

TrupH

TrupH™ Measurement System

In this technical note, the Nernst equation is reviewed, and various components (measuring electrode, reference electrode, diaphragm, etc) of a TrupH measurement electrode are described. The interplay between these components, as well as their importance to accurate pH measurements, is also presented.

The NERNST Equation

pH measurements are used to determine the active hydrogen ion concentration in an aqueous solution. Three methods can be used for the direct determination of the pH value:

- 1 The visual method: the color of pH sensitive indicator (litmus) paper is compared to a standard color scale.
- 2 The photometric method: a spectrophotometer measures the peak absorption wavelength of a pH sensitive dye (phenolphthalein) in the solution.
- 3 The potentiometric method: an electro-chemical measurement that relates pH to the potential created by a chemical reaction between metals and hydrogen ions in the solution.

For bioprocess applications, the first two methods require drawing a sample from the bioreactor or fermentor, which is not only labor intensive, but precludes real-time feedback control. The potentiometric method is the only pH measurement which can be used as a continuous, in-line measurement for real-time control of bioprocesses.

The Potentiometric Method The potentiometric measurement method is based on the Nernst equation which describes the relationship between the galvanic potential of a defined electrode assembly and the chemical activity of the ion concentration being measured. The underlying principle of pH measurements is very similar to that of a battery, or galvanic cell.

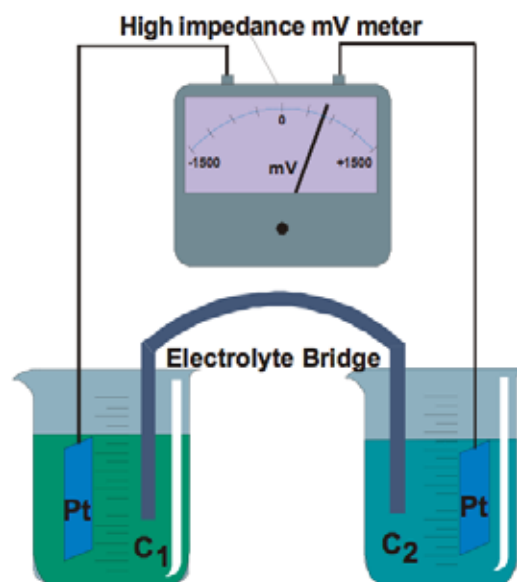
A pH electrode assembly consists of a measuring electrode, which is sensitive to the ion activity, and a reference electrode (or cell), similar to the one depicted on the right side of Figure 1. Although Figure 1 shows the half cells as spatially independent (for clarity), the reference half cell is generally contained in a separate compartment inside the same housing used for the measuring half cell. The pH is then obtained by measuring the

potential difference between the sampling electrode and the reference electrode. The operation of an electrode assembly in its simplest form is presented here.

Consider two electrodes (each a thin plate of polished platinum), each immersed in an aqueous solution. Assume that the two solutions have different hydrogen ion concentrations (C_1 and C_2), but that both are saturated with pure hydrogen gas and are at the same temperature, T . Each electrode will then generate a unique potential that reflects the active hydrogen concentration of the solution in which the electrode is immersed.

To be able to measure this potential, the electrical circuit must be closed: i.e., the two solutions must be connected by a salt bridge (electrolyte bridge) and the two electrodes must be connected to a high impedance voltmeter. Because the current in the electrical circuit is negligible, the chemical composition of the two solutions is not altered. Furthermore, the salt bridge forms a phase boundary between solutions C_1 and C_2 .

Figure 1 Example of a simple pH electrode assembly for measuring the pH of solution C_1 using reference solution C_2 . Two separate cells, joined by an electrolyte bridge are shown. The two electrodes are connected to a high impedance voltmeter.



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The difference in active hydrogen-ion concentration in the solutions will generate a potential difference between the two platinum electrodes. This potential, E, is related to the active hydrogen-ion concentrations, C₁ and C₂, by the Nernst equation:

$$E = \frac{R \cdot T}{n \cdot F} \times \log \frac{C_1}{C_2}$$

Where E is potential difference (in mV), T is the temperature of the solutions (in Kelvin), n is the charge number of the ion being measured (n=1 for hydrogen ions), R is the ideal gas constant (8.31439 J/mol/K) and F is the Faraday constant (96495.7 C/mol). Conveniently, since pH is described as the log of the activity, and the potential, E, across the glass electrode also has a log dependence on activity, it necessarily follows that the generated potential is a linear function of pH.

