

The Essentials of pH Measurement Design, Installation, Maintenance, and Improvement

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Abstract

While the concept of the pH measurement that was first published 100 years ago remains essentially the same, significant technological improvements in glass formulation and construction and reference electrode design have increased pH electrode life and performance. Considerable experience has been gained in terms of electrode installation methods for difficult process conditions as the scope of pH applications has expanded. Yet much of this practical expertise has not been documented and the ability of embedded diagnostics and calibration records and wireless devices to eliminate common problems and provide smarter and more effective maintenance has not been explored.

This paper addresses the essential aspects of each major phase of a successful pH measurement implementation from selection, installation, calibration, to performance monitoring. The relative merits of various measurement types and principles, application strong points and watch-outs, installation practices, factory and field calibration methods, wiring and grounding problems, troubleshooting, and online diagnostics are concisely discussed. The examples focus on demanding industrial applications that require 0.01 to 0.02 pH accuracies despite harsh conditions from sterilization-in-place in biopharmaceutical processes and high reaction temperatures, salt, polymer, and crystal concentrations in chemical processes. The paper concludes with recent test results of wireless pH measurements in a bioreactor and looks forward into future improvements.

Principles

100th Anniversary of the Extraordinary Rangeability and Sensitivity of pH

The concept of the pH measurement as the negative logarithm of the hydrogen ion concentration was first published in 1909 by Soren Sorensen of the Carlsberg Laboratory of Copenhagen. 100 years later, the glass pH electrode is still the most prevalent online composition measurement in the process industry. The logarithmic relationship offers an incredible rangeability and sensitivity far beyond the capability of any other common

field measurement. For the 0-14 pH scale, the glass electrode can measure 14 orders of magnitude change in hydrogen ion concentration. At 7 pH, the glass electrode can detect changes in the hydrogen ion concentration to the eight decimal place.

Effect of Process Concentration and Temperature on Process pH

More exactly pH is a function of hydrogen ion activity as defined by Equations 1 and 2. Most pH measurements are in extremely dilute water solutions where the hydrogen ion concentration is the same as the hydrogen ion activity. In Equation 3, this one to one relationship corresponds to a unity activity coefficient. In some chemical reactors, the concentration of ions or non-aqueous solvents is high enough to cause the activity coefficient to significantly decrease. In these applications, the pH can change even if the hydrogen ion concentration is constant if the concentration of ions and solvent changes.

The product of the hydrogen and hydroxyl ion concentration in a water solution depends upon the water dissociation constant (pK_w) per Equation 4. The water dissociation constant changes with temperature on the average about -0.03 per °C which for a given hydroxyl ion concentration causes the pH to change -0.03 per °C for strong basic solutions. This change in solution pH with temperature is not corrected by the standard temperature compensator. A 8.3 pH hot waste stream at 50 °C that cools down to 25 °C by the time it reaches the effluent discharge will be above 9 pH, possibly in violation of an environmental constraint. Not shown here is that the change in the dissociation constants of weak acids and weak bases with temperature will also affect the pH.

$$a_H = 10^{-pH} \quad (1)$$

$$pH = -\log(a_H) \quad (2)$$

$$a_H = \gamma * c_H \quad (3)$$

$$c_H * c_{OH} = 10^{-pK_w} \quad (4)$$

Where:

a_H = hydrogen ion activity (gm-moles per liter)

c_H = hydrogen ion concentration (gm-moles per liter)

c_{OH} = hydroxyl ion concentration (gm-moles per liter)

γ = activity coefficient (1 for dilute solutions)

pH = negative base 10 power of hydrogen ion activity

pK_w = negative base 10 power of the water dissociation constant (14.0 at 25°C)

Glass Electrode

The most popular pH sensor in chemical and waste treatment processes is the combination electrode that consists of a glass measurement electrode surrounded by a

reference electrode. A spherical or hemi-spherical glass bulb has a pH sensitive surface that develops a millivolt potential (E_1) that is proportional to pH of the process. The inside surface of the glass electrode also develops a potential that corresponds to a 7 pH buffer. The sensing of pH depends upon a thin hydrated layer on the glass surface. If the surface in contact with process is in the same condition as the surface on the interior of the bulb, the difference in the millivolt potentials between the interior and exterior glass surfaces can be described by the Equation 5, which is a simplification of the Nernst Equation. The standard temperature compensator corrects for the change in the millivolts generated per pH unit by the temperature factor in Equation 5. Typically an RTD sensor embedded in the electrode is used to provide automatic compensation that effectively keeps the temperature factor at 298 °K (25 °C) in Equation 5. At 25 °C we have Equation 6 with the often stated potential for the glass measurement electrode of -59.16 millivolts/pH. If you plot pH versus millivolts per Equation 6, the intercept is at 7 pH and 0 millivolts. The slope is -59.16 millivolts, which corresponds to 100% efficiency. As the pH electrode ages, the slope and efficiency decreases.

