Precision Sensor News

"What's Causing My pH Measurement Drift?"

Jane explained to us that her pH measurement was drifting at the start of her fermentation. The sensors appeared to respond alright during the initial standardization sequence. Immediately after the standardization step, the sensors would begin to drift. We studied the data, looked at the graphs, and outlined the process conditions. Our investigation of the process uncovered the key contributor to the drift: a phenomenon called Liquid Junction Potential. A pH sensor's reference half cell provides a stable potential after a chemical equilibrium is achieved. One of the components of the reference half cell is the liquid junction (a.k.a. frit, ceramic diaphragm, reference junction). The liquid junction is a ceramic compound that links the internal potassium chloride salt bridge with the process chemistry producing the millivolt potential pathway. Most pH measurement problems are associated with the liquid junction. The liquid junction's chemical equilibrium can be altered by many process conditions. Steam sterilization, caustic rinse cycles, and pure water rinses all affect the potential of the liquid junction. As part of the decontamination procedure, Jane used a caustic rinse cycle of concentrated sodium hydroxide at 80ºC for 1 hour. The caustic cycle was followed by a pure water rinse, then by a dry air flush. Exposing the sensor to this type of decontamination cycle altered the liquid junction's normal chemistry of saturated potassium chloride. Subsequent exposure of the sensor to fermentation media produced a period of chemical equilibration at the liquid junction resulting in drifting pH measurement.

As Jane's data and graphs indicated, once the liquid junction potential returned to "normal" the pH measurement remained steady. She could wait for the electrode to reach equilibrium, perhaps an hour, then perform the grab sample calibration. However, Jane's group decided to remove the pH sensors during the caustic rinse cycle and have reported a remarkable improvement.

Basic Sensor Design
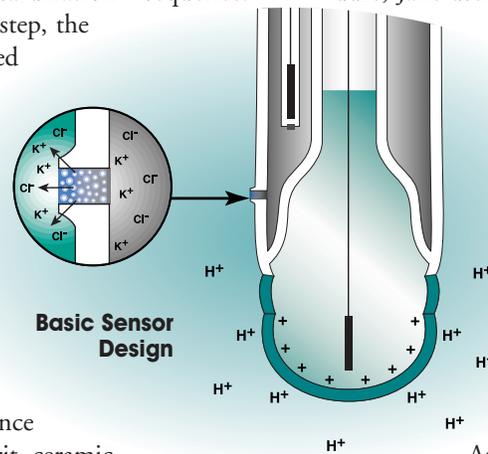
Guidelines for Choosing a Housing

The electrode housing is designed to hold and protect the pH electrode while inserting it in the bioprocess vessel. There are various types of side entry ports and different groups of housings to fit each port type. That's why the first step is to identify the diameter and type of port on the vessel. It is also a good idea to confirm the length of the port to ensure 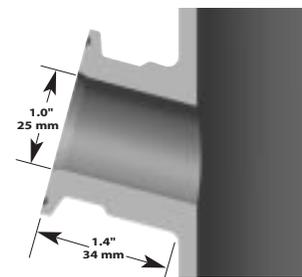the O-ring will seal properly. Once this information is gathered, choosing from a few designs will be easy. The three most common ports found on pilot and production scale vessels are:
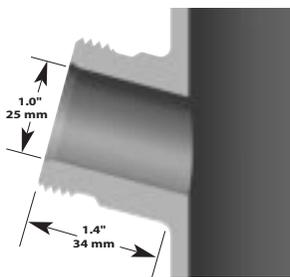
Standard 25 mm Side Port
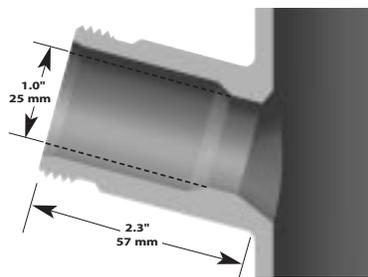
B. Braun 25 mm Safety Port