If we consider a ten-fold difference in active hydrogen concentration between C₁ and C₂ (which corresponds to one unit step on the pH scale), we obtain a potential difference called the Nernst potential, U_N, at process temperature, T, given by:

$$U_N(T) = \frac{R \cdot T}{n \cdot F} \times \log \frac{10 \cdot C_2}{C_2} = \frac{R \cdot T}{n \cdot F} \times \log(10) = 58.16 \frac{T [K]}{293.15} \text{ mV}$$

From the Nernst potential equation, we see that the Nernst potential is, similarly to hydrogen ion activity, temperature dependent. The term “RT/nF (Log (10))” is sometimes called the Nernst or slope factor. Table 1 illustrates this temperature dependence over a wide range of process temperatures. Typical bioprocess temperatures are highlighted in pink. Even over the limited bioprocess temperature range, the Nernst potential changes almost 3 mV, or 5%, which can introduce significant error into the pH measurement. Therefore, temperature compensation is critical in achieving accurate pH measurements for bioprocess control.

Figure 2 illustrates the relationship between the pH scale and the Nernst potential. 1 molar aqueous HCl corresponds to a pH of 0, while 1 molar aqueous NaOH corresponds to a pH

of 14. These boundaries for the pH scale lie 7 pH units from the center point of neutrality (pure water). In Nernst potential units, they correspond to measured voltages of +407.12 mV and -407.12 mV, respectively. In other words, the voltage measurement requirements to read the Nernst potential for the entire pH scale from 0 to 14 is 814.24 mV or approximately 1 V. Similarly, at 25°C, for every pH unit change, the total measured potential will (ideally) change by 59.16 mV.

T °C	U _N mV	T °C	U _N mV	T °C	U _N mV
0	54.20	35	61.14	70	68.08
5	55.19	40	62.13	75	69.08
10	56.18	45	63.12	80	70.07
15	57.17	50	64.12	85	71.06
20	58.16	55	65.11	90	72.05
25	59.16	60	66.10	95	73.04
30	60.15	65	67.09	100	74.04

Table 1 Nernst potential as a function of temperature

The precision of the voltage measurement of the Nernst potential by a pH meter/transmitter therefore directly determines the precision of the pH measurement loop. The accuracy of the pH measurement, however, requires that in order to correctly measure the actual Nernst potential, the electrical circuit formed by the meter/transmitter, cable, and pH electrode, must have minimal offsets and impedance loading. For more details on the pH scale, please refer to the technical note entitled “pH Measurement Definitions”. For more details on practical pH measurements and potential errors, please refer to the technical note entitled “Practical pH Measurements”.

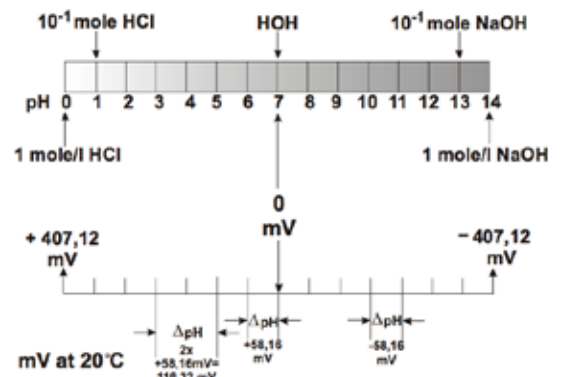
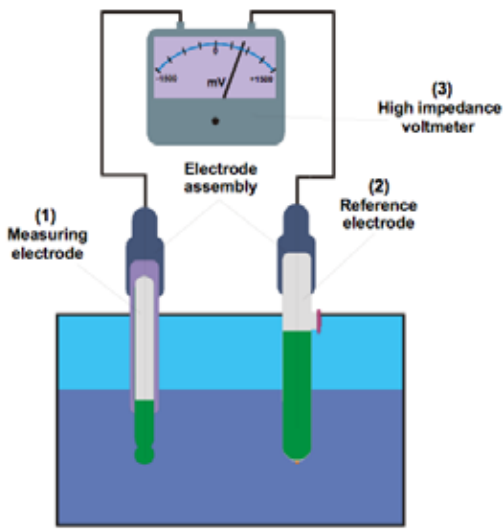


Figure 2 pH Scale related to the Nernst potential.



The pH Measurement System

The basic pH measurement system, shown in figure 3, consists of three components:

- 1 a measuring electrode, sensitive to pH,
- 2 a reference electrode, and
- 3 a high impedance voltmeter.

