The Everyman's Guide to the Miraculous but Misunderstood ORP Sensor

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Everyone in the water and wastewater industry knows and measures pH. Conductivity is a concept we all readily grasp. Dissolved oxygen and free chlorine are easy to understand since they refer to actual chemicals.

But ORP is another matter. If you know that it stands for oxidation-reduction potential then you are already in a select minority. And if you can really explain what it means then you are in an elite club.

It's precisely because ORP is so poorly understood that we sell about 8 pH sensors for every ORP sensor. Yet, if more people understood just how powerful this 3-letter parameter is we would triple our sales. There is a good chance that you may be one of the many who are missing out on the power hidden in an ORP measurement.

1. What ORP Means

Chemicals are like people. There are givers and there are takers. In the chemical universe the givers are chemical compounds or elements that give electrons to those in need. The takers are those compounds that need and take electrons. In the human race, for every giver there has to be a taker. So it is in chemistry. Electrons don't just float around in water. For every molecule, atom or ion that coughs up an electron there must be another species that can grab it for its own selfish purpose.

The process of giving an electron is called "oxidation" and the process of grabbing an electron is "reduction." One molecule is especially famous for being a "taker"—oxygen. O_2 molecules are ruthless in their pursuit of taking electrons from any poor chemical capable of giving it one or—more frequently—two. A schematic of an oxidation-reduction reaction is shown in Figure 1. In this drawing compound B could be oxygen.

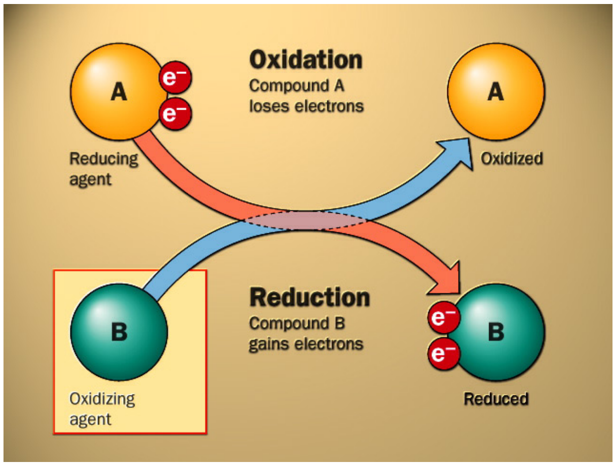

Figure 1 - Schematic of Oxidation Reduction. Compound A gives up two electrons and compound B takes the two electrons

The giver is very often a metal such as iron or sodium. In one case known to us all 4 oxygen atoms gang up on 3 iron atoms and steal a total of 8 electrons. The two elements then marry and form Fe_2O_3—or good old rust. In chemical parlance we would write these two reactions as:

Oxidation: $Fe \rightarrow Fe^{+3} + 3e^-$

in which the +3 superscript means that the poor iron atom has lost 3 electrons and consequently ends up with a positive charge.

On the other side of the swap is greedy oxygen in which each oxygen molecule takes four electrons to form 2 oxygen atoms each with a doubly negative charge.

Reduction: $O_2 + 4e^- \rightarrow 2O^{2-}$

We call these reactions “half reactions” because neither one can proceed by itself. They must go together and the number of electrons that the iron atoms give up has to equal the number of electrons that the oxygen molecules take. That’s why 2 iron atoms link up with 3 oxygen atoms and we combine both half reactions to give us the following full reaction:

$4\,Fe + 3O_2 \rightarrow 2Fe_2O_3$.

Our knowledge of oxygen stealing electrons dates back over two centuries to the great French scientist who lost his head in the French Revolution—Antoine Lavoisier. Tony both discovered oxygen and its propensity to cause rust. Hence the term “oxidation.” Since oxidation was originally intended to mean the addition of oxygen then it’s easy to see that the term “reduction” comes from opposite process of removing or reducing oxygen. Since the eighteenth century chemists have uncovered thousands of reactions that combine elements or compounds that give up electrons and others that gobble them us but we still use the terms “oxidation” for the former and “reduction” for the latter.

Since oxidation and reduction reactions always occur together we term the pair of reactions as oxidation-reduction or “redox” for short. If you know how a battery works then it should be immediately apparent that, as long as the oxidation reaction is physically separated from the reduction reaction and we force electrons to flow on a wire then we have a battery, or “galvanic” device. We characterize batteries by their voltage output—or “potential”—and that is exactly how we measure a redox reactions. Instead of volts we use millivolts (mV)—hence the name oxidation-reduction potential (ORP).

We would like to attach a mV reading to just the oxidation or the reduction part of a redox pair but we know we can never measure one without the other. So we create a standard reaction to which we arbitrarily assign an ORP value of 0 mV. That reaction is the reduction of hydrogen ions to hydrogen gas—the “standard hydrogen electrode” (SHE):

$2H^+ + 2e \rightarrow H_2$

This should sound familiar to anyone who has studied pH electrodes. Standard hydrogen electrodes require bubbling hydrogen gas through a 1 Molar solution of hydrochloric acid (i.e. pH 0). Figure 2 is a schematic of galvanic cell in which nickel oxidizes (i.e. is the reducing agent) and a standard hydrogen electrode serves as the oxidizing agent.

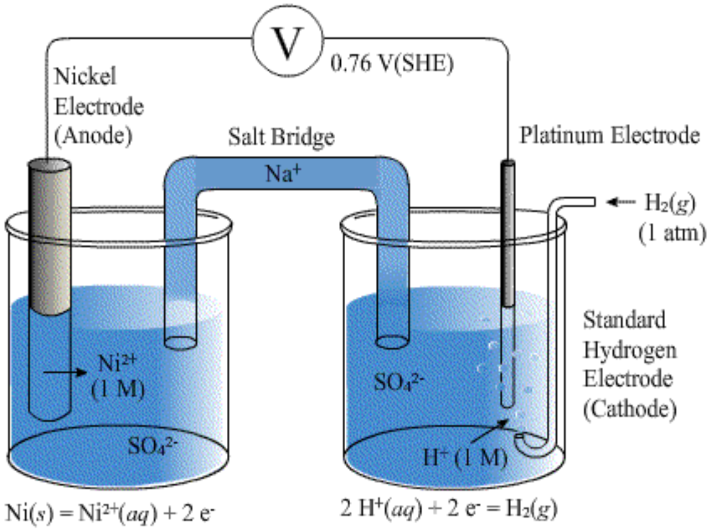

Figure 2 - Oxidation of Nickel with a standard hydrogen electrode

You don't have to be an experienced chemist to realize that using a hydrogen electrode in a working sensor is not very convenient. For this reason electrochemists have largely switched over to a more benign standard reference electrode that is created by immersing a silver wire in a saturated potassium chloride solution. Simple chemistry inside this electrode results in the pure silver in the wire being in equilibrium with silver chloride in solution. This redox reaction is:

AgCl + 2e- → Ag + Cl^-.

This should also look familiar because the silver/silver chloride electrode is the reference electrode in virtually every combination pH probe sold today. Now you can see why an ORP probe and a pH probe differ only by virtue of their process electrode and have the same reference electrode.

The question you should be asking yourself is just what the ORP value of the Ag/AgCl reaction to the H^+/H_2 reaction. The answer is 230 MV at 25 ^{0}C. So if a redox reaction is reported relative to the Ag/AgCl reaction and you want to know what the redox value is relative to the SHE just add 230 mV. (Remember though that this is true only at 25 ^{0}C.) The sad truth is that authors who report ORP values in the literature, more often than not, do not state which zero reference they are assuming. Fortunately for us practitioners who live in the real world and use real probes with real Ag/AgCl reference electrodes the values we read on our ORP analyzers are the ones we report. Adding 230 mV is just one act of mental drudgery that we would rather not add to our complicated lives. So when you see ORP values of, say 650 mV, that is recommended for disinfection you can assume that this is the value you will measure with your ORP probe consisting of a Pt process electrode and Ag/AgCl reference electrode.

