH electrode itself.

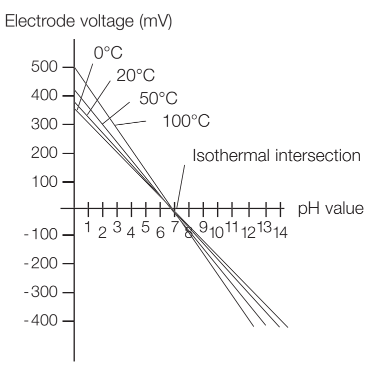

Figure 15: Temperature-dependency of the pH electrode

A combined electrode is characterised by its slope and neutral voltage. Both these variables are therefore determined during calibration and displayed by the pH measuring unit (Chapter 2.3.1).

Whereas the neutral voltage of good electrodes is a constant, the slope of the pH electrode is a function of temperature. For example, whilst the signal of the pH electrode varies by about 59 mV per pH unit at +25 °C, the slope at +10 °C is only about 56 mV/pH, rising to 66 mV/pH at 60 °C. Therefore, the same electrode in a sample with constant pH of 4.0 will emit a voltage of about 168 mV at 10 °C, 177 mV at +25 °C and 198 mV at +60 °C, plus its neutral voltage.

The pH measuring unit takes account of this temperature function: after calibration it always plots the slope of a pH electrode converted to a reference temperature (usually +25 °C).

It should again be noted here that in pH measurement, the temperature response of the electrode and never that of the sample is tested. pH and temperature always constitute a single unit when quoting measurement results. Only pH values obtained at the same temperature can be compared with one another.

Modern pH meters with a 2-line display for simultaneously displaying the two measured variables and pH electrodes with built-in temperature sensor make the user's work much easier.

2.3.4 Testo buffer solutions with calibration reservoir

It is important to clean the probe prior to calibration in order to avoid contamination of the buffer solution. However, small amounts of the substance being measured, small solid particles or similar will always get into the buffer solution. For this reason, calibration should always be carried out in an appropriate container (example beaker glass) and the buffer solution should be poured away once completed. The new Testo pH buffer bottles with calibration reservoir greatly simplify this process while also saving buffer solution. A calibration reservoir is located in the head part of the 250 ml bottles. The reservoir is filled by pressing the bottle. The calibration fluid in the reservoir is poured away once calibration is complete; the remaining fluid remains in the bottle. This ensures that the fresh buffer solution is not contaminated. The Testo pH buffer solutions are available for pH values 4.01; 7.00 and 10.01.

Figure 16: Easy and fast calibration using a calibration reservoir

2.4 Taking a measurement

Before commissioning, the measuring unit and electrodes should first be visually inspected to ensure that they are in perfect condition. If necessary, the measuring system should then be calibrated in accordance with the manufacturer's specifications.

Then proceed as follows:

a. Select the appropriate electrode and measuring unit for the application (see Chapter 4.2).

b. Check the electrode (fluid level, glass breakage. Open the sealing stopper before measuring).

c. Connect the electrode to the pH meter.

d. Rinse the electrode with water and dab dry. Do not rub, because rubbing can generate electric charge on the glass membrane, delaying the display.

e. Dip the electrode in the measuring solution and stir briefly. Then leave it to stand. Make sure that the electrode is immersed so far that at least the diaphragm is covered by the solution. It is possible that a slightly different pH is measured in stirred than in standing solutions. Generally, the "unstirred" pH is more accurate.
In the case of probes with a protective cage, make sure that no air bubbles adhere to the glass membrane or diaphragm.

f. Wait until a stable measured value is attained (e.g. with the aid of an automatic "hold" function) and read off, print, store or transfer the value directly to PC.

g. Rinse the electrode with tap water and store in accordance with the manufacturer's specifications.

h. The temperature of the solution must be logged together with the pH value. This condition applies to all pH measurements and all pH measuring systems.

It is not required to attach an electrode to instruments with permanently attached electrodes.

3. Practical aspects of pH measurement

3.1 Daily handling of the pH electrode

3.1.1 Storage conditions

One important rule applies to storage:

A combined electrode should always be stored in the solution used in the reference system.

The reason for this rule is that the storage and reference solutions will then have the same salt concentrations, whereas they would not if the electrode was stored in distilled water or buffer solution. In the latter case, ions may migrate or water may diffuse from the incorrect storage solution through the diaphragm into the electrode, diluting the reference electrolyte.

As a result, measurement would become very slow and imprecise.

However, in emergencies, storage in buffer solution (if possible pH 4) is preferable to dry storage. Dry storage destroys the swell layer of the glass membrane and also causes the reference system to dry out. After the pH membrane has dried out, the pH electrode must be regenerated for a few hours in distilled water before measuring again. It must then be stored in the appropriate storage solution.

Usually, the reference solution used in pH electrodes is a solution with a very high salt concentration. Since the reference solution and storage solution should be of matching concentratiom the storage solution also has a very high salt concentration. In practice, as a result, salt crystals are often formed.

These crystals can be easily recognised by the formation of a white coating on the electrode shaft and outside on the wash cap. This coating is harmless to the electrode and can be easily rinsed off in water. It therefore does not represent any loss of quality. Standing storage of the electrodes reduces this crystallisation.

3.1.2 Cleaning

Electrodes should always be cleaned:

– before calibration (before dipping in a buffer solution),
– before measurement and
– after measurement.

Cleaning is necessary to ensure that

– the buffer solutions are not contaminated (change in pH)
– the measured substance is not contaminated
– the electrode is fit for the next measurement.

The electrodes should be rinsed with (warm) water. If necessary, allow the water still adhering to the electrode to run off carefully into a soft paper towel.

The possibilities of regenerating the electrodes are described in Chapter 3.2.3.

Rubbing the pH membrane can result in electric charges on the glass membrane, causing considerable delay in displaying the correct measurement value.

When taking measurements in highly viscous or sticky media, the electrode must be cleaned in (warm) water immediately after measuring i.e. before the measured substance dries on the electrode.

For these and other critical measuring media, special electrodes can be used on the basis of manufacturers' recommendations.