A detailed description of each basic component is presented in the sections that follow.

Figure 3 Three components of a basic pH measurement system: measuring and reference electrodes, and high impedance voltmeter.

The Measuring Electrode

The purpose of the measuring electrode is to determine the pH value of an aqueous solution.

A platinum/hydrogen electrode was originally used (1897) to measure the hydrogen ion concentration in aqueous solutions. The hydrogen electrode consists of a platinum plate or rod that is coated with platinum black, and is exposed to a flow of hydrogen gas. A silver wire coated with silver chloride serves as a reference electrode in the measurement loop. Today, the hydrogen electrode still serves as a laboratory reference standard, because it can yield extremely accurate results. However it is no longer used for practical measurements in bioprocess applications, because it is difficult to use.

The Measuring Electrode

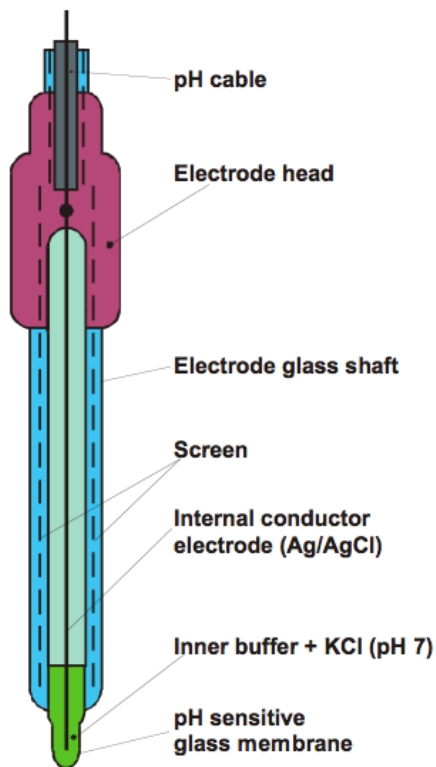
The development of the glass measuring electrode enabled simple and reliable pH measurements for bioprocess applications. Owing to their inherent reliability and measurement accuracy when combined an electronic readout, glass electrodes have become the de facto standard for pH measurements today. In turn, pH control has now become as common as temperature, dissolved oxygen, and mass balance in bioprocess control.

The shaft of a pH electrode (figure 4, blue) is made from glass that is highly resistant to hot alkaline solutions and whose electrical resis-

tance is several times greater than that of the membrane glass. The shaft glass is insensitive to pH changes and has thick walls to be mechanically rigid and robust.

The glass membrane, which detects changes in pH, is cylindrically shaped with a bulb at the end, and is fused to the glass shaft (figure 4, green). The glass membrane is made from special glass that is hydrogen ion sensitive. The glass electrode is partly filled with a buffer solution, normally having a pH value of 7. A defined amount of potassium chloride (KCl) is added to this internal buffer.

The Construction of a Glass Electrode



A silver wire coated with silver chloride (Ag/AgCl) is inserted into the glass electrode (figure 4, black). This wire serves both as the Ag/AgCl electrode immersed in the internal buffer solution, as well as the conducting wire from the electrode to the core of the pH cable (figure 4, grey) found at the top of the electrode.

Figure 4 Schematic diagram of a glass pH measuring electrode.

The Glass Membrane

Although many types of glass can produce a potential difference proportional to the hydrogen ion concentration in an aqueous solution, only certain special types of glass, such as Mc-Innes glass (Corning 015), can produce galvanic potentials that follow the Nernst equation over a wide pH range. The improvement of these special glasses is an ongoing research effort at electrode manufacturers world-wide.

When the membrane glass of a measuring electrode comes into contact with an aqueous solution, it forms a thin gel layer, approximately 10^{-4} mm thick, between the glass surface and the solution (figure 5). In fact, without the gel layer there can be no pH measurement. For a completely dry electrode, it takes approximately one to two days for the gel layer to fully develop. Therefore, a measuring electrode must be hydrated for a minimum of 24 hours prior to use. For this reason, Finesse delivers all TrupH electrodes already hydrated (the membrane is kept wet with a KCl solution in a plastic cap), so that they are ready for immediate use.

The thickness of this gel layer depends on the quality and composition of the membrane glass, as well as the temperature and the pH value of the measured solution. As the internal side of the glass membrane is in contact with the inner buffer (an aqueous solution of pH 7) a gel layer is also formed on the inside of the glass membrane (figure 5). The thickness and composition of the gel layer determine the response time and the characteristic slope of the glass electrode. Therefore the gel layer is of critical importance to the electrode performance.

