

## The Ten Things You Should Know about pH and ORP

*As a manufacturer our technical support department receives a steady flood of phone calls or e-mails for problems concerning the measurement of pH and ORP. Over half of these calls turn out to be the result of a misunderstanding of how pH and ORP measurements are made and how they should be interpreted. So here is a list of the ten things anyone in the business of measuring the pH or ORP of their process should know that will make his or her job more stress-free.*

### 1. pH measurements are only good to 0.1 pH units.

Probes are made of electrodes and electrodes are funny things. They are the only electronic component that don't have specifications listed in their data sheets. One major figure of merit, the impedance of the glass electrode, is on the order of tens of Megaohms and can vary by a factor of two. Making them is still an art form.

Cross sensitivity to other ions (e.g. sodium), non-linearity at very high or very low pH, contamination of the electrolyte and differences between any two electrodes limit the accuracy of measurement. Expecting accuracy of greater than 0.1 pH units is expecting a lot.



### 2. Speaking of accuracy... It's not the same as precision.

A ruler with 1/8" markings is accurate but not very precise. A micrometer with 0.001" markings but an incorrect zero is precise (or reproducible) but not accurate. For a consistent process a pH probe can achieve precision of results to within 0.02 pH units but its accuracy will always be limited by variables such

as calibration, very high or low pH, ionic interference or electrostatic charge build-up. Careful, routine calibration will narrow the gap between the accuracy of readings closer to the lower level of precision.

### 3. ORP measurements are only good to $\pm 10$ mV.

Once again the measurement of ORP might be characterized by a high precision but the accuracy of the reading is constrained by the nature of its one point calibration, as explained in point 6, and the non-buffered calibration solutions that allow the ORP value of the calibration solutions to change over time. Whereas the buffered composition of pH calibration solutions insures that they will change minimally an ORP calibrations solution is a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts. Just the addition of air to the mixture will increase the ORP of the mixture.

### 4. ORP measurements are relative.

The process electrode is nothing more than a platinum (or gold) band upon which oxidation / reduction (REDOX) reactions take place. To complete the circuit—as in all potentiometric devices—requires a reference electrode. Usually that is the same Ag/AgCl electrode used in a pH probe so the REDOX potential that you read is the difference between the Pt band process electrode and the Ag/AgCl reference electrode. What matters most with an ORP measurement is its change to a standard that has been internally established.

### 5. Accurate pH calibration requires two points.

Calibration measures the response of an instrument as one changes the measurement variable in a known way. For pH measurements that measurement variable is the concentration of hydrogen ions. One calibrates a pH probe by drawing a line through points representing the response of a pH probe to more than one  $\text{H}^+$  ion concentrations (or pH values). Therefore calibration requires at least two points. Nearly all pH calibration is done with two solutions from the list of three: 4, 7 and 10.



## 6. ORP calibration is usually done with one point.

This sounds like a reversal of point 4 but it's not. ORP is not a measure of any one species (e.g.  $H^+$  ions or oxygen molecules). It measures the collective REDOX potential of everything in the water. Furthermore calibration solutions, e.g. 200 mV and 600 mV solution, are two completely different mixtures of reagents, with each having its own calibration slope and offset. You can't construct one calibration curve using two different solutions. Therefore all we can do is choose one solution and calibrate for it. We suggest a 600 mV solution since that is close to the target of most water treatment facilities. However you can always check the accuracy of your ORP analyzer with as many calibration solutions as you desire.

## 7. ORP measurements can be slow.

Stick an ORP probe in a calibration solution and you will get a steady reading within 20 seconds. Take the same probe and stick it in a glass of tap water and it might take 15 minutes for the reading to settle to the 200-300 mV that is typical of tap water. The response of the process electrodes to the REDOX reactions that take place on the surface of a Pt electrode depends on the speed of the many reactions that give the potential and the rate at which molecules diffuse through the water. The  $Fe^{2+}$  and  $Fe^{3+}$  ions that comprise most of the ORP value in calibration solutions react very quickly with the Pt but the chlorine species (usually HOCl) and dissolved oxygen that make up tap water react much more slowly. So the key to successful ORP measurement is insuring that you allow enough time for the probe to equilibrate.

## 8. pH measurements must be temperature compensated to be accurate.

A pH measurement is the determination of  $H^+$  ions in solution. Higher temperature causes the chemical activity to increase and the pH reading to increase accordingly. So we must remove the temperature effect by measuring it and using the well known Nernst equation to correct it for the reading at 25°C. (The correction is quite simple. The pH value is proportional to temperature when the latter is an absolute value (i.e. in Kelvins)).

## 9. ORP measurements are affected by temperature but are NOT corrected for it.

An ORP value simply reflects the ability of whatever is in the water to oxidize whatever contaminants are in the water. Of course oxidation speeds up at higher temperatures. But since ORP measures the rate of chemical reactions and not any one chemical species there is no need to correct it. What you see is what you get. Nonetheless, when you report ORP values it's a good idea to state the temperature at which the reading was taken. It is common to report ORP values at 25°C so that there is a basis of comparison with other readings.

## 10. Some probes last longer than others but none last forever.

Over time chemicals in the process make their way through the junction or salt bridge and into the pH 7 buffer that bathes the reference electrode. Most probes are combination style which means that the reference electrode and process electrode are "combined" in one glass envelope. This usually makes it impossible to recharge the KCl electrolyte solution that surrounds the reference Ag/AgCl reference electrode. For this reason combination probes last about a year. Some manufacturers allow one to change the KCl electrolyte which prolongs the lifetime of their combination probes.

Differential probes, such as the Aquamatrix P/R60 series, are comprised of two separate pH measuring circuits—one in a constant pH 7 bath and the other for the process—having a grounding rod in common. This arrangement eliminates ground loops and also allows a reference solution and junction (or salt bridge) that can be changed at will. These probes also contain a buffer amplifier that convert the low current signal into a high current one. Differential probes cost more but their very long lifetimes can actually make them cost competitive. Their accuracy is also unsurpassed.

Nonetheless all electrodes lose their efficiency as the glass becomes contaminated and/or eroded by the process. While most combination probes will last about a year a differential probe will last about at least five.

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