Before moving on let me do what no self-respecting magician will—reveal to you how we get the redox numbers in the preceding paragraph and in the ones that follow. It's a fairly simple equation first set forth by Walter Nernst a century ago. Nonetheless for those of you who are squeamish about mathematics avert your eyes and skip to the next paragraph containing the English language.

$$E_{\text{red}} = E^{\ominus}_{\text{red}} - \frac{RT}{zF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}}$$

In this equation E_{red} is the potential we measure, E^0_{red} is the potential under standard conditions of concentration and temperature, R is the so-called universal gas constant--8.314 J K^{-1} mol^{-1}, T is the absolute temperature in Kelvin, z is the number of electrons being swapped in the redox reactions, a_{red} is the activity (almost the same as the concentration) of the reducing chemical and a_{ox} is the activity of the oxidizing chemical.

Whether you've made it through the above math or fled in terror here is the cool part. Do the arithmetic for the part of factor RT/zF and, when z=1 (one electron changes hands) and T = 298 K (or 25 ^{0}C) and you get our beloved 59.16 mV value. Because the next component in the Nernst equation you can see that, for every ten-fold increase in oxidant concentration (or ten-fold decrease in reductant concentration) you get an increase in the voltage of 59.16 mV.

One characteristic of redox reactions that you ignore at your own peril is that they all proceed at very different rates spanning a range of seconds to hours. A pH measurement takes on the order of seconds because it is a potentiometric measurement that is not based on real chemistry going on at its electrodes. Galvanic—or amperometric--probes on the other hand, are based on redox reactions that take place at the process electrode. Every probe in the water operator's toolbox, except one, relies on the chemistry of just the one species it measures (such as oxygen or ammonia). That one exception is the ORP sensor whose platinum electrode plays host to every conceivable reaction. Some, such as the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation mentioned above, are very fast. Others, such as the oxidation of organic compounds by hypochlorite, are very slow. The consequence is that I can put my ORP sensor in 600 mV calibration solution that relies on the iron redox reaction and get a reading in 20 seconds but put the same probe in a glass of tap water and wait 15 minutes for the reading to settle down. If you have a process that you want to control and that changes on the order of seconds ORP measurements may not work. Fortunately that is rarely the case in our industry.

Now that we know we can quantify any redox reaction by attaching a potential to it we can understand another important characteristic of materials. We initially said that some atoms, molecules or ions are electron givers—reducing agents—and some are electron takers—oxidizing agents. In truth that is not quite true. When two chemical species get together the one with the higher oxidation potential is the oxidizing agent and the other is the reducing agent. So a chemical that is an oxidizing agent with one partner can turn into a reducing agent with another. Take copper for example. As a metal it readily gives up electrons to oxygen to form copper oxide, the beautiful green patina we see on copper roofs and weather vanes. But put a plate of copper oxide in water with a plate of zinc and the zinc then becomes the reducing agent (the electron giver) and copper oxide becomes the greedy oxidizing agent and grabs electrons to revert back to shiny copper metal. In fact ships, oil platforms, tanks and other marine structures that are constructed of steel usually have zinc plates attached that are called sacrificial anodes. The constant stream of electrons the zinc releases to the steel keep the latter from rusting away. When the zinc has oxidized down to nothing it is simply replaced with new zinc.

In Table 1 we've listed the most common redox half-reactions and their potentials. A negative value for a reaction means that the reaction is "energetically favored," i.e. it wants to go in the direction of left to right. All the reactions in the table are tabulated such that the chemical species in question gobbles up electrons, i.e. is a reducing reaction. That's why an oxidation reaction has a positive potential: it wants to go from right to left. As you can see from the first row in the right hand column all of the reaction potentials are referenced against the standard hydrogen electrode.

Since all redox reactions in the real world combine an oxidation half-reaction and a reduction half-reaction we can describe any commonly found redox reaction by taking "one from column A and one from column B." Two halves do indeed make a whole.

Table 1 - Standard Redox Potentials

Half reactions with negative potentials are reducing reactions. Those with positive potentials are oxidizing reactions.

Reduction Half-Reaction	E^o_{red}	*Oxidation Half-Reaction*	E^o_{oxid}
$K^+ + e^- \rightleftharpoons K$	-2.924	$2\ H^+ + 2\ e^- \rightleftharpoons H_2$	0.0000...
$Ba^{2+} + 2\ e^- \rightleftharpoons Ba$	-2.90	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.158
$Ca^{2+} + 2\ e^- \rightleftharpoons Ca$	-2.76	$Cu^{2+} + 2\ e^- \rightleftharpoons Cu$	0.3402
$Na^+ + e^- \rightleftharpoons Na$	-2.7109	$O_2 + 2\ H_2O + 4\ e^- \rightleftharpoons 4\ OH^-$	0.401
$Mg^{2+} + 2\ e^- \rightleftharpoons Mg$	-2.375	$Cu^+ + e^- \rightleftharpoons Cu$	0.522
$H_2 + 2\ e^- \rightleftharpoons 2\ H^-$	-2.23	$I_3^- + 2\ e^- \rightleftharpoons 3\ I^-$	0.5338
$Al^{3+} + 3\ e^- \rightleftharpoons Al$	-1.706	$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2O_2$	0.682
$Mn^{2+} + 2\ e^- \rightleftharpoons Mn$	-1.04	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.770
$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$	-0.7628	$Hg_2^{2+} + 2\ e^- \rightleftharpoons Hg$	0.7961
$Cr^{3+} + 3\ e^- \rightleftharpoons Cr$	-0.74	$Ag^+ + e^- \rightleftharpoons Ag$	0.7996
$S + 2\ e^- \rightleftharpoons S^{2-}$	-0.508	$H_2O_2 + 2\ e^- \rightleftharpoons 2\ OH^-$	0.88
$2\ CO_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2C_2O_4$	-0.49	$OCl^- + H_20 \rightarrow Cl + OH$	0.90
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	-0.41	$HNO_3 + 3\ H^+ + 3\ e^- \rightleftharpoons NO + 2\ H_2O$	0.96
$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$	-0.409	$Br_2(aq) + 2\ e^- \rightleftharpoons 2\ Br^-$	1.087
$Co^{2+} + 2\ e^- \rightleftharpoons Co$	-0.28	$2\ IO_3^- + 12\ H^+ + 10\ e^- \rightleftharpoons I_2 + 6\ H_2O$	1.19
		$CrO_4^{2-} + 8\ H^+ + 3\ e^- \rightleftharpoons Cr^{3+} + 4\ H_2O$	1.195

$Ni^{2+} + 2 e^- \rightleftharpoons Ni$	-0.23	$Pt^{2+} + 2 e^- \rightleftharpoons Pt$	1.2
$Sn^{2+} + 2 e^- \rightleftharpoons Sn$	-0.1364	$MnO_2 + 4 H^+ + 2 e^- \rightleftharpoons Mn^{2+} + 2 H_2O$	1.208
$Pb^{2+} + 2 e^- \rightleftharpoons Pb$	-0.1263	$O_2 + 4 H^+ + 4 e^- \rightleftharpoons 2 H_2O$	1.229
$Fe^{3+} + 3 e^- \rightleftharpoons Fe$	-0.036	$Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightleftharpoons 2 Cr^{3+} + 7 H_2O$	1.33
		$Cl_2 + 2 e^- \rightleftharpoons 2 Cl^-$	1.3583
		$HOCl + H^+ + 2e$- $Cl + H_20$	1.49
		$MnO_4^- + 8 H^+ + 5 e^- \rightleftharpoons Mn^{2+} + 4 H_2O$	1.491
		$Au^+ + e^- \rightleftharpoons Au$	1.68
		$H_2O_2 + 2 H^+ + 2 e^- \rightleftharpoons 2 H_2O$	1.776
		$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.842
		$O_3 + 2 H^+ + 2 e^- \rightleftharpoons O_2 + H_2O$	2.07
		$F_2 + 2 H^+ + 2 e^- \rightleftharpoons 2 HF$	3.03

2. Why ORP Matters

It turns out that oxidation reactions are behind two of the most common reactions in water and wastewater processing:

1. In wastewater one kind of bacteria are little chemical factories that take ammonia and oxidize (or “nitrify”) this chemical to nitrite. Another species further oxidizes the nitrite to nitrate. Then, in a reversal of bacterial philanthropy another set of bacteria that is deprived of oxygen anaerobically reduces the nitrate to nitrogen gas, which then floats harmlessly off into the atmosphere. The natural and usual course of action is to measure dissolved oxygen concentrations—keeping it high enough during the nitrification stages and low during the anaerobic (denitrification) stage. This is the role of the aerator which insures that the water has sufficient dissolved oxygen—about 4 to 8 ppm (or at least 50% saturation).