3.1.3 Testing

The simplest test of a pH electrode is visual inspection. The following points should be examined:

Test point	Remedy
Is the power plug of the instrument dry?	Dry with a hair drier
Is the electrode cable OK?	Replace (for electrodes (with plug-in head)
Is the plug-in head of the electrode and the cable connection dry?	Dry with a hair drier
Is any mechanical defect visible on the electrode (breakage or crack on the glass membrane)	Replace the electrode
Is the reference electrolyte OK (level, correct electrolyte, colour, etc. ...)?	Top up

Other test possibilities:
One simple and rapid check is to take a measurement in buffer solutions. In this case, after calibration, the instrument must display the value of the buffer solution. The tolerated error naturally depends on the accuracy of the buffer, the electrode used and the procedure adopted for the previous calibration. It should be noted that the pH of the buffer must be read off for the relevant measuring temperature, e.g. pH 7.07 at 10 °C. The same value must also be displayed by the instrument in measuring mode.

A more precise check of the pH electrode is provided by recalibration (zero point and gradient). Here, the manufacturer's specifications must be taken into account, since they also contain the acceptable tolerances. A modern pH measuring unit indicates if a pH electrode is no longer suitable for measurement by issuing an error message. In addition, electrode ageing can be recognised from the calibration data (zero point and slope of the electrode). Please refer to the manufacturer's specifications for precise details.

3.2 Error sources

3.2.1 Chemical factors

Chemical factors are generally considered to be all impurities that affect electrode response (see Figure 17).

One extreme example is pH measurement of hydrofluoric acid. This acid attacks the pH glass very aggressively and can destroy it. One remedy is to use special pH membrane glass.

Especially in weakly buffered waters, care must be taken to define the pH only in a closed, bubble-free vessel (cf. Chapter 3.2.5). Since in general even the transport of a sample leads to a temperature change, measurements should always be taken on-site.

Another source of error, e.g. for samples from groundwater or in the case of raw water samples from the tap, is the CO_2 in the air, since it causes carbonic acid to form in the sample. Within a day, the pH can fall by more than 0.1 pH unit for this reason alone.

3.2.2 Physical influences

The main factors here are mechanical damage to the glass pH membrane (see Figure 17). Today's common pH electrodes with glass membrane are therefore protected by a plastic protective cage, if the design so permits.

In the case of cracking or fissuring of the pH glass, the electrode must be replaced, because otherwise correct measurement is no longer guaranteed.

3.2.3 Electrode ageing and measurement errors

pH electrodes are electrochemical sensors. The “life curve” of an electrode begins in practice with production. From this moment, chemical processes continually take place all over the electrode. For example, the swell layer on the pH membrane is generated and consumed. However, these chemical processes are also one of the reasons why an electrode ages.

The life span of the combined electrode is in general 1-3 years. It is mainly defined by the reference system and by the measuring and storage conditions.

Extreme stresses, such as very high pH values and high temperatures and/or mechanical load, reduce the life span to a few months or even a few weeks or only days. In a strong alkaline environment (pH >13) the pH glass is severely attacked at high temperatures. By contrast, even very strong acids (pH <1) generally do not affect the life span of the pH electrode (cf. Chapter 3.2.4).

Rule of thumb:
A temperature increase of 10°C halves the life span of the pH electrode.

The ageing effect can be kept within reasonable limits by calibration. The electrode must be replaced at the latest when its slope drops below e.g. -52 mV/pH at 25 °C. These specifications are made by all Testo pH meters.

Recognising signs of ageing in the pH electrode:

- Increased electrode response time
- Increased sensitivity to rubbing of the glass membrane (electrostatic effects)
- Increased cross-sensitivity of the electrode, e.g. to sodium ions,
- Reduced slope,
- Change in neutral voltage

Practical aspects of pH measurement

How can a pH membrane be regenerated?

The pH membrane can be partially regenerated by etching with diluted hydrofluoric acid.

Proceed as follows:

– Dip the pH glass membrane for about 1 minute in a solution of sodium fluoride (c = 1 mol/l) and hydrochloric acid (c = 2 mol/l)

– Then dip the electrode for about 1 minute in hydrochloric acid (c = 2 mol/l)

– Finally, rinse the electrode carefully and recondition for 1 day in distilled water. Then store in the storage solution.

This type of regeneration can only be performed a few times.

Warning:
Special precautions must be taken when handling hydrofluoric acid!

Another, milder possibility is regeneration with 4% NaOH and finally with 4% HCl for 5 minutes each. This process is gentler on the membrane and can be repeated several times if necessary.

If these treatments have no effect, the electrode must be replaced.

Measurement distortions are often caused by extraneous influences on the pH or reference system.

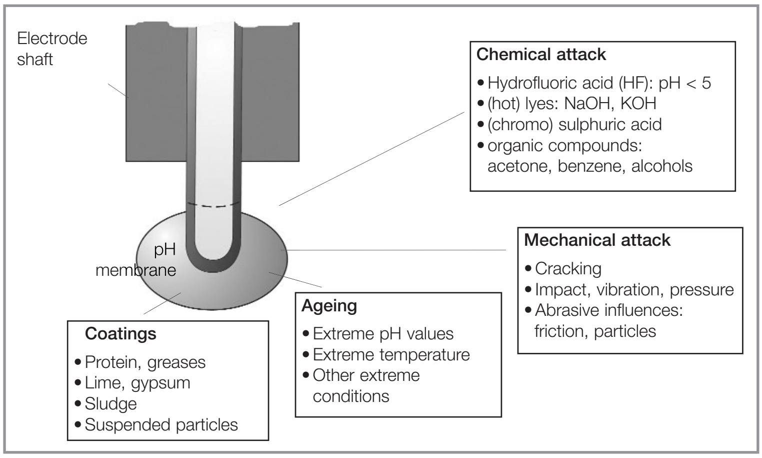

Figure 17: Possible disturbance influences on a pH membrane

Practical aspects of pH measurement

It is a little known fact that almost 80% of all measuring problems can be traced back to the reference system of the pH electrode.

Possible causes of measurement errors relating to the reference system:

- Evaporation of reference solution,
- Penetration of measuring solution,
- Defective or clogged diaphragm,
- Defective or wrong reference electrolyte (for refillable electrodes),
- Incorrect preservation
- Incorrect storage.