Reference Electrode

There must also be a reference electrode whose internal electrolyte is in contact with the process to complete the circuit through the process liquid. For the combination electrode shown in Figure 1 there is concentric porous ring called a “liquid junction” around the glass bulb for the potassium chloride reference electrolyte to move through to reach the process. Since potassium and chloride ions migrate at the same rate (equitransferent), the ions arrive at the process at the same time so that the potential (E_5) at the liquid junction is zero. Since the reference junction by design is porous, process ions can migrate into the reference electrode. Process ions rarely migrate at the same speed. An excess of process ions builds up in the liquid junction until a potential becomes large enough to stop further migration of ions. The liquid junction potential (E_5) changes until this equilibrium is reached. For dilute low ionic strength aqueous solutions between 4 and 10 pH, this potential is quite small (e.g. 15 millivolts). As process ions move into the liquid junction, they can plug the junction. Plugging reduces the contact of the reference electrolyte with the process, which increase the resistance (R_6) of the junction. If process ions can continue to freely move inside the reference electrode, additional extraneous potentials are formed. Chemical attack of the internal silver-silver chloride reference electrode can occur that changes the internal reference potential (E_4). This contamination of the internals of the reference electrode is commonly termed “poisoning”. Reference electrodes in chemical and waste treatment processes typically have multiple junctions to protect the inner sanctum of the internal electrode and use gels or porous solids to retard the migration of process ions. When acids or bases participate in chemical reactions, the acid and base concentration is large and consequently the ionic strength is high enough to cause a relatively large liquid junction potential. Often these chemical reactions require tight control (e.g. 0.02 pH). If the liquid junction potential is larger than the allowable pH measurement error, a flowing reference junction is used where a continual flow of electrolyte into the process is maintained to sustain a small constant liquid junction

potential. Another application for a flowing junction is water so pure there is concern of loss of insufficient ions in the process. In this case, the flow of electrolyte into the process is used to sustain electrical continuity between the reference and measurement electrode.

$$E_1 - E_2 = 0.1984 \cdot (T + 273) \cdot (7 - \text{pH}_1) \quad (5)$$

at $T = 25 \text{ }^\circ\text{C}$:

$$E_1 - E_2 = -59.16 \cdot (\text{pH}_1 - 7) \quad (6)$$

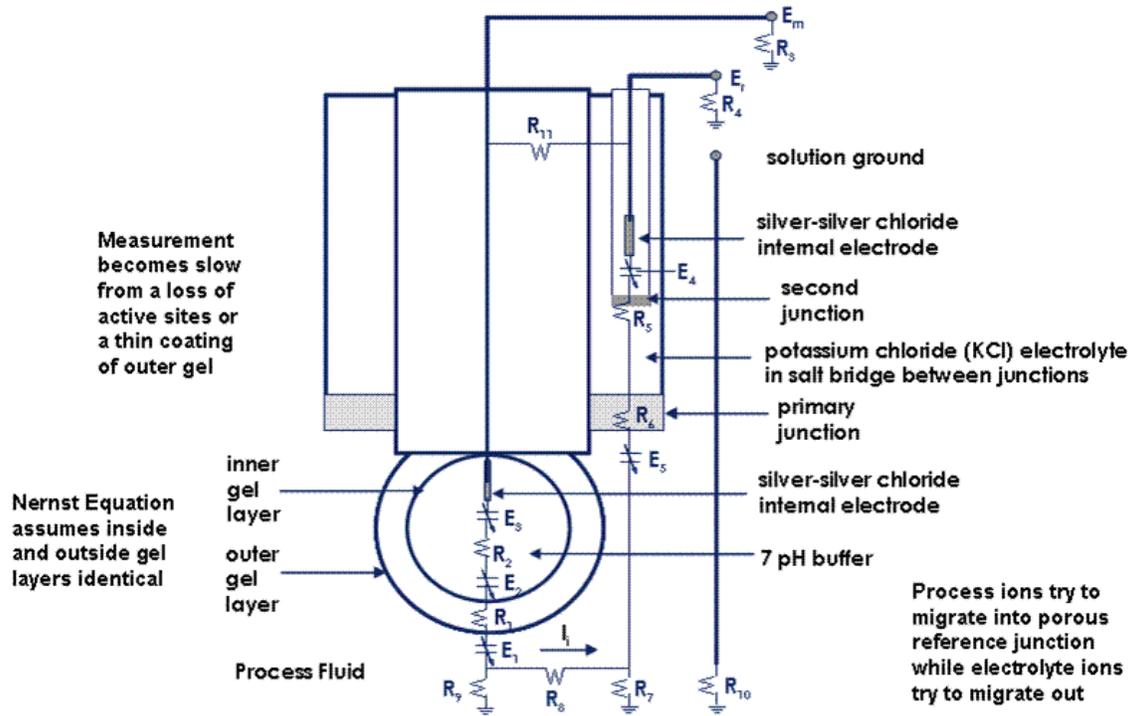


Figure 1. Combination pH electrode - The potential (E_1) developed at the glass electrode surface is indicative of the process pH. Changes in the hydrated glass surface layer activity and shunt resistance (R_{11}) are corrected by a slope calibration adjustment. Changes in the liquid junction potential (E_5) are corrected by a zero (offset) adjustment.

Resistances

The resistances in the path between the internal electrodes in the glass and measurement electrodes shown in Figure 1 are normally all small compared to the glass measurement electrode resistance of 20 to 200 megOhms. The current flow is extremely small making the potential drop across these resistances negligible. The process fluid resistance (R_8) is

negligible except for non-aqueous solvents or ultra pure water. The resistances to earth ground should all be large enough to suppress noise from electromagnetic interference and ground loops.