2. In water treatment, disinfection in the form of chlorine or hypochlorite works by oxidation of bacterial cell walls. Regardless of the source of chlorine going into the water it is hypochlorous acid, HOCl, that forms and acts as the bacterial genocide. At high pH values, HOCl breaks up into OCl^-, which also disinfects albeit at a lower efficacy. Both species are collectively called “free chlorine” which distinguishes them from the ordinary, ubiquitous chloride ion, Cl^-, which does nothing except make our food and oceans salty. Naturally, chlorine analyzers are used to dose the right amount of chlorine gas or liquid hypochlorite to keep the free chlorine concentration in the right range. However chlorine analyzers really only measure HOCl and, since the concentration of this

species depends on pH, the analyzer must measure the pH and mathematically correct the reading for it in order to furnish a measurement for free chlorine.

3. Chlorine in its various forms is the runaway favorite for disinfecting water but it is not the only choice. Chlorine's heavier cousin on the periodic table is bromine and doesn't give the scary health consequences of chlorine. It does however form bromates which are not welcome visitors to our water. Chloramine is also a less toxic chlorine containing compound but is not as strong an oxidant as its pure cousin. Ozone is also a very good oxidant and is often used in pre-treatment. It is typically measured directly by its absorption of ultraviolet light. Chlorine dioxide is a strong oxidant used for primary disinfection. It has been finding increased use primarily because it is more stable at typical pH values in water treatment plants.

In sum, we have here in the world of water and wastewater treatment oxygen, chlorine with a supporting cast of ozone, chorine dioxide, bromine, chloramine, hypochlorite and ozone. We'll pretend that UV disinfection does not exist.

So far every chemical we've mentioned is an oxidant. Is there any need whatsoever for chemicals that reduce? The answer is "some." Oxidation is the process of breaking down and killing bacteria and that's what we do when we process wastewater or make clean water fit for drinking. But there are two exceptions.

The first such exception is the anaerobic process of converting nitrate to nitrogen gas; this so-called denitrification is a reduction reaction of nitrate in which bacteria provide the electrons. These bacteria always do their work in low oxygen oxygen conditions.

The second case for reducing agents is in preparing water for boilers. Oxygen and boilers or steam turbines are a deadly combination. At the high temperatures common to all boilers dissolved oxygen corrodes the steel pipe at an accelerated rate. To scavenge oxygen sodium sulfite (or hydrazine) is added to reduce the oxygen and convert it to water. Interestingly, really low oxygen (< 10ppb) creates a different kind of corrosion problem with iron pipes so operators need to insure that, in these systems, the dissolved oxygen remains at a very low but finite level.

Since oxidants oxidize organic matter, by definition then, organic matter are reducing agents. Their large sizes and large quantities assure that they carry a lot of reduction potential.

So if oxidation and reduction are two competing forces that find themselves on opposite sides of a game of tug-of-war then the overall potential of the overall mix of chemicals should give one grand total—the ORP of the solution. That is exactly what an ORP sensor measures.

Oxidation and reduction reactions are found in just about every phase of water and wastewater treatment and involve as many different chemicals as there are processes. To make sure that the processes are optimized all we need to do is measure and control the redox potential, i.e. the ORP. That's why the ORP sensor really is one of the most powerful tools in the water quality instrumentation toolbox.

3. How ORP Probes Work

An ORP sensor is uniquely powerful because it is a "bottom line" instrument. It doesn't care about specific chemicals in the water. It simply wants to know the redox potential of everything in the water. Whether it's ozone, chlorine, dissolved oxygen or gas it doesn't care. It only "cares" that whatever is in the water can break down the contaminants whether they be microbes or natural organic matter.

So now that we understand what ORP is we can now understand how to use it. Finding basic information on how to make and interpret ORP measurements is as easy as finding out how to make a nuclear warhead. But with just a little effort you can become an ORP expert.

Every electrochemical sensor requires two electrodes: One electrode is immersed in the process and the other is a reference that is immersed in a standard solution. We are all familiar with the pH probe. For a combination probe the reference electrode is a silver (Ag) wire immersed in KCl-AgCl solution. For a differential probe the reference electrode is a fully independent electrode identical to the process electrode and immersed in pH 7 buffer.

To make an ORP sensor we need an electrode that allows all the possible redox reactions to take place. To do so we simply replace the process electrode of a pH probe with a platinum (or gold) band attached to a lead wire. The Pt band does one thing—it provides a catalytic surface upon which redox reactions can take place. Everything else about the probe is identical to pH probes including the reference electrode.

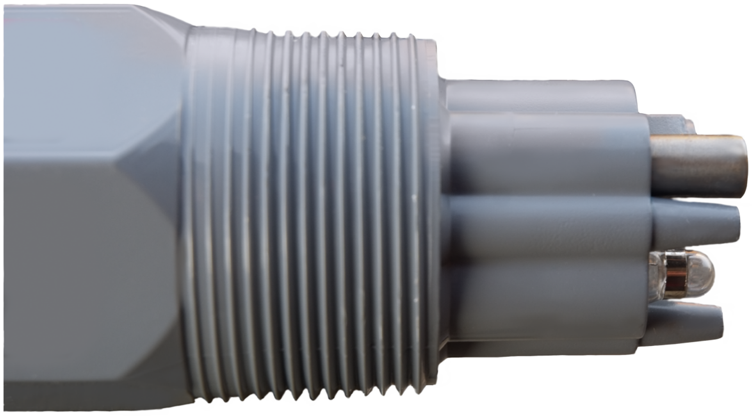

Figure 3 - This front end of an Aquametrix differential probe shows the process electrode, which consists of nothing more than a Platinum band and a lead wire that connects to the pre-amp.

Unfortunately not all reference electrodes are equal so the reading that one probe gives may be different from another. This is especially true when comparing a combination probe with a differential probe. The former has a reference electrode that is simply a Ag/AgCl wire in a saturated KCl solution. The latter is an electrode of an Ag/AgCl in saturated KCl solution immersed in pH 7 buffer solution. So not only are the redox values of the two reference electrodes different, the redox value of the differential probe will be different for any of the different pH 7 buffer solutions that one can buy or make up.

Because it is simple to change the reference solution of a differential probe we conducted the following test: We used our own 594 mV ORP standard solution and calibrated a probe with pH 7 buffer solution. We then replaced the ph & buffer solution with standard solutions from three manufactures plus fresh pH 7 buffer solutions and compared the readings. To get some idea of the accuracy of the test we measured the output of the probe with two charges of fresh pH 7 buffer.

The results are shown in Table 2. This table brings good news. The two independent checks of ORP output with pH 7 buffer differed by 15 mV—approximately the expected accuracy of 10 mV. All four choices for reference solution are within 15 mV of each other. So we can see from the results that the different reference solutions produce ORP output that are close together. Furthermore, the one-point standardization that we are about to discuss, can eliminate any difference between choices of ORP reference solution.

Table 2 - ORP Probe Output for Four Choices of Reference Solution. The probe was calibrated using 6 month old pH 7 buffer solution in the reference well

pH 7 Buffer (aged)	pH 7 Buffer (new)	ATI Buffer Solution	Hach Buffer Solution	Aquametrix Buffer Solutions
594	608 / 603	617	603	617

As an experienced pH probe power user you are thinking that this disparity amongst reference electrodes is simple to resolve. Just calibrate. And you would be approximately correct. I mean “approximately” because we don’t really calibrate an ORP probe; we standardize it. Here’s the difference:

When one calibrates a probe (to an analyzer of course) one measures the response of the probe to a known standard. A calibration curve is, at its simplest, a straight line and two points determine a line. For a straight line calibration we report a slope and an intercept, the latter of which is the response of the sensor at zero input. That’s why we use two standard solutions to calibrate a probe. For a pH probe we use two solutions that are two of three possible solutions: pH 4, 7 and 10. We measure the probe output in mV as a function of pH. Of course we know that the slope should be close to 59.16 mV/ pH unit at 25 ^{0}C.) For dissolved oxygen we measure the probe output for a probe sitting in air which is 21% oxygen. We usually don’t measure a second point because we don’t have a second standard as convenient as air. We can dissolve a reducing agent like sodium metabisulfite into a container of water (Hey we know what that means!) to wipe out nearly all of the dissolved oxygen to get a second calibration point. But most of the time we just assume a calibration point of zero probe output at zero dissolved oxygen.