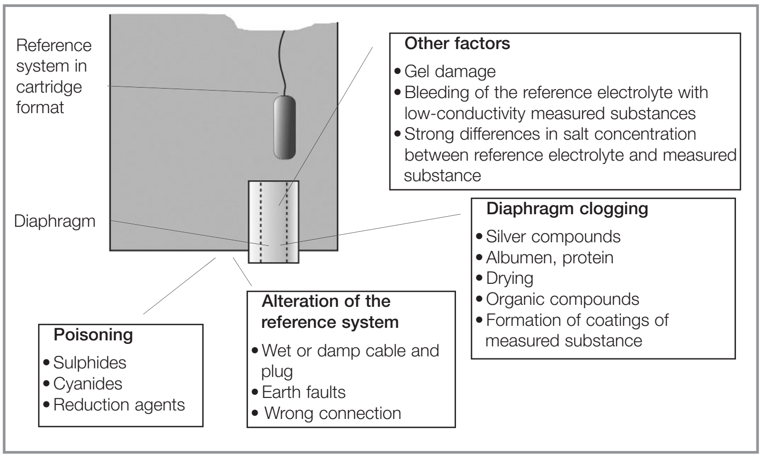

Figure 18: Influences affecting the reference system

A suitable diaphragm and therefore a suitable pH electrode must therefore be very carefully selected (see Chapter 4.2.1).

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Practical aspects of pH measurement

Two examples are given below to illustrate the correct choice of diaphragm.

– Example: Drain water measurement:

In drain water, a conventional ceramic diaphragm becomes very rapidly clogged. This clogging is caused by e.g. silver sulphide, because silver from the reference electrolyte reacts with sulphide from the measured substance. This process can be recognised by a black diaphragm. Incorrect measurements occur due to the lack of electron flow.

The problem can be remedied by using a special diaphragm in combination with a silver-free reference electrolyte. In this case, a large diaphragm with a single large pore ("single pore") will not be blocked up, unlike a diaphragm with very many small pores such as the ceramic diaphragm. Bonding the silver from the reference electrolyte in a reference cartridge also prevents the additional formation of silver sulphide. Here, the Testo electrode Type 05 with single pore diaphragm can be used or testo 206 pH 1 or 206 pH 3 with electrode type 05 can be used.

– Example: Meat measurement

Conventional pH penetration electrodes with ceramic diaphragms clog up very quickly. The spongelike ceramic diaphragm has a large number of small openings that are closed by the protein compounds. A thin, often hardly noticeable film of grease often forms on the diaphragm. This results in very slow response times which in turn lead to almost constant pH value displays.

Using a special hole diaphragm in combination with a gel electrolyte can significantly reduce electrode contamination caused by protein compounds. Faster measurement and a longer lifetime are guaranteed. testo 205 with hole diaphragm or testo 230 with pH probe type 13, which have the same diaphragm design, are recommended for this type of measurement.
Both probes have the advantage of being very robust on account of the low amount of glass.

3.2.4 Acid and alkali errors

Acid and alkali errors are errors that occur at pH values below about 1 or above about 12. These errors can be recognised by the non-linear electrode characteristic in these ranges (Figure 19).

pH values above about 12, especially in standard pH glasses, are indicated as "sodium or alkali errors". Solutions with very high pH values generally also contain a high concentration of alkali ions (Na+, K+, etc.). The sodium error of a pH electrode can in fact be explained by cross-sensitivity of the pH membrane to these ions. In other words, the pH glass is also measuring the concentration (activity) of the alkali ions.

The negative output voltage of the pH electrode in the alkali range is thereby shifted towards the positive direction, and so the pH reading displayed by the pH measuring unit will be too low.

This undesirable effect can be reduced by using special glass membranes. Additional calibration using a pH buffer with a high pH is also recommended. Special electrodes are used in this case.

The same also applies to "acid errors", i.e. measurement errors in highly acidic solutions (pH < approx. 1). However, this effect is not as significant in metrology as the alkali error, and will therefore not be described in detail here [1].

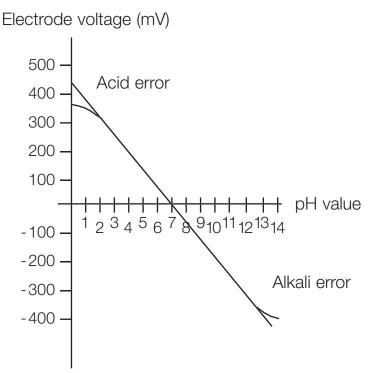

Figure 19: Alkali and acid errors of a pH electrode

3.2.5 Media low in ions

Media are considered low in ions if they have a low salt content (salt concentration) within the mmol/l range (millimoles per litre). The effects of this low salt content are reflected in low conductivity (< 100 µS/cm). Conductivity can be determined with the Testo conductivity meters testo 240 or testo 252. In addition, the low salt content has the effect of increasing the resistance of the diaphragm. This transfer resistance is caused by the fact that the reference electrolyte is considerably diluted by the ion-weak measuring medium in the diaphragm. The release rate of the reference electrolyte is thereby considerably reduced. The pH electrode therefore responds much more slowly to changes in pH.

The resulting errors can amount to a few pH units in extreme cases.

By using special diaphragms (single-pore diaphragm or ground-glass diaphragm), this contact problem can be largely prevented.

The addition of a small quantity of high-purity salt with neutral pH (potassium chloride) to the measuring solution is often recommended as a means of increasing ion strength. This measure reduces the response times of the pH electrode. However, the additive also modifies the balanced concentrations in the measuring solution, and this change also affects the pH value. General rules cannot be given here, and so users will have to decide on a case by case basis.

The most extreme case of an ion-weak medium is without doubt high-purity water. In this case, you should always use only a ground-glass diaphragm and flow-type measuring cells made of ionweak glass. The addition of neutral salt cannot be recommended in this case. Moreover, with pure water, particular care must be taken to ensure good electrical shielding and earthing during measurement (see Chapter 3.2.6).

