YOKOGAWA

TECHNICAL NOTE

ANALYTICAL

Best Practice pH Installation and Maintenance Manual

Tech Note: TNA1505

vigilantplant®

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PREFACE

The Measurement Loop

Basic Components: In order, to effectively measure pH, every measurement loop (instrumentation and sensor) must include certain essential components. There must be an analyser/transmitter to take the signal from the sensing elements and convert it into a useful output for indication and control. The sensor/electrode part of the loop contains at least three elements: (1) reference electrode; (2) measuring electrode and (3) a temperature electrode. In addition, quality low-noise cabling between the sensors/electrode and the instrument is necessary to insure an accurate measurement.

Analyzer/Transmitter: Selecting the proper instrument for a specific application involves answering some basic questions. (1) What is the “area classification” for the application (general purpose, Class 1, etc.); (2) What output requirements are necessary (4-20 mA, alarm contacts, etc.); and (3) are the power input requirements (115 VAC, 24VDC, etc.). With this information, selecting the appropriate analyzer or transmitter is an easier task. Additional considerations for selection would be whether “diagnostics” or other advanced features are desired.

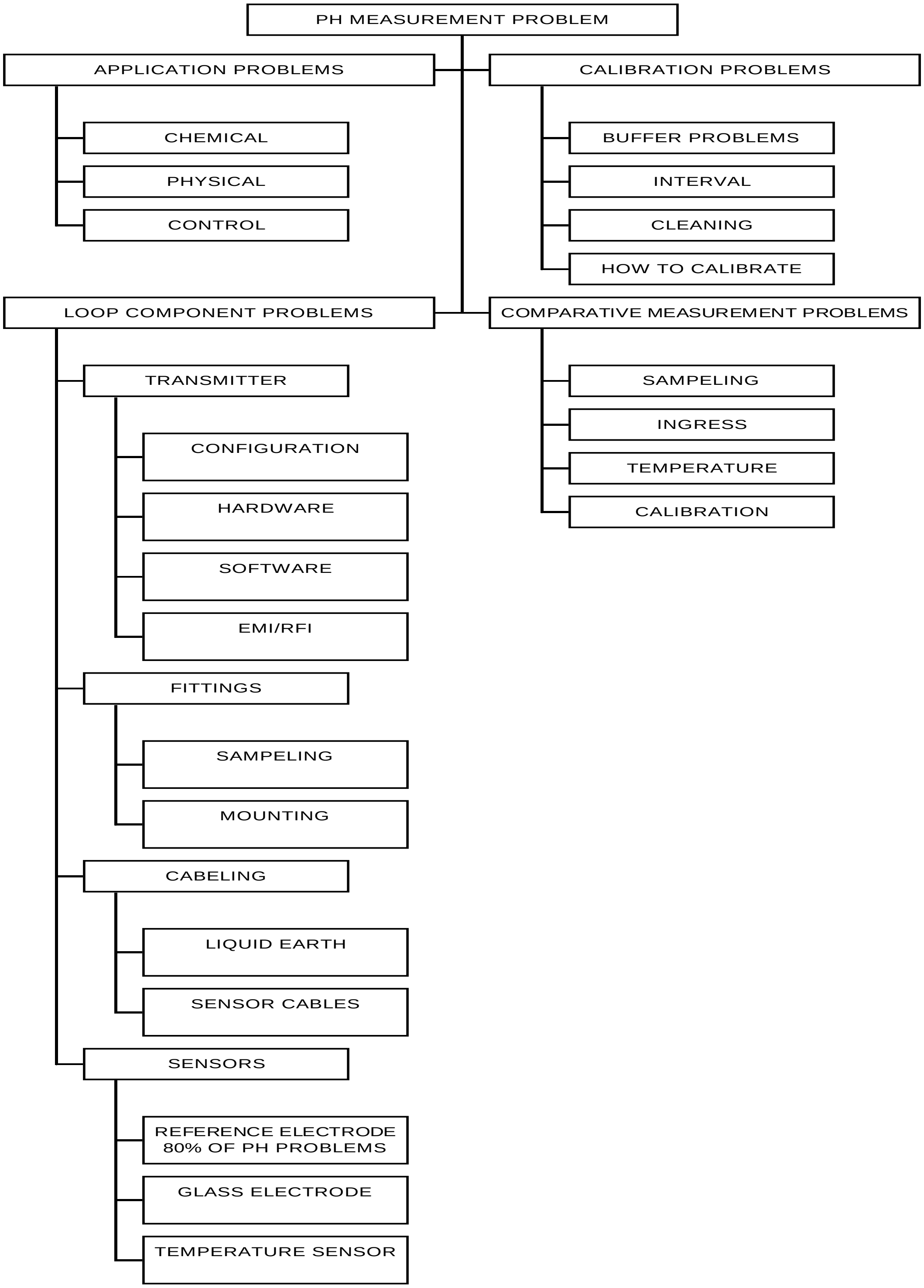
Sensors/Electrodes: The “business end” of the measurement loop is the sensor (electrode assembly). These components must come in direct contact with the process in order to obtain the measurement and are therefore exposed to the effects of the process (temperature, abrasion, chemical attack, etc.).

> *Reference electrode:* The primary purpose of the reference electrode is to provide a stable "reference" voltage from which to make the pH measurement of the process. Conventional reference electrodes also provide electrochemical continuity (complete the measurement circuit) between itself and the measuring electrode.
>
> *Measuring (glass) electrode:* This electrode is constructed with a unique glass membrane which senses the increase or decrease in pH value and provides an equivalent millivolt change to the pH analyzer/transmitter.
>
> *Temperature electrode:* In addition to measuring pH, the measuring electrode is also affected by temperature. The third electrode in the measurement loop, the temperature electrode, is used to compensate for the effects of process temperature changes on the measuring electrode. Thus assuring that the pH reading is due to actual pH changes and not to the affects of a change in the process temperature.

The desire is to achieve an accurate, reliable measurement with a reasonable electrode life expectancy while minimizing frequency or complexity of maintenance that is required/ needed. When a quality pH sensor system is undamaged, cleaned and properly calibrated it will provide a measurement that is accurate and reliable. Even if an electrode is in a process that does not cause coating, plugging, abrasion or other problems, it still must be calibrated periodically to correct for aging of the sensors and the non-recoverable changes to the electrodes that take place. These effects of aging usually happen slowly therefore, calibration should not be necessary more frequently than about once a month in typical general purpose applications. If more frequent calibration is needed, it is usually because (1) the process is aggressive; (2) the electrode cleaning process was not effective; (3) the routine calibration was not properly executed; (4) the pH readings are temperature dependent or (5) the wrong electrodes have been selected for the application.

Measurement results obtained from dirty or faulty electrodes can be anything from slow response, to a completely erroneous reading. Example: If a film remains on the pH sensor after cleaning, then measuring error can be interpreted as a need for re-calibration. Since, these changes are reversible with correct cleaning; this is a key step in the maintenance process. Therefore, the accuracy of the pH measurement depends upon the frequency of your maintenance and the frequency and method of periodic maintenance depends largely on the application. However understanding what causes the difficulties in pH measurements, a stable and accurate pH measurement can be accomplished. Troubleshooting a pH system can be an annoyance, but the following intentionally general advice can be used as a starting point. Now the question becomes where do you start?

PROBLEM CLASSIFICATION



- PH MEASUREMENT PROBLEM
  - APPLICATION PROBLEMS
    - CHEMICAL
    - PHYSICAL
    - CONTROL
  - CALIBRATION PROBLEMS
    - BUFFER PROBLEMS
    - INTERVAL
    - CLEANING
    - HOW TO CALIBRATE
  - LOOP COMPONENT PROBLEMS
    - TRANSMITTER
      - CONFIGURATION
      - HARDWARE
      - SOFTWARE
      - EMI/RFI
    - FITTINGS
      - SAMPELING
      - MOUNTING
    - CABELING
      - LIQUID EARTH
      - SENSOR CABLES
    - SENSORS
      - REFERENCE ELECTRODE 80% OF PH PROBLEMS
      - GLASS ELECTRODE
      - TEMPERATURE SENSOR
  - COMPARATIVE MEASUREMENT PROBLEMS
    - SAMPELING
    - INGRESS
    - TEMPERATURE
    - CALIBRATION

10 QUICK QUESTION FOR DIAGNOSIS

As the problem classification shows there are a multitude **of possible causes** when you experience a problem with your pH measuring system. The effect the problem has on your system can probably be classified in one of the following areas:

1. Indication **fixed at pH7.**
   Probably the glass electrode is broken, or there is a short circuit between the glass and reference side. Replace the glass electrode or remove the short circuit.