But ORP calibration presents us with a totally different dilemma. Since ORP is not a single chemical species or parameter we have no control variable to vary. No Calibration is possible. What we can do is mix up a solution of chemicals that we know will give us a known potential that we can measure. We measure the potential in mV and adjust the analyzer until the reading is what we know it ought to be. This is what we call a “standardization.” Could we do a second standardization? Yes, but if we adjust the analyzer to match the expected voltage of the second standard then the first standard would no longer match. Fortunately we can take faith in Mr. Nernst and feel confident that the slope of an ORP sensor with concentration of redox agents is 59.16 mV for every ten-fold increase (decrease) of oxidizing (reducing) agent.

For calibration there are three solutions that have been used for decades. We summarize them in Table 3.

	Oxidant/Reductant	Recipe	ORP (vs. Ag/AgCl)
Light's Solution	Fe^{+2} / Fe^{+3}	2.64 g $K_4[Fe(CN)_6]$ * 3 H_2O and 2.06 g $K_3[Fe(CN)_6]$ * H_2O in 500 mL buffer pH 7.00 at 25°C	476 mV
Zobell's Solution	Fe^{+2} / Fe^{+3}	1.861 g $Fe(NH_4)_2\ (SO_4)_2$ * 6 H_2O and 2.411 g $Fe\ NH_4\ (SO_4)_2$ * 12 H_2O in 500 mL 1 M H_2SO_4 at 25°C.	229 mV
Quinhydrone	Quinone / Quinhydrone	pH 4 or pH 7 buffer saturated with Quinhydrone	pH 4 - 263 mV pH 7 – 86 mV

Table 3 - Three commonly available ORP Standard Solutions

Now that we are ORP sensor experts we can discuss how to actually use them.

4. ORP Measurements in the Real World

4.1. ORP to Monitor Disinfection

Let's start with the most common use of ORP—to measure disinfection that is generally done by chlorine. As we mentioned earlier, what we call "chlorine" is hypochlorous acid, or HOCl. The oxidation reaction that kills microbes can be found in Table 1 is:

$HOCl + H^+ + 2e^- \rightarrow Cl + H_2O;\ E_0 = 1.49\ V$

In water treatment facilities a chlorine analyzer is ubiquitous and required by EPA standards to insure that there is enough residual chlorine in the distribution system. In wastewater treatment we are less concerned with residual chlorine and more concerned with making sure that we get the job of killing bacteria done. Most measurements of dissolved chlorine report "free chlorine" which is the total of HOCl and OCl^-. An amperometric Cl analyzer measures only HOCl so, without pH correction, an amperometric chlorine sensor is likely to underestimate the concentration of free chlorine. In fact for pH over 7.5 the HOCl concentration is less than 50% of total chlorine and drops to less than 15% at pH 8.5. That's why chlorine analyzers calculate the free chlorine concentration using the pH value that is either input manually or measured with a separate pH sensor.

Alternately we can set the ORP value on our controller to a value that will disinfect. As Table 4 shows, an ORP of 650 mV will do the job. As long as we are clear that this value refers to an ORP value that is relative to the Ag/AgCl reference and we calibrate our ORP sensor with a good standard then we can be confident that whatever is in the water is killing bacteria.

Table 4 - Survival Times of Pathogens at Three ORP Values.[1]

	Survival (seconds)		
ORP Value (mV)	<485	550 to 620	665
E. Coli 0157:H7	> 300	<60	<10
Salmonella spp.	>300	>300	<20
Listeria	>300	>300 S	<30
Thermotolerant Coliform	> 48 hours	> 48 hours	<30

Spa and pool vendors will often sell an ORP analyzer as the only tool for measuring the disinfection of the water. Though you can also run a water treatment facility using an ORP analyzer alone I don't know of any that actually do. Being able to measure the chlorine (or ClO_2 or NH_2Cl) is necessary for the operator in the WTF to control the dosing of disinfectant. There is simply too much at stake in a municipal water treatment facility to forego the addition of a chlorine analyzer that can, at the very least, give an indication of disinfectant concentrations. One very prudent strategy is to calibrate the ORP level against the chlorine measurement. In fact some so-called chlorine analyzers are actually ORP analyzers that have been calibrated to effective chlorine concentrations.

The bottom line is that ORP measurements don't just give a layer of redundancy for disinfection monitoring. They actually give a better indication of the true disinfecting abilities of the water.

4.2. ORP as a Measurement of Dissolved Oxygen

As we discussed above dissolved oxygen (DO) is the primary tool in wastewater processing that breaks down organic matter using aerobic, nitrifying bacteria. For this application a DO analyzer seems an obvious choice. While I would be the last person to suggest that a wastewater should make do without a dissolved analyzer an ORP sensor will provide complementary information to that from a DO sensor and, in one sense, actually do a better job

Check out Figure 4 below. These measurements come from wastewater treatment at a dairy plant. The dissolved oxygen measurements come from an electrochemical sensor. One can see that the pH and ORP measurements change in measureable terms but the DO measurements are stuck at zero when the DO falls to levels below about 2 ppm. One can argue that an optical DO analyzer would have done a better job measuring low concentrations. The fact still remains that the ORP sensor clearly measures the reducing chemistry of an anoxic or anaerobic environment while a DO analyzer only works in an oxidation environment.

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[1] T.V. Susulow, *Oxidation-Reduction Potential for Water Disinfection Monitoring, Control and Documentation* , ANR Publication 8149, Univ. of California at Davis

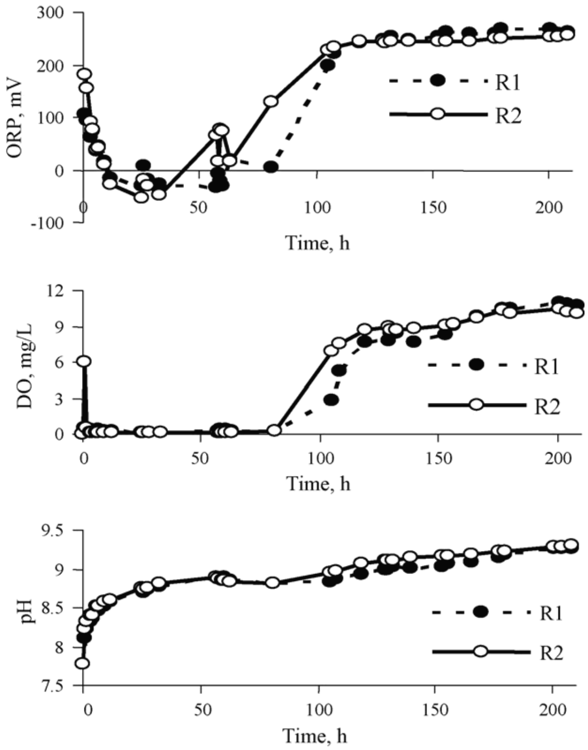

Figure 4 - Plot of ORP, DO and pH vs. Treatment Time at a Dairy Plant Wastewater Aeration Tank[2]. Notice that the DO measurements for the first 70 hours are pegged at zero whereas the ORP and pH measurements change significantly.

The reason for ORP measurements providing more accurate information of DO than the measurement of DO itself at very low concentrations should come as no surprise. We only need take another look at the Nernst equation to realize that the voltage from an ORP sensor varies linearly with the logarithm of the concentration of oxygen. This is not ideal for measuring moderatemlevels of DO. For instance, if the DO concentration changes from 1 ppm to 10 ppm the ORP will change by only 59.17 mV (at 25 ^{0}C of course)—certainly easily measureable but not preferable to the direct DO measurement. On the other hand, when the DO concentration drops from 0.1 ppm to 0.01 ppm our DO analyzer is effectively stuck at zero yet our OPR analyzer records the same hefty 59.16 mV!