Sanitary Flanged 25 mm Side Port

pH Electrode Troubleshooting

Many pH system measurement problems are directly related to the pH electrodes' performance. Incorporating a simple troubleshooting procedure into the existing SOP (standard operating procedure) will enable you to quickly identify troubled electrodes and ultimately improve the pH measurement. A pH electrode produces 59.2 millivolts per pH unit @ 25ºC. A properly functioning electrode will respond quickly after exposure to a given buffer. In addition to displaying the pH value, some pH instruments may also display the electrode's millivolt output. pH buffers are a formulation of salts that are designed to produce a specific pH value and corresponding millivolt value. Below is a table of some of the more popular buffers with their pH and millivolt values. pH buffers 7.00 and 4.01 are very stable and readily available from most buffer suppliers. The use of fresh buffers that are temperature controlled to 25ºC will minimize test error.

pH buffer @25°C	pH electrode millivolt output
4.01	+176.9
6.86	+8.3
7.00	0
9.18	-129.0
10.01	-178.1

% Slope Calculation

In addition to mV output and response time, the "% slope" is another important indicator of pH electrode health. However, some transmitters do not automatically calculate it. Follow this procedure to calculate it manually.

Test Procedure

1. Set the instrument's pH/mV switch to the mV mode.

2. Rinse the electrode thoroughly with DI water.

3. Insert the electrode in the 7.00 buffer solution and record the response time and mV output. Note: If you're unable to get a stable reading this may indicate liquid junction problems.

4. Rinse the electrode thoroughly with DI water.

5. Insert the electrode in the 4.01 buffer solution and record the response time and mV output.

6. Use these mV readings to calculate % slope.

Calculations

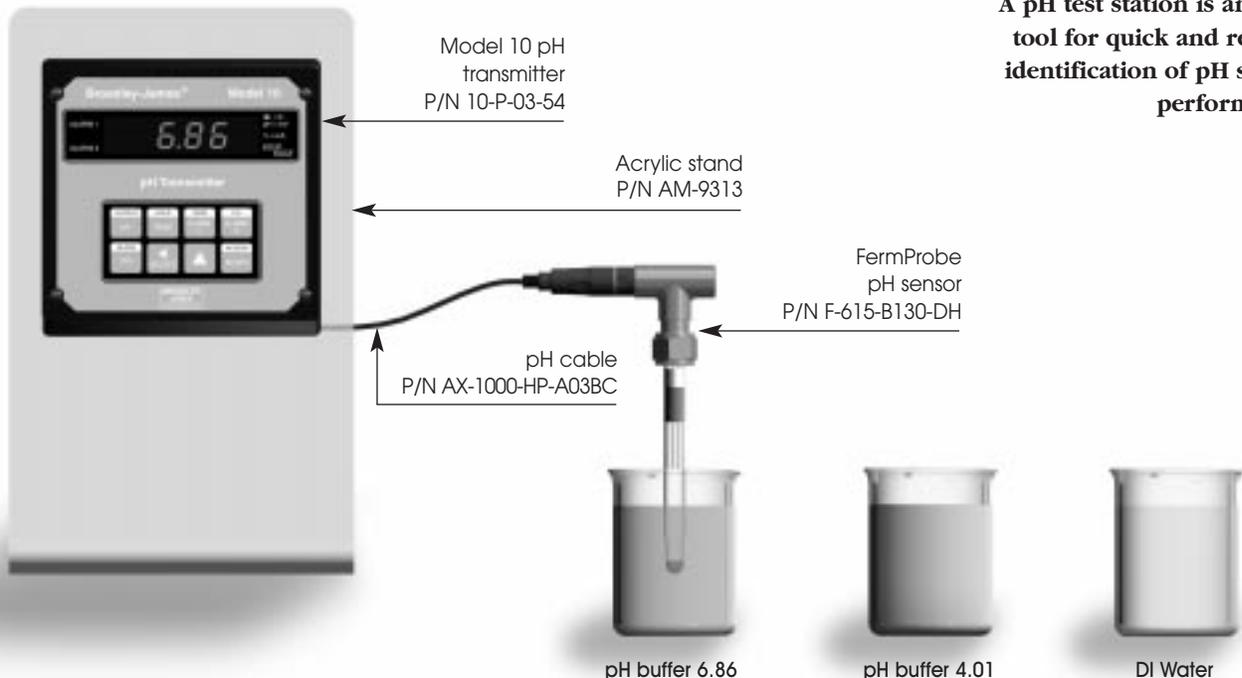Actual mV reading in 7.00 pH buffer: -7.4 mV
Actual mV reading in 4.01 pH buffer: +164.6 mV

Actual Span = +164.6 - (-7.4) = 172.0 mV

Theoretical Span = 176.9 - 0 = 176.9 mV   (see table on left)

$$\% \text{ Slope} = \frac{\text{Actual Span}}{\text{Theoretical Span}} = \frac{172.0 \text{ mV}}{176.9 \text{ mV}} \times 100 = 97\%$$

The recommended % slope range is between 91% and 100%.