2. Your **comparative measurement** shows different values than the on-line meter.
   Refer to chapter 8 on comparative measurements.

3. You experience problems at **calibration.**
   Refer to chapter 5 on buffers and calibration.

4. **Unstable** or noisy readings, **drifting** values or **off-scale** readings.

The easiest thing to do first in these cases is to have a look how your system performs when the electrodes are in their **reference pH buffers**.

However, before doing so the following checklist of most common faults and errors may be helpful:

1. Are there any **error messages** on the display? If so refer to chapter 7 and 10.
2. Have the **cables** been shortened or lengthened? Make sure that no wire is touching the transmitter house. See chapter 8
3. Is the **liquid earth** connected? Check if terminal 14 is connected. For further information refer to chapter 7.
4. Are the **electrodes clean** and in good shape? Refer to chapters 3, 4 and 10.
5. Has the **installation** been manipulated or changed in any way? If yes return it to its original state when possible. Else refer to the different chapters about mounting cabling and electronics.
6. In case you are using a **flowing** type **reference electrode**, check that it is properly filled and flowing. Make sure to use the correct concentration of KCl. Refer to chapter 3.
7. Are **cables and connectors** dry, in good shape and not touching any part of the electronics housing? Refer to chapter 8.
8. Does a short circuit between terminals 13 and 15 give a stable reading near pH 7? If no see chapter 7.
9. Are the electrodes immersed in the measuring liquid? See chapter 6.
10. Does the loop show the right values for the different buffers, but is unstable in process? Refer to chapters 6 and 11. You probably have a control or installation problem.

If you are not able to solve your problem through these 10 questions, we advise you to read each chapter carefully. It will give you a better understanding of pH loop installation and maintenance.

Note: Before manipulating the installation it is good practice to note the impedances, asymmetry and slope values. These can help to assess the real problem.

INSTALLATION CONSIDERATIONS

Achieving accurate and reliable readings using a traditional pH analyzer is challenging, however with the right equipment and proper maintenance, stable and accurate pH measurements can be accomplished. The first obstacle all instrument engineers who have ever installed a pH system on a process plant have been confronted with the choice of how to present the sample. It is possible to mount the sensors in:

- An Immersion assembly (dip probe) in an open tank, closed vessel, or flowing channel or flume.
- An insertion assembly direct in the process.
- A flow through assembly in a sample by-pass line.
- A retractable assembly with process isolation (also known as a withdrawable under pressure fitting).

It is of course possible to expand the list, and introduce sub-divisions, but these are the basic categories.

How to Choose?

The application usually restricts the available choice for you. So you can start by eliminating what is not considered suitable. Take for example slurry applications, in most cases, the customer will not be prepared to consider a sample by-pass loop, because of the possibility of solid settling, and blocking the sample lines. In-line flow installations, (direct insertion and sub-assemblies) are seen as troublesome in continuous processes, because it is hard to gain access for maintenance.

The position in the process stream may be important. In this case the use of an immersion fitting can be indicated to make the measurement direct in the reaction tank, hence minimising delay time for accurate dosing control.

The alternate situation can also apply where a measurement needs to be placed further downstream to allow adequate mixing, or reaction time.

Gaining in popularity is the retractable electrode holder, which combines the benefits of the direct insertion, with the ease of accessibility of the by-pass measurements. The things, which stop this solution from being universally accepted, are the higher maintenance aspects of the mechanical moving parts, and the extra constraints placed on the (combined) sensors. Some manufacturers try to compensate for the restrictions imposed in the retractable design, by incorporating self-calibration systems. It is better to promote the use of individual sensors for those applications where the demands of the process are too severe.

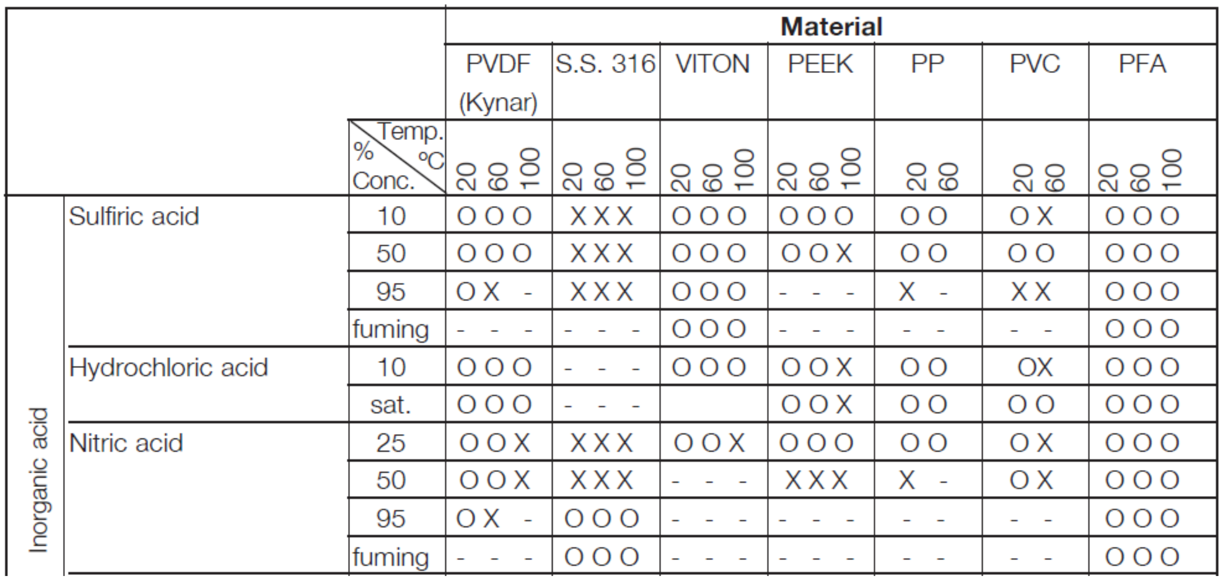
Choosing the right materials?

Materials of construction of the storage tanks, sample lines, measurement housings may contaminate the water/process due corrosions of leaching of plastics. Let’s use an ultrapure water systems for example, Table 1 shows a brief list of known acceptable materials of construction *arranged in order of preference*. To prevent the increase of static potentials a stainless steel flow chamber is recommended. Since most plastics are not completely gas tight, such a chamber will also prevent the absorption of CO2 from the air

Table 1
(Arranged in order of preference)

- Teflon (tetrafluoroethylene)
- Tefzel (trifluoromonethylene)
- Tantalum
- Titanium
- Pure block tin
- High-purity quartz
- PVDF (polyvinylidene fluoride)
- Polyethylene
- Polypropylene
- Borosilicate glass
- 304 L Stainless Steel
- 304 Stainless Steel
- 316 L Stainless Steel
- 316 Stainless Steel
- 321 Stainless Steel
- PVC (polyvinyl chloride)

However, you can see that for every application and process media there are acceptable and unacceptable materials of construction that can be used.



			Material						
			PVDF (Kynar)	S.S. 316	VITON	PEEK	PP	PVC	PFA
		% Conc. / Temp. ºC	20 60 100	20 60 100	20 60 100	20 60 100	20 60	20 60	20 60 100
Inorganic acid	Sulfiric acid	10	O O O	X X X	O O O	O O O	O O	O X	O O O
		50	O O O	X X X	O O O	O O X	O O	O O	O O O
		95	O X -	X X X	O O O	- - -	X -	X X	O O O
		fuming	- - -	- - -	O O O	- - -	- -	- -	O O O
	Hydrochloric acid	10	O O O	- - -	O O O	O O X	O O	OX	O O O
		sat.	O O O	- - -		O O X	O O	O O	O O O
	Nitric acid	25	O O X	X X X	O O X	O O O	O O	O X	O O O
		50	O O X	X X X	- - -	X X X	X -	O X	O O O
		95	O X -	O O O	- - -	- - -	- -	- -	O O O
		fuming	- - -	O O O	- - -	- - -	- -	- -	O O O

Which is easiest to maintain?

The sample by-pass flow fitting has to be the top contender. The use of small bore piping to bring the sample to the fitting means that it can be easily and cheaply mounted in the most convenient place for access.

Isolation valves, flushing water and drain lines can easily be added to minimise the operator contact with process fluids. The measurements can be grouped together conveniently to provide a comfortable working environment for the technician who will maintain the systems. This rates very highly for convenience, safety and accuracy. (We will explore later how accuracy is affected by the installation.)

