Technical Note
Calibration of pH Sensors

Performance Series pH / ORP Sensors

It's a common analogy is that a pH sensor functions just like a battery. Both devices rely on an electrochemical reaction to output a voltage. Over time the battery gets weak and eventually dies. pH sensors also lose signal over time and eventually fail to respond to changes in pH. Because of these facts, periodic verification and calibration of the pH should be performed to ensure that the sensor is maintaining accuracy.

pH Sensor Basics: Glass & Reference

To continue the analogy, a battery is compromised of two half cells - Cathode & Anode. A pH sensor also uses two half cells - Glass & Reference.

The glass electrode half cell is responsible for producing a millivolt (mV) potential that varies with changes in pH. This relationship is based on the Nernst equation as 59.16mV per pH unit at 25°C *(assuming a theoretically perfect sensor)*. There are many technical papers on the relationship between voltage, pH, and temperature so we will not go much further with this document; however there are several important points to recognize.

- At 7pH the sensor will output 0mV. This is referred to as neutral pH and represents the isopotential point of the pH scale.
- The mV response varies with temperature thus the pH signal is typically corrected back to a globally recognized value of 25°C.
- Temperature compensation accounts for changes in the response of the glass electrode. It does not take into account the effect of temperature on process chemistry (molecular disassociation). Advanced pH analyzer will be able to compensate for this effect.

The reference half cell forms the rest of the pH circuit so that voltage can be measured. As the name suggests, the reference half cell produces a stable potential voltage (reference voltage) that is not influenced by changes in pH. Again, there are several important points to consider with the reference electrode.

- There are multiple designs for reference electrodes that produce different potentials. Barben pH sensors employ a Ag/AgCl element in a KCl electrolyte solution.
- The KCl salt solution must have an electrical "bridge" with the glass electrode to form a circuit. This bridge is typically a porous membrane that allows the electrolyte to come in contact with the process fluid which the glass electrode is immersed in. This porous membrane is referred to as the "reference junction".

A simplified illustration of a pH measurement system

The glass measurement electrode and the reference electrode combine to form the pH sensor.

The pH analyzer is really a high impedance voltmeter.

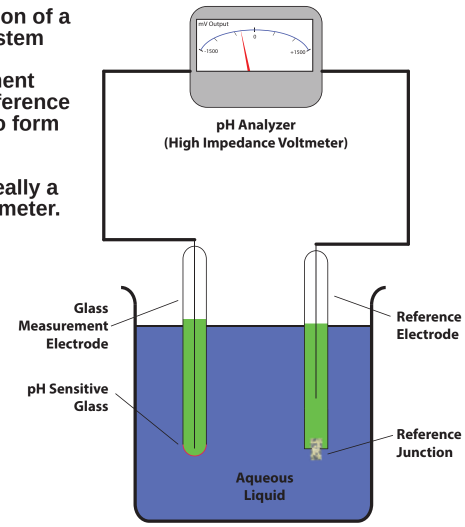

Figure 1

Calibration Basics

As the pH sensor ages the mV response will change. This can occur for several reasons. The glass measurement electrode will lose sensitivity as it is exposed to changing pH. The potential of 59.16mV per pH units will decline. The reference electrode may also contribute to error in the reading. The KCl electrolyte used in the reference electrode can become depleted, diluted, or even poisoned over time. This occurs when there is liquid mass transfer between the process liquid and the internal electrolyte. These changes in the electrolytes will cause the stable reference potential voltage to fluctuate causing error in the overall signal. In the case of poisoning the mV signal might even increase causing pH reading lower or higher then expected.

Initial calibration of a new pH sensor is done in liquid buffer solutions. Buffers provide a stable pH value that the sensor can be checked against. There a many formulations and types of buffer solutions on the market today. Once again there is a wealth of information available on buffer formulations and their usage thus this paper will not get into details. Here are some important considerations with buffers.

- Buffer pH values will change with ambient temperature. Modern pH analyzers will have buffer tables and the ability to compensate for temperature.
- Buffers have shelf life and will degrade with exposure to air.
- After use the buffer should be disposed of. Do not pour back into the bottle.