A continuous exchange of hydrogen ions (H+) in the gel layers and the solutions takes place on both sides of the membrane. This ion exchange is controlled by the H+ concentration of both solutions. If the sample solution is alkaline, the H+ ions migrate out of the gel layer, and a negative charge is developed on the outer gel layer. Furthermore, as the hydrated gel layer forms, a voltage potential develops between the surface of the glass and the aqueous solution being measured. A potential is developed on each side of the glass membrane.

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If the H^+ ion concentrations of both inner and outer solutions are the same (on both sides of the glass membrane), the ion exchange stops after equilibrium has been reached between the H^+ ions in the solutions and the H^+ ions in the gel layers. Both sides of the membrane glass will have the same potential, and the potential difference will be 0 mV.

However, if the H^+ ion concentrations between the inner buffer and the outer solution are different, a potential difference will develop between

the inner and outer surfaces of the membrane glass. Because the inner solution of the electrode is at a constant pH value, the inner surface potential remains constant. Therefore, the potential difference that is measured across the glass membrane will be proportional to the difference in pH between the inner (constant) buffer and the outer (sample) solution.

In order to actually measure the potential difference (called the membrane potential) the membrane glass itself must be conductive. The glass is therefore usually doped with ions of an alkali metal (Li^+ in most present-day glasses or Na^+ ions in older membrane glasses) that achieve mobility within the membrane glass.

The glass membrane shown in figure 5 is a sphere. Glass membranes, however, can be made in many different shapes, including, but not limited to, hemispherical ends, flat ends, and pointed ends. The membrane glass is generally very thin (~25 to 200 μm) and the various shapes lead to a set of design trade offs. The spherical ends have the lowest impedance and fastest response time, but they break the most easily, whereas the flat ended probes are the most rugged but have the slowest response time and the highest impedance. TrupH glass membranes are optimized to achieve the best compromise in response time, impedance, and robustness for bioprocess applications.

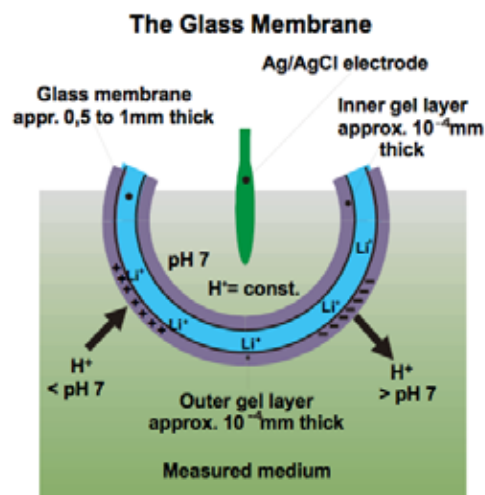


Figure 5 Formation of gel layers on the inner and outer surfaces of the membrane glass. A potential is formed across the glass membrane that is proportional to the pH difference between the measured medium and the inner buffer solution.

The Reference Electrode

The reference electrode represents a well-defined electrical connection between the measured medium and the pH meter. Simply put, the reference electrode provides a stable voltage (typically 0 mV, or as close as possible to zero) connection to the sample solution, in order to close the pH measurement loops and determine the measuring electrode's voltage. The accuracy of the pH measurement is often determined by the reference electrode and therefore the choice of reference electrode is of significant importance. An ideal reference electrode should produce a predictable potential that follows the Nernst equation. A stable reference electrode should also have a low temperature coefficient and minimize hysteresis as a function of temperature.

Similarly to the measuring electrode, a reference electrode typically consists of an internal electrode immersed in a defined electrolyte. In contrast to the measuring electrode, the reference electrolyte must be in contact with the sample solution (medium). Over time, various reference systems have been investigated, but only two systems, the mercury-mercurous chloride (calomel) and the silver-silver chloride (Ag-AgCl) reference electrodes have been found to be sufficiently reliable in providing an accurate and stable reference potential.