A decrease in the high impedance shunt resistance (R_{11}) can cause a loss of the electrode slope (efficiency). The degree to which the measured potential is decreased will depend on the relative magnitudes of the glass electrode impedance and the impedance of the shunt. In one case of bad sensors with low shunt resistances, at room temperature the sensors had low slopes (short-spanned), but at higher temperature the sensors had adequate slopes for that temperature. This was due to the decrease in glass impedance at higher temperature, which decreased the effect of the high impedance shunt.

How bad can it be? If you look at the resistance (R_{11}) of the high impedance shunt as a multiple of the resistance (R_1) of the high impedance glass electrode ($R_{11} = n * R_1$), you can get an idea of how much the measured electrode efficiency would be lowered:

| n | <u>Efficiency</u> |
|-----|---------------------|
| 100 | 99% |
| 50 | 98% |
| 20 | 95% |
| 10 | 91% |
| 5 | 67% (bad electrode) |

The decrease in the shunt resistance (R_{11}) can be accelerated by aging due to the exposure of o-rings and seals to a harsh process, which could attack the materials of construction and introduce some leakage, as well as the effects of prolonged heating on the internal potting materials, which could break down over time. The decrease has little to do with the glass electrode itself, but with the integrity of the sensor construction over prolonged periods. It is also likely that at least some high impedance shunting may be built into the sensor.

Selection

Transmitter

In the selection of the transmitter, key features should be considered. The transmitter should provide solution pH temperature compensation in addition to the standard Nernst temperature compensation. Additionally, the transmitter should provide assistance during buffer calibrations and diagnostics for the transmitter and its electrodes.

- A configurable solution temperature compensation should correct the pH measurement for changes in solution pH, which avoids the error of making a

pH adjustment to a hot solution to correct a pH offset due to temperature alone, and eliminates the seemingly inexplicable difference between the lab and on-line measurements in hot processes.

- All solutions above 7 pH will exhibit at least some decrease in pH with increasing temperature, due to changes in the dissociation constant of water, which can be compounded by changes in the dissociation constants of weak acids and weak bases.
- Solutions below 7 pH can also exhibit temperature dependence due to changes in weak acid dissociation constants with temperature.
- The sensor millivolt signal and temperature, as well as the calibration constants (sensor slope and zero offset) should be accessible as an aid in troubleshooting.
- The calibration routines provided by the transmitter should allow time for sensor stabilization, and include temperature compensation for buffer pH changes with temperature to avoid calibration errors.
- The transmitter should include diagnostic fault alarming for the sensor and transmitter itself, as well as calibration errors.

Electrodes

The selection of the right glass largely depends upon the pH range and temperature. Some suppliers offer low pH glass that minimizes the acid error below 1 pH, high pH glass that minimizes the alkalinity (sodium ion) error above 10 pH, low temperature glass that prevents an excessively high glass resistance below 10 °C, a high temperature glass that slows down the aging process that accelerates for temperatures above 25 °C, and a glass that withstands repeated steam-in-place (SIP) sterilizations. Many suppliers offer a single general purpose (GP) glass that address many of these issues well enough to avoid the complication of selecting, stocking, and replacing a multitude of special glasses. However, the life of GP glass in high temperature and SIP applications can be unacceptable. Figure 2 shows that a high temperature glass can double the life expectancy at 50 °C and higher temperatures.

Flat glass electrodes are promoted to minimize coatings and abrasion. The fluid velocity, electrode shroud, location, and probe holder geometry plays a bigger role than glass surface design in preventing coatings and abrasion. Most of the success in reducing coatings was achieved by a narrowing of the probe holder increasing the fluid velocity at the surface. Flat glass electrodes have a more limited pH range and thinner glass with stress points. The spherical or hemispherical bulbs are more accurate and rugged but public perception still creates a sizeable although declining market for flat glass.

The selection of the reference electrode has the ultimate goal of keeping the reference potential as constant and small as possible despite extremes in process composition and the presence of solids or sticky fluids. High and variable concentrations of acids, bases, ions, and non-aqueous solvents can cause large and fluctuating liquid junction potentials. Ultra low conductivity solutions increase the resistance of the path from the reference to

the glass and are prone to EMI, fluid velocity induced errors, and variable liquid junction potentials. Coatings and particles can plug the reference and create a large reference resistance and liquid junction potential. Finally, contamination of the reference with process chemicals is extremely disruptive to the reference electrode potential and can seriously degrade the reference internals to the point of failure.