The retractable assembly is seen by many as the best way of mounting sensors. Indeed it has much to be said for it. When the retractable is combined with the flush port option it does have many of the advantages of the sample by-pass systems

Direct insertion and sub-assembly installations can often be sited to enable maintenance to take place without interrupting the process, despite measuring in the process stream.

In critical applications a good way is to use dual lines, with changeover valves, so that there is a duty and stand-by regime in operation.

The immersion assembly can be hard to handle, especially in the longer versions. Some of the problems are that it is heavy, long, slippery and dirty when it comes out of the process. Given a little thought and a very small extra investment, a simple gantry equipped with a pulley can make regular calibration much easier. Add a water supply to wash the probe, a drain for the waste and an adjustable stand for the buffer container, and maintenance becomes a matter of simplicity.

The measurement is important to you, not because you like to measure pH, but for what it does for you. It must be done to ensure high quality, maximise production yield or meet regulatory compliance. In any case it is only a means to an end. The measurement also costs you money as an overhead on your production costs. The measurement should take place with the minimum of effort, to help to keep these costs low. We try to achieve this with well-specified equipment, and this goes a long way to meeting your needs.

A stage further in the process is to help him choose where and how to make his installation. The Yokogawa product offering has the widest range of materials of construction, flange and pressure ratings available anywhere.
We can often place measuring systems directly in places where the competition would require expensive sampling systems. In addition we have the broadest range of sensors.

By working with the customer to provide the maintenance fitter with little aids, as described for the immersion assembly, the time required to service a sensor system is reduced. Simple weather protection for systems mounted outside gives similar benefits. This not only affects his costs, but also the accuracy of the measurement.

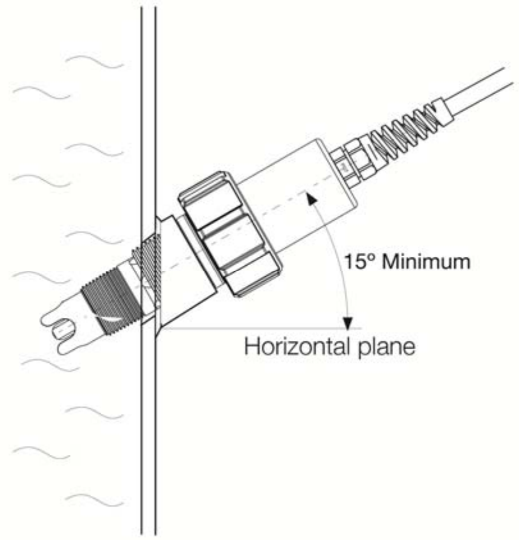
How Does the Installation Affect Accuracy?

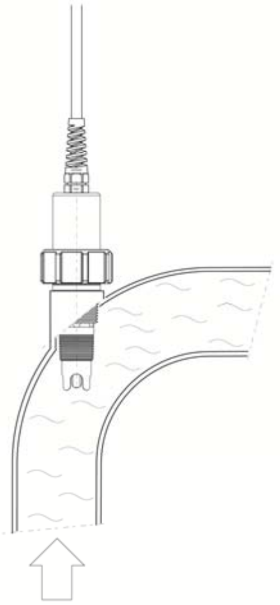
By making the job of the maintenance technician less difficult! When you make it easy for him to work on the sensor system, he will repay that small investment by doing a better job. He will not even realise he is doing it. Because the working environment is planned, he automatically works better because he only needs to concentrate on the task, and not the problems.

The simplest example is mounting sample by-pass systems at a convenient working height. But also immersion fittings and retractable systems should be mounted in easy to reach places. I can testify from personal experience that sample systems mounted either too high or too low can be not only awkward to work on, but even dangerous. Mount them at chest height, with easy access, and even accidental sensor breakage is kept to a minimum.

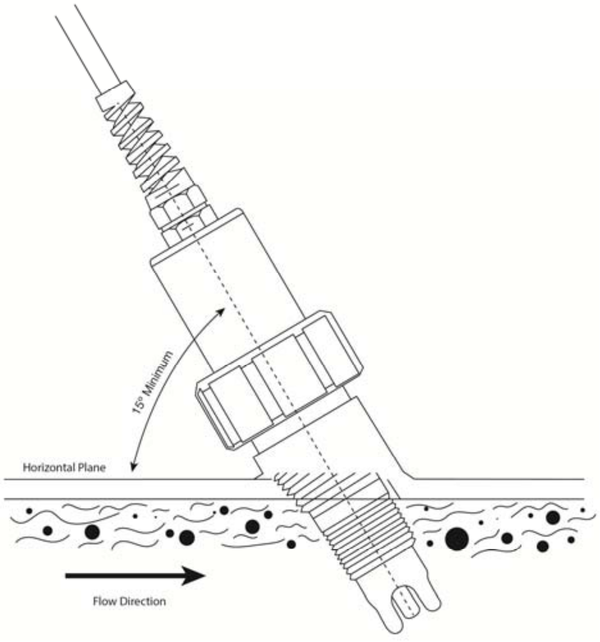
Proper Mounting

For optimum measurement results, most pH sensors should be installed in a location that offers an acceptable representation of the process composition and **DOES NOT** exceed the specifications of the sensor. Some sensors are designed with NPT threaded connections on both ends of the sensor to allow installation in a wide variety of applications. Others require placement into a holder that are designed for versatile in-line, immersion or off-line installation. For best results the sensor should be mounted with the process flow coming towards the sensor, and positioned at least 15° above the horizontal plane to eliminate air bubbles in the pH glass bulb (see Figure below).





However, there are some applications that contain heavy particulates where the ideal installation design is to place the sensor tip in direction with the flow.



Can we mount pH sensors upside down?

Most of the pH sensors with glass membrane cannot be mounted upside down. To absorb the thermal expansion of the internal buffer there is always a considerable air bubble in the sensor.
When the sensor is mounted upside down the reference element can lose the contact with the electrolyte because it inserts in air instead of electrolyte. The FU24 pH sensor from Yokogawa can be used in upside down application, because it has a special design which reduced the size of the air bubble. This allows for 360° mounting capability.

Pure water sampling

In this case the flow for a fitting with a content of approx 500 cc should be limited to 200) 300 cc/min. Only then the reference electrode can make good electrical contact with the reference electrode, and will the reference electrode not be washed out.

ELECTRONICS

Design

The system is designed to minimise the effect of external influences. The Yokogawa amplifiers feature dual high impedance input amplifiers in a differential configuration with liquid earth. This system is used to ensure compatibility with most available sensor combinations. It also provides excellent noise rejection, minimising stray signals that can affect industrial pH measurements. Earth loop currents in damp and damaged cabling are eliminated by equipotential screening.
Measuring and reference electrode inputs are amplified separately against the liquid earth sensor.
The input impedance's of both amplifiers are very high (> 10exp13 ohm)

Installation

Install the converter in a reachable place, preferably at eye height. Make sure it is as close as possible to the probes. Long cables between the transmitter and the sensors make maintenance (calibration) difficult. We advise a maximum length of 10m to prevent interference.
Make sure that all cable glands are waterproof to prevent water coming in to the transmitter.
Do not expose the transmitter to continuous sunshine. It is advised that in such cases a protection hood is used.

Periodic maintenance

Transmitters require very little periodic maintenance. The housing is sealed to IP65 standards, and remains closed under normal operation. Users are required only to make sure the front window is kept clean in order to permit a clear view of the display and allow proper operation of the pushbuttons. The window can be cleaned using a soft damp cloth. To deal with more stubborn stains, a neutral detergent may be used. Never use harsh chemicals or solvents!
Make sure the unit is reassembled properly after opening, to avoid water ingress and condensation.

Checks

The proper functioning of the transmitter can be done using a signal (mV and Pt100 (0)) simulator. With this instrument the correct functioning of all parts of the measuring loop can be checked.
The electronics are of course checked by a watchdog. In case of problems, error codes will be generated.In case you doubt the proper functioning of the transmitter, you can quickly verify what the system does when 0 mV is applied to the input. Simply short circuit input terminals 13 (reference) and 15 (measuring side). The display should read a stable 7 pH +/- AS potential. If not the transmitter is probably defective.

