pH measurement

A practical guide to the installation, operation, maintenance and calibration of pH electrodes

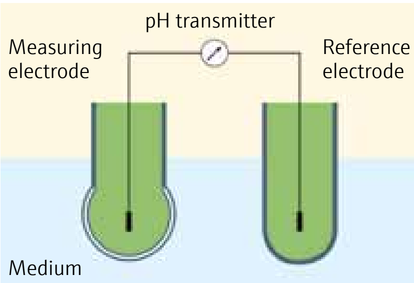
Endress+Hauser
People for Process Automation

Contents

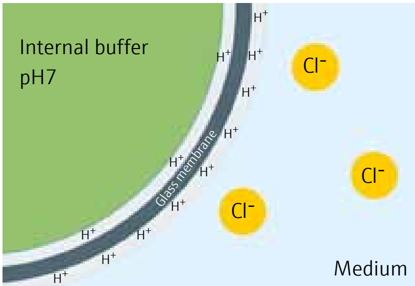
The pH measuring principle

pH measurement is the measurement of a liquid's acidity or alkalinity and is used in a wide range of applications such as product quality monitoring, process control and effluent monitoring.

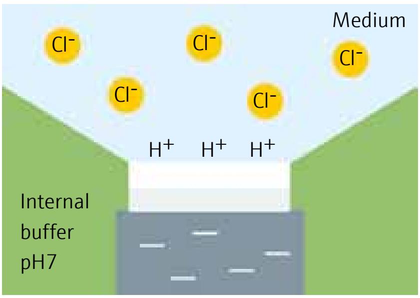
In typical glass electrodes the measurement is based upon a special pH-sensitive glass membrane (gel layer) where the surface reacts to the hydrogen ion (H^+) content of the measured solution. This is measured relative to a reference electrode that is also in contact with the process medium (via the diaphragm or liquid junction). This resulting potential difference is measured by the transmitter and is converted directly into a pH value.



The pH measuring principle



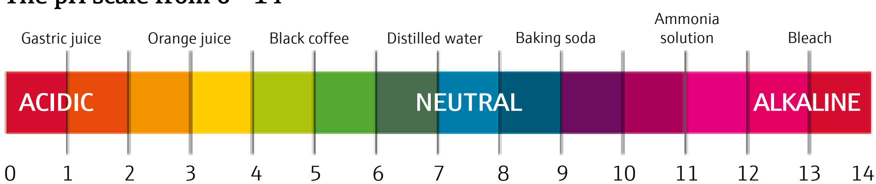
Membrane of a glass pH electrode



How an IsFET electrode works

Apart from using a glass membrane, the pH value can also be measured by an ion-selective field effect transistor (ISFET). Here the sensing part of the electrode is a transistor with drain and source that are isolated from the 'gate'. The hydrogen ions at the gate cause a current flow through the transistor and the related voltage is processed as in glass electrodes.

The pH scale from 0 - 14



Memosens: say goodbye to moisture ingress

Memosens digital sensor technology has proven its worth in tens of thousands of measuring points worldwide. It's non-contact inductively coupled connection completely eliminates the problem of moisture ingress and measurement distortion.

Memosens digital pH electrodes

All calibration and operation information is stored in a chip in the sensor head. This means that the electrodes can be calibrated offline away from the process and under controlled conditions such as a laboratory or maintenance workshop.

This both simplifies the maintenance process and maximises electrode lifetime as these vital processes can be carried out more effectively and without time constraints. Additionally, using two or three electrodes per measuring point means that electrodes can be fully regenerated and then 'rested' in between use.

When the electrode is ready for cleaning and calibration, it can simply be replaced with one that is calibrated and ready for use. The fouled electrode should then be taken back to the maintenance area for cleaning and regeneration (using the procedures detailed in this document).

Interrogation of the Memosens electrodes gives information on operating hours and conditions that the electrode has been exposed to. Additional calibration data such as delta slope, zero point and the number of sterilisations (where applicable) are essential tools in predictive maintenance.

The result is up to 30% longer sensor lifetime compared with traditional analogue sensors – and significant time and cost savings for your plant!

Memobase Plus: measure, calibrate, document

The Memobase Plus software tool allows simultaneous measurement and calibration of multiple electrodes in a controlled environment using your laptop or PC. This results in a simplified and optimised maintenance and calibration effort that is fully traceable and documented.

Memobase Plus effectively turns your computer into a calibration and measuring station, by connecting the sensors to your PC via USB. Up to four sensors can be managed simultaneously in any combination. Operation is simple and intuitive, as the software automatically identifies the sensors and the user is guided through calibration and maintenance procedures. Fully FDA 21 CFR Part 11 compliant, Memobase Plus is ideal for use in the highly controlled and regulated life sciences industry.

