APPLICATION NOTE – pH

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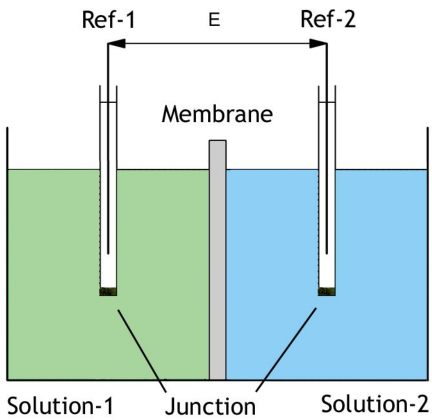
What is pH?

The pH is a measurement for the acidity or alkalinity of a solution. In pure water the hydrogen ion (H+) and hydroxyl ion (OH^-) concentrations are equal at 10^{-7} M (25°C). To provide a convenient and effective means of defining acidity and alkalinity, the pH is defined as the negative logarithm of hydrogen activity:

$$pH = -\log [H^+]$$

The heart of a pH measuring system is a membrane made from special pH-selective glass on which a very thin layer of hydrogen ions is formed when dipped in water. At high pH values, this layer will have a low hydrogen concentration. However, at low pH values a large number of H^+ ions diffuse in the layer. By measuring the generated electrical potential (E) in the layer the corresponding pH can be computed.

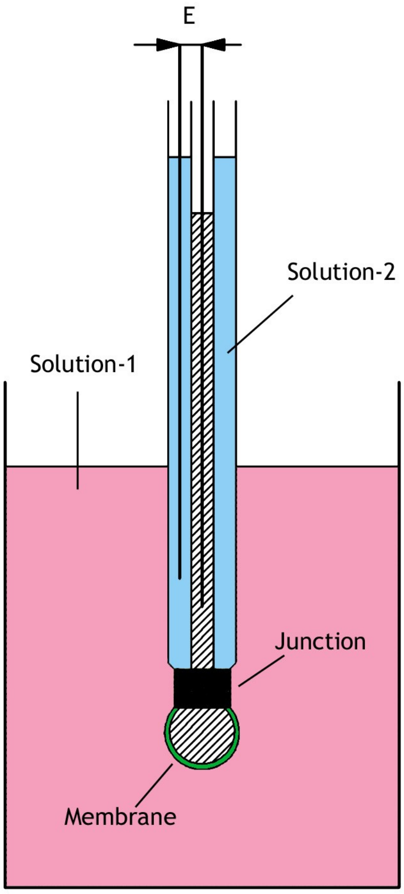


Solution-1: sample to be measured
Solution-2 : known buffer solution (7 pH)
Reference-1: silver wire in a salt-bridge (KCl)
Reference-2: silver wire in a salt-bridge (KCl)
Membrane layer-1: H^+ ions generated by the sample
Membrane layer-2: H^+ ions generated by the buffer

The potential (E) between both wires will vary with the pH difference between sample and known buffer according the Nernst-equation (-59.2 mV/pH at 25°C). A salt-bridge around each wire prevents direct metal contact with the solutions by using a wet junction for a stable electrical behaviour.

Combination Electrode

A combination electrode is an indicating and a reference electrode combined into a single body that is easy to use and popular because of its compactness. A minimum amount of sample is required due to the close proximity of the pH responsive membrane and the liquid junction.



Junction Types

Glass combination electrodes mostly feature an anti-fouling annular ceramic junction. The annular junction is formulated with a special ceramic which encircles the glass bulb. Numerous pores in the ceramic provide lower resistance and more stable pH readings. The epoxy body combination electrodes come standard with a specially formulated porous ceramic plug junction.
Sleeve junctions provide the highest flow rate for difficult samples.

A double junction reference is constructed with an Ag/AgCl inner chamber and a chemically compatible reference solution in the outer chamber. It is recommended for samples containing organic compounds, proteins, heavy metals, and other compounds that interact with silver, such as bromides, iodides, cyanides, and sulphides.