CABLES AND CONNECTORS

When you need optimal pH or ORP (Redox) measuring results, the complete measuring loop not only requires highly qualified sensors and transmitters but also the special purpose sensor cables.
The program of Yokogawa includes a range of low-noise cables for accurate transmission of low voltage signals even in areas where interference is present. They have a shield with internal anti-noise sheath and can be connected to all pH and ORP (Redox) electrodes fitted with an 0-connector.

At the electrode end the cables are provided with a socket having spring gilded contacts for secure connection to the sensor. The combination electrode plug and cable socket is watertight and temperature resistant up to 125 °C. It meets the requirements of IP 65.

Where a convenient installation is not possible using the standard cables between sensors and converter, a junction box and extension cable may be used. The total cable length should not exceed 50 meters (e.g. 5 m fixed cable and 45 m extension cable). In the case of systems using dual high impedance sensors (e.g. Pfaudler 18), then the cable length is restricted to 20 meters (fixed cable only, no extension with WF10).

Errors caused by damp electrode cables or connections.

It is of the greatest importance to protect the electrode cables and connections from ingress of moisture. This may reduce the insulation resistance of the cable connections causing a partial short circuit and consequently an erroneous reading. Often it happens that cable is broken. The online impedance control allows to detect errors caused by moisture or broken cable. Immersion fittings particularly may be subject to condensation when fitted in low temperatures processes.

Solutions:
a. Purging the fitting with dry air or nitrogen.
b. The addition of silica-gel or any other moisture absorbing material.

Errors caused by shortening the electrode cables

Often, it is usual for installation technicians to cut off surplus cable lengths. This is done despite the availability of different cable lengths. The shortening is strongly to be dissuaded. To prevent “inside radiation” of disturbances the cables are supplied with a special layer of graphite for screening. This layer can be removed very difficult but after shortening the cable length regularly measuring errors are stated (e.g. instability) or are strongly “manual” sensitive. The cause of the measuring error was the result of a strongly decreased isolation resistance between core and screen of the electrode cable. For cables of the glass electrode this isolation resistance must be over 1000 times the resistance across the glass membrane.

Interferences by stray voltages in the liquid

In many industrial applications the voltage potential of process liquids is significant and cannot be neglected when making pH measurements. This voltage level may be due to a number of causes, a full study of which is too complex to be covered in this article. It is essential therefore, that the liquids are earthed at the point where the pH value is to be measured. This can be easily achieved when metal fittings are used. When plastic fittings are used they should be fitted with an Liquid Earth (Solution Ground) electrode of suitable metal.

Errors caused by poor installation

When commissioning a pH measuring system, care should be taken that the electrode connectors do not become wet, or fouled with fine deposits. Particular care should be taken if the electrodes are removed for tests, or pressure testing of the pipe, and are left unprotected. If this occurs any dirt should be carefully removed from the electrode connections and the cables removed and, either thoroughly dried, or preferably replaced.

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CHOOSING THE RIGHT ELECTRODES

Choosing the right equipment?

Every application is different and has its own difficulties; knowing potential nuisances of an application helps to ensure that the proper electrodes are selected from the beginning. A pH sensor has four components: a measuring electrode, a reference electrode, a temperature electrode and a solution ground/liquid earth. Each of these electrodes serves a purpose; however, the measuring and reference are the most critical. There are different versions of each electrode to combat known difficulties in various pH applications.

Measuring electrode - The correct selection of a glass electrode for a particular application can only be made if details of the components of the measuring loop and their significant properties are known. Example, in pure water to counter the low response speed and the effect of the alkali components on the glass electrode, a low-impedance glass is recommended. There are different versions of pH measuring glass available on the market and the following points should be considered when selecting the proper glass electrode:

- selection of the glass membrane (sensitivity of the glass electrode (mV/pH))
- chemical resistance of the glass membrane

pH sensitive glass has the particular property that alkali metal ions present in the texture of the glass are exchanged with H^+ ions of the liquid.

What is the benefit of using heavy duty glass?

Heavy Duty Glass is the description of pH sensors that feature a wall thickness of the sensitive glass membrane of approximately 1 mm. All customers who consider pH sensors as fragile will benefit from this feature. Also applications corrosive to Glass like hot alkaline solutions with high salt content or processes with risk of HF (Fluoride containing waters at low pH) will benefit from heavy duty features.

Reference electrode - The reference electrode is the most important piece in the measurement setup besides a liquid earth/ solution ground element. The purpose of the reference electrode is to provide a constant reference voltage as well as completing the pH measuring circuit. In order to have electrochemical continuity between the measuring electrode and the reference electrode a liquid junction/diaphragm is required.

The reference system may be poisoned by the penetration of "unwanted ions" in the salt solution. To overcome this problem an eletrolyte and diaphragm is used to connect the metal/metal salt with the process liquid (see fig.4).

A constant flow of electrolyte from the reference electrode prevents poisoning of the electrolyte around the reference pin. The KCl can be liquid or Gel. In Gels, the KCl will diffuse out of the junction. Gels do not require (cannot) be refilled and diffuse at a slower rate. If liquid, the KCl will diffuse and flow out of the junction (this is what is called a flowing reference) solving some problems we'll discuss in a moment.

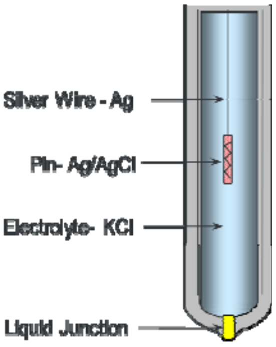
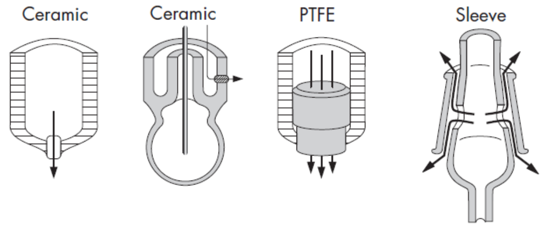


Figure 4: Reference Electrode

Along with different types of KCl solution there are also different types of junctions that can be used:

- Ceramic
- Porous Teflon
- Glass sleeve capillary element



The Reference electrode is the weakest link in the measurement system being the problem in 80-90% of all applications.

- Typical modes of Reference Failure
    - Plugging
    - Fouling
    - Poisoning
    - KCl Depletion
    - Pressure Spikes (causing pumping of KCl out of the electrode)

What is electrode replacement expectancy?
Typical Applications - Expect to replace (3) Reference Electrodes for every (1) Measuring.
Harsh Applications - Expect to Replace (10) Reference Electrodes for every (1) Measuring.
Minimum Life expectancy - Junction Poisoning

- Symptoms to be aware of:
    - Severe discoloring (turning brown or black in color) of the Junction
    - Discoloration is not removed with cleaning

However, knowing the process allows you to select the right reference system for the process. Each electrode has their own advantages and were made to solve particular issue.

When should we use a flowing reference?
In pure water for example, because of the low conductive properties of high purity water, a flowing reference is needed. The purpose of the flowing reference is to release just enough ions to carry the measurement signal and to complete the measurement circuit. With a standard nonflowing reference the internal KCl solution will be depleted causing a short sensor life.

Flowing references are very useful in applications that have a high potential for plugging of the junction. If you use a sensor where the KCL is always flowing out (see fig.6) of the sensor, as long as the reservoir is full then the only potential for process ingress is if the process pressure exceeds the pressure applied to the KCl chamber.

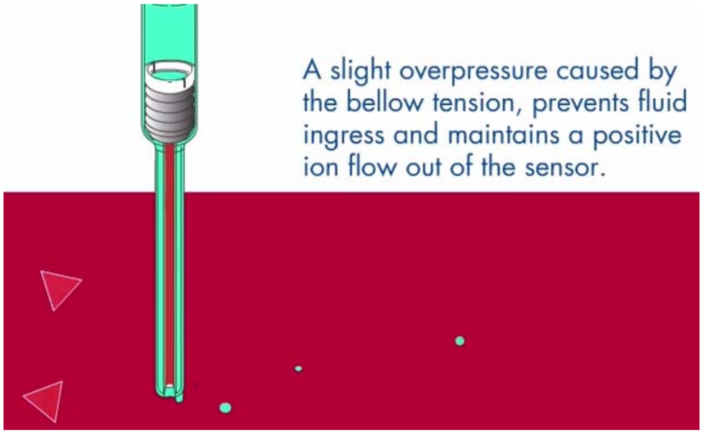


Figure 6: Flowing Reference Electrode (Bellomatic, SR20-AC32)

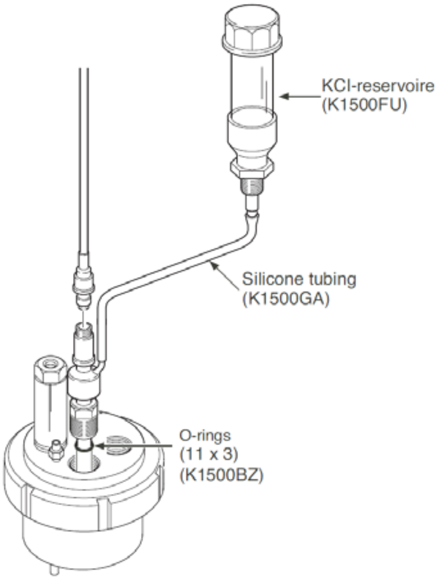


Figure 7: KCl reservoir installation example

When should we use salt bridge over flowing reference?
Flowing reference cell and salt bridge have the same purpose: to prevent diffusion through the junction and fouling of the sensor. Sometimes a salt bridge is easy to retrofit existing installation where you experience sensor troubles. You keep the same reference sensor but place it inside the KCl chamber of the salt bridge.