3.2.6 Overall system

This section will highlight the need to take account of the entire measuring environment or system environment in the actual pH measurement. Most of the sources of error discussed here are caused by the high membrane resistance of the pH electrode.

The combined electrode itself, as described in Chapter 2.2, represents a high-ohmic source of electric voltage. Its pH-dependent output voltages are in the mV range (approximately -400 mV to +400 mV). Standard commercially available pH electrodes have typical membrane resistances of between 5 and 1000 MOhm ($5x10^6$ to $1x10^9$ Ohm).

Also, since the voltage source of the pH electrode can only supply very little current, the measurement input of the pH meter must have a roughly 1000 times greater input resistance in order to ensure clear measurement. This requirement is only met by specially designed measuring instruments (pH meters) with an input resistance of more than 10^{12} Ohm.

A pH measurement must therefore never be taken with a standard voltmeter, since these instruments generally only have an input resistance of up to about 20 MOhm.

These facts also mean that the signals are highly susceptible to electromagnetic interference, due e.g. to solenoid switches close to the system or to static charges on people, e.g. because of plastic floors in buildings (chemistry laboratories).

The connecting cable between the electrode and the meter must therefore be as short as possible and must be shielded. Special cables with additional inner shields and with a protective, electrically conductive outer braid are used for this purpose. Interruption of this shielding at any point between the pH electrode and pH meter results in the familiar "hand-sensitive" effect: the pH display becomes unstable and varies with the movements of the operator.

The maximum permissible cable length is about 5 metres. For longer distances between the pH electrode and the meter, the use of additional amplifiers (impedance transformers) is recommended. These amplifiers are usually screwed directly on to the plug-in heads of the pH electrode. The existing cable can then be simply re-used.

The meters themselves can be protected e.g. by a metal coating on the side of the housing, by careful selection of the electronic components and by special precautions when producing the printed circuit tracks.

In special cases (such as high-purity water or organic solvents) the measuring vessel may itself have to be included in the shielding. In this case, we speak of measurements in a Faraday cage.

The effects of electric or magnetic fields on the measuring system are described under the general term "electromagnetic compatibility" (EMC). German and international draft standards have been drawn up to deal with these effects [9]. The requisite high resistance described above for the measurement may be lost due to leakage currents in the event of moist or even wet connectors or meter sockets.

Consequently, the insides of the connector plugs and/or sockets must always be kept perfectly dry. Any moisture can be removed by careful treatment with hot air (hair dryer). To remove solid deposits (salts, etc.), the plugs and/or sockets must then be carefully rubbed with a soft dry cloth.

Various systems are waterproofed from the electrode to the meter. The specified protection classes (usually IP54, IP65 or IP66) usually only refer to the fully connected state, i.e. with all the components interconnected. Even meters with sockets protected against water ingress must be dried as described above after contact with water.

– Earth loops

In particular in the case of mains-powered measuring systems, care must be taken to avoid earth loops. Earth loops occur when more than one component of the system (measuring solution, measuring vessel, meter, reference electrode, external printer, external recorder, power pack, stand, stirrer, analogue outputs, PC interfaces etc.) are connected to earth simultaneously at two different points. Here, two different points mean, for example, the earth of the mains connection and the generally accidental earth connection of the above components.

The resulting closed circuit (or the current flowing in it) can cause significant measurement distortions, unstable displays and even destruction of the reference system. Since earthing of the system components is often unintended by the measurer and can therefore vary with time, these earth loops are not easy to recognise. The described distortions in the measured values can therefore not always be detected. Only systematic working methods can remedy this problem (see below).

One remedy is methodical earthing of each component at a single point (earth of the mains connection or water pipe). When additional equipment, such as printer or PC interface, is added to the meter, perfect electrical isolation must also be ensured. The appropriate parts are available in the Testo list of accessories.

Assuming careful handling, errors or faults in the meters themselves only occur rarely today. Modern meters run through a self-test of all important components after switching on. Any faults are automatically signalled both during the self-test and during subsequent operation by appropriate error messages from the meter.

4. Example applications and selection criteria

4.1 Example applications

4.1.1 Bakery

Here, pH measurement is e.g. used to control dough rising. High pH values in the mixture result in a loss of volume and unpleasant solidity of the baked products. Biscuits tend to crumble if the pH is too low. A pH of 7 to 8 is considered ideal. pH monitoring can help to produce longer-lasting constant quality.

Recommended: testo 206-pH 2 with penetration electrode for pliable materials or testo 230 with pH electrode type 03.

4.1.2 Meat products

Figure 20: pH measurement in the meat producing industry

The significance of pH for the meat production industry has now become self-evident. For meat and other food products, pH is a very important aid in quality assessment and in deciding whether to use particular semi-finished and finished products. Particularly maturing meat highly dependent on the pH value.

Example applications and selection criteria

The pH value of all meat products must fall within the range from pH 4.5 to pH 8. Moreover, the distinction is drawn between three different types of meat:

DFD meat (dark-firm-dry)
Normal meat
PSE meat (pale-soft-exudative)

The following diagram shows the pH curves of different types of meat after slaughter.

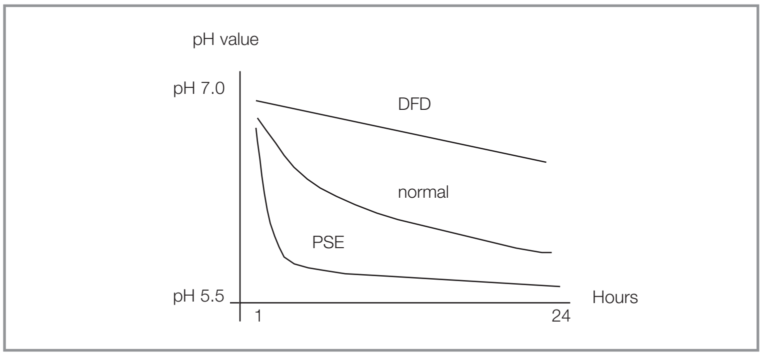

Figure 21: pH curves of different types of meat

It can be seen that the pH of DFD meat drops very slowly, whilst the pH of PSE meat falls relatively rapidly. The rate at which the pH falls can provide indicators of the meat's suitability for particular processing applications. PSE meat is not suitable for the production of raw ham because of its high drying losses and pale colour.