Membrane Types

- General and low temperature glass is especially suited for low temperature, non aqueous solutions and pH measurements under 12 pH.
- Universal glass is best suited for most pH measurements where minimal or no Na^+ is present. It is a low-resistant glass with a very fast and stable response and is designed for pH ranges of 0 to 13 and temperatures of 0° to 135°C.
- High pH, low sodium ion error glass is especially formulated for continuous, long-term use at high temperatures, particularly in strong alkaline solutions above pH 11. It experiences negligible Na^+ ion error above 13 pH. The impedance of the glass is much higher than other glasses, and a slower response will be experienced at room temperatures and below. Response time will increase as the temperature is elevated.

Internal Reference Types

Calomel reference electrodes (Hg/Hg_2Cl_2) can give very accurate potentials. Both its reproducibility and potential stability are superior to those of the Ag/AgCl electrode, although only at a constant and relatively low temperature. Calomel is subject to a constant and relatively low temperature fluctuation with a temperature limitation of 80°C.

Silver/silver chloride reference (Ag/AgCl) electrodes are largely hysteresis-free and can be used at higher temperatures with lower temperature coefficients. Ag/AgCl is the best general purpose reference with a wide temperature range (-5° to 110°C).

Reference Construction

Refillable Reference Cell: selected for high accuracy, stability, and longer electrode life. Refillable types sacrifice convenience and ease of maintenance.

Sealed Reference Cell: sealed gel-filled reference electrodes are designed for convenience where minimal maintenance is required. Slightly lower accuracy and shorter life must be taken in account.

Electrode Construction

Glass Body Electrodes: ideally suited for most routine pH measurements for accuracy, high temperature, and ease of cleaning.

Epoxy Body Electrodes: a good choice for applications where rough handling and breakage are a major problem.

Maintenance

A pH electrode is active and stable only after wetting! For this purpose it must be immersed for **at least ten hours** in a 3...4 M KCl solution. During short interruptions (e.g. storage) the electrode should be immersed in a 3...4 M KCl solution. In doing this it is always kept ready for use. When the interruption is longer than a month, refill the closing cap with 3...4 M KCl and plug it on the electrode tip in order to protect the glass bulb. Before use, ensure that the reference part of the electrode is topped up with a 3...4 M KCl solution.

Avoid a low pressure inside a refillable electrode! Therefore always remove the closure from the refilling aperture during the measurements as well as during the calibration. This allows the saltbridge solution to flow through the ceramic liquid junction and prevents contamination of the electrolyte. For the same reason, the inside level should always be higher than the outside level of the measuring solution. Close the refilling aperture again when storing the electrode.

A polluted electrode may be cleaned with a soft detergent or 0.1 M HCl. Greasy substances may be removed with acetone or alcohol **(never do this with plastic electrodes!)**.

If the electrode is polluted by proteinaceous materials (such as blood), it should stand in a cleaning solution overnight and then be cleaned with distilled water before use. The pH electrode wears away by being used. If the electrode tends to respond slower and calibration becomes difficult, even after cleaning, it should be replaced by a new one.

Good Measurement Practices

- While calibrating or measuring all solutions should be stirred gently (e.g. with a magnetic stirrer) to ensure the electrode gives a true representation of the beaker contents.
- Calibration solutions should be chosen which have values near the expected sample value.
- Only fresh calibration solutions should be used! Changing all solutions daily is a good practice.
- All solutions should be maintained at equal temperature.
- Rinse the electrode twice between measurements: first thoroughly in distilled water and then with a small amount of the next sample to be measured.
- Allow the electrodes sufficient time to stabilise while calibrating or measuring. A stability indicator on most of our meters prompts the user when readings should be taken.

Frequently Asked Questions

Q. If I order a pH meter, what accessories do I need to use with it?

A. You need a pH electrode and at least two pH buffers, one at pH 7 and the other at either pH 4 or 10.

Q. My colleague is using an ORP electrode to measure the same solutions as I, but our readings are not even close. Could there be something wrong with my electrode?