At low and stable temperatures (< 80°C), calomel electrodes have high output voltage stability and high accuracy (~ hundredth of a millivolt). However, Ag-AgCl electrodes are the most widely deployed, because they are easy to manufacture,

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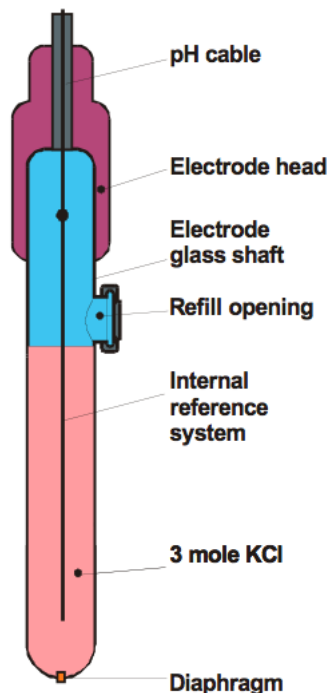


Figure 6 Schematic diagram of a reference electrode.

have a fast stabilization time for most process temperatures (between -30°C and 135°C), and exhibit very reproducible behavior. Furthermore, Ag-AgCl reference electrodes remain stable and accurate during large temperature fluctuations and at high temperatures (up to 135°C). All TrupH electrodes employ the silver-silver chloride reference system.

Figure 6 illustrates the design of a Ag-AgCl reference electrode. The internal electrode consists of a silver chloride coated silver wire which is immersed in 3 molar KCl solution. The KCl solution fills the glass body (figure 6, pink) of the reference electrode. In non-gel-filled (non Finesse) electrodes, the reference solution must be topped up on a regular schedule through the refill opening. The silver wire is also connected to the pH cable in order to provide the reference voltage.

A diaphragm (normally a small porous ceramic rod) is fitted at the bottom of the reference electrode to permit the potassium chloride to diffuse into the sample liquid (medium). The electric circuit of the pH measurement loop is completed when the silver-silver chloride wire is connected via a coaxial cable to the pH meter/transmitter.

The Combination (Single Rod) Electrode

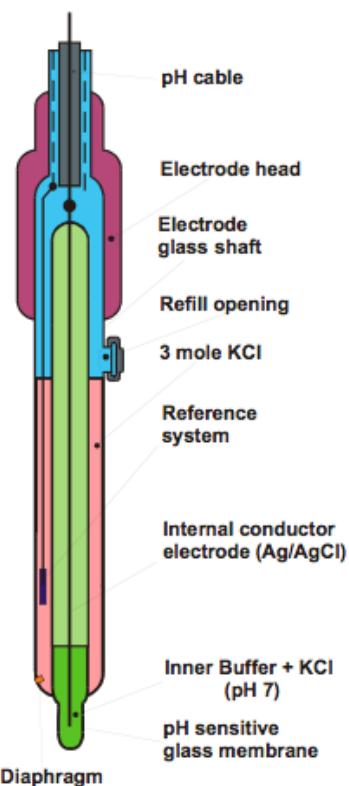


Figure 7 Schematic diagram of a combination (TrupH) electrode.

Since 1947, electrode manufacturers have combined the measuring and reference electrodes into a single device called the combination electrode. The combination electrode simplifies the pH measurement and provides a convenient solution to the end user. Combination electrodes are now employed in almost all bioprocess applications. TrupH electrodes are gel-filled combination electrodes.

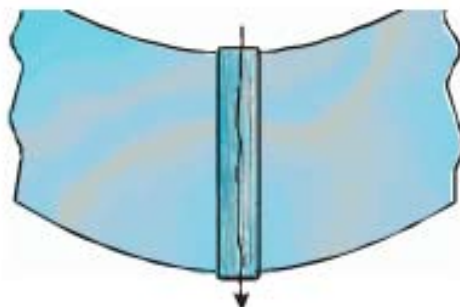
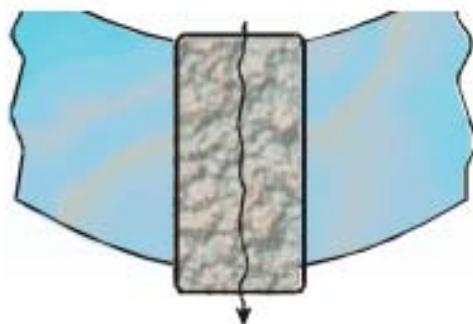
In a standard combination electrode (figure 7), the reference electrode (pink) is built into concentric space surrounding the measuring electrode (green). The concentric space is filled with reference electrolyte and contains the internal reference system. A diaphragm near the bottom of the reference chamber serves as the junction between the KCl reference solution and the sample liquid (medium). Because the reference electrolyte is a conductive medium, it further acts as a screen for the measuring electrode.

However, reference electrodes based on a liquid reference electrolyte are maintenance intensive because their electrolyte level must be controlled and regularly topped up. The development of gel-filled reference electrodes, such as the Finesse TrupH electrode family, provides an almost maintenance-free product.