4.3. ORP for Biological Phosphorus Removal

We’ve talked about the breakdown of organic matter by oxygen and microbes by strong oxidants—generally chlorine. In the former case, oxygen is used by aerobic bacteria to oxidize ammonia to nitrite and, next from nitrite to nitrate. It is the absence of oxygen

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[2] P.M. Ndegwa, Li Wang & V.K. Vadella, *Potential strategies for process control and monitoring of stabilization of dairy wastewaters in batch aerobic treatment systems*, Process Biochemistry **42** (2007), 1272-1278.

that allows anaerobic bacteria to grow and reduce nitrate to nitrogen, the latter of which floats harmlessly to join the 79% of our atmosphere that is nitrogen gas. Nitrogen is one of two major nutrients that feed algae. The other is phosphorus. When nutrient levels rise in our surface waters algae grow and consume oxygen. One only needs to see this so-called eutrophication of a small pond or the Chesapeake Bay to see the ecological damage an overabundance of nutrients can create.

The removal of phosphorus—or phosphate to be more precise—through biological means has replaced chemical removal in most plants because of the former's independence from chemicals. Biological phosphorus removal, like nitrogen removal, requires an anaerobic stage and an aerobic stage, thus setting the stage for ORP monitoring. Unlike its nitrogen counterpart the sequence of microbes is anaerobic and next aerobic

In the anaerobic phase fermentative bacteria break down polyphosphates (phosphate polymers) for energy and use this energy to convert organic matter into chemicals called fatty acids that store energy. This release of phosphate into the liquor seems to the opposite of what we want to do but the next stage, using the same bacteria, more than compensates. These so-called phosphate accumulating organisms then gorge on the free phosphate and create a biomass of their stuffed little microbe bodies that can be removed as sludge. (The reason for the first stage of phosphorus release is that that the anaerobic conditions kill off the aerobic nitrifying bacteria that would interfere with the phosphorus accumulating bacteria in the second stage.)

Just like the process of removing nitrogen, we can monitor ORP levels to insure that the phosphate accumulating bacteria live in an environment characterized by an ORP -140 mV[3] to -250 mV[4] and that they can next dine in the comfort of an aerobic environment characterized by an ORP of 220 to 280 mV[5]. Once again we can monitor DO to control the anaerobic – anoxic – aerobic environments but our DO measurements are stuck at zero when the process is anaerobic. ORP measurements, on the other hand, merrily chug along in all three environments.

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[3] P.Huaing, S. Qin, Q. Zhao and X. Guo*, Quick Start-up of Mudanjiang Wastewater Treatment Plant and Factors Influencing Phosphorus Removal*, Global NEST Journal, **8** (1), 1-8, 2006.

[4] D. Obaja, S. Mac_e, J. Costa, C. Sans, J. Mata-Alvarez, *Nitrification, denitrification and biological phosphorus removal in piggery wastewater using a sequencing batch reactor*, Bioresource Technology, **87** (1), 103-111, 2003,

[5] D.S. Lee, C.O. Jeon and J.M. Park, *Biological Nitrogen Removal with Enhanced Phosphate Uptake in a Sequencing Batch Reactor Using Single Sludge System*, Water Research, **35** (16), 3968-3976, 2001.

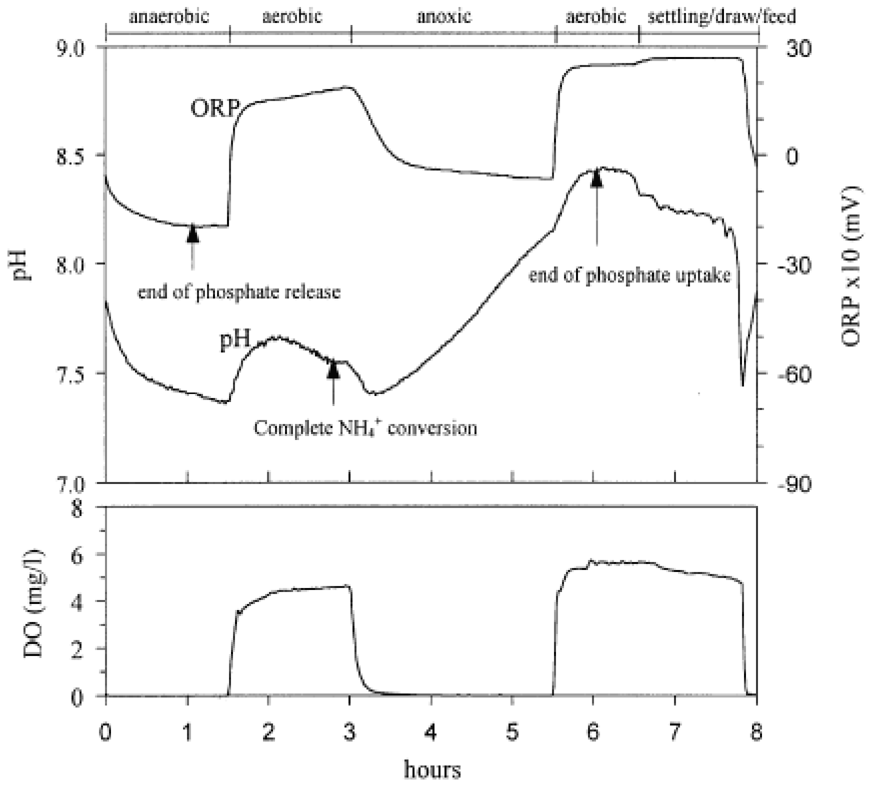

Figure 5 - Sequence of Anaerobic to Aerobic Sequences in Phosphate Removal. Note that the DO measurement pegs at zero during the anaerobic phase but that the ORP measurements continue to track the process. From Lee et al (Ref.5).

4.4. Chrome Plating

Although chrome plating has lost its luster (pun intended) compared with the heyday of chrome bumpers and appliances in the fifties and sixties, it is still a big industry. You don't have to work for the EPA to know that one form of chromium in the highly oxidized state Cr^{6+}--or Cr (VI) in our drinking water is a major health threat. To remove this nasty positive ion metal finishers add a sulfur-containing reducing agent--usually sodium bisulfite ($NaHSO_3$) or sodium metabisulfite ($Na_2S_2O_5$) that adds three electrons to Cr(VI) to turn it into Cr(III) the latter of which forms compounds that are insoluble in water and settle onto the bottom of the treatment tank.

As a newly minted ORP expert you instantly recognize that adding chemicals to reduce nasty Cr(VI) to benign Cr(III) is a job for an ORP analyzer. It is easy to foresee that, as we add the sulfur reducing agent, more and more Cr (VI) converts to Cr (III) and the oxidation potential drops. When all of the Cr (VI) has been tied up the ORP reading on an analyzer will stop dropping and level off. In this way we perform something that is familiar to anyone who adds a reagent to a sample and watches for a dramatic color change when our chemical of interest is all used up. We all know this as a "titration." The decrease in ORP readings from 600 mV to 240 mV is shown in Figure 6a[6].

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[6] Ed. By H.F.Liu and B.G. Liptak, CRC Press, *Wastewater Treatment*, Chapter 7, 1999.

If titrations with an ORP analyzer excite you then get ready for the second such one in the treatment of chrome plating wastewater. Cyanide is another nasty chemical that must be rendered harmless. In this case a two stage oxidation by sodium hypochlorite (NaOCl) first converts cyanide (CN^-) to cyanate (CNO^-) and, in the next, the same hypochlorite, but at lower pH, converts the cyanate to a mixture of harmless carbon dioxide, nitrogen, sodium chloride and sodium hydroxide. As we can see in Figure 6b we can monitor this two-stage reaction as a two-stage titration using our multi-purpose ORP analyzer. (What we have not discussed is the crucial role that pH serves in these reactions. Oh but if only we had more time.)