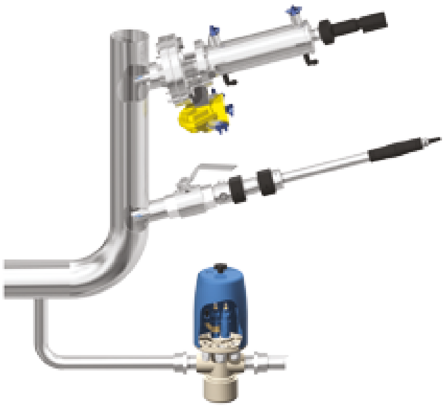
Memocheck: test your measuring points

- **Memocheck service tool:** Provides a quick and easy test of wiring and installation. It can also be used on site to troubleshoot a system which has already been commissioned, to establish possible causes of error.
- **Memocheck Plus qualification tool:** Verifies the process data independently of the sensor, so you can be absolutely sure of your readings.
- **Memocheck Sim qualification* and service tool:** Offers multi-parameter checks in just one handheld device. Installation, commissioning and troubleshooting are performed quickly and easily.

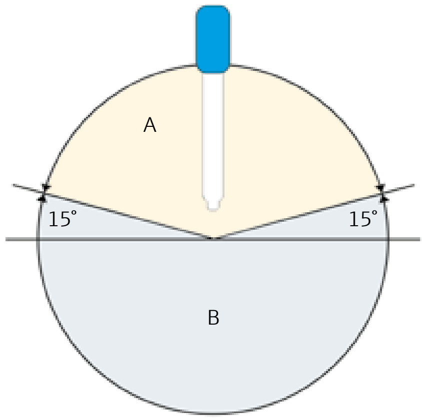
* Can be used as a qualification tool with the optional quality certificate.

Installing your pH electrode

Choice of installation assembly is vital in ensuring optimum pH measurement. Unless specifically designed for upside down mounting, the electrode must be installed at least 15° from the horizontal.



Typical pH assembly installations.



A = Permitted angle, B = Not permitted.

Using the correct insertion technique is vital to prevent breakage of the delicate glass electrode. Endress+Hauser electrodes are designed so that the thread of the sensor is on a freely-rotating head. This means that the electrode can be held in place while the threaded part is rotated in order to correctly screw the electrode into the assembly - the electrode can be removed in the same way.

Should the entire electrode head be turned in order to insert/remove it, this can result in breakage. Particular care should also be taken where there are O-rings inside the assembly.

Carefully rotate the threaded part only!

Cleaning your pH electrode

The electrode should be cleaned regularly (depending on application) and *always* prior to attempting any calibration. A coating on the pH electrode membrane and/or diaphragm (reference junction) will impede the proper calibration and operation of the pH electrode. Even if not obviously visible to the eye, it is possible that a thin biofilm can form that will block the membrane and/or diaphragm.

Choice of cleaning fluid

This is dictated by the process medium to which the electrode is exposed (water alone is usually not sufficient). Often simple household washing up liquid can provide an effective cleaning detergent.

General coating

- Rinse well with clean water, dry and then soak in 5% HCl for 15 minutes.
- Rinse well with clean water and dab dry with a soft cloth.
- Soak the electrode in 3M KCl solution for a minimum of one hour then calibrate.

Inorganic coating

- Rinse well with clean water, dry and then soak in 0.1M tetrasodium EDTA solution for 15 minutes (maximum).
- Rinse well with clean water and dab dry with a soft cloth.
- Soak the electrode in 3M KCl solution for a minimum of one hour then calibrate.

Protein coating

- Rinse well with clean water, dry and soak in 5% HCl for 15 minutes (or 0.1M HCl and 0.1% pepsin).
- Rinse well with clean water and dab dry with a soft cloth.
- Soak the electrode in 3M KCl solution for a minimum of one hour then calibrate.

Grease and/or oil coating

- Rinse with detergent or ethanol solution.
- Rinse well with clean water and dab dry with a soft cloth.
- Soak the electrode in 3M KCl solution for a minimum of one hour then calibrate.

Silver sulfide coating/blockage

- Soak in 0.1M thiourea for 15 minutes, rinse with clean water and dry with a soft cloth.

Tips

- Remove tough deposits with hydrogen peroxide or sodium hypochlorite.
- Prepare a 5% HCl solution by adding 15ml concentrated HCl to 85ml water.

Calibrating your pH electrode

Once the pH electrode has been suitably cleaned and regenerated, it is then ready for calibration. Using an appropriate choice of pH buffers (typically to bracket the measuring range), perform the calibration by following the instructions in the transmitter. A two-point calibration is typically carried out.

It is vital to ensure that pH buffer solutions are stored correctly in between use (in sealed bottles and under ambient conditions) and that no contamination occurs. In between buffer use, the electrode should be rinsed with clean water and dabbed dry with a soft cloth.

Ideally, calibration should be performed under controlled conditions. Attempts to remove a sensor from a high temperature process and immediately calibrate may result in error as the temperature sensor tries to stabilise.