If the process reacts with KCL or cannot be contaminated with KCl you can use a salt bridge filled with another solution like NaNO3. In high temperature applications the maintenance may be even less with a salt bridge because the reference cell is under reference conditions. Refilling of the large reservoir is easy and does not need to be done frequently.

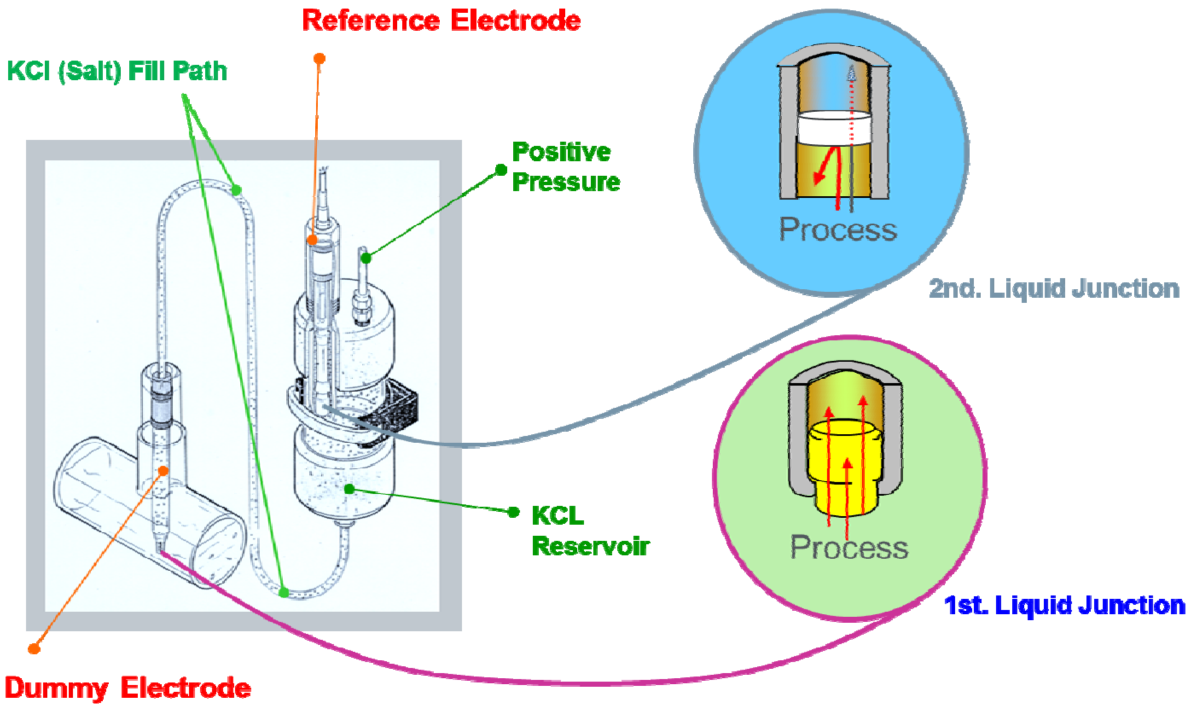


Figure 8: Salt Bridge Installation

Liquid Earth/ Solution Ground - To counter the effects of noise (static charge) it is essential that the equipment setup include a liquid earth/solution ground.

Temperature electrode - To ensure accurate temperature compensation it is recommended that the pH system include a built in temperature electrode.

Quick Reference Sensor Selection:

The following chart can be used as a quick reference guide for some of the most commonly used Yokogawa sensors.

UNIQUE pH Sensor	FEATURES	WHERE TO USE IT
PH20 "Tempress"	♦ Patented pressure compensation panels ♦ Chemically resistant PVDF construction ♦ Double junction reference ♦ Integral Pt1000 temperature element for enhanced accuracy ♦ Simple maintenance by comprehensive design	♦ Process that is prone to pressure spikes ♦ Process that may poison the reference
PH87/97 "Hot Tap"	♦ Simple design and rugged construction ♦ Integral J-Box for easy wiring ♦ Anti-Blowout guard ♦ Optional Solid-State reference system ♦ "Hot-tap" applications with ball valve ♦ Titanium sheath for chemical protection ♦ Adjustable insertion lengths ♦ Cost effective, long life ♦ Built-in solution ground	♦ Process that requires retractable assembly ♦ Process that contains slurry, abrasives, or pulp stock ♦ Process that may poison the reference requires Solid-State reference option
FU20	♦ Easy removal of sensor without twisting cable ♦ Pressure rating up to 145 psi ♦ Integral Pt1000 temperature element for enhanced accuracy ♦ Simple maintenance by comprehensive design ♦ Ion trap designed for sensor life extension and acts as a double junction	♦ All applications where quick removal of the sensor and no compromise in safety is needed
FU24	♦ Easy removal of sensor without twisting cable ♦ Pressure rating up to 145 psi ♦ Integral Pt1000 temperature element for enhanced accuracy ♦ Automatic compensation for changes in process pressure ♦ Simple maintenance by comprehensive design ♦ Ion trap designed for sensor life extension and acts as a double junction	♦ For harsh chemical applications were large temperature/pressure variations results in early depletion of KCl ♦ Harsh pH applications were an all-in-one style body is desired ♦ Extremely clean water ♦ Extremely dirty, coating process ♦ Upside down or 360° mounting is needed ♦ All applications where quick removal of the sensor and no compromise in safety is needed ♦ Process that is prone to see pressure and temperature changes
Heavy Duty/ High Temp.	♦ Glass 15 times thicker than regular sensors ♦ "L Glass" for use in Temps. >130ºC and high pH ♦ Metal foil screening ♦ Maximum pressure: 1000kPa (10 bar) ♦ Bulb membrane for general purpose ♦ Dome shaped membrane for "Heavy Duty" applications	♦ Process with solids or abrasives ♦ High temperature process ♦ Process with pH > 12
SR20-AC32 Bellomatic	♦ Automatic compensation for changes in process pressure ♦ Constant, positive flow of KCl ♦ Large electrolyte reservoir	♦ Extremely clean water ♦ Extremely dirty, coating process ♦ Process with poisonous ions ♦ Applications that see pressure changes

UNIQUE pH Sensor	FEATURES	WHERE TO USE IT
SC25	♦ Sterilizable pH sensor ♦ Heavy duty glass for higher temperature and alkaline applications up to 130°C. ♦ Can be used in low conductivity (>10µS)	♦ Process that is prone to pressure spikes ♦ Process that may poison the reference ♦ Mono and Tri ethylene glycol (meg/teg) ♦ All-in-one 12mm design (pH/Ref/Temp/LE)
PH18	♦ Sterilizable pH sensor ♦ All enamel construction ♦ No reference electrode or junction ♦ Easy installation and commissioning ♦ No routine maintenance ♦ Flexible installation options ♦ 140ºC, 15 bar (284ºF, 214 psi)	♦ Process where KCL is forbidden ♦ ‘Process containing a low water content ♦ High process temperature and pressure ♦ Process with rapid pressure/temperature changes ♦ Fermentation processes ♦ Dairy product manufacture
pNa (SM23-AN4 or SC24V)	♦ Sodium reference electrode ♦ No reference junction ♦ No electrolyte ♦ 120°C	♦ Process where KCL is forbidden ♦ Applications with high and stable salt concentrations ♦ Brine applications ♦ Fermentation processes ♦ Electrolysis processes ♦ Cheese manufacturing

Maintaining your pH Monitoring System

Why Is Sensor Maintenance Required?