Months

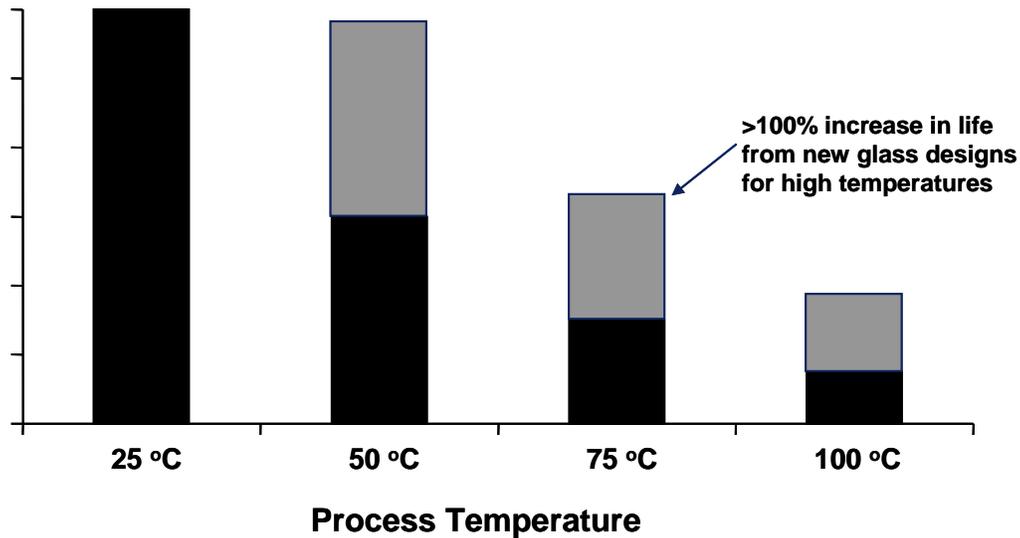


Figure 2. Life Expectancy of High Temperature and General Purpose Glass Electrode - New glass designs offer a 100% increase in electrode life at elevated temperatures.

Process pH

pH measurements in water solutions below 2 pH or above 12 pH are strong acid or base solutions with concentrations approaching the percentage range. These concentrations are usually better measured using conductivity measurements.

- Very low pH measurement can suffer errors from acid effects on the pH electrode and large potentials on the liquid junction of the reference electrode.
- In addition to liquid junction potential, high pH solutions can severely shorten the life of the pH electrode, especially at high temperatures, and the measurement itself is subject to alkalinity errors (also termed sodium ion errors), which offset the pH below the actual pH value.

Process Temperature

Higher temperatures shorten the life of pH electrodes, and exposure to high temperature lengthens the response time, leading to a slugging response to pH changes. The traditional approach to high temperature situations has been to use a sample stream with

sample cooling, which increases installation and maintenance costs and creates measurement time delays. Today there are alternatives available:

- pH electrodes have been designed for continuous high temperature exposure to provide a reasonable life under these circumstances.
- A second case is SIP (Steam in Place) pH sensors, which are designed to withstand a relatively short exposure to high temperature, primarily for sterilization in the biotech industry.

Process Concentrations

To properly function, a reference electrode should maintain a standard potential, which is a function of the silver ion dissolved in its fill solution, and maintain electrolytic contact with the process by diffusion of potassium chloride ions through its liquid junction. The potassium and chloride ions in a reference fill solution diffuse through a reference at an equal rate, so there is a net charge balance across the liquid junction. Potassium chloride is said to be equitransferent.

- Ions from the process, diffusing into the liquid junction are likely not equitransferent, and so a potential, called liquid junction potential, develops in opposition to the charge imbalance created by unequal diffusion rates of positive and negative ions.
- Certain ions in process can precipitate or complex the silver ions upon diffusing into the reference electrode, the most common being sulfide, bromide, iodide, and cyanide, and can effect the functioning of the reference electrode in two different ways:
 - Poisoning: Reduction of the silver ion concentration in the innermost portion of the reference electrode causes silver ions on the silver-silver chloride wire to dissolve, and once all of the silver chloride has dissolved a large offset in the potential (and the pH measurement) is produced, and the reference electrode must be replaced.
 - Plugging: A second effect can be precipitation of silver within the liquid junction, blocking the diffusion of ions into the process and thus opening the pH measuring circuit, and causing the pH measurement to drift.
- Reference electrodes have been designed to retard the migration of process ions into the reference electrode by using multiple liquid junctions, an outer reference fill of potassium nitrate to lower silver ion concentration, and gelled fill solutions to prevent ion transport by thermal convection.
- In extreme cases, where there are high concentrations of harmful ions in the process, a flowing reference is required, which uses a flow of fill solution into the process to make electrolytic contact to prevent incursion of process components into the reference. Flowing reference electrodes are maintenance intensive due to the need to keep an adequate reservoir of fill solution, and maintain a pressure on the fill sufficient to overcome process pressure.

Process Conductivity

Low conductivity processes (conductivity less than 50 $\mu\text{S}/\text{cm}$) can create problems for pH measurements, largely due to effects on the liquid junction of the reference.

- Large and unstable liquid junction potentials can develop in low conductivity water samples due to spurious concentration changes within the liquid junction, which cause an overall unstable pH measurement.
- A pH sensor designed for low conductivity must be used for these applications, and the current approach for dealing with liquid junction instability is to use a flowing reference or a pressurized reference to ensure that the liquid junction is always filled with reference fill solution.
- pH sensors for low conductivity are almost always mounted in a flow-through configuration (described in the “Installation practices” section) to better control sample flow rates and prevent contamination of very pure water with electrolyte from the reference electrode.
- Applications involving the detection of acidic or basic contaminants in ultra-pure water (conductivity near 0.055 $\mu\text{S}/\text{cm}$) are better served using conductivity measurements, which are more sensitive to low levels of contaminants and much easier to apply than pH.

Non-Aqueous and Mixed Solvents

Generally, pH sensors design and the interpretation of the pH measurement is based on a tacit assumption that measurements are being made in water solutions.

- When the water content is below 40%, the pH reading can be shifted due to solvent effects on the hydrogen ion activity, and the pH electrode can lose sensitivity due to drying, which make it necessary to periodically rewet the electrode with water.
- Fully non-aqueous solvents can greatly shift the pH scale, acidic solvents shifting it downward, basic solvent shifting it upward, while solvents that are neither acidic nor basic can extend the pH range.
- The dissociation constants of acid and bases will change in the concentration of the solvent and water
- The dissociation constant and hence the neutral point for the solvent is different than for water. For example, the dissociation constant for pure methanol is 16.84 versus a water dissociation constant (pK_w) of 14 for water at 25 °C. The neutral point of a methanol solution is 8.42 pH at 25 °C.
- The interface between the liquid junction of the reference and a non-aqueous or mixed solvent can result in large junction potentials.
- When considering applying a pH sensor to a mixed solvent process, the materials of construction of the sensor should be reviewed to avoid solvent attack on o-rings and seals, which can result in leaks and sensor failure.