TrupH electrodes use pressurized PHERMLYTE™ (3 mol/l KCl electrolyte in gel form) reference electrolyte that keep the liquid junction of the reference electrode clog-free. The diaphragm is made from ceramic (COATRAME™). The glass shaft is often reinforced with an outer sleeve.

The Diaphragm

The diaphragm is a critical component of the reference electrode. It provides an electrolytic interface between the Ag-AgCl electrode and the sample solution. In most electrodes, the diaphragm consists of a porous ceramic plug fused into the glass wall of the electrode at the lower end of the reference electrode.



The PHERMLYTE™ electrolyte reference system allows pH measurements down to pH 0, survives operating temperatures above 90°C, and is resistant to organic solvents. pH measurements utilizing the PHERMLYTE™ reference system are both reliable and accurate. Furthermore, because the KCl saturated gel is free of AgCl, there is no possibility of silver sulphide contamination when measuring the pH value of solutions containing sulphides.

For bioprocess applications, TrupH electrodes that use the PHERMLYTE™ electrolyte are suitable for steam sterilization, autoclave, and clean-in-place.

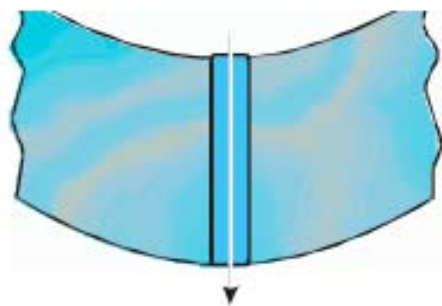
Various diaphragm types (differing in construction and shape) are available. Each type has its advantages and limitations. Normally, the measurement application determines the use of a specific diaphragm type. TrupH electrodes use a 1 HP Coatramic diaphragm (porous ceramic). The five types of most widely used pH electrode diaphragms are:

a Porous Ceramic Diaphragm

- Most frequently used today
- High chemical resistance
- Easy to manufacture.
- Reproducible electrolyte flow
- Because of its large surface, vulnerable to contamination.
- TrupH electrodes combine a COATRAME™ ceramic diaphragm and PHERMLYTE™ reference electrolyte for bioprocess applications

b Platinum Fiber Diaphragm

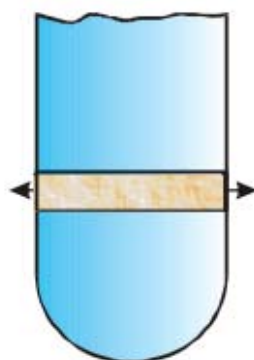
- Consist of very fine platinum wires that are loosely spun together and fused into the glass
- Electrolyte flow is less reproducible than ceramic diaphragms
- Good resistance to contamination



c SINGLE PORE™ Diaphragm

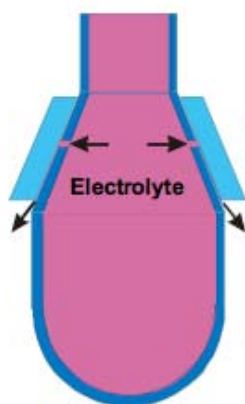
- Strictly speaking, not a diaphragm at all
- Very small glass capillary allows a larger leakage rate than a ceramic or platinum diaphragm
- Constant and reproducible electrolyte flow
- Minimal clogging or contamination
- Most accurate and repeatable results.

During a traceability test in 1997, the German Federal Physical Technical Institute (PTB) demonstrated that SINGLE PORE™ pH electrodes have the best accuracy in the marketplace (“Traceability of pH measurement” by Petra Spitzer; ISBN 3-89429-877-4 or ISSN 0947-7063).



d Annular Ceramic Diaphragm

- Formed by a porous ceramic layer between two glass tubes
- Direction of the measured medium is not critical owing to the annular shape of this junction
- The electrolyte flow is not reproducible
- Mainly applied in gel-type electrodes



e Ground Sleeve Diaphragm

- Ideally suited for suspensions or emulsions (easily cleaned by pulling up the glass sleeve) and low ionic solutions or in non-aqueous media
- Electrolyte flow rate depends on the roughness of the ground glass surface of the sleeve and the tightness of the sleeve fit.
- Not suitable for applications where the pH electrode is subjected to vibration (loosens the diaphragm sleeve)

For bioprocess applications, the COATRAMIC™ diaphragm is the best choice and provides the greatest performance and reliability advantages to TrupH electrodes. Because it does not clog easily, a TrupH electrode is more resistant to bio-fouling and requires less maintenance than competing products.