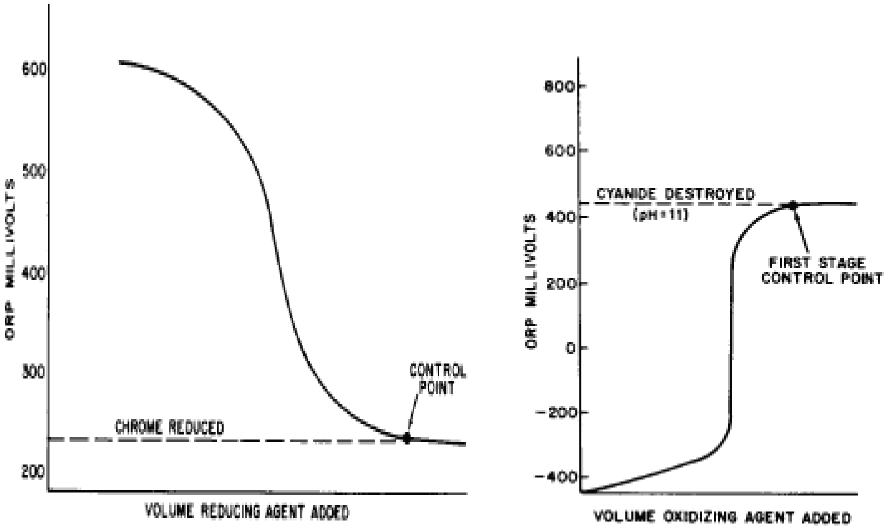

Figure 6 - Reduction of Chromium (VI) and Oxidation of Cyanide as monitored by ORP Measurements. (From Reference 6). In both cases, we know that the job of ridding the wastewater of these two dangerous chemicals is done when the ORP value levels off.

4.5. And Everything in Between

One day I'll write a book on the many splendor things that ORP measurements can do. For now I'll just leave you with a few other applications in wastewater treatment that can be monitored and controlled thanks to the wonderful ORP analyzer.

That rotten egg smell coming out of sewage, volcanoes and outbursts from our lower digestive system is hydrogen sulfide—H_2S. It's a good thing this chemical is so pungent because, molecule-for-molecule, it is more lethal than hydrogen cyanide. On the other hand, the bacteria that produce H_2S from the reduction of sulfate ($SO4^{2-}$) are beneficial in wastewater treatment because they are food for anaerobic denitirifying bacteria. These bacteria do their best work at ORP values between -50 and -250 mV[7]. The production of hydrogen sulfide and volatile fatty acids is collectively called malodor production.

Methane is a gas that we do not want coming out of manholes but we do like to come out of landfills. Reduction of carbon compounds to methane occurs at ORP values -175 and -400 mV[7]. In landfills the methane is produced from bacteria deep within the rotting compost in an anaerobic or anoxic environment and is piped away to generate electricity. The production of methane in landfills for cogeneration is in competition with the production of hydrogen sulfide. By insuring that there is just enough oxygen to keep the ORP between -180 and -230 mV Khanal and Huang discovered that they could maximize the methane production and minimize the sulfide generation[8].

In addition to methane and hydrogen sulfide production there is a large class of reduction reactions that microbes carry out anaerobically to produce weak acids known as volatile fatty acids and alcohols. (Now you know why beer makers keep oxygen out of the fermentation kettles.) These reactions are actually just intermediate steps in the breakdown of fats so that phosphorus accumulating organisms can do their work to release and then gobble up phosphate. They occur over a wide range of ORP values from -100 mV to -450 mV[9].

We are all familiar with the corrosion of steel, iron and copper at normal temperatures. At high temperatures that exist in boilers corrosion can eat away a stainless steel pipe in a matter of days. For this reason the water that is fed into boilers is de-aerated to less than 10 ppb of dissolved oxygen. It turns out that about 5 ppb of oxygen will give a protective oxide coat in carbon steel that prevents further corrosion and that reducing the DO below this will actually increase corrosion. We also know that flow can remove the protective coat in a process known as flow accelerated corrosion (FAC). In 1986 FAC in Virginia Power's Surry Nuclear Power Plant resulted in a high pressure explosion that killed four workers.

One might assume that a DO analyzer that measures very low concentrations of oxygen would be the obvious choice for this process. But we've already been through the arithmetic that tells us that small amounts of dissolved oxygen are better measured with an ORP meter.

5. Learn this stuff and become an ORP guru

Congratulations. You just graduated with a Bachelor's Degree in the ORP School of Survival. If you want to earn your Masters from the comfort of home all you need now is to understand a few basic truths about ORP that the casual user does not. For this you don't need to learn any more technical information; you only need apply what you already know.

5.1. Why is the ORP of Pure Water NOT Zero?

This seems like a no-brainer. In pure water there are no reactions taking place. Therefore the ORP should be zero. So why is it that, when I stick a sensor in the water, it

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[7] M.H. Gerardi, *Oxidation-Reduction Potential and Wastewater Treatment*, New England Interstate Pollution Control Commission Newsletter, Winter 2007.

[8] S.K. Khanal and J. Huang, *ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater*, Water Research, **37**, 2053-2062, 2003.

[9] M. G. Barajs, A. Escalas and R. Mujeriego*, Fermentation of a low VFA wastewater in an Activated Primary Tank*, Water SA, **28** (1), 89-98 , 2002.

creeps slowly to a value such as 100 mV. Why does it seem like oxidation is taking place in an inert medium? Andy why, when I Google this question, do I come up with zero explanations?

Answer this question and you've earned your stripes. Here we go: It is true that water and other relatively inert substances don't react. (Duh… That's why they're called "inert.") But being inert is not the same as having zero oxidation potential. The latter implies that there is indeed chemistry in the form of swapping electrons taking place and that the potential change is zero. So to define the ORP of pure water is like trying to describe the colors in a black-and-white photo. The reason why we watch the read-out attached to an ORP probe slowly change is simply because the water that we thought was pure is not pure at all. Whatever is in the air will saturate the water sample. That means our pure water will load up on oxygen and oxygen, as we all know, is an oxidant. The nitrogen that comprised 79% of the atmosphere really is inert and adds nothing to the ORP value. So we think we are measuring the ORP of distilled water but we are really measuring the ORP of dissolved oxygen.

The ORP of tap water is almost always much higher—200 to 300 mV. That's because of the residual chlorine that most municipal water treatment facilities add to treated water to insure that the water that was disinfected at the WTF stays disinfected when it comes out of your tap.

5.2. Why ORP Calibration is a One Point Deal

We've been through in Section 3 this but, for the sake of completeness, let's just repeat the one lesson almost no one learns.

To reiterate why we can't calibrate an ORP analyzer in the usual sense let's look at pH calibration. As with any calibration we vary the quantity of the parameter we want to measure and plot the output for each parameter value. For pH we measure the voltage output of the probe for 2 or 3 pH values (or hydrogen ion concentrations). How does the probe voltage depend on the pH? Easy—it's our good friend the Nernst equation. Fortunately pH is on a logarithmic scale because the voltage varies linearly with the log of$[H^+]$ (i.e. -pH). We already know that the slope of the calibration curve should be –59.16 mV at 25 ^{0}C.

Figure 7 is an actual calibration of a probe to three pH buffer solutions. In real life most of us only use two buffer solutions but the more points the better the accuracy. A linear least squares fit through the data gives us our calibration parameters. (If least squares fitting is too distant in your memory suffice it to say that it is the straight line that comes closest to matching the three data points.) The slope is the efficiency of the probe and, not surprisingly, is close to the expected 59 mV. The intercept represents the voltage output of the probe at pH 7 (not zero) that, if we do the arithmetic, is 8.31 mV—close enough to zero for government work.