When a quality pH sensor system is undamaged, cleaned and properly calibrated it will provide a measurement that is accurate and reliable. Even if an electrode is in a process that does not cause coating, plugging, abrasion or other problems, it still must be calibrated periodically to correct for aging of the sensors and the non-recoverable changes to the electrodes that take place.

These effects of aging usually happen slowly therefore, calibration should not be necessary more frequently than about once a month. If more frequent calibration is called for, it is usually because (1) the process is aggressive; (2) the electrode cleaning process used was not effective; (3) the routine calibration was not properly executed; (4) the pH of the process is temperature dependent or (5) the wrong electrodes have been selected.

Users desire an accurate, reliable measurement with a reasonable electrode life while minimizing the frequency or complexity of maintenance that is needed. However, ensuring the electrodes are clean and calibrated will always involve some amount of maintenance.

The measurement results obtained from dirty or faulty electrodes can be anything from slow response, to a completely erroneous reading.

Therefore, the accuracy of the pH measurement is directly dependent upon the frequency of maintenance, and the maintenance frequency (and also the method used) is directly dependent upon the importance and/or aggressiveness of the process.

NOTE

The following periodic maintenance advice is intentionally general in nature because pH sensor maintenance is highly application specific.

General Maintenance Procedure

The basic maintenance procedure for pH sensors/electrodes includes: (1) **Check** to see if electrodes need to be cleaned; (2) **Cleaning** the electrodes properly, then (3) **Re-checking** to see if the cleaning was effective and finally, (4) **Calibrating** the electrodes when it is necessary.

Checking and Cleaning the pH Electrodes

All pH electrodes should be cleaned on a periodic basis. The frequency of this cleaning is dependent upon the severity of the process (potential for coating or fouling) the electrodes are exposed to. An easy way to determine if the electrodes need to be cleaned is to, remove them from the process and wash them off with either DI or Tap water. Place the electrodes in a pH 4.01 buffer. If the displayed value is within 0.10 pH of the buffer value, the electrodes can be considered clean. Put the system back on-line.

Checking: To determine if the electrodes need cleaning, remove them from the process and rinse them off with either DI or Tap water. Place the electrodes in a pH 4.01 buffer and allow the reading to stabilize. If the displayed value is within **0.10 pH** of the buffer value, the electrodes can be considered clean and the system can be placed back on-line. If the displayed value is outside the 0.10 tolerance, the electrodes should be cleaned.

Cleaning: A variety of cleaning solutions can be used depending on the coating effects of the process on the electrodes. Typically a 5 to 10% solution of HCl (or Muriatic) works well.

1.) First, rinse off the electrodes/sensor in just plane water to remove any heavy process coating using a soft brush, taking care not to damage the electrodes.

2.) Immerse the electrodes in the cleaning solution for 1-2 minutes, agitating them regularly. The pH reading will drop below 1.00 pH. Use the soft brush to clean off any remaining coating deposits.

3.) Once the reading has stabilized, remove the electrodes from the acid and rinse them thoroughly with clean water to avoid contaminating the buffer solution used in the next step. The pH of the rinse water should be close to pH 7.

pH glass is a porous glass and retains some of the last solution in which it was immersed. When you place the electrodes in the rinse water you may notice the pH reading settle out between pH 3 or 4. This means there was still some acid in the pH glass. After the reading has stabilized, wash the electrodes again in fresh rinse water. The pH will again climb and may settle out between pH 5 or 6. If so, some cleaning acid may still remain. wash the electrodes again, or until the final reading is close to pH 7.

4.) Place the electrodes back in the pH 4 buffer solution. If the displayed value is within **0.10 pH** of the buffer value, the electrodes are clean and do not require calibration. Put the system back on line.

If the pH value is outside the tolerance (0.01 pH), then a two point buffer **calibration** is require.

NOTE

EXA mains powered instruments allow users to do “on-line” cleaning of the pH electrodes and automatically check if the cleaning was effective. This capability can eliminate the manual “Check” step for the user.

Buffers and Calibration

Buffers

pH Buffer solutions are an indispensable tool for maintaining an accurate pH measurement. A pH measurement loop requires regular calibration of the electrodes to compensate for their aging and deterioration, therefore it is essential to have a reliable standard with which to do this calibration. This is the task of pH buffers. They are the reference points to which the measurement electrodes are calibrated. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. Consequently, if the buffers are not accurate themselves, the calibration serves no useful purpose.

The fundamental concept of buffers is that it is a solution designed to maintain its rated value even with the intrusion of contaminants. Buffer solutions are one which resists large changes in pH following the addition of either an acid (H+) or a base (OH-). This is because the weak acid and its conjugate base can react with both the acid and base. A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid, mixed in a 1:1 ratio (equilibrium). These are called N.I.S.T. Buffers. National Institute of Standards and Technology **(**NIST), formerly known as the National Bureau of Standards (NBS); is a federal technology agency that develops and promotes measurement, standards, and technology.

The level of contaminants a Buffer can withstand before becoming inaccurate has a great deal to do with how close to equilibrium the solution is in the first place. The pH of such a solution is calculated by the following formula:

pH = pKa+log(salt)/(Acid)

If the Salt/Acid ratio is 1, then we have:

pH = pKa, because log 1 = 0

N.I.S.T. lists the pKa values for buffers at 25ºC:

4.008- Potassium Hydrogen Phtalate
6.865- Potassium Dihydrogen Phosphate/ Disodium Phosphate
9.180- Sodium Teraborate Decahydrate (Borax)

Therefore, the pH values for the most stable buffer solutions are 4.01, 6.865 and 9.18 respectively *after rounding* at 25°C. These are the equilibrium values at which the buffer can accept the maximum level of contaminants before becoming inaccurate. This is commonly referred to as the "buffer capacity." The constituents of these liquids are defined by international standards like **DIN19266, IEC 726 and NIST**. What Buffer values do you use… 4.00, 7.00, and 10.00? If you use 4.00, 7.00, and 10.00 you are not using N.I.S.T. Buffers, you are using what are known as Technical or “Traceable to N.I.S.T.” Buffers. You can tell a N.I.S.T. Buffer from a Traceable Buffer because no N.I.S.T. Buffer at reference temperature (25ºC) is a whole number and all traceable buffers are whole numbers (4.00, 7.00, and 10.00).

A Traceable or Technical Buffer is made by taking the N.I.S.T. formulations for true buffered solutions and adjusting them away from the 1:1 ratio to get the whole number, 4.00, 7.00, or 10.00. This was done 15-20 year ago because with the past old Analog Transmitter it was simpler and straightforward to read a whole number during calibration. Which would you be able to see better on the transmitter below in Figure 9, a pH of 6.86 or a pH of 7.00? The answer is simple 7.00 without a doubt.

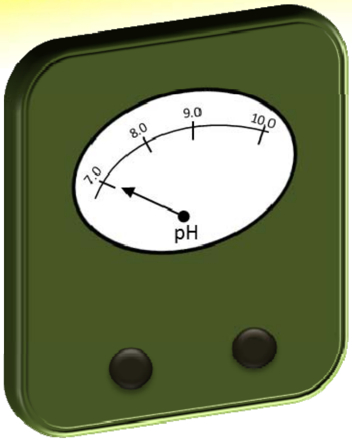


Figure 9: Analog Display

Examples of the N.I.S.T. buffers used by YOKOGAWA are shown in **Table 2.** Buffer solutions prepared from these substances conform to the recommendations of the DIN Standards Committee and the National Institute of Standards and Technology (NIST). The substances were chosen for their particular suitability as calibration standards for precision pH meters. Examples of the Traceable buffers are shown in **Table 3**. All Yokogawa pH Transmitters are preprogrammed with N.I.S.T. Buffer tables for calibration. Refer to **Technical Note TNA0905 "PH450 Analyzer Programming Customer Buffer Tables"**, before calibrating a Yokogawa EXA PH series transmitter with Traceable or Technical Buffers; you will need to program the buffer table to reflect the buffer table of the buffer you are using. Refer to **Technical Note TNA0919 "PH450 Analyzer Free Programmable Buffer Tables"** for help.