In principle, a diaphragm should provide a deliberate leak of the reference electrolyte solution into the sample medium and simultaneously prevent unrestricted mixing of both solutions within the reference electrode. Penetration of the measured

solution into the reference electrolyte and the subsequent poisoning of the reference system does occur frequently, however, especially when the measured solution is pressurized.

Some pH electrodes use a pressurized reference electrolyte vessel in order to counteract the penetration of the measured solution through the diaphragm. As a rule of thumb, a differential pressure of 100 kPa (above the pressure of the measured solution) will normally suffice. As a result, a small amount of reference electrolyte solution will penetrate the sample solution, which is generally

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not of significance to the process. Pressurization does provide benefits by decreasing the reference electrode resistance into the 0.1 kΩ to 2 kΩ range, improving the reproducibility of the measurement, and preventing the diaphragm from clogging.

Note that before a TrupH electrode is immersed into the sample solution, the stopper which closes the diaphragm must be removed! Otherwise, a pH measurement cannot be obtained.

Measuring the Electrode Potential Difference

The pH measuring and reference electrodes form the pH measurement loop within the sample solution (see figure 9). The underlying principle of the pH measurement loop is very similar to that of a battery or galvanic cell, both of which produce an output potential (or e.m.f) as a result of an electro-chemical reaction.

The difference in potential between the measuring and reference electrodes is a function of the sample solution pH value. According to the Nernst equation, this voltage should change by 59.16 mV for each pH unit at 25°C. In principle, such a voltage change should be straightforward to measure. However, in practice the voltage measurement is difficult because the electrical impedance of the glass electrode, and especially of the glass membrane, are very high, so that the pH measurement loop cannot produce a meaningful current (not even large enough to detect with the moving coil of a DC voltmeter). Therefore, any measurement method that draws current from the pH measurement loop will reduce the output voltage and distort the actual voltage reading.

The reference electrode's connection to the test liquid may have an impedance of several kΩ, while the measuring electrode's impedance can range from ten to several hundred MΩ depending on the electrode design. Note that the measuring and reference electrodes are in series, and as such their impedances are additive. The total resistance of a glass membrane therefore varies between 10 MΩ and 1 000 MΩ at 25°C, and increases further with decreasing temperature. The upper limit of membrane resistance is about 5 000 MΩ (5 x 10⁹ Ω).

The fact that the total electrode impedance is often very large poses a problem for accurately measuring the voltage generated. In order to achieve a measurement accuracy of ±0.1 pH units, the internal resistance of the meter/transmitter must

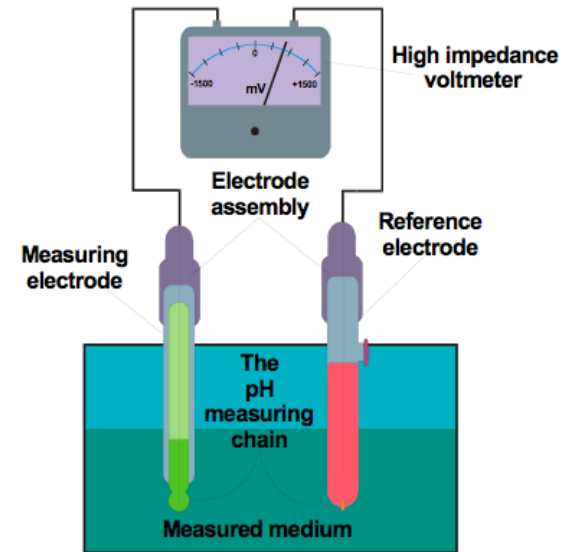


Figure 9 pH measurement loop showing the measuring and reference electrodes, and a high impedance voltmeter.

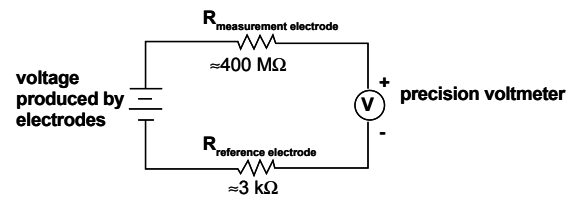


Figure 10 Electrical schematic of a typical pH measurement loop

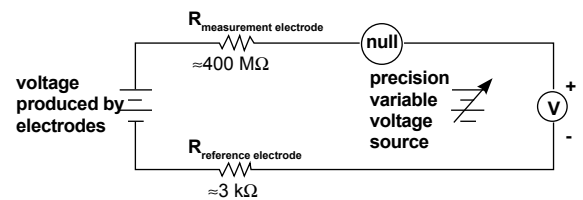


Figure 11 Electrical schematic of circuit that overcomes high impedance of pH electrode

exceed the resistance of the measuring electrode at least one hundred fold. A membrane resistance that is too high will produce erroneous readings on the electronic readout of the pH value. For practical purposes, the pH meter/transmitter should have an internal resistance of at least 10^{12} ohms.