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The effects of temperature on buffer solutions are highlighted on the labeling for this buffer solution.

Figure 2

Two Point Calibration

A new pH sensor should go through a two point calibration. One buffer solution should be 7pH. Using an neutral buffer ensures a good zero point to reference. The second buffer solution is typically either 4ph or 10pH. A 3pH Δ is enough difference for the analyzer to perform an accurate slope calculation. Slope corresponds to the efficiency of the glass electrode and is expressed as a percentage. A theoretically perfect sensor will have a slope of 100%. In reality, a new sensor will have a slope of 97% to 99%. A new sensor will respond very quickly when moved from 4pH to 7pH buffer. Once the slope gets below 80% the response of the pH sensor will be noticeably slower. Replacement of the sensor should be considered. Here are the important considerations with a two point calibration.

- The slope indicates the sensitivity of the glass electrode. Recording slope values over time will provide an on-going indication of the health of the sensor.
- Two point calibrations should always be performed for new sensors. Ongoing, two point calibration may be suitable in less aggressive processes close to neutral 7pH.
- Rinse the sensor in tap water when changing between buffer solutions to avoid cross-contamination.
- The speed of response between buffers should be < 30 seconds. If response is slower then additional cleaning or replacement may be required.
- 4ph buffer is highly recommended. It has less temperature error and tends to have longer shelf life then 9.18pH or 10pH buffers.
- If the pH analyzer has a manual calibration option then select this option over automatic calibration.

Grab Sample Calibration for Barben pH Sensors

To achieve the best accuracy in harsh chemical processes, initial two point calibrations should be followed up by one point grab sample calibrations. As mentioned earlier in this paper, changes in the reference half cell can also impact the accuracy of the pH reading. A one point grab sample corrects for these changes in the reference. The procedure is listed below.

- Remove Barben pH sensor from the process. Clean as necessary. (see separate cleaning Tech Note for additional information).
- Reinstall the pH sensor into the process and give it time to reach process temperature.
- Take a sample of the process near the sensor installation and measure the pH using a laboratory style pH electrode. This measurement should be done in the field to avoid any temperature changes. Swirl the sensor back and forth in the sample for best results.
- Use the reading from the laboratory electrode to offset the pH value in the analyzer.

Questions often come up regarding the laboratory electrode used in grab sample calibrations. This probe is typically a simple combination glass electrode connected to handheld electronics. The probe should have built-in temperature compensation. Consider a separate, external temperature RTD if the sample temperature varies greatly from ambient temperature and highest accuracy is required. Barben Analyzer Technology recommends a laboratory electrode which uses a liquid KCl electrolyte. This ensures that the laboratory electrode chemistry matches the process sensor chemistry. The laboratory probe should have a large aperture style junction.

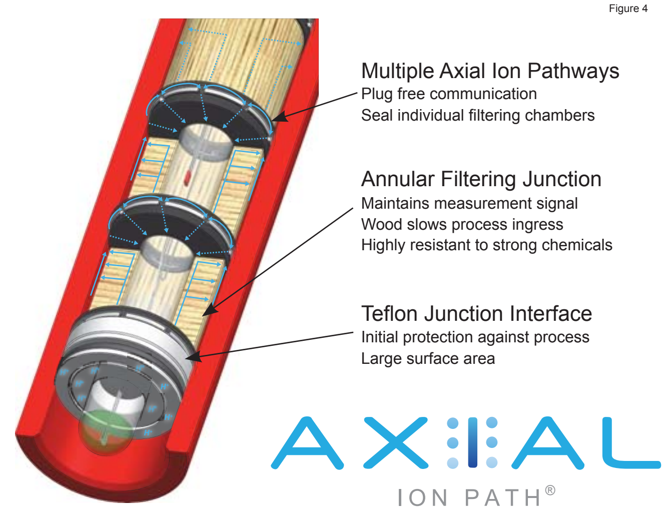
Great example of a two point calibration station. Two buffers and rinse water. An example of a laboratory style pH electrode can also be seen in this photo.