Model 10 pH transmitter
P/N 10-P-03-54

Acrylic stand
P/N AM-9313

FermProbe pH sensor
P/N F-615-B130-DH

pH cable
P/N AX-1000-HP-A03BC

A pH test station is an ideal tool for quick and reliable identification of pH sensor performance.

pH buffer 6.86   pH buffer 4.01   DI Water

Temperature Compensation

Temperature changes will cause the pH electrodes' millivolt output to change. This is called the Nernstian response. Temperature will also affect the pH of the process. This is called the solution temperature coefficient. One can compensate for the Nernstian response by incorporating a temperature compensation scheme. In processes where the normal operating pH is close to the assymetry potential (pH of 7 or 0 mV) temperature compensation usually isn't an issue.

Automatic Temperature Compensation (ATC) is the most popular method for pH correction due to the Nernstian response. In this method, a separate temperature sensor is positioned near the pH electrode. The temperature sensor's signal is incorporated in an algorithm (the Nernst equation) with the pH electrode's signal and a corrected pH measurement is displayed. Some electrodes have built-in temperature sensors. The disadvantage with this type of device is the lag time for temperature equilibration. It may take several minutes for temperature equilibration to occur.

This is a problem for many microprocessor-based transmitters that have programmed time constants for acceptable signal stability. It's also a problem when one considers that most pH calibration procedures are time limited.

The table below indicates how much temperature variation is allowable to achieve an error of less than 0.01 pH units.

Permissible Temperature Variation for Error of Less Than 0.01 pH

pH of Media	7	6 or 8	5 or 9	4 or 10
Max Temp Variation °C	∞	2.7°	1.3°	0.9°

pH Unit versus Temperature

| °C	mV per pH Unit
0	54.20
20	58.16
37	61.54
40	62.13
80	70.07

Retractable or Stationary Housing

The ability to retract a sensor from the process during a run is an appealing feature for many processes. Most biopharmaceutical processes depend on the pH and/or dissolved oxygen measurements for control and/or data trending purposes. If, for some reason, the electrode malfunctions during the run, a retractable style housing allows you to remove it for testing and/or replacement. The ability to remove it does, however, come at an expense.

Retractable housings are more expensive to purchase and to service versus their "stationary" counterparts. The cost of O-rings and the labor to replace them can add up very fast. The retractable housings' initial cost is about 5 times the cost of a stationary style housing. Maintenance costs associated with a stationary housing are a fraction of those for a retractable housing. Improper or infrequent maintenance of a retractable housing may result in contamination.

In a retractable housing there are several moving parts, over a dozen O-rings and seals, and threaded connections that raise contamination questions. A stationary style housing, such as the one shown on right, usually has only 2 O-rings and no moving parts.

Another important issue when considering what type of housing to choose is the desired insertion length of the sensor. In a retractable housing the insertion length of the sensor is less than 3 inches. As mentioned in an article in our Summer 1998 Precision Sensor News, the insertion length of pH and D.O. sensors is sometimes a critical parameter.

Snap Ring
Retaining Nut
O-ring AS-209
O-ring AS-111
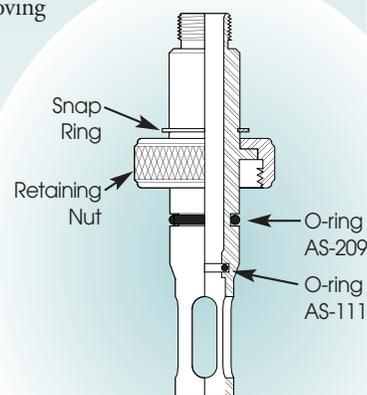
Model 330 housing— cutaway view

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