- The application itself should be examined in the laboratory before going to an on-line measurement, to prevent surprises on-line from the above and other nonlinear effects that are a function of solvent concentration.

Sensor Coating and Cleaning

Undissolved solids and liquids in a process solution can coat a pH sensor, decreasing its response time or even making it unresponsive to changes in solution pH.

- A sample flow rate of 5 ft/sec or greater can reduce the accumulation of fouling material, through the turbulence created.
- Alkaline deposits can be removed with dilute acid (5% HCl) or vinegar, while acid deposits can be removed with mild caustic (1% NaOH caustic soda).
- Organic deposits (oil and grease) can often be removed with a detergent solution, but more tenacious coating may require the use of a solvent, which should be carefully chosen to avoid attack on the sensor's o-rings and seals.
- The sensor's exposure to any cleaning solution should be limited to avoid contamination of the liquid junction by the cleaning solution.

Specifications

The exact specifications depend upon the manufacturer. The following example is representative of the range of operating conditions, performance, process connections, and wetted materials of construction offered.

- **Sensor Specifications:**
 - **General Purpose pH Sensor**
 - Process Connections: 1 in. MNPT
 - Materials of Construction: Tefzel®1, glass, ceramic and Viton®1
 - Temperature Compensation: Automatic 0 to 85°C
 - Maximum Pressure: 790 kPa (100 psig) at 65°C
 - **High Temperature pH Sensor**
 - Wetted Materials: Titanium, Ryton3, Teflon®1, glass, and EPDM: Options, Viton®4 or Kalrez®5
 - Operating Temperature: 5°C to 155°C
 - Maximum Process Pressure and Temperature: 285g kPa (400 psig) at 155°C
 - Process Connections: Insertion/Submersion, 1 inch compression process connector
 - Process Connection: Retraction, can be inserted through a 1-¼ inch or 1-½ inch ball valve

- Maximum Pressure at Retraction or Insertion 524 kPa (64 psig) 21 inch sensor length, 343 kPa (37 psig) 36 inch sensor length
 - **Low Conductivity pH Sensor Assembly**
 - Accuracy: ± 0.05 pH
 - Noise: < 0.02 pH; Drift: < 0.05 pH per week
 - Conductivity Range: > 0.4 $\mu\text{S}/\text{cm}$
 - Sample Temperature: 0°C to 70°C
 - Sample Pressure: 5 to 10 psig – drain to atmosphere
 - Sample Flow Rate: 60 to 180 ml/min (1- 3 gph)
 - Wetted Materials: Silicone, polycarbonate/ polyester, glass, stainless steel, PVDF, Viton
 - Reference Electrode: Flowing, open capillary
 - Process Connections: $\frac{1}{4}$ in. FPT
 - **Steam-in-Place (SIP) pH Sensor**
 - Temperature Range: up to 105°C (steam up to 140°C)
 - Pressure Range: max 600kPa (72 psig) at 105°C
 - Wetted Materials: Glass, ceramic and EPDM o-ring USP VI
 - Process Connector: Pg 13.5 connector
 - Dimensions: 12 mm OD, shaft length 120 mm, 225 mm, or 325 mm
- **pH Transmitter Specifications**
 - pH Range: 0 to 14
 - Accuracy: ± 1 mV @ $25^\circ\text{C} \pm 0.01$ pH
 - Repeatability: ± 1 mV @ $25^\circ\text{C} \pm 0.01$ pH
 - Stability: 0.25% / year @ 25°C
 - Temperature resolution: 0.1°C ($\leq 99.9^\circ\text{C}$); 1°C ($\geq 100^\circ\text{C}$)
 - Digital Communications:
 - Fieldbus (pH): Four AI blocks assigned to pH, temperature, reference impedance, and glass impedance.
 - HART (pH): PV assigned to pH. SV, TV, and 4V assignable to pH, temperature, mV, glass impedance, reference impedance, or RTD resistance.
 - Diagnostics: The internal diagnostics include:
 - Calibration Error, Sensor Failure, High Temperature Warning, CPU Failure, Low Temperature Warning, Input Warning, ROM Failure, Glass Impedance Warning, Glass Impedance Failure, Reference Impedance Warning, and Reference Failure

Installation Practices

In general, pH sensor location should be chosen to meet the following objectives:

- (1) safe and convenient access for calibration and maintenance

- (2) permissible process conditions (e.g. temperature and pressure)
- (3) representative mixture (no stagnation, layering, or short circuiting of reagent)
- (4) optimal fluid velocity for minimum coatings and abrasion
- (5) minimum transportation delay

pH sensors should be mounted at least 10° above horizontal to promote good reference electrode function (gravity assistance to electrolyte) and to avoid air bubbles in the pH electrode fill solution being in contact with the pH sensitive surface of the electrode.