A. There is nothing wrong! Because ORP is a relative measurement, it is almost impossible to compare two ORP electrodes directly. ORP electrodes come equipped with bands made up of platinum, gold or silver. Each band type will give you a different reading in the same solution. Even if the electrodes are of the same band type, the leak rate through the reference junction will affect your readings.

Q. Can I measure the pH of a gas?

A. The only way to measure the pH of a gas is to dissolve it into distilled water and measure the mixture. Technically, the pH of the distilled water/gas mixture will be that of the gas.

Q. How do I take soil measurements?

A. Prepare the sample by combining a 10 g soil sample with distilled water (total volume should be 50 ml), mixing thoroughly, and allowing the mixture to settle for 10 minutes. Carefully insert the pH electrode and allow readings the stabilise.

Q. Why is a double junction electrode better than a single junction electrode?

A. A double junction electrode is less likely to become clogged because the second junction is located higher up in the probe out of contact with the sample.

Q. How often do I need to calibrate my pH meter?

A. Before each use or set of uses.

Q. How can you unclog a pH electrode? How can you restore a dry pH electrode?

A. First check the interior wire. If corrosion is evident, replace the electrode. If not, then soak the electrode in pH 4 buffer solution at 50°C for 2...4 hours. Restore a dry electrode by soaking it in tap water after rinsing out the refill chamber with distilled water and refilling with the proper solution.

Q. How far can my pH electrode be from my meter? What if it is too far?

A. The maximum distance an electrode can be from a pH meter is about 60 m. If the distance is greater, you will need a transmitter. Use either a transmitter or purchase an industrial electrode with a built-in transmitter. A transmitter will allow you to use your electrode up to 300 m from your meter provided you are not in a noisy environment.

Q. If measuring the entire range of pH what buffers should be used?

A. At least 3 buffers, e.g. pH 4, 7 and 10.

Q. What pH electrode do I use for a specific application?

A. Follow the general rules below for selecting the right pH electrode:

- Glass bodied pH electrodes may be used in most sample types.
- Epoxy bodied pH electrodes are designed for rugged environments, multiple-user situations, and field or plant applications. Epoxy bodied pH electrodes should not be used in organic solvents.
- For situations containing proteins, sulphide, and TRIS, use double junction electrodes.
- For viscous or dirty samples, use sleeve junction electrodes for best results and easy cleaning.

Q. How do I store my pH electrode?

A. Proper electrode storage maximises electrode performance and extends electrode life. There are two ways to store a pH electrode:

- Use a 3...4 M KCl solution.
- As a temporary substitute use 200 ml of pH 7 buffer to which 1 gram of potassium chloride (KCl) has been added. For long-term storage information refer to the appropriate pH electrode instruction manual.

Note: never store your electrode in distilled water!

Q. What filling solution do I use?

A. The recommended filling solution depends on the type of electrode. Some electrodes have sealed references and do not require filling solution. For refillable pH electrodes, use a 3...4 M KCl solution.

Q. How do I clean my pH electrode?

A. The solution used to clean a pH electrode depends on the possible contaminants. Use the guide below to choose the appropriate solution:

- For general cleaning soak the electrode in 0.1 M HCl or 0.1 M HNO_3 for 30 minutes.
- For removing stubborn deposits and bacterial growth, soak the electrode in a 1:10 dilution of household laundry bleach for 15 minutes.
- For removal of protein deposits soak the electrode in 1% pepsin in 0.1 M HCl for 15 minutes.
- For removal of inorganic deposits soak the electrode in 0.1 M tetra sodium EDTA for 15 minutes.
- For removal of oil and grease rinse the electrode with mild detergent or methanol. After any of the cleaning procedures, thoroughly rinse the electrode with deionised water, drain and refill the reference chamber, and soak the electrode in storage solution for at least 1 hour.