Figure 3

Advantages of Single Point Grab Sample Calibration

Why is the additional grab sample calibration successful in improving accuracy? Figure 4 shows a cross-section of a Barben pH sensor. The Axial Ion Path® reference can be seen surrounding the internal glass measurement electrode. This reference design is extremely successful in combating contamination in processes with high temperatures/pressures and strong chemicals. Upon initial installation, this reference design will experience some initial voltage offset as liquid mass transfer occurs between the process and the electrolyte. Grab sample calibrations remove this offset and ensure that the best accuracy is maintained. Calibration frequency may actually lessen as equilibrium is reached and the reference stabilizes.

Figure 4



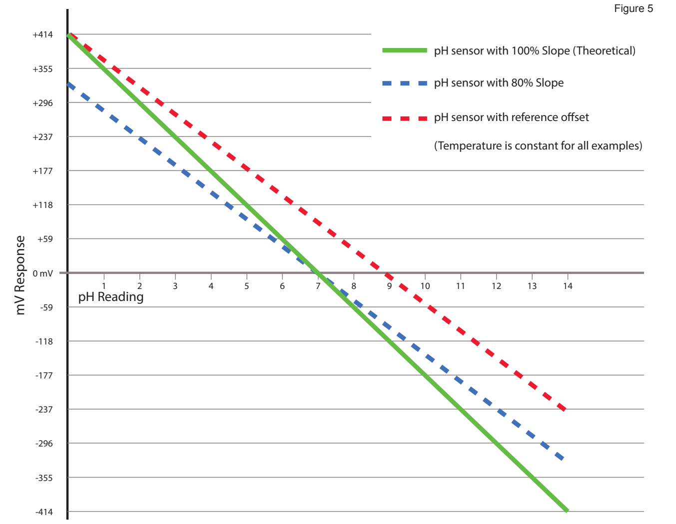
Calibration Summary

The chart in Figure 5 provides a graphical representation of the response of several pH sensors. The green line represents a theoretically perfect sensor with 0mV at neutral 7pH and 59.16mV per pH unit across the entire range of measurement. In reality pH sensors will degrade over time. A sensor that has seen loss of efficiency due to the glass will see the slope change. This can be seen with the blue line in the graph. The sensor has a slope value of 80%. It will output less voltage per pH unit when compared to the perfect pH sensor of the green line.

If our sensor with 80% slope now experiences some voltage offset due to contamination of the reference half cell then the line may shift. This shift can be seen as the red line on the graph.

The two point calibration will correct the blue line. The single point grab sample calibration will correct the red line. Both calibrations are important!

Figure 5



The above graph shows the effect of slope and offset on the sensor response. The blue line shows how a sensor with 80% slope puts out less mV's per a given pH value than a new sensor (represented by green line). This can be corrected via a two point buffer calibration.

The red line shows the effect of reference offset on our blue line sensor. Note that the mV response is skewed high. This error can be corrected by a one point grab sample calibration.

Final note, errors caused by slope are not seen at 7pH (isopotential point). The error becomes more of an issue as the pH moves AWAY from neutral towards 0 or 14pH.

Sensor Storage & Shelf Life

pH sensors need to be kept hydrated in order to function. Sensors are shipped from the factory with a small, liquid filled cap. Save this cap! If the sensor is taken out of service for any length of time the cap can be reused to keep the sensor tip wet. Potable water or buffer solution work equally well for this purpose. If the sensor will be stored for long periods of time then mold can form in the cap. The mold is not harmful and can be easily cleaned off prior to usage. If mold is a concern use diluted 4pH buffer solution. The acidity of the solution will prevent mold from forming inside the cap.

A final battery analogy, pH sensors have a shelf life just like a battery does. It is typical for the sensor to lose 5% of its efficiency for each year of storage. If a sensor has not been used for some time check its response in buffer solutions. A 5 minute soak in dilute (3-5%) hydrochloric acid is also effective in restoring the sensitivity of the electrode.

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A pH sensor with liquid filled cap prior to shipment. The black electrical tape helps to secure the cap and prevents leakage.

Figure 6

Contact Us

Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of Ametek.

Ametek has nearly 14,000 colleagues at over 120 manufacturing locations around the world. Supporting those operations are more than 80 sales and service locations across the United States and in more than 30 other countries around the world.

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