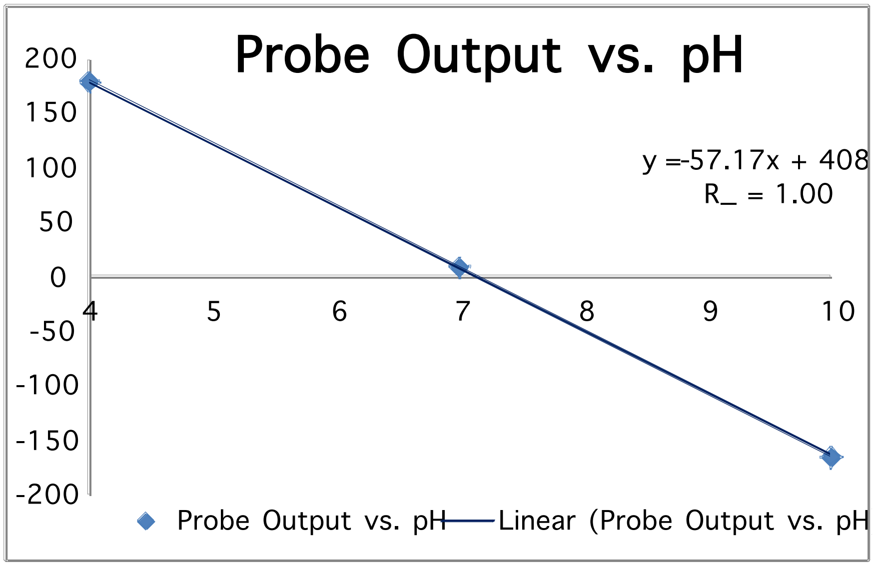

Figure 7 - Calibration of a pH analyzer. We measure the probe response at 3 pH values and measure the best fit straight line to determine the slope and intercept of a linear calibration curve. Not surprisingly the slope is very close to 59 mV/pH that we expect.

So how should we calibrate an ORP analyzer? Again we fall back on the Nernst equation for fitting the output of the probe to a variable that goes on the x-axis. But what is that variable? For pH calibration it was the log of [H^+], i.e. pH itself. Likewise, for ORP calibration, the variable on the x-axis should be the log of the oxidant species divided by the log of the reductant species. The only problem is that this redox pair is different for every calibration solution. In particular, Light's and Zobell's solutions are two entirely different chemical systems so no one Nernst equation using both calibration measurements is possible.

All we can do is make up a solution of a redox pair of chemicals whose ORP we know from a textbook and measure the voltage output of our ORP probe. If the voltage is different from the textbook value we simply dial in the correct voltage on the analyzer until the readout gives us the correct number. That's not a calibration. That is a standardization.

5.3. Why Good Probes go Bad

The ORP process electrode is nothing more than a platinum band that is wired to the reference electrode in a combination probe or the pre-amp in a differential probe. Unlike a pH electrode there is no gel layer that must be keep moist at all times. Platinum is an inert metal and is loath to react with other chemicals.

Still bad things can happen to good ORP electrodes. Sulfur compounds and some organic compounds can adsorb onto the platinum surface and therefore "poison" the electrode. In other environments algae can grow on the electrode surface. While the algae undergo photosynthesis they emit oxygen which is picked up by the Pt electrode as an increase in ORP. In both of these cases the symptoms of a compromised ORP electrode is that the probe does not change much when its environment does.

If you want to know if an ORP probe is dead and gone or just a little sick stick it in a weak acid. You should see a change in ORP value within 15 seconds. If not then it's time to get out a soft brush and detergent and do a little cleaning.

Cleaning an ORP sensor is not much different than cleaning a pH probe. For minimal cleaning use a soft brush and detergent. For a sensor that may have scaling built up (i.e. calcium carbonate deposits) soak the probe in 0.1 M hydrochloric acid (HCl). If you don't have any available just grab some white vinegar. For a probe that has seen serious fouling (e.g. from algae) use household bleach that has been diluted with an equal amount of tap water. For serious build-up of scale or fouling polish the Pt band with sandpaper that is grade 600 or higher.

5.4. What is the connection between pH and ORP?

At this point we understand that pH and ORP are very different beasts even though, to an untrained eye, the probes look identical. But is there any correlation between pH and ORP?

The answer is yes and—I hate to have to bring it up again—and the Nernst equation tells us why. In a nutshell: For every unit rise in pH, ORP increases by 59 mV (at 25 ^{0}C). (You do recognize that famous number, 59 mV, don't you?) Though H^+ ions do not themselves oxidize or reduce other chemicals they are a necessary part of most redox reactions. As an example we take the ubiquitous oxygen reduction:

$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

As you can see oxygen cannot do its job unless some hydrogen ions accompany it to give themselves up in the service of making water. Note that for every hydrogen ion for every one electron and that is why ORP varies rises and falls by 59 mV per pH unit. There are other examples, such as the famous ammonia → nitrate → nitrite in which the ratio of hydrogen ions to electrons is greater than 1 and the change in ORP with pH is more than 59 mV.

This relationship holds true as long as the chemical on the right hand side of the reaction is tightly bound, as it is in water. If it is acidic then it will release its own hydrogen, which will lower the balance of hydrogen ions on the left side of the reaction. This lowers the ratio of hydrogen ions to electrons and, consequently, the change of 59 mV/pH drops.

There are also cases in which a species other than hydrogen ions are able to provide the charge balance to make the reaction go. For example take the reaction:

$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$

In this reaction copper is the sacrificial lamb and gives up it electrons to reduce Fe^{+3} to Fe^{+2}. In this case pH has no effect on ORP values.

The bottom line is that hydrogen ions are omnipresent in water and in our blood and plays a supporting role in the chemical reactions that take place. In most of these, when pH goes down, ORP goes up. The lesson for water treatment workers is to make sure you control your pH (usually meaning that it is basic). Otherwise your ORP values will drop and you will find yourself dosing more oxidant when you really ought to be dosing acid.

5.5. A Question of Accuracy

Check the datasheet for a pH probe such as ours and you will see a precision of 0.01 pH units. Many users mistakenly think that this means that their readings will be accurate to within 0.01 units of the correct pH value. In actuality pH measurements are only accurate to within about 0.1 pH unit. The same is true for ORP measurements. The precision for an ORP sensor is approximately 5 mV but its accuracy is 10- 20 mV.

Precision and accuracy are too different things. I have a tape measure that has markings every 1/64” but the front of the tape that has the little latch has worn down so that there is “slop” in the measurement of 1/8”. My tape measure has a precision of 1/64” and a precision of 1/8”. Accuracy is a measurement of how close to the truth our instrument is whereas precision defines how fine of a measurement we can take. Typical ORP measurements are accurate to no better than 10 mV. As with pH or any other measurement frequent calibration will minimize an ORP analyzer’s accuracy and bring it closer to the tighter precision value.

ORP measurements, moreover, are open to more sources of error than a pH sensor. For one thing ORP standards are not buffered like pH calibration standards. A buffered standard is one that resists changes in its value. You can pour a few drops of acid in pH 7 buffer and the solution pH will hardly change. The chemistry of weak acids guaranties this stability. ORP standard solutions (and conductivity standards as well), on the other hand, will change their value upon addition of other chemicals. For instance when we make up our ORP standards we let the solution sit for several hours before taking final measurements. As oxygen from the air dissolves into the solution the ORP rises. As the calibration solution sits the chemistry between iron compounds changes the actual ORP reading.

Fortunately, effective disinfection requires that the ORP of the water is between 650 and 800 mV. Accuracy to within 10 mV is good enough.

5.6. ORP Measurements Require Patience

We already talked about this but it does bear repeating in this section. An ORP measurement is an aggregate of every possible redox reaction in the water. In a standard solution such as Zobells’s or Lights, the redox reactions in a standard solution consist mostly of conversion between Fe (iII) and Fe (III)) and is very fast. On the other hand the redox reactions in a glass of ordinary tap water consists of several reactions involving different chlorine species and can be very slow. Just how slow is illustrated in Figure 8 which is taken from the work of Steininger and Pareja[10]. This is one experiment you can try at home just to see how slow an ORP measurement can be. Had one stopped the measurements illustrated in Figure 8 one would incorrectly measure the actual ORP values of the water sample and conclude that the 7 sensors were all calibrated to different standards when, in fact, they agree to within 1% of each other.

If you need to measure the ORP of aqueous solutions in mere seconds ORP analyzers may not be the best choice.

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[10] J.M. Steininger and C. Pareja, *ORP Sensor Response in Chlorinated Water*, NSPI Water Chemistry Symposium, 1996.