Q. Do pH buffers and filling solutions have a shelf-life?

A. The typical shelf-life for pH buffers and filling solutions is 2 years unopened and 6 months open. For best results, the pH buffer bottles should be sealed promptly to avoid carbon dioxide absorption.

Q. What is a good pH electrode slope range?

A. The acceptable slope range is 92% to 102%. Slopes below 92% indicate that the electrode may require cleaning or if cleaning does not help, the electrode should be replaced. Slopes above 102% indicate that the pH buffers are contaminated.

Q. What is a good pH electrode ISO-pH range?

A. The acceptable slope range is 6.5 to 7.5 pH. Values outside this range indicate that the electrode may require cleaning or if cleaning does not help, the electrode should be replaced.

Q. Do I need an Automatic Temperature Compensation (ATC) probe?

A. The most common cause of error in pH measurements is temperature. The slope of a pH electrode is highly dependent of temperature, and pH buffer values and sample values change with temperature. For the most accurate results an ATC probe is always recommended. There are three advantages for using an ATC probe. The meter recognises a particular pH buffer and autocalibrates with the correct pH value at the current temperature. The meter calculates and stores the correct slope value. The meter automatically adjusts the stored slope in memory to display the temperature adjusted pH value of the sample.

Q. What is the best absolute accuracy I can achieve?

A. Measuring errors depend on the electronic accuracy of the meter (generally 0.01 pH), the accuracy of the two buffers (generally 0.02 pH) and the chemical behaviour of the electrode. This results in an error of minimum 0.05 pH provided the sulutions are stirred. It is better to consider 0.1 pH as the best possible absolute accuracy. In extreme situations like measuring very low or high pH measurements, difficult solutions, or temperatures far from room temperature will increase the errors.

Q. Why will my pH system no longer autocalibrate?

A. When the pH system will not autocalibrate, the meter, pH electrode and pH buffers should be checked systematically. If your meter has a mV mode, measure the electrode mV in pH buffers:

- The electrode mV in a pH 7 buffer should be 0 ± 30 mV.
- The electrode mV in a pH 4 buffer (at 25°C) should be 160 to 180 mV more than the value in pH 7.
- The electrode mV in a pH 10 buffer (at 25°C) should be 160 to 180 mV less than the value in pH 7.
- If the mV values are outside of the above ranges, clean the pH electrode. If cleaning does not return the mV to an acceptable range, replace the electrode. Note: as long as the pH electrode has a slope between 92% and 102%, the electrode should be working properly. The pH buffers should be replaced if the measured mV values are outside of the acceptable ranges. Contaminated buffers may slightly contribute to shifted mV values.

Q. My pH electrode is drifting. What should I do?

A. There are three possible causes for electrode drift:

- If the electrode is new (or has been dry) and drifting, the electrode may not be properly conditioned. Refer to the appropriate electrode instruction manual for details.
- If the electrode is stable in buffers but not in the sample, the electrode may be incompatible with the sample or application.
- If the electrode is drifting in buffers and samples, the electrode may require cleaning.

Q. What should I do to measure in ethanol?

A. Basically, you need a pH electrode with a low resistance pH bulb, and the reference portion of the electrode should have a double junction design with an outer chamber that is refillable. Take a 10 ml aliquot of the regular 4 M KCl fill solution and dilute it to volume with the ethanol in a 100 ml volumetric flask. Use this solution to fill the reference chamber of the electrode. Ethanol solutions require the correct type of liquid junction, that is, one that is easily renewed and cleaned. An open liquid junction or sleeve junction electrode is recommended. The proper functioning of the glass electrode depends on the hydration of the glass layer which takes place on the surface of the pH sensitive glass membrane during soaking and measurement in aqueous solutions. As long as the electrode is frequently rehydrated, accurate measurements in non-aqueous or partly aqueous solutions such as ethanol are also possible. You are going to have dehydration of the pH bulb and reference junctions with the ethanol. You will have to switch out the electrodes for rehydration every few days. This can be accomplished by soaking in a slightly acidic buffer such as pH 4 buffer.