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# Properly Measure Ions in Solution

*Here's how to decide whether to use pH, oxidation reduction potential, conductivity, or resistivity — either singly or in combination.*

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**W**hen choosing an analytical instrument to monitor solutions, it is important to carefully consider what is being measured, and whether a different or additional measurement might offer improved process control. In this article, we look at four common measurements — pH, oxidation reduction potential (ORP), conductivity, and resistivity — and how best to employ them.

## Understanding pH

The most common — yet misunderstood and misused — measurement is pH. It simply measures the hydrogen ion activity in a solution. To the novice, this means the acidity or alkalinity of the solution, normally translated to the range of 0–14 pH. Always, however, keep three important points about pH in mind:

1. The measurement is logarithmic. A solution with a pH of 6 has ten times the concentration of hydrogen ion ( $10^{-6}$  Mol/L) as a neutral solution of pH 7 (which contains  $10^{-7}$  Mol/L concentration of  $H^+$ ). A pH 5 solution has ten times the concentration of a pH 6 solution, and 100 times the concentration of a neutral solution, and so on. This feature makes pH control quite difficult. It also means that measurement of the acidity of the solution is relatively insensitive to changes in concentration — a doubling of the acid concentration results in pH changes of only -0.3 pH.

2. pH only measures the free hydrogen ion, or disassociated acid molecules,

not the total acid in solution. Hence, two solutions with a pH of 4 still can have dramatically different concentrations of acid. A solution containing a “strong acid” (such as hydrochloric), which disassociates completely, requires a smaller concentration of acid to achieve the pH reading of 4.0. A “weak acid” (such as acetic), however, does not disassociate completely; therefore, a pH of 4.0 will contain a much greater amount of total acid.

3. The pH range of 0–14 is misleading. First of all, the true pH of a solution may, in fact, be less than 0, or greater than 14. In addition, today's glass measuring electrodes do not read this complete range accurately. At pH values less than 1.5, an electrode signal begins to drift significantly, and at  $pH > 12.5$ , two different phenomena that can cause significant process problems occur. The first is commonly referred to as sodium ion error. The presence of large quantities of positive sodium ions acts to confuse the sensitive glass membrane. This results in a lower-than-actual pH measurement. Figure 1 shows the actual effect. The second is that the concentrated caustic solution begins to etch the sensitive measuring glass surface, causing reduced sensitivity and, subsequently, lower-than-actual pH readings. Always remember that a “high pH” electrode is designed only for more accurate but brief measurements in high pH, not for prolonged exposure or control.

The unfortunate reality of this situation is that, in a control environment, an

erroneously low pH reading can prompt the addition of caustic, causing additional etching of the glass, and reducing the glass sensitivity even more — a Catch 22 scenario that eventually will drain an entire reserve of caustic soda.

### Oxidation reduction potential

ORP gauges the electron activity in a solution. To the novice, this translates to a measurement of the concentration of oxidizers or reducers in a solution. Common oxidizers include chlorine, sodium hypochlorite, ozone, and bromine. Common reducers include sodium sulfite (also known as sodium metabisulfite), and sulfur dioxide.

The most common oxidation processes include disinfection, such as of cooling towers and bottling lines, and destruction of cyanide in plating waste treatment and hydrogen sulfide gas in scrubbing towers. The most common reduction processes include chrome reduction in waste treatment, and dechlorination of treated waste prior to discharge. In each of these cases, an agent being added donates or accepts

the electrons required for the actual oxidation or reduction.

The ORP measurement then translates literally to the overall “potential” or strength that the solution has to complete the process. For example, a solution with an ORP of 650 mV will be “stronger” than one with an ORP of 500 mV — and therefore will complete the oxidation of the desired species at a faster rate. Water with no oxidizer or reducer present will have an ORP of approximately 250 mV, because of the design of the electrode and some minimal activity of the dissolved oxygen normally present. The addition of oxidizers to the solution will cause the ORP value to rise, while reducers will make it drop towards zero, or even to a negative value.

### Conductivity and resistivity

The measurements of conductivity and resistivity are closely related. Both gauge the ability of a solution to conduct electricity. Normally, however, the true purpose of either measurement is only as a counting tool for the number of ions present.

