

Understanding pH Troubleshooting and Diagnostic information

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?

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 25°C. 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 than 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.

Now how do I use this information to relate to what I am seeing online?

Below are some 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 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 its potential. When the millivolt offset is $\pm 30 - 45\text{mV}$, it is advisable to replace the reference electrode.

Another reason for drifting could be caused by process solutions containing sulfides or sulfur bearing species, which 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 $30 - 45\text{ K Ohms}$, 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 an 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 then 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 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 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, then there is no good electrical contact between electrolyte and process. This results in diffusion potential that is directly measured as error. The chemical composition of pH buffers is different from process liquids. So 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 on 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 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 in 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 (and reference) via the solution ground. In case of a broken 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.