A pH electrode for this application must be insensitive to protein contamination, because otherwise its life span and reaction time are very rapidly reduced. Also, position-independent measurement is essential, because the measuring points, e.g. in different halves of the pig, are at different heights. A gel electrode is recommended in this case.

Recommendation: testo 205 one-hand pH meter for the meat industry, testo 206-pH 2 or testo 230 with pH electrode type 13.

Figure 22: pH measurement during raw sausage maturing

4.1.3 pH measurements in the environmental sector

Water-tight instruments in compact design are ideal for the drinking water, waste water sectors or when neutralising condensate in heating engineering (condensing boilers). A pH value of between 6.5 and 9.5 is defined for drinking water in the Drinking Water Ordinance. pH values below 6.5 promote the ingress of lead, copper and zinc from water pipes. The pH value has to be measured and adjusted regularly to minimise this metal charge. In the case of waste water, biological reactions in "bio materials" only take place in a specific pH range. The increase in pH is monitored over a specific time period.

Recommended instruments: testo 206-pH 1 or testo 230 with probe type 04 pH.

Figure 23: pH range in the biological stage of waste water treatment

4.1.4 Photography

The pH in development, fixing and other photographic solutions defines the quality of the finished photograph. Colour film developer must have a pH of about 12.4. It is recommended to take a sample (for example a beaker glass) from large processing machines.

Recommendation: testo 206-pH 1 or testo 206-pH 3 with probe type 04 or testo 230 with probe type 04.

Figure 24: pH value of developer in a large photo laboratory

4.1.5 pH measurement in industry

The application of pH meters in industry is highly complex and the choice of probe depends mainly on the types of electrode possible in the solutions being measured. Usually, high standard glass electrodes or gel electrodes with hole diaphragm are recommended.

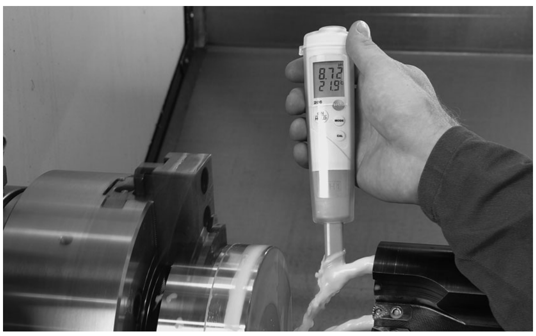

Figure 25: Determining the pH value of the lubricating and cooling membrane in a turnery

The pH value of lubricants used for turning and milling is taken as an example for pH measurement in the metal-working sector.

The lubricants are slightly basic on account of their ingredients. However, the pH should not exceed 9.0 as otherwise it will not be possible to hold turning parts properly in the jaw chuck. Additionally, itchiness will occur if there is skin contact. Because the lubricant is pumped around constantly (reuse) the pH value increases from the original 7.5 to 9. Fresh lubricant should be added or all the lubricant should be replaced.

Recommended: testo 206-pH 1 or testo 230 with probe type 04.

4.1.6 Other example applications from A to Z

Agriculture	Iron and steel
Bacteriology	Jam production
Beverages	Laundry
Brewery	Leather processing
Brine	Manufacture of dyes
Carpet manufacture	Meat and fish conservation
Cement production	Medical applications
Ceramics	Metal refining process
Cheese dairies	Metal treatment
Cleaning technology	Neutralisation processes
Confectionery	Oil tests
Cosmetics	Paper and paper pulp
Dairy industry	Petroleum
Dental care products	Pharmaceutical products
Dye works	Pigment manufacture
Eggs	Quality control
Fermentation reactions	Swimming baths
Fertilisers	Textile industry
Fish farming	Tobacco
Foundry work	Vegetables
Gelatine	Water tests
Glue manufacture	Yoghurt manufacture
Health	Zoology

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Application examples and selection criteria

4.2 Correct choice of electrode and instrument

The following tables provide an overview of the suitability of electrodes and instruments for the respective measurement application and requirement.

	Effluent examples	General aqueous solutions	Aquaria	Beer, fruit juice, wine	Butter, joghurt, cheese	Substances containing egg white	Emulsions, aqueous	Emulsions, part aqueous	Earth (suspensions)	Extreme pH values (pH<1, pH>13)	Penetration meas. in meat	Penetration meas. in fruit, veg.	Substances containing hydrofluoric acid	Galvanic sewage	Hot lyes	Highly viscous aqueous solutions	Solutions low in ions	Jams	Cosmetic products	Leather manufacturing	Milk	Rain water	Brine	Swimming pools	Soaps, detergents	Aqueous suspensions	Part-aqueous suspensions	Pastry, bread	Part-aqueous sol. <10% H_2O	Part-aqueous sol. <10% H_2O	Temperatures up to +80 °C	Temperatures up to +100 °C	TRIS buffer solutions	
Universal electrode Type 01 pH	+	+	+	0	–	–	0	0	0	0	–	–	–	0	–	–	–	–	–	0	0	0	0	+	0	0	–	–	0	–	0	–	0	pH
Laboratory electrode Type 02 pH	0	+	+	0	–	–	0	0	0	+	–	–	0	0	0	0	0	–	0	+	0	0	+	+	0	0	–	–	0	0	+	0	0	pH
Universal electrode Type 04 pH	+	+	+	0	–	–	0	0	0	0	–	–	–	0	–	–	0	–	–	0	0	0	+	+	0	0	–	–	0	–	–	–	0	pH/°C
Special electrode Type 05 pH	+	+	0	+	–	0	+	+	+	+	–	–	0	+	–	–	0	–	–	0	0	+	+	+	+	+	+	–	0	0	–	–	0	pH/°C
Penetration electrode Type 03 pH	0	0	0	0	+	+	+	+	+	–	+	+	–	0	–	+	–	+	+	–	+	–	+	0	+	+	+	+	0	0	–	–	–	pH/°C
Penetration electrode Type 13 pH	0	+	0	0	+	+	+	0	0	0	+	+	–	0	0	+	0	+	+	+	+	+	0	0	0	0	+	+	0	+	–	–	–	pH/°C
Immersion probe Type 04 T	0	+	0	0	0	+	+	+	+	–	–	–	–	–	–	–	+	0	0	+	0	+	0	+	0	+	+	0	+	+	+	+	0	°C
Immersion probe Type 15 T	+	+	+	+	–	0	+	+	0	+	–	–	+	+	+	0	+	0	0	+	+	+	+	+	+	+	+	0	+	+	+	+	+	°C
Penetration probe Type 25 T	+	+	+	+	+	+	+	+	+	–	+	+	–	–	–	+	+	+	+	+	+	+	+	+	0	+	+	+	+	+	+	+	0	°C
Redox electrode Type 06 mV	+	+	+	0	–	–	0	0	+	–	–	–	–	+	–	–	–	–	0	0	0	+	+	+	0	+	0	–	+	0	+	0	–	mV

