Making accurate pH measurements

When it comes to obtaining accurate pH measurements, three's the charm

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About the Author

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Fred has taught accredited course work and authored numerous articles relating to pH, ORP and conductivity measurements. Past publications include "What Is pH and How Is It Measured?", a primer on the use of pH instrumentation, and "Electrical Conductivity Measurements" in the "Process/Industrial Instruments and Controls Handbook", Fourth Edition, by McGraw Hill, Douglas M. Considine Editor.

Like the old saying goes, give a man a watch and he always knows what time it is. Give him two watches and he never knows the correct time. Ah, but give him three watches, let him average the two closest times, and he will be fairly close to a correct time.

What do watches have to do with pH? In this article, we will tie the analogy of accurate time to pH measurement and show how to make more accurate, dependable and believable pH measurements by using three pH sensors.

So how do we measure a pH process accurately?

pH buffers and labs The first thing needed for accurate pH measurements is an accurate reference or starting point, and that is the pH buffer. This is the standard by which a pH sensor is calibrated.

Sensors are cleaned (hopefully) and immersed into buffer solutions of 7 and 4 pH to set the zero and slope of the sensor. When this is set and accurate, the sensor is calibrated and will be able to measure correctly.

But what happens when the process does what it does so well, and starts to coat or otherwise add error to the sensor measurement? What about potential ground loops that may or may not be present on any given day? How do you ensure that the pH value you are seeing is correct?

Figure 1: Technician taking a sample for comparison in the lab. She better hurry, because if it cools off the pH reading may change.

Some will take a grab sample (Figure 1) and run it to the lab for a quick comparison. What if they take a bathroom or cigarette

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break on the way to the lab? The sample has the chance to change over this time in temperature and absorb some CO_2 from the atmosphere. Both of these things will lead to a different reading between the on-line sensor and the lab.

Just a few more considerations: What if the lab meter is not temperature compensated, or manually adjusted to an incorrect temperature of the sample? Was the sample taken from the exact same location as that of the measuring electrode of the on-line sensor? These differences will cause an error between the two readings.

Two or three sensors? A diligent process designer may install a second pH sensor into the process, average the two readings, and use that average as an accurate value for the pH measurement.

Sounds good on paper, but in practice this is not a reliable method. Why? First, it is important to understand that no two pH sensors are alike. In buffers, maybe, but as soon as the sensors are subjected to the process and the dynamics of the process are imparted onto the sensors, each sensor will have a different take on what the process pH represents.

One of the differences may be that one sensor has been hit with a contaminant and shifts its pH reading, affecting the average of the two sensors. Therefore, the overall average does not reflect the true pH of the process. A second difference may be that each sensor is seeing a different pH based on where they are mounted within the process.

If the sensors are mounted in a tank, perhaps one sensor is closer to a mixer than the other sensor, or one sensor is closer to a reagent addition line. In each case, one sensor is not seeing the same value as the other. Streaming potentials (an electric current that occurs when an electrolyte is driven through the sensor) may also affect the pH value, depending on where the sensor is mounted in relation to the other sensor. Bottom line: Having two sensors is no better than having just one sensor.

The best way around the dual sensor approach is to use three sensors. Just as giving a man three watches and having him average the two closest times to come up with an accurate time measurement, the same applies for three pH sensors. The three sensors should be mounted as close to each other as possible to minimize any differences in the above mentioned scenarios.

The three sensors should be looked at as individual entities where one throws out or disregards the reading obtained by the sensor that shows the largest difference from the other two sensors, and then averages the reading of the two remaining sensors for a reasonable interpretation of the true process pH.

Won't three pH sensors be costly? The answer is, it will cost a little more up front but in the long run, the cost savings will be much greater.

In some applications, like the chemical, pharmaceutical and food industry - where product can be very expensive - process plants are willing to pay a little more to ensure higher quality and larger, end-result cost savings. Applications where three sensors would provide large cost savings through accurate measurement include: any process where tight pH control will save reagents, increase product quality, prevent process upsets, or damage equipment, or where fines may be levied if pH outfall is outside regulatory requirements.

Figure 2: A multi-channel transmitter, such as this Endress+Hauser CM444, can take three pH sensor inputs and average the two closest readings.

And now, with new devices like multi-channel transmitters (Figure 2) with three-input capability and digital sensor technology, it doesn't have to be so expensive. In other words, you don't need three pH transmitters - just three pH sensors and one transmitter.

The multi-channel transmitter detects differences among the three pH sensors and calculates an average value. That value then is sent to the control system, where the system uses this average as the basis for making decisions on the operation of the process.

By using three pH probes and a single transmitter, you can shorten working time in highly critical applications.

A clean pH sensor yields accuracy For a pH sensor (Figure 3) to maintain its accuracy, it must remain clean. The glass measuring electrode cannot become coated and the reference electrode assembly must similarly not become coated, plugged or otherwise contaminated by the process solution.

The coating or scaling might be removed using a water jet from a faucet or spray bottle. More entrenched coatings may require the use of a gentle brush to carefully remove the coating. Depending on the nature of the scale or coating, you may find it necessary to dip the sensor in a hot water solution, maybe in a beaker of 250 ml containing 5 ml or so of Dawn® dishwashing detergent. Lightly scrub the electrode for a few seconds to facilitate cleaning.

For more aggressive coatings you may have to dip the brush in a 2% HCI acid solution and then lightly scrub the electrode for a few seconds. Alternatively, you may have to soak the sensor (electrode area) in a similar solution for a few minutes to really work at attacking the contaminant. Immediately after cleaning/soaking, rinse the sensor in water and then let the pH sensor soak in tap water or a 7 pH buffer solution for a few minutes to stabilize.

One advantage of a three-sensor system is that it's easier to determine when a sensor needs to be cleaned. If one sensor reads pH consistently different than the other two, then it probably needs to be cleaned and calibrated. Without such a system, the plant has no way of knowing when a sensor needs service, and typically performs cleaning and calibration on a scheduled basis. In some cases, when the sensor is perfectly fine, this is a waste of time.

With a modern digital pH sensor and a multi-channel transmitter, it is easy to replace a questionable sensor with one that has been pre-calibrated and awaiting its turn in the rotation.

In the end, it's important that whatever method is used to determine the pH of a process - single, double or triple redundant measurements - the pH sensors must be clean to obtain a reliable and accurate pH value.

Figure 3: Typical pH sensor.

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