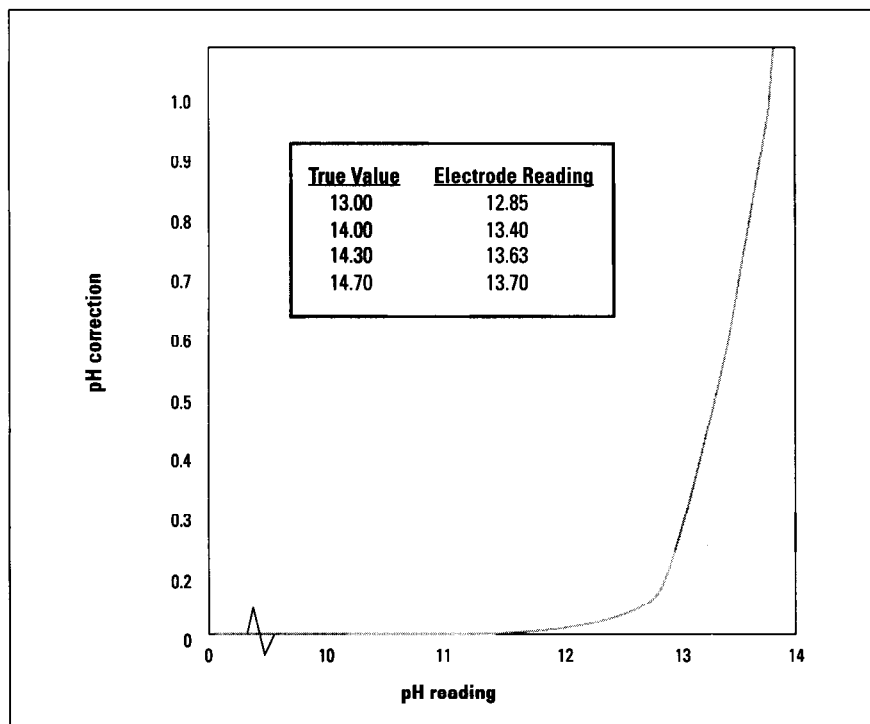
When a solution is resistive to electrical current flow, owing to a lack of ions, the proper measurement is resistivity; the magnitude of resistance can exceed 18 million ohms ( $M\Omega$ ) (using a standard 1 cm cell — that is, two 1  $cm^2$  electrodes 1 cm apart from each other). To achieve resistive or pure water, several steps of water purification such as deionization, reverse osmosis, or ultrafiltration must be used.

In contrast, conductivity is used when ions are present in the solution, making it conductive to electrical current. Conductivity, in fact, has a very large range of measurement depending upon the application. The low end is for relatively clean solutions, such as well water, or water after a small amount of treatment such as deionization, while mid-range can handle applications such as recirculated cooling tower or rinse tanks. The high end includes very concentrated solutions of acids, bases, or salts.

### Choosing the right measurement

*Conductivity vs. pH.* As stated earlier, pH measurement can be difficult in very high or very low pH conditions. Many times, conductivity can provide a more accurate measurement for these applications. One important advantage of conductivity is that it generally is a linear measurement with respect to concentration — that is, if the concentration of ions in the solution doubles, its conductivity doubles as well. (At very high concentrations, however, ion concentration hinders ion mobility, resulting in lower conductivity with increasing concentration; the relationship still is nearly linear, though.) Compared to pH, this can provide significantly more resolution for monitoring changes in concentration.

At the extremes of pH, electrode drift occurs more easily than true changes of concentration. One example of this is in the measurement of sodium hydroxide. Consider a 5% NaOH solution such as often used for cleaning solutions. With conductivity



■ Figure 1. Curve illustrates sodium-ion-induced error at 25°C.

as the measurement, a +0.5% control range can be achieved (namely, 220,000–240,000  $\mu\text{S}$ ). The pH of this same solution will be greater than 14, and problems with sodium error and etching of the glass will be significant. In concentrated solutions containing a single acid, base, or salt, conductivity can offer greater accuracy, more stable readings, and lower maintenance than a pH system. Table 1 lists some sample solutions read for both pH and conductivity.

Note, however, that conductivity monitors all ions present in solution. So, if the intent of a process (like in waste treatment) is to neutralize, then pH is the only measurement that can be used.

In recirculated neutralization processes, such as the air scrubbing of acid fumes in sodium hydroxide, it is becoming quite common to monitor both pH and conductivity. Control of pH insures that the concentration of caustic is sufficient to neutralize the acid fumes as they occur, while the conductivity measurement is used to prevent "salting out" at the bottom of the scrubber. The continued neutralization of the acid produces salts as byproducts. This results in the pH decreasing (caustic being neutralized), while the conductivity increases (from additional salt content). Sodium hydroxide is replenished from the low pH indication, while solution will be drained off and replaced with fresh solution when the conductivity is too high.

**ORP vs. pH and ORP.** The measurement of ORP often is performed in conjunction with pH — as this can provide improved control in some cases. (Figure 2 shows such an installation for a water-treatment system.) In disinfection or other oxidation applications involving chlorine, it has been found that the pH does affect the activity of the chlorine in water. Specifically, the form in which the chlorine exists in the water changes with pH. As pH increases, the chlorine changes from a strong oxidizer, HOCl (hypochlorous acid), to a weaker,

**Table 1. pH vs. conductivity for sodium hydroxide.**

Conc. (Wt. %)	Normality	Conductivity	True pH	Measured pH*
2%	0.510	95,000 $\mu\text{S}$	13.7	13.3
4%	1.043	175,000 $\mu\text{S}$	14.0	13.4
6%	1.597	250,000 $\mu\text{S}$	14.2	13.5
8%	2.173	305,000 $\mu\text{S}$	14.3	13.6
10%	2.772	360,000 $\mu\text{S}$	14.4	13.6

\*Difference stems from sodium ion error even though measurement was taken with best-available low-sodium-ion-error formulated glass electrode.