Table 4: Electrode and instrument selection

+ suitable
0 suitable in limited cases
– not suitable

Your requirement	testo 230	testo 205	testo 206
pH measurement	x	x	x
mV measurement	x		
°C measurement (via pH electrodes)	x	x	x
mS/cm measurement			
1 point calibration		x	x
2 point calibration	x	x	x
3 point calibration		x	x
Automatic temperature compensation pH	x	x	x
Buffer bottles with dosing head		x	x
Gel storage cap		x	x
IP 54 protection class	x		
IP 68 protection class		x	x
Separate NTC temperature probe	x		
Calibration data display	x	x	x

Table 5: Criteria for instrument selection

5. References

[1] H. Galster; pH-Messung; Grundlagen, Methoden, Anwendungen, Geräte; VCH Weinheim, (1990)

[2] DIN 19266; pH-Messung - Standardpufferlösungen, (10/1971)

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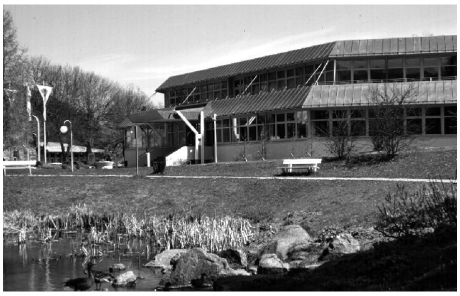
[9] pr-EN 50082, Teil 2 sowie pr-EN 50081, Teil 2; Elektro-Magnetische Verträglichkeit

6. Presentation of Testo measuring instruments



The Company

Testo was founded in 1957 and is now one of the worldwide leading manufacturers of portable electronic measuring instruments for . . .

- **Air Conditioning/Refrigeration Engineering**
  Measures temperature, humidity and air flow to maintain a healthy ambient climate for people and ideal conditions for the production and storage of sensitive products.
- **Heating systems**
  Efficiency measurements facilitate energy savings.
  Safety measurements during installation and servicing prevent personal injury and property damage (gas heating systems).
- **Food quality**
  Regular temperature monitoring measurements prevent the multiplication of microorganisms (e.g. salmonella).
- **Emissions**
  Controlling combustion processes is good for the environment and saves resources. Product quality assurance by checking decisive process parameters.
- **Industry**
  Measurement engineering for quality assurance during production. Thermal fluctuations in the manufacturing process influence the quality of the products. Temperature monitoring provides a basis for quality assurance. In the laboratory sector of the chemical and pharmaceutical industry, it is vital to have efficient and accurate readings which can be processed on a PC. Testo measuring instruments fulfill these requirements.

Employees

1,100 employees (570 of them in Lenzkirch) develop, manufacture, sell, maintain and calibrate in accordance with DIN EN ISO 9001:2000.

Presentation of Testo measuring instruments

Training

Every year Testo offers training opportunities in the industrial, commercial and technical sections of the company. We also offer internships and have placements for polytechnic degree students.
Testo also offers commercial and technical apprenticeships.
Since 1979 Testo has successfully trained more than 135 young people.

Customer consultations

We welcome the opportunity to give advice to our customers from the industrial and contracting sectors as well as from official authorities.

From Lenzkirch worldwide

The Lenzkirch high-tech manufacturer Testo exports almost 60 % of its precision measuring instruments. Testo is represented in all corners of the world by 25 subsidiaries and 50 agents.

Future-oriented research

Approximately 70 of the 570 employees in Lenzkirch are involved in research, development and marketing. We have a higher-than-average commitment to research. The main aim is to offer even better solutions to our customers for their measurement tasks.

Measurement instruments for air conditioning and the environment

Testo has been developing and manufacturing portable flue gas analysers for the protection of our environment since 1980.

Qualified all-round service

Testo is also there for you after your purchase. Our worldwide service offers fast help. A 24 hour service is offered in most countries.

A market leader

Testo's high quality (DIN EN ISO 9001 certificate), its reasonable prices and customer-friendly service have made Testo a market leader in the portable measuring instrument sector.

ISO 9001 TESTO QUALITY certified

testo 205

testo 205 is a compact one-hand measuring instrument, i.e. there is no line between the pH probe and instrument electronics. A temperature measurement tip is located in the patented Testo pH probe so that the temperature can be measured directly in spite of the penetration tip. The probe head can be changed (spare part). The probe has a long service life on account of the hole diaphragm and the gel electrolyte and has a particularly fast response time and is insensitive to dirt (e.g. protein).

This all makes testo 205 the ideal measuring instrument for the food industry, and in particular meat processing.