Table 2

EXA AUTO CAL NBS BUFFER TABLE				
TEMPERATURE		**pH Value**		
°C	ºF	pH7	pH4	pH9
0	32	6.98	4.00	9.46
5	41	6.95	4.00	9.40
10	50	6.92	4.00	9.33
15	59	6.90	4.00	9.28
20	68	6.88	4.00	9.23
25	77	6.86	4.01	9.18
30	86	6.85	4.02	9.14
35	95	6.84	4.02	9.10
40	104	6.84	4.04	9.07
45	113	6.83	4.05	9.04
50	122	6.83	4.06	9.01

Table 3

TYPICAL NBS *TRACEABLE* BUFFER TABLE				
TEMPERATURE		**pH Value**		
°C	ºF	pH7	pH4	pH9
0	32	7.13	4.00	10.34
5	41	7.10	4.00	10.26
10	50	7.07	4.00	10.19
15	59	7.05	4.00	10.12
20	68	7.02	4.00	10.06
25	77	7.00	4.00	10.00
30	86	6.99	4.02	9.94
35	95	6.98	4.02	9.90
40	104	6.97	4.04	9.85
45	113	6.97	4.05	9.82
50	122	6.97	4.06	9.78

Temperature Dependence

The temperature dependence of the pH of a buffer solution is generally specified in terms of measured pH values at certain discrete temperatures. Since the Yokogawa EXA PH series instruments are preprogrammed with N.I.S.T. Buffer tables, you can see from table 1 above that as the temperature changes the pH of the buffer solution also changes. So if during calibration the temperature compensator needs to be immersed in the buffer liquid, an automatic adjustment for temperature variations will be done in the transmitter. Any pH value listed is only meaningful if the measuring temperature is also specified. High caustic Buffers (9.18 and 10.00) are the most temperature sensitive buffer that can be used. pH 4 Buffer is the most temperature stable buffer that can be used.

~ BE AWARE ~

- Solutions with a pH above 7 (base or caustic) are particularly sensitive to the ingress of atmospheric C0$_2$. When C0$_2$ from the air dissolved in the caustic buffer the conductivity increases and the pH value

decreases. Why? Because the Carbon Dioxide from the air dissolves and forms Carbonic Acid… this causes the pH value to go down. The longer the caustic buffer sits open to air or the older the Buffer is, the greater the ingress of the $C0_2$, the buffer values will be low. Therefore it is good practice to only use the 9.18 pH buffer for checking the upper range of the transmitter, and use 6.86 and 4.01 pH Buffers to perform calibration.
- Solutions showing any sign of contamination must be discarded immediately and fresh solutions used.
- No solution should be used for more than a month after preparation, as it may no longer be accurate.
- Solutions should be stored in tightly sealed, preferably air-tight bottles made of polythene or borosilicate glass.
- Solutions used in calibration should NOT be returned to the original bottle, as they will contaminate the buffer.

Calibration

A pH measurement loop requires regular calibration of the electrodes to compensate for their normal aging and also deterioration caused by the process. Typically this is done about once a month. There are two commonly used methods of calibration; Automatic and Manual. Both achieve the desire results of adjusting for the aging (diminishing accuracy) of the electrodes. Users should choose the method which best suits their maintenance requirements and capabilities.

- **Automatic Calibration**
  EXA instruments offer internally programmed buffer tables, to calculate the buffer value at the actual temperature during the calibration. In addition, the stability of the reading is automatically calculated and when the reading has stabilized fully, automatic adjustments of slope and asymmetry values are made. A menu driven system prompts the operator through a simple, foolproof routine.

- **Manual Calibration**
  EXA also offers this method, where the operator decides the actual pH value to enter. Manual calibration is most often used for single-point adjustment of the asymmetry potential, by comparison method (grab sample). Manual calibration can also be used to perform a full 2-point calibration with solutions other than the NIST buffers that are listed in the calibration tables. In this case, the solutions are applied sequentially as in the AUTOCAL method, but the user determines the adjustment of reading and stability.

- **A Third Alternative**
  Yokogawa pH Analyzers offer a third means for calibration called **Sample Calibration**. This function allows users to input. The operator activates the “SAMPLE” calibration routine, at the same time as taking a representative process sample. After determining the pH of this sample by independent methods, (in the Lab for example) the reading can be adjusted. While the sample is being analyzed, EXA holds the sample data in memory, while continuing to control and read pH normally.

NOTE

During manual calibration the temperature coefficient remains active and all readings are referred to 25 °C. This makes grab sample calibration easy and accurate. However, if the manual calibration technique is used for buffer calibration, the temperature coefficient must be set to zero in maintenance mode in the "TEMP" routine.

However, no matter the method chosen the procedure should always be the same. Always use fresh buffer solutions to avoid the possibility of introducing errors from contaminated or aged solutions. Buffers supplied as liquids have a limited shelf life, especially alkaline buffers, which can absorb $C0_2$ from the air. Yokogawa strongly recommends NIST (primary) buffer standards in order to ensure the best accuracy and best buffer capacity is available.

1.) Rinse the electrodes thoroughly with clean water to remove any remaining cleaning solution. Then, immerse the electrodes in the first buffer solution (usually the neutral 6.87pH buffer) and let the measurement stabilize.

2.) Adjust the meter reading to the pH value of the buffer solution according to the method selected (automatic or manual).

3.) Rinse the electrodes with clean water to remove the traces of the first buffer. Then, immerse the electrodes in the second buffer solution usually 4.01 or 9.18 depending on the measuring range) and let the measurement stabilize.

4.) Adjust the meter reading to the pH value of the buffer solution according to the method selected (automatic or manual). A check for correct calibration can now be done by immersing the sensor again in the first buffer solution (after rinsing) to see if the reading is accurate. If it is not, the calibration should be repeated.

WARNING

During buffering the liquid earth and the temperature compensator must be Connected and the buffer solution temperature must be within the technical specification limits as indicated on the type plate.

The Basics…What does your Calibration tell you?

There are four Main Parameters for pH Troubleshooting:

1. Asymmetry / Zero
2. Slope
3. Impedance 1 (Measuring electrode impedance)
4. Impedance 2 (Reference electrode impedance)

Most commercial instruments will be able to give you an Asymmetry / Zero and Slope reading. pH system with a solution ground/ liquid earth and advanced sensor diagnostics will also be able to provide you impedance values. Understanding the purpose of each of these allows us to know where our problems with our pH system maybe and where to start.

The Asymmetry Potential (AS) also referred to as the millivolt offset, is an indication of the condition of the **reference electrode**. Theoretically when the electrodes are placed in a buffer 7, the millivolt output from the electrode pair (pH and reference) should be zero. If you have an asymmetry of 20, your pH sensor would be generating 20mV's at 7ph instead of theoretically 0mV's. Most problems with the asymmetry will be caused by the reference sensor. Some of the causes of the millivolt offset are depletion of the Potassium Chloride (KCl) from the reference electrolyte or the reference electrolyte becomes poisoned with the process solution. When the millivolt offset is +/- 30mV, it is advisable to replace the reference electrode. The reason for this is because of the NERNST Equation determined that every pH change is equal to 59.16 mV at 25ºC. If your pH system has zero of 30 mV then you are adjusting an offset equal to 0.5 pH.

The Slope (SL) also referred to as the efficiency of the electrode is an indication of the condition of the **measuring (glass) electrode.** The slope is displayed in a percentage (%) value, with 100% being ideal. When the electrode is new, the slope should be in the upper 90% range. As the electrode ages and loses efficiency, the slope and response of the electrode will start to decrease. The slope value is updated each time a two point calibration is performed and usually only small changes in the slope value should be noticed. One of the main reasons the electrode may have a low slope value, is because it was not cleaned before calibration, making it less efficient. If a low slope value is noticed, clean the electrode with a 5-10% HCl solution for a minute, rinse it thoroughly with clean water and recalibrate. Depending on the application and response time required, it is advisable to replace the pH electrode when the slope value is in the mid to low 80% range.

Conditions that cause low slope readings:

1. Consumed sensor (old pH sensor, check serial numbers for date) – replace measurement sensor
2. Poisoned sensor – Try cleaning, soaking in pH buffer and then recalibrating sensors. If it doesn't correct it replace the measurement sensor.
3. Dirty Sensor – Clean then recalibrate.
4. Cracked sensor – Impedance 1 will be low. Replace measurement sensor.
5. Wet/shorted cable – Ohm out cable, replace cable if bad.

Conditions that cause high slope:

1. Improper calibration – if someone calibrated with a US 10 buffer but auto calibrates the unit in NIST 9 buffer it will cause a slope above 100%.
2. Poisoned sensor – Try cleaning, soaking in pH buffer and then recalibrating sensors. If it doesn't correct it replace the measurement sensor.
3. Static charge – Place a ground in the pH buffer and recalibrate.