The optimum slope for a fully functioning pH electrode is -59.2mV/pH. The slope will gradually deteriorate as the electrode ages with use. The factory default warning alarm is -55mV/pH in Endress+Hauser transmitters, however, the lower limit of this is typically dependent upon the criticality of the measurement.

Electrodes should be discarded if the slope falls below 85% (-50mV/pH)and attempts to clean and regenerate the electrode have failed.

Storage and regeneration of your pH electrode

Storing your pH electrode

pH electrodes are supplied hydrated, i.e. a rubber cap filled with 3M KCl that keeps the membrane and diaphragm wet. It is important not to discard the rubber caps as they can be re-used for short-term storage.

If stored correctly (using the protection cap filled with electrolyte) in ambient conditions, pH electrodes can have a shelf life of around 12 months without any impact upon sensor function.

Note: Never allow the membrane and diaphragm to dry out! Brief periods in air are unavoidable from time to time but must be kept to a minimum.

Rehydrating your pH electrode

The glass membrane of a pH electrode is similar to a contact lens and as such it is vital that it is kept fully hydrated in order to maintain the 'gel' layer that is so important in the measurement process.

If the pH electrode dries out in the process or during storage, soak the electrode in 3M KCl solution for 24 hours (or at least overnight) or 60°C 3M KCl solution for six hours.

If the pH electrode is allowed to dry out for a significant period of time, regeneration may not be possible. It is important to also consider that even if the sensor is regenerated, it may have a reduced lifetime. Endress+Hauser Memosens electrodes display a high glass membrane impedance alarm to alert you to this problem.

Reactivating the glass membrane

Physical or chemical damage to the glass membrane may result in sluggish performance of the electrode. Use of a 10% solution of ammonium biflouride creates a very dilute hydrofluoric acid to 'etch' a fine layer and reactivate the membrane.

- Dip only the glass bulb of the pH electrode in the solution for 60 seconds then immediately dip in 5M HCl to neutralise the strong base.

- Rinse well with water then soak the electrode head in 3M KCl overnight before rinsing and calibrating.

pH measurement FAQs

What should the slope of my pH electrode be?
The theoretical slope of a pH electrode is -59.16mV/pH. The minimum acceptable slope is dependent upon the criticality of your measurement. Electrodes should always be discarded if the slope falls below 50mV.

How long will my pH electrode last?
This depends upon the process that the electrode is being used in. The more harsh the application, i.e. extreme pH and/or temperature, presence of harsh chemicals, poisoning ions and/or abrasives and high flowrates, will all impact on sensor lifetime.

How often should I clean and calibrate my pH electrode?
Again this depends on the process. Heavily fouling processes will require more frequent cleaning and calibration. It is important to tailor the regime to suit each individual application. For example, monitoring the delta slope value (difference between latest and previous calibration) is a good indicator of whether calibration is required more frequently.

How long will my buffer solutions last?
Opened bottles of buffer should be discarded after six months. Alkaline buffers may deteriorate more quickly as they absorb CO_2 from the air. Never re-use buffer solutions, i.e. *do not* pour back into the bottle after use. Always store buffers correctly - in sealed bottles under ambient conditions.

What should I do if my pH electrode fails calibration?
Ensure that the electrode has been properly cleaned. Leave it (ideally overnight) in 3M KCl (potassium chloride) electrolyte to fully hydrate and regenerate and then repeat the calibration. Ensure buffers have been stored correctly and not contaminated. If these steps fail, the electrode may require replacement.

Why is temperature such an important factor in pH measurement?
pH varies with temperature and is not linear. The effect of temperature upon the pH depends upon each particular process matrix. The pH of a process at 15°C will not be the same at 80°C. It is more pronounced at more alkaline pH levels.

What is the appropriate way to store a pH sensor when not in use?
The electrodes *must* be kept hydrated! Use electrolyte, pH4 buffer solution or tap water - *never* use deionised water.

Can a pH sensor be installed upside down?

No. In most cases the electrolyte inside the sensor is liquid. If the sensor is <15° from the horizontal then air pockets can form in the glass bulb of the electrode. If upside down installation is required, then an appropriate electrode for this application must be used such as the Ceragel CPS71D (BU version) or the Ceramax CPS341D.

Ceramax CPS341D

What should the flow velocity be?

Typically in the region of 2-3m/s (less for low conductivity applications).

Why is conductivity important in pH measurement?

Very low conductivity (<50μs/cm) can result in a phenomenon called liquid junction potential. This is due to the very low ionic strength of the process medium relative to the high concentration of ions in the electrolyte. A specific electrode with a high outflow of electrolyte is required to minimise this. The flowrate should also be controlled and a stainless steel assembly used.

UK

Endress+Hauser Ltd
Floats Road
Manchester
M23 9NF

Tel: 0161 286 5000
Fax: 0161 998 1841
info@uk.endress.com
www.uk.endress.com

PU01052C/22/EN/01.14

Endress+Hauser
People for Process Automation