Figure 26: pH value of meat during dissection

Technical data for testo 205

Parameter	pH / °C
Sensor	pH electrode / NTC
No. of measurement channels	2
Measurement range	0 to 14 pH
Resolution: pH	0.01 pH
Resolution: Temperature	0.1 °C
Accuracy: pH	± 0.02 pH
Accuracy: Temperature	± 0.4 °C
Temperature compensation	Automatic
Display	LCD, 2 lines, 0 to 70 °C
Probe	Screw-in pH / °C probe modules
Measurement rate	2 measurements per second
Application temperature	0 °C to +60 °C
Storage temperature	-20 °C to +70 °C
Battery type	4x lithium button cell LR44
Battery life	80 h (Auto Off 10 Min)
Housing	ABS with soft coating around handle Protection class IP 65
Dimensions	197 x 33 x 20 mm
Weight	69 g

Table 6: Technical data on testo 205

A summary of product features

- Combined penetration tip with temperature probe
- Measurement tip can be changed by user
- Maintenance-free gel electrode
- Built-in backlit display
- Audible key feedback
- 2 line display
- Automatic full-scale value recognition
- 1, 2, or 3 point calibration possible

testo 206-pH 1

The testo 206 product line consists of 3 instruments.

testo 206-pH 1 has a measurement head for pH measurement in liquids. The pH value and temperature are measured simultaneously and shown in the two-line display. The measurement head can be easily replaced if necessary. Thanks to Testo's probe technology, the probe is still highly robust, fast and insensitive to dirt and has a long service life. 1, 2 or 3 point calibration is possible. The set includes TopSafe (water-tight protection case), a belt holder and a spill-proof storage cap (gel).

Figure 27: pH value during the manufacture of fruit juice

Applications for testo 206-pH 1

- pH measurement in the environment sector (water, waste water, ...)
- Condensate neutralisation (heating engineering/condensing boiler)
- pH applications in industry (e.g. lubricant pH value)
- pH measurement in the food sector (e.g. fruit juice production)
- Generally: Liquid substances in all sectors

testo

Presentation of Testo equipment

Technical data of testo 206-pH 1

Parameter	pH / °C
Sensor	pH electrode / NTC
Number of measurement channels	2
Measurement range	0 to 14 pH
Resolution: pH	0.01 pH
Resolution: Temperature	0.1 °C
Accuracy: pH	± 0.02 pH
Accuracy: Temperature	± 0.4 °C
Temperature compensation	Automatic
Display	LCD, 2 line, 0 to 70 °C
Probe	Screw-in pH / °C probe modules
Measuring rate	2 measurements per second
Application temperature	0 °C to +60 °C
Storage temperature	-20 °C to +70 °C
Battery type	1x CR2032
Battery life	80 h (Auto Off 10 Min)
Housing	ABS with Top Safe, Protection class IP 68
Dimensions	197 x 33 x 20 mm
Weight	69 g

Table 7: Technical data for testo 206-pH1

testo 206-pH 2

testo 206-pH 2 was developed for soft substances. It is possible to carry out efficient measurements in yoghurt, cheese, meat products, sausage, mash or skin cream. This instrument has a built-in temperature probe for automatic temperature compensation. A 1, 2 or 3 point calibration is possible. A TopSafe (water-proof protection case), belt holder and spill-proof storage cap (gel) are included in the Set.

Figure 28: Quality control during the production of skin cream

Applications of testo 206-pH 2

- Milch and milk products (yoghurt, cheese, ...)
- pH value of mash during the production of spirits
- pH during delicatessen production (e.g. salad dressing)
- Application in cosmetics sector (cream production)
- pH checks during meat processing

Presentation of Testo measuring instruments

Technical data for testo 206-pH 2

Parameter	pH / °C
Sensor	pH electrode / NTC
Number of measurement channels	2 channels
Measurement range	0 to 14 pH
Resolution pH	0.01 pH
Resolution Temperature	0.1 °C
Accuracy pH	± 0.02 pH
Accuracy Temperature	± 0.4 °C
Temperature compensation	Automatic
Display	LCD, 2 line, 0 to 70 °C
Probe	Screw-in pH / °C probe module
Measurement rate	2 measurements per second
Application temperature	0 °C to +60 °C
Storage temperature	-20 °C to +70 °C
Battery type	1x CR2032
Battery life	80 h (Auto Off 10 Min)
Housing	ABS with Top Safe, Protection class IP 68
Dimensions	197 x 33 x 20 mm
Weight	69 g

Table 8: Technical data for testo 206-pH 2

testo 206-pH 3

testo 206-pH 3 is intended for connection to external pH probes. All of the pH probes are connected with this plug-in adapter via the BNC plug-in connection. If Testo pH probes with temperature sensor are used, the temperature reading is shown in the display and the temperature is compensated automatically. If the instrument does not find a temperature sensor at the BNC socket, a manual setting of the temperature value is possible. This instrument can also have a 1, 2 or 3 point calibration. Two different starter kits are available, in which in addition to a standard pH probe (Testo pH probe Type 01 without or Type 04 with temperature probe), TopSafe (water-tight protection sleeve) and the belt holder are included.

Figure 29: pH value check in laboratories

Applications for testo 206-pH 3

- All of the probes on the market can be connected with the BNC adapter. Testo probes with temperature measurement facilitate automatic temperature compensation.
- Ideal for pH measurements in the laboratory
- pH monitoring in the environmental sector (water quality, earth samples)
- pH checks in the industrial sector (e.g. photo process baths)

Technical data for testo 206-pH 3

Parameters	pH / °C
Sensor	pH electrode / NTC
Number of measurement channels	2 channel
Measurement range	0 to 14 pH
Resolution pH	0.01 pH
Resolution temperature	0.1 °C
Accuracy pH	± 0.02 pH
Accuracy temperature	± 0.4 °C
Temperature compensation	Automatic
Display	LCD, 2 line, 0 to 70 °C
Probe	Screw-in pH / °C probe modules
Measurement rate	2 measurements per second
Application temperature	0 °C to +60 °C
Storage temperature	-20 °C to +70 °C
Battery type	1x CR2032
Battery life	80 h (Auto Off 10 Min)
Housing	ABS with Top Safe, Protection class IP 68
Dimensions	197 x 33 x 20 mm
Weight	69 g
	Refer to the documentation on the respective probe for information about the pH and temperature accuracy.

Table 9: Technical data testo 206-pH 3

testo 230

testo 230 is a pH meter with a separate temperature probe socket which has the advantage that standard temperature probes from the Testo range can be connected directly so that temperature measurements can be carried out. This "Two in One" meter saves you purchasing a separate thermometer. Unlike testo 205 and testo 206 instruments, the meter processes DIN/NBS buffers and has a wide range of different probes available for different applications.