**Figure 2. Water-treatment unit relies on both pH and ORP controllers.**

slower-acting oxidizer, OCl<sup>-</sup> (hypochlorite ion), decreasing the oxidation potential or ORP. Although the ORP measurement alone does indicate the true oxidizing capability of the solution, controlling the pH in addition to the ORP can keep the chlorine in its more active state and provide more efficient use (and, thus, lower total use) of the oxidizer. Bromine and fluorine behave in a similar manner.

Another important oxidizer, ozone (O<sub>3</sub>), has not been found to be affected by pH. This is simply because the form of the ozone in the water does not change with the pH of the water. Therefore, ORP

alone can provide good measurement and control for ozone applications.

**ORP vs. residual (free) chlorine.** A monitor for residual chlorine often is specified when the true process application is oxidation. This can be misleading as the residual chlorine monitor does not take into account the level of activity that the chlorine present may have — which, as stated earlier, can vary significantly depending upon pH. In fact, the World Health Organization (WHO) proved in 1968 that the killing of *E. coli* bacteria depends upon ORP, not free residual chlorine. Indeed, in 1972, WHO set a standard

for public swimming pool disinfection based on ORP.

If the process being performed is oxidation or reduction, then ORP is the preferred measurement. If pH is tightly controlled, ORP and ppm of residual chlorine can be correlated quite well.

In other applications, the presence (or absence) of chlorine specifically must be measured accurately. For instance, this is required to protect some reverse osmosis filters. Chlorine concentration of 1 ppm or greater can damage some membranes, and thus must be monitored carefully. If the actual presence of chlorine, not its activity level, is important, then residual chlorine is the preferred measurement.

**Conductivity vs. resistivity.** Conductivity and resistivity are essentially the same measurement, but at different ends of the scale. The actual measurement unit of conductivity is the inverse value of resistivity — formerly termed the mho, it has since been renamed after its founder, Siemen (S). Table 2 lists some equivalent values in conductivity and resistivity, and indicates the most appropriate measurement ranges for each.

While it is true that both values indicate the actual conductivity or resistivity of the solution, significant errors in readings can occur when the incorrect instrument is used for an application. The problem occurs in the compensation taken to eliminate the effect of temperature from the raw, measured value. Most conductivity instruments use a simple, linear temperature compensation, which is accurate in solutions with conductivity greater than 1  $\mu\text{S}$ , and amounts to approximately 2.0% for each degree change in temperature from 25°C (in water). In solutions with conductivity less than 1  $\mu\text{S}$ , the effect of temperature becomes much more significant, and is no longer a simple linear relationship. It, therefore, is critical to insure that the instrument being used will compensate for temperature correctly in the range of the application. To moderate-

**Table 2. Equivalent readings for conductivity and resistivity.**

Resistivity, $\Omega$	Conductivity, $\mu\text{S}$	Solution
<b>18,000,000</b>	0.056	Clean (pure water)
<b>10,000,000</b>	0.1	↓
<b>1,000,000</b>	<b>1.0</b>	↓
100,000	<b>10.0</b>	↓
10,000	<b>100</b>	↓
1,000	<b>1,000</b>	↓
100	<b>10,000</b>	Dirty ("salty" water)

Measurements in boldface are in "correct" ranges for the application.

ly confuse the issue, it is common in European countries to use only the conductivity scale, and instruments are made accordingly.

#### Calibration concerns

Once the measurement instruments are selected, they must be installed and calibrated. For applications of pH, ORP, and conductivity, a wet calibration of the complete system should be performed. This insures the accuracy of the combination of the complete system of sensor and controller or transmitter. For pH, a standard two-point calibration with pH buffer solution is used. For ORP, a similar calibration, but using quinhydrone (a reducing agent), is performed. Like chlorine, its activity is pH-sensitive, and, therefore, it is placed into pH buffer solutions to insure known calibration values. These calibrations should be repeated on a regular basis, normally once per month for most applications. Conductivity calibration requires standard solutions. A single, standard solution in the range of conductivity of the application normally is sufficient for a one-point calibration of the system.

Resistivity calibration unfortunately is much more complicated. In the high purity ranges of this application, standard solutions are unstable and, therefore, are inaccurate. The best method is to electrically calibrate the instrument using resistors (at 25°C to disable any compensation), and to use a sensor certified for accuracy in cell

constant, that is, the size of and distance between the electrodes.

The sensors used in conductivity and resistivity do not deplete over time like the pH and ORP electrodes; therefore, regular monthly calibration is not necessary. Generally, an annual calibration is sufficient for these systems.

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#### Further Reading

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