- **Submersion Mounting** involves a sensor at the end of a conduit that extends below the lowest possible surface level in a process vessel or pond.
 - It is the most inconvenient mounting configuration because the sensor and the conduit must be removed for maintenance or calibration, and sensor replacement can be labor intensive.
 - Care must be taken to make a watertight seal between the sensor and the conduit, and backfilling the conduit is advisable to avoid leakage of process fluid into the cable end of the sensor, which can cause shorts.
- **Insertion Mounting** has the sensor mounted in a pipe tee, or through the side of a pipe or vessel, in a location where electrodes will be fully immersed in a representative process mixture and air or bubble entrapment can be avoided.
 - The sensor should be provided with a quick-disconnect mounting accessory or a cable connector to allow it to be withdrawn from the process without having to unscrew the sensor and consequently not having to remove the cable from the analyzer or junction box to avoid twisting and damaging the sensor cable.
- **Retraction Mounting** allows a pH sensor to be mounted in an insertion configuration and be withdrawn by pulling it back behind a valve, which can be closed, and eliminates the need to drain the pipe or vessel.
 - Withdrawal can be done manually or using a pneumatic or electric actuator.
 - The pressure and temperature limits, and the operational procedure of the retraction device should be strictly observed to prevent ejection of the sensor or release of process fluid.
- **Flow-through Mounting** can consist of a sensor with female threads or flanges to mate with process piping, or can simply be an insertion sensor mounted in a tee or flow chamber.
 - The term flow-through is usually taken to mean a pH sensor mounted in a side stream off the main process, and is the only mounting choice when sample cooling, pressure reduction, or filtration and separation is required to make the measurement.
 - When fitted with isolation valves, this mounting configuration is the most convenient because it allows the sample flow to be shut off and the line drained for sensor calibration and maintenance.

- The major drawbacks to flow-through mounting are the added expense of providing a sample bypass, the delay introduced by the transport time of getting the sample to the sensor, and the loss of sample to drain, unless provision is made to return the sample to the process.

Calibration Methods

pH transmitters are factory calibrated for an accurate milliVolt potential measurement, but due to variations in pH sensors and ageing effects, initial and routine pH sensor calibration is necessary.

- **Buffer Calibrations** use two buffer solutions, usually at least 3 pH units apart, which allow the pH analyzer to calculate a new slope and zero value, corresponding to the particular characteristics of the sensor to more accurately derive pH from the milliVolt and temperature signals.
 - The slope and zero value derived from a buffer calibration provide an indication of the condition of the glass electrode from the magnitude of its slope, while the zero value gives an indication of reference poisoning or asymmetry potential, which is an offset within the pH electrode itself.
 - The slope of pH electrode tend to decrease from an initial value relatively close to the theoretical value of 59.16 mV/pH, largely due in many cases to the development of a high impedance short within the sensor, which forms a shunt of the electrode potential.
 - Zero offset values will generally lie within ± 15 mV due to liquid junction potential, larger deviations are indications of poisoning.
 - Buffer solutions have a stated pH value at 25°C, but the stated value changes with temperature especially for stated values that are 7 pH or above. The buffer value at the calibration temperature should be used or errors will result.
 - The values of a buffer at temperatures other than 25°C are usually listed on the bottle, or better, the temperature behavior of the buffer can be loaded into the pH transmitter allowing it to use the correct buffer value at calibration.
 - Calibration errors can also be caused by buffer calibrations done in haste, which may not allow the pH sensor to fully respond to the buffer solution.
 - This will cause errors, especially in the case of a warm pH sensor not being given enough time to cool down to the temperature of the buffer solution.

- pH transmitters employ a stabilization feature, which prevents the analyzer from accepting a buffer pH reading that has not reached a prescribed level of stabilization, in terms of pH change per time.
- **pH Standardization:** Standardization is a simple zero adjustment of a pH analyzer to match the reading of a sample of the process solution made using a laboratory or portable pH analyzer. Standardization eliminates the removal and handling of electrodes and the upset to the equilibrium of the reference electrode junction. Standardization also takes into account the liquid junction potential from high ionic strength solutions and non-aqueous solvents in chemical reactions that would not be seen in buffer solutions. For greatest accuracy, samples should be immediately measured at the sample point with a portable pH meter. If a lab sample measurement value is used, it must be time stamped and the lab value compare to a historical online value for a calibration adjustment. The middle signal selected value from three electrodes of different ages can be used instead of a sample pH. The periodic standardization based on data analytics can be automated greatly reducing need for samples freeing up operations, lab, and maintenance technicians.
 - Standardization is most useful for zeroing out a liquid junction potential, but some caution should be used when using the zero adjustment.
 - A simple standardization does not demonstrate that the pH sensor is responding to pH, as does a buffer calibration, and in some cases, a broken pH electrode can result in a believable pH reading, which may be standardized to a grab sample value.
 - A sample can be prone to contamination from the sample container or even exposure to air; high purity water is a prime example, a referee measurement must be exposed to a flowing sample using a flowing reference electrode.
 - A reaction occurring in the sample may not have reached completion when the sample was taken, but will have completed by the time it reaches the lab.
 - Discrepancies between the laboratory measurement and an on-line measurement at an elevated temperature may be due to the solution pH being temperature dependent. Adjusting the analyzer's solution temperature compensation (not a simple zero adjustment) is the proper course of action.
 - It must be remembered that the laboratory or portable analyzer used to adjust the on-line measurement is not a primary pH standard, as is a buffer solution, and while it is almost always assumed that the laboratory is right, this is not always the case.