Figure 30: testo 230 – pH-Set 2

Different set combinations are available:

pH-Set 1 Universal:
testo 230 pH meter, battery, 2 electrode clips, buffer set
pH 4, 7, universal electrode type 04 pH, Instruction manual, Set case.

pH-Set 2 Food:
testo 230 pH meter, battery, 2 electrode clips, buffer set
pH 4, 7, penetration electrode type 03 pH, 50 ml storage solution, S7-BNC electrode cable, instruction manual, Set case.

pH-Set 3 Affordable:
testo 230 pH meter, batteries, 2 electrode clips, buffer set
pH 4, 7, universal electrode type 01 pH, instruction manual, Set case.

Technical data for testo 230

Measuring ranges	0 to 14 pH -50 to +150°C ± 1999 mV
Resolution	0.01 pH 0.1°C 1 mV
Accuracy ±1 digit	± 0.01 pH ± 0.4°C (-50 to -25°C and +75 to +99.9°C ± 0.2°C (24.9 to +74.9°C) ± 0.5 % of reading (+100 to +150°C) ± 1 mV (0 to 999 mV) ± 2 mV (1000 to 1999 mV)
Temperature compensation	man -10 to +150°C auto -50 to +150°C
Operating temperature	0 to +40°C
Storage/Transport temperature	-20 to +70°C
Display	LC display, two lines
Connections	BNC compatible socket for pH or ph/°C Mini DIN socket for temperature probe
Battery life	Approx. 100 h
Weight	180 g (incl. battery)
Other features	IP 54 °C/°F ABS housing material Auto-Off

Table 10: Technical data for testo 230

testo 230 applications

testo 230 is a combination of a full pH meter and a high standard thermometer in a compact, water-proof housing.

The redox voltage can determined via the redox electrode type 06.

The instrument has automatic temperature compensation and can be calibrated in the pH range with standard as well as with DIN buffers.

testo 240

testo 240 combines a complete conductivity measuring instrument and a fully-fledged thermometer in a compact, waterproof housing. Measurement errors at high conductivities and deposits on the electrodes are avoided on account of the 4 electrode engineering used. The salt level (NaCl) of an aqueous solution can be determined directly.

Figure 31: Measuring conductivity in the brine during the processing of ham

testo 240 applications

- Long service life of measurement cell due to 4 electrode engineering
- Extremely wide measurement ranges with only one measurement cell
- Easy, user-friendly operation
- Measurement of salt level (NaCl)

Presentatio of Testo measuring instruments

Technical data for testo 240

Probe type	Conductivity measurement cell	NTC	Calculated variable
Meas. range	0 to +2000 mS/cm	-50 to +150°C	+1 to +200000 mg/l NaCl
Accuracy ± 1 digit	± 1 % of reading (0 to +2000 mS/cm)	± 0.5 % of reading (+100 to +150°C) ±0.2°C (-25 to +74.9°C) ±0.4°C (-50 to +25.1°C) ±0.4°C (-75 to +99.9°C)	± 1.2 % of reading (+1 to +200000 mg/l NaCl)
Resolution		0.1°C (-50 to +150°C)	0.1 mg/l NaCl (+1 to +200000 mg/l NaCl)
Display		LCD 2 line	
Operating temperature		0 to +40°C	
Storage tempertature		-20 to +70°C	
Battery type		9 V block battery	
Life		60 h	
Dimensions		168 x 72 x 27 mm	
Weight		170 g	
Warranty		2 years	

Resolution max. 0.1 µS/cm
Temperature compensation automatic
Temperature coefficient: 0 to 5 %/°C linear
Compensation in accordance with the non-linear function
Natural water corresponding to DIN 38404 from 0 to +50°C
Autom. measuring range switchover (conductivity)
Auto-OFF function
°C/°F

Table 11: Technical data for testo 240

Spill-proof storage cap

pH probes must be stored in moist conditions in order the prevent the swell glass from drying out. Testo has developed a leak-proof storage cap for the new testo 205 and testo 206 pH meters. The gel corresponds to the otherwise usual 3 molar potassium chloride. Spillage does not occur on account of the gel consistency. It is important to clean the electrodes thoroughly prior to immersing them in the storage gel. The robust plastic cap with KCl gel is attached directly to the belt/wall holder. The cap can also be attached directly (without belt/wall holder) on the instruments. Spare caps are available separately or in a set of 3.

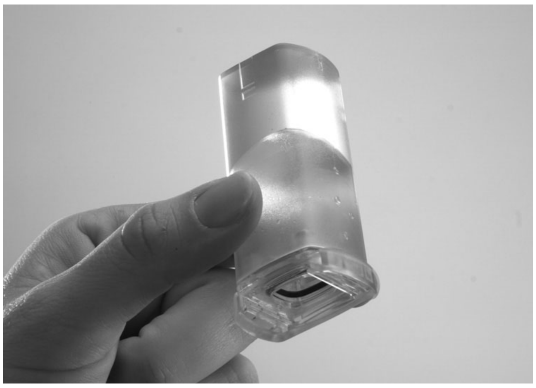


Figure 32: Storage cap for pH probes with spill-proof KCL gel

testo

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Copy this page as often as possible and fax or return the completed form by post.

Suggestion for improvement / Product information request

To:

Sender:

Name ______________________

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Address ______________________

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Tel. ______________________

Fax ______________________

Date ______________________

☐ I would like more information on the following products:

☐ testo 205/206/230 (0981 1124) ☐ testo 230 (0981 3434) ☐ testo 240 (0981 3434)

☐ Measurement Engineering for Transport and Storage of food (0981 1014)

☐ Measurement Engineering for Restaurants, Catering and Supermarkets (0981 1024)

☐ Monitoring instruments for food production (0981 1034)

☐ Handbook: Temperature measurement in the food sector (0981 4353)

We are grateful for all suggestions for improvement in order to keep this pH handbook up to date and work them into a new edition.

☐ I have the following suggestion(s) for improvement:

Chapter	Page	Topic	Suggestion

Notes

Notes

You will find the addresses of our subsidiaries and agents worldwide
at **www.testo.com**.

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