The Reference Impedance (RZ) also referred to as the resistance of the **reference junction**, is an indication of a precipitate (blockage) forming in the reference junction and that the electrode needs cleaning. This resistance is also influenced by the conductivity of the process solution. Typically a clean reference junction will have a resistance of less then 10-15k Ohms, but in low conductivity solutions, RZ values between 200 and 500 K Ohms are not uncommon. When the RZ value starts to approach 30 -35 K Ohms, the electrode will start to have a slow upward drift. When the reference impedance exceeds 100 K Ohms an error message should appear in the analyzer.

Conditions that cause Reference Impedance High alarms:

1. Reference sensor dirty – clean sensors
2. Reference sensor depleted – Replace/refill sensor.
3. Damaged/open cable – test cable if bad replace.
4. Poisoned Sensor – Replace/refill Sensor

Conditions that cause Reference Impedance 2 Low alarms;

1. Cable wet/shorted

Some instrumentation will also provide you with a **measuring glass** impedance value. This is used traditionally for alarms to indicate faulty equipment.

Conditions that cause Glass electrode Impedance 1 High alarms:

1. Measurement sensor cable disconnected/bad
2. Measurement sensor bad – replace measurement sensor.

Conditions that cause Glass election Impedance 1 Low alarms:

1. Cracked measurement sensor – replace measurement sensor
2. Wet/Shorted cable – replace cable
3. Poisoned sensor – Try cleaning, soaking in pH buffer and then recalibrating sensors. If it doesn't correct it replace the measurement sensor.

TROUBLESHOOTING

Once the system is calibrated and functioning properly, there are still problems that can occur with the measurement. Below are a few commonly seen issues and possible remedies.

Drifting:

This is seen when a pH probe is placed online and over time the reading starts to drift up or down. As the **Asymmetry Potential (Zero millivolt offset)** becomes greater, the electrode will have a tendency to drift over time and more frequent calibrations will be required to compensate for the drift. Some of the causes of the millivolt offset are depletion of the Potassium Chloride (KCl) from the reference electrolyte. This is common in gel-filled reference electrodes are used in the wrong applications such as being used in high purity water applications. When the concentrated reference electrolyte (KCl) and the low conductivity (mineral free) process solution meet at the reference junction, the process solution leaches the salt from the reference electrolyte causing the reference potential to become unstable.

Another reason is the reference electrolyte becomes poisoned (figure 10) with the process solution. This is most evident in process applications where the process pressure is greater than 1 ATM. When the process pressure is greater than the pressure inside the electrode, the process solution is forced into the reference electrode, contaminating the electrolyte and changing it’s potential. When the millivolt offset is ±30 - 45mV, it advisable to replace the reference electrode.

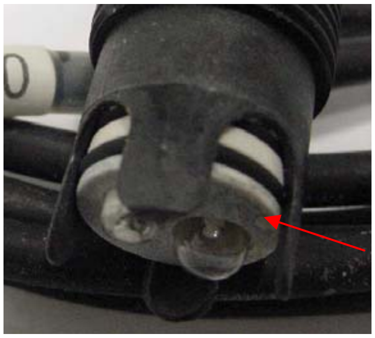


Figure 10: Poisoned Junction

Another reason for drifting could be caused process solutions containing sulfides or sulfur bearing species, react with the silver chloride in the reference electrolyte, causing insoluble precipitates to form in the reference junction. These precipitates cause a high electrical junction resistance, which leads to non-reproducible diffusion potentials, causing the electrode to have a slow constant upward drift. When the RZ value starts to approach 30 -45 K Ohms, the electrode will start to have a slow upward drift.

Noisy Readings:

The Reference Electrode because it is often open (via the junction) to the process, is the weakest link in the measurement loop and very susceptible to the interference of stray voltages in the liquid. In many industrial applications the voltage potential of process liquids is significant and cannot be neglected when making pH measurements. This voltage level may be due to a number of causes, a full study of which is too complex to be covered here. It is essential therefore, that the liquids are earthed at the point where the pH value is to be measured. This can be easily achieved when metal fittings are used. When plastic fittings are used they should be fitted with an earthling (solution ground) electrode of suitable metal.

One way to test if stray voltages are causing errors is to take the pH system off line and place it into a process grab sample. If the reading is stable and does not drift in the grab sample and then it drifts when it is placed back online, then you know it is the sample line. Another way to verify that is to place a jumper in the analyzer between the reference terminal and the solution ground terminal. If the reading locks in place then you have proven again that it is noise within the sample media that is traveling through the reference electrode into the transmitter causing unstable readings.

Slow Response Time:

Sluggish or slow response times are indication of coating or plugging of the junction. This could even be caused by a film on the glass sensor that cannot be seen with the naked eye.

A variety of cleaning solutions can be used depending on the coating effects of the process on the electrodes, but typically a 5 to 10% solution of HCl works well.

1. Rinse off the sensor in just plain water to remove any heavy process coating.
2. Immerse the electrodes in the cleaning solution for 1-2 minutes, agitating them regularly. Use a soft brush to clean off coating deposits without damaging the electrode.
3. The electrodes must them be rinsed thoroughly with clean water to avoid contamination of the calibration buffers with the cleaning chemicals.

Another reason is that as the electrode ages and loses efficiency, the slope and response of the electrode will start to decrease. The slope value is up dated each time a two-point calibration is performed and usually only small changes in the slope value should be noticed. One of the main reasons the electrode may have a low slope value is because it was not cleaned properly before calibration, making it less efficient.

On-line pH Measurement is wrong, but reads correctly in the buffers:

This is the well-known pH problem that we call Diffusion Potential. If the sensor junction is plugged, the electrical contact between electrolyte and process is poor. This results in diffusion potential that is directly measured as error. The chemical composition of a pH buffer is different from the process liquid, therefore when the junction is in bad condition, you calibrate for this error in the pH buffers, but they are different from the process. An easy check is to look at the diagnostic information in the pH analyzer: Is the Asymmetry Potential high or the Slope low. If yes then most likely you have this problem. Another cause can be the infamous ground loop current. This can be the case when you use pH sensors without solution grounding.

Errors seen resulting from cracked membranes:

A minute crack in the membrane of a glass electrode is not always visible to the naked eye. Frequent temperature shocks may give minute cracks in the membrane with consequently measuring errors. In this case the analyzer reading is 0 mV and the analyzer shows a reading of pH 7, because most pH sensors using internal buffer with pH 7. If you place the sensor is a buffer with pH 4 the instrument would still read 7 pH. For neutralization processes (set point is typically pH 7) this is very critical and dangerous situation for environment and plant are possible. Without additional diagnostic, the error will not be detected. The analyzer and pH systems that incorporate a solution ground and online impedance sensor diagnostics frequently check the impedance of the pH membrane via the solution ground. In case of a broken glass membrane an alarm is possible to generate.

Process pH Measurement Do Not Match Laboratory Measurement:

When they do not match, there is a problem and it is natural that the in-line analyzer is considered the "wrong" one, because the laboratory is the reference method and the in-line measurement is just a tool to control the process. Anyway when they do not match, you must find the reason:

1. Are both analyzers accurate? To check this both analyzers must be validated, not calibrated. So you take 2 or 3 fresh buffer solutions and measure these solutions with both analyzers. Do not make any adjustment. Please take a piece of paper and write down the values and judge the results. If one of them is wrong by 0.1 pH or more then that one needs to be calibrated. Once you have done so, you must repeat the validation test.
2. Compare apples with apples: The in-line measurement and the laboratory analyzer must measure the same sample at the same pressure and the same temperature. In other words, bring the teapot to the kettle and not the kettle to the teapot. It is possible to measure at the lab at reference temperature and the in-line measurement at process temperature. But this can only be done when the in-line analyzer is properly compensated for temperature. You can check this by taking a hot sample, insert the sensor in hot sample and let the sample cool down to 25 degrees. Only when the reading does not change, you have proper temperature compensation. If the reading changes, calculate the change in delta pH / delta temperature and program this coefficient in the analyzer if you have the capability.
3. Have reasonable expectations. If both analyzers have an accuracy of 0.1pH, you can accept differences in readings up to 0.2 pH. 4. Take into account properties of the process. As example we take boiler feed water. This sample is ultrapure water with traces of Ammonia or Morpholine to increase the pH. This sample is completely unbuffered. So as soon as it is exposed to ambient air the pH will drop due to absorption of Carbon dioxide from the air.