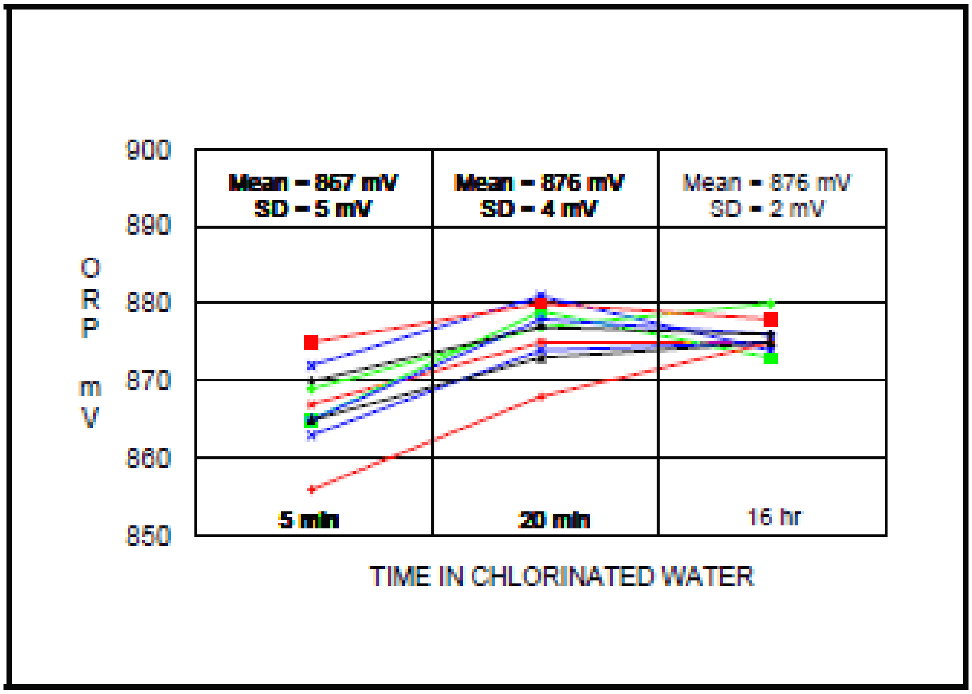

Figure 8 - Time Response of ORP Sensor in Chlorinated Water. (Ref 10)

5.7. Calibration Solutions are rarely NIST traceable

If you can't trust your calibration solution then you can't trust your measurements. Look at any pH calibration solution (including ours) and you'll see "NIST traceable" written on the label. This means that the instrument that was used to measure the solution was itself calibrated using a NIST (National Institute of Standards and Technology) analyzer. This, in turn, means that the analyzer was calibrated using calibration solutions that are themselves NIST traceable.

Making a NIST traceable pH calibration solution is straightforward. One needs only follow the recipe to be assured that the mixture of phosphate salts will produce the correct pH. The buffering capacity of the solution insures that its pH value will not change much.

But making a NIST traceable ORP calibration solution is much more difficult. As we discussed in Section 5.5, making a calibration consisting of two redox pairs (such as a ferric and a ferrous salt) is much dicier. There is no buffering capacity of the solution to resist changes in the solution ORP value and, because ORP is an aggregate property of the solution, anything in the water can and will affect the ORP value.

If someone advertises you a NIST traceable solution with an accuracy of ±1 mV be afraid. Be very afraid. As in ORP measurements themselves, expecting better than 10 mV accuracy from an ORP calibration solution is expecting too much.

5.8. Why pH Measurements Are Temperature Compensated and ORP Measurements are not.

You are probably aware that pH measurements must be temperature compensated in order to give an accurate pH measurement. This is because a pH probe doesn't really measure the hydrogen ion concentration directly. It measures the difference in potential between the reference and process electrodes by virtue of the difference of hydrogen ion concentrations. The potential varies linearly with temperature (as those who were brave enough to read about the Nernst equation can clearly see).

Put it this way: If we take a glass of vinegar and warm it up while we record the voltage coming out of our pH probes we will see that voltage rise. But the hydrogen ion concentration can't possibly change so we have to make a correction. At the risk of further trauma by bringing back the Nernst equation, we use that relationship to give us the hydrogen ion concentration or pH value. Temperature compensation insures that we always read the correct pH no matter what the temperature of the sample is.

ORP measurements also follow the Nernst equation and the voltage of an ORP sensor will increase when we turn up the heat on our sample. But ORP is not the measurement of a chemical species that is derived from a measurement of the voltage of the probe. It IS the measurement of the voltage. At the risk of being repetitive, ORP measurements are bottom line measurements. The values simply reflect the ability of whatever is in the water to oxidize whatever contaminants are in the water. Of course oxidation speeds up at higher temperatures.

So does this mean that there is no need to attach a temperature element to an ORP probe? The answer is a resounding "no." We still need to understand how effective our process is at oxidizing or reducing "stuff "in the water and we can't do that if it turns out that a high ORP reading was the result of a very hot sample instead of an adequate supply of, say, hypochlorite or oxygen. When we report ORP values we also report the temperature. As a practice we report ORP values at 25 ^{0}C. In this way we are able to compare the redox abilities of one solution with another. How do we report the ORP value at 25 ^{0}C when we measured the process at, say, 37 ^{0}C? Easy—just use the Nernst equation. Are you getting the hint that, even if you hate math, you really should know the Nernst equation?

5.9. Combination or Differential

So far we have discussed ORP sensors as if they were all alike. For the most part that's true. The vast majority of pH/ORP probes are "combination" probes. This means that the reference and process electrodes are "combined" inside one glass envelope. The reference electrode is our old friend, the Ag/AgCl wire, immersed in a KCl solution. This makes for a simple, compact, and inexpensive probe. Over time the process permeates the reference electrode and invariably contaminates it. Since the reference electrode is completely sealed inside the glass envelope, there is no way to replace its contaminated solution. For this reason combination probes can maintain their accuracy for—on average—1 to 2 years. Furthermore, any ground loops that make their way into either the reference or process electrode affect the accuracy of the reading.

Differential probes address both the problems of reference electrode contamination and ground loop errors. By splitting the two electrodes and referencing them both to a common titanium ground rod, the following benefits occur: The reference electrode can now be coupled into the process via a replaceable salt bridge. When the reference solution becomes contaminated, one simply discards it and replaces it with fresh solution. The “salt bridge” that provides the permeable junction between the process and the reference electrode is also replaceable.

The addition of the ground rod splits the measurement circuit containing the process and the reference electrodes into two high impedance circuits containing the common titanium return electrode. A differential probe therefore measure pH or ORP by subtracting the reference circuit from the process circuit—hence the term “differential.” The added advantage of the differential circuit is that any ground loops that find their way into the measurement are automatically subtracted, thus giving the sensor higher precision

Rather than lasting 1 to 2 years, the differential probe lasts anywhere from 5 to 10 years, depending on the application. The Aquametrix differential pH/ORP probes have roots that go back to the original Karl King patent four decades ago[11].

5.10. The Final Word

The ORP sensor is fundamentally different from every other sensor used in water quality instrumentation. It is the only sensor that measures a property of water rather than a chemical species. That property is oxidation-reduction, or redox, potential. The world of water chemistry is overwhelmingly dominated by reactions in which the chemical constituents swap electrons amongst themselves. Those reactions drive such vital processes such as disinfection, nitrification, denitrification, phosphate removal, methane production, hydrogen sulfide removal, precipitation of heavy metals and corrosion. This wide variety of chemical reactions underscore just how powerful the ORP sensor is.

The lack of understanding of just what ORP means is the reason most users shy away from installing it in their installation. I firmly believe that if all system operators understood ORP sales of the sensors would be an order of magnitude higher than what it is today. Though an ORP analyzer can replace a chlorine analyzer or a dissolved oxygen analyzer it is not my intention in writing this paper to advocate doing so. It is simply a very powerful tool that can insure that a chemical process we need to control is proceeding as necessary.

Like any sensor, ORP analyzers have their limitations that must be understood. Probably the most important one is the slow response that can occur in relatively clean water. But, once understood, there is probably no other instrument that can be used in so many different processes related to water and wastewater treatment.

Mark Spencer holds a PhD in physical chemistry. He is the president of Water Analytics, the company that manufactures the Aquametrix line of water quality instrumentation. He spends his spare time writing technical articles that can be understood by all because he is a nerd who actually thinks that topics like ORP are way cool.

To find out more about ORP and other esoteric but important topics e-mail Mark at mspencer@wateranalytics.net or call him at 978-749-9949.

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[11] Karl King,*Self-Compensating Electrode System*, United States Patent 3,862,895, 1975.