Maintenance

Middle Signal Selection

The best solution in terms of reliability, maintainability, and accuracy is the use of the 3 pH electrodes with different durations of process service and automatic selection of the middle value for the loop process variable (PV). The return on investment for the additional electrodes from improved process performance and reduced life cycle costs is typically more than enough to justify the additional capital costs for biological and chemical processes if the electrode life expectancy has been proven to be acceptable in lab tests for harsh conditions. The use of the middle signal inherently ignores a single failure of any type including the most insidious failure that gives a pH value equal to the set point. The middle value reduces noise without the introduction of the lag from damping adjustment or signal filter and facilitates monitoring the relative speed of the response and drift, which are indicative of measurement and reference electrode coatings, respectively. The middle value used as the loop PV for well tuned loops will reside near the set point regardless of drift. A drift in one of the other electrodes is indicative of a plugging or poisoning of its reference. If both of the other electrodes are drifting in the same direction, the middle value electrode probably has a reference problem. If the change in pH for a set point change is slower or smaller for one of the other electrodes, it indicates a coating or loss in efficiency, respectively for the subject glass electrode.

Diagnostic Information

The first level of diagnostic information in a pH transmitter is the fundamental measurements made by the transmitter and sensor, which include milliVolt input, temperature, and the resistance of the temperature element.

- The source of a questionable pH measurement can be determined as being due to the temperature measurement or the milliVolt measurement by examining their values, as in the case of a failed temperature sensor, which indicates a process temperature that is fantastically low or high.
- pH transmitters also provide internal diagnostic routines, which can provide the user with real time fault and warning information. These can be divided into the following categories:
 - Transmitter diagnostics alert the user to electronic and CPU problems with the transmitter itself, which can either indicate that the validity of the measurement has been compromised, or in the extreme situations, that the transmitter electronics should be replaced.
 - Sensor diagnostics can indicate problems with the pH sensor itself, or problems with the process.
 - These include milliVolt measurements out of range, which indicate a sensor has been miss-wired, or there is a major sensor problem.

- Temperature measurements will trigger alerts if they are too low or high and outside the operating range of the measurement, as well as failures in the temperature element such as shorts, opens, or miss-wiring.
- Calibration errors are triggered by sensor calibration constants (slope and zero) being out of the normal range, which indicate a sensor failure or procedural errors on the part of the user.
- Advisory messages do not indicate a problem with transmitter or sensor function, but do let the user know that calibrations, simulations, and other events are or have taken place.
- Glass pH Electrode Impedance Diagnostics:
 - Glass pH electrode impedance is in the range of 10's to 100's of megOhm and is strongly temperature dependent.
 - A crack or break in the glass electrode creates a short, which results in an impedance of 1 megOhm or less.
 - Detecting broken or cracked pH electrodes requires impedance measurement circuitry with temperature compensation and the simple setting of a low impedance alarm.
- Reference Electrode Impedance Diagnostics:
 - The overall impedance of a reference electrode is a sum of the resistances of its components with the largest being the liquid junction, and is typically in the range of a few kOhm. This junction resistant is due to the limited volume of current carrying electrolyte within the liquid junction.
 - Coating or blockage of the liquid junction increases the impedance of the liquid junction, as will a pH sensor that is no longer immersed in liquid.
 - Detection of coating or blockage involves setting a high reference impedance alarm, as reference impedance increases due to coating or blockage are gradual; it is useful to use two levels of impedance high alarms to indicate a warning and a failure.

Asset Management

If the analyzer is provided with digital communications such as HART or Foundation Fieldbus, asset management software can provide a remote window into analyzer function and settings. Diagnostic information can accessed remotely, and diagnostic alert provided to operators and control systems in real time using asset management software. In addition to simply alerting the user of a problem, the software can provide information on the root cause of the problem by combining the alert with live measurements and configuration information, which allows troubleshooting to be done before making a trip to the analyzer. Remote access to analyzer configuration makes it possible to review measurement and temperature compensation settings, and transfer a complete configuration to an analyzer from another analyzer or from a configuration template

composed in the software. Calibration can be performed remotely based on a grab sample analysis or knowledge of the process composition during a particular stage of a process. Asset management software records all of the above information with timestamps, which makes it possible to review events and configurations conveniently without the need to keep paper records.

Wireless

WirelessHART pH devices conduct a measurement every second but are set up to transmit an updated value only if the change in measurement from the last transmitted value is great than the “resolution” setting or the elapsed time since the last transmitted value is greater than the “refresh time” setting. The “refresh time” provides periodic reporting usually every 16 seconds for pH. The “resolution” setting provides exception reporting on an as need basis, which can reduce the number of transmissions by an order of magnitude. Battery life can be extended to 5 or more years.

The cost savings in the elimination of wiring design and installation are obvious for new projects. Less obvious is the savings in maintenance and relocation costs. Cable does not need to be relocated to different or new cable trays and conduits and re-terminated at different or new panels. WirelessHART devices automatically report alerts without interrogation and can reconfigured and monitored remotely. Often WirelessHART devices have the latest advances in sensor technology, such as finer resolution (e.g. 0.001 pH) and a more accurate monitoring of glass resistance.

The untethered portability of wireless transmitters are particularly useful in the dynamic environment of process research and development and flexible manufacturing. For example, a pilot plant at the University of Texas for research of new technologies for CO₂ capture and demonstration of customer designs for distillation column packing has documented significant savings in relocation and setup costs to meet changing equipment configurations and control objectives. WirelessHART devices are being used for the same reasons on single-use-bioreactors (SUB) mounted on carts that can be wheeled for connection to analyzers and other process equipment.