In short, a conventional voltage meter's internal resistance is generally too low to perform this measurement without affecting the circuit and the pH measurement. The problem is represented in the electric circuit schematic shown in figure 10.

Even a very small current traveling through the high resistances of each component in the circuit (especially the measurement electrode's glass membrane), will produce relatively substantial voltage drops across those resistances, thereby seriously reducing the voltage seen by the meter. Making matters worse is the fact that the voltage differential generated by the measurement electrode is very small, in the millivolt range (~ 58.16 millivolts per pH unit 20°C). The meter used for this task must be very sensitive and have an extremely high input resistance.

This problem is often solved by using a more clever circuit (see figure 11) which allows a more precise measurement.

In the circuit shown in figure 11 (a common design for pH electronics), a precision voltage supply is adjusted until zero current flows through the circuit, thereby creating a null. The voltmeter is connected in parallel with the supply and can be viewed to obtain a voltage reading. With a null reading, there should be zero current in the pH electrode circuit, and therefore no voltage dropped across the resistances of either electrode, giving a precise reading of the "measuring electrode's" voltage at the voltmeter terminals. The fundamental premise of this approach is that it is easier to find a null than to precisely measure a set voltage, namely a small number with large sources of error.

Wiring requirements for pH electrodes are stringent and stipulate clean connections and short distances of wire (10 yards or less, even with gold-plated contacts and shielded cable) for accurate and reliable measurement.

General Observations for Troubleshooting TrupH Electrodes

The comments provided below relate to the practical operation of pH electrodes. Please note that some of these observations may not be relevant for your specific bioprocess application. These comments are intended to provide the end user with some insight into potential problems encountered when operating pH electrodes, and summarize briefly a few troubleshooting tips. If you encounter any difficulties operating TrupH electrodes in your process, please contact your local Finesse representative for detailed technical support.

- All pH electrodes have a finite life, and that lifespan depends greatly on the type and severity of service. In some applications, a pH electrode life of one month may be considered long, and in other applications the same electrode(s) may be expected to last for over a year. Storage in a buffer solution of pH = 4 should maximize the storage life.
- Because the glass (measurement) electrode is responsible for generating the pH-proportional voltage, it is the one to be considered suspect

if the measurement system fails to generate sufficient voltage change for a given change in pH (approximately 58.16 millivolts per pH unit at 20°C), or fails to respond quickly enough to a fast change in test liquid pH.

- If a pH measurement system "drifts," creating offset errors, the problem likely lies with the reference electrode, which is supposed to provide a zero-voltage connection with the measured solution.
- Because the pH unit is a logarithmic representation of hydrogen or hydroxyl ion concentration, there is an enormous range of process conditions represented in the 0 to 14 pH scale. Also, due to the nonlinear nature of the logarithmic scale, a change of 1 pH unit at the top end (12 to 13 pH) does not represent the same quantity of chemical activity change as a change of 1 pH at the bottom end (from 2 to 3 pH). Control system engineers must be aware of this dynamic if there is to be any hope of controlling process pH to a stable value.

- The following conditions are hazardous to measurement with glass electrodes: high temperatures, extreme pH levels (either acidic or alkaline), high ionic concentration in the liquid, abrasion, hydrofluoric acid in the liquid, and any kind of material coating on the surface of the glass.
 - Temperature changes in the measured liquid affect both the response of the measurement electrode to a given pH level, and the actual pH of the liquid. Temperature measurement devices can be inserted into the liquid, and the signals from those devices used to compensate for the effect of temperature on pH measurement, but this will only compensate for the measurement electrode's mV/pH response, not the actual pH change of the process liquid.
 - Calibration of the pH meter can be affected by:
 - Contamination of electrolyte solution
 - Electrolyte evaporation
 - Decay of Ag/AgCl wire
 - Decay of the reference junction
 - Aging of glass electrode and gel layer
- Acknowledgements: We would like to Erich K. Springer for his contributions to this technical note.*