Wireless transmission can eliminate wiring termination mistakes and ground loops. While only about 10% of the installations suffer from ground potentials and noise, these problems are difficult to track down. When a lab meter is connected to the electrode, the noise or shift in pH often goes away, which indicates one could get rid of the problem by eliminating the wiring. A recent comparative test of conventional wired versus new WirelessHART pH transmitters on a single-use-bioreactor had some interesting test results. The SUB had a mammalian cell culture that was very sensitive to pH. A resolution setting of 0.01 pH was requested but was mistakenly set at 0.01%, which translated to about 0.001 pH. The pH loop was able to control to within 0.002 pH of set point while reducing the number of communications by 60% by the use of exception reporting with the incredibly fine 0.001 pH resolution setting in the WirelessHART

transmitter, which is beyond the stringent 0.02 pH control requirement of bioprocesses. Confirming the suspicions that noise from grounding problems could be eliminated with wireless transmitters, spikes in the conventional wired transmitter trend did not appear in the WirelessHART transmitter pH trend chart. Figure 3 shows the SUB test results.

Some chemical process would need a 0.01 to 0.05 pH resolution setting whereas for chemical waste treatment a 0.1 pH resolution setting should be good enough. In any case, the resolution setting should be greater than the noise amplitude and less than the allowable deviation from set point in order to deal with process disturbances. Coarser resolution settings correspond to a greater reduction in communications and commensurate increases in battery life.

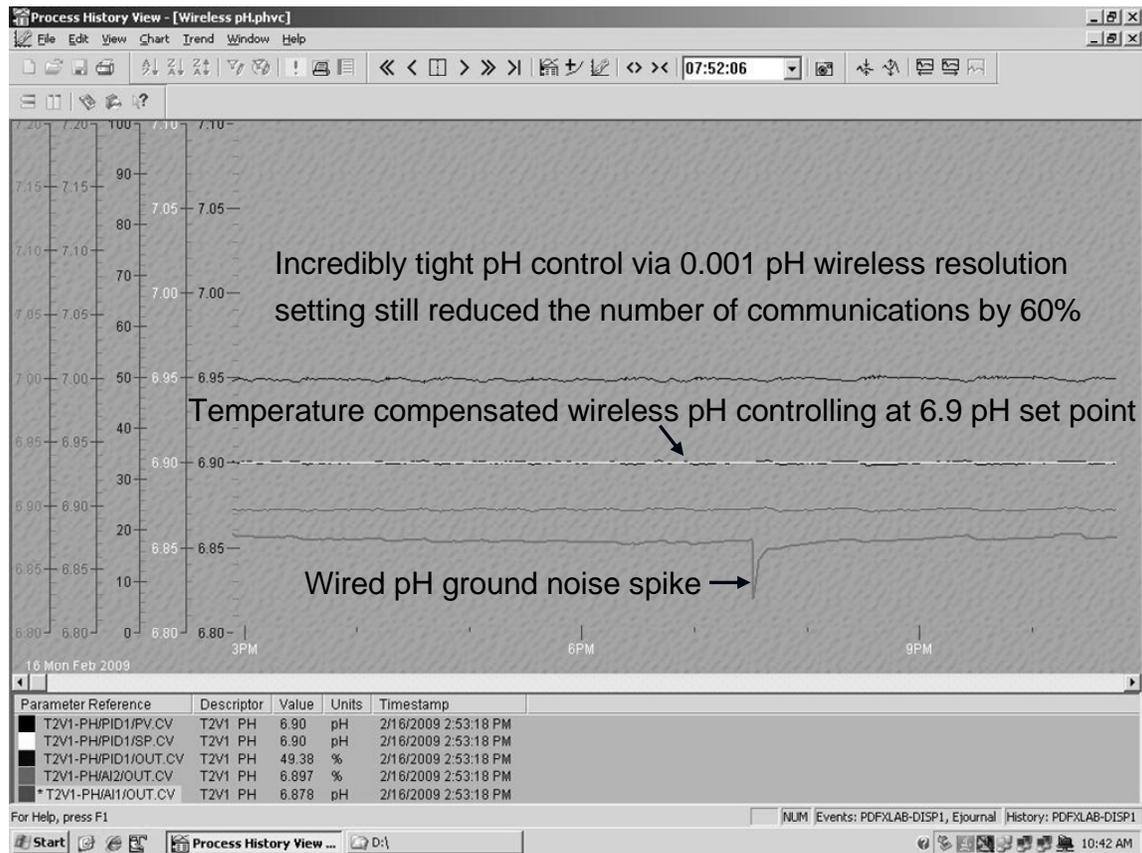


Figure 3. Performance of a WirelessHART for control and a wired pH transmitter for monitoring. The WirelessHART transmitter was able to control pH to within 0.002 pH of set point and eliminated the spike seen in the wired pH transmitter.

The future is wireless. Sensors will have embedded chips with calibration records. There will be an increase in the type of diagnostics as manufacturers get smarter about detecting and interpreting the impedance changes in the glass and reference electrode. As users become more aware of the actual problem, there should be an increased interest in being

able to fix rather than replace the electrodes. To address this potential market some electrodes now offer the ability to easily pop out and snap in a new reference junction.

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