FUNDAMENTALS OF ORP CALIBRATION

WHAT ORP MEASURES AND WHY WE WANT TO CALIBRATE IT

The measuring signal (typically, voltage) in majority of the process analytical measurements is a function of some physical or chemical property of the process liquid. For example, the pH-sensor produces an electrical signal proportional to some level of acidity or pH level of the liquid its immersed it. The calibration method for this type of measurement is plotting read signal versus property of the liquid. The two-point calibration is most commonly accepted. The ORP is drastically different type of measurements! There is no direct one-to-one property/concentration correspondence. ORP is only an indicator if the process liquid has a reducing or oxidizing potential.

Since the ORP measurement is a direct measurement of the millivolt output of the ORP sensor, and the voltage measurement of an analyzer is very stable over time, some people question why it is standardized at all. In fact, earlier analog ORP analyzers were calibrated using a millivolt source just to check the accuracy of the millivolt measurement of the analyzer. This procedure is referred to as a factory calibration. Some people argue that two-point calibration is preferable because it may give an advantage of greater accuracy. Well, it turns out to be a myth. The goal of this application note is to detangle common misconception

ORP STANDARDS

All process analytical measurements require a standard for calibration. Usually the standard come with specified range of accuracy at the specified condition, such as temperature for example. In case of ORP the temperature and the type of the reference electrode are specified.

Some ORP standards are referenced to a standard hydrogen electrode (SHE), which is 0 mV by definition. Some standards are referenced to an Ag/AgCl electrode, which is used in RAI ORP sensors. Two ORP standard solutions are in common use: Light's solution and ZoBell's solution. Their properties are summarized in the table below.

CALIBRATION
ONE-POINT CALIBRATION (STANDARDIZATION)

With a one point calibration, we assume that the ORP analyzer will read 0 mV at 0 mV. The reason for doing a single point ORP calibration is that the millivolt potential measured by the analyzer is the difference of the ORP electrode and the reference electrode, which has a potential of about 200 mV at room temperature. The ORP read by the analyzer should be close to specified value of the known standard. An ORP sensor is commonly checked by placing it in a solution of known ORP and confirming that the measured ORP matches the ORP of the standard to within some limit, usually within ±10 mV. If the ORP is too much in error, the analyzer reading is offset to match the known ORP, by doing the single point standardization.

CHECKING THE ORP RANGE

Having a two point range checking ties the measurement to two known millivolt values, offset and slope value, and may make a user more confident of the measurement. But given the ±10 mV or so repeatability of the ORP sensor itself, it does not provides any more accuracy than a single point calibration. On top of that, ORP is not temperature compensated, so if the measurement is not done at 25 C, any benefit gained would be likely lost.

Because a few of standards having different ORP are available, the sensor can be checked at two or more points (do not confuse it with two-point calibration), but a multiple point calibration possible only in certain limited applications. To understand why, it is necessary to review some basic ideas of oxidation reduction chemistry.

	Composition	ORP at 25ºC vs sat'd Ag/AgCl
Light's solution	0.10 M each Fe+2 and Fe+3 from ferrous and ferric ammonium sulfate in 1.0 M H2SO4	+476±5 mV
ZoBell's solution	0.0033 M each Fe(CN)6-4 and Fe(CN)6-3 from potassium ferrocyanide and ferricyanide in 0.1 M KCl0.489"	+229±5 mV

ORP OF A SPECIFIC REDOX COUPLE (TWO-POINT CALIBRATION)

ORP is a measure of the ratio of the concentration of the reduced and oxidized forms of a chemical. A good example is ferrous (Fe^{+2}) and ferric (Fe^{+3}) iron. Ferric iron is the oxidized form and ferrous iron is the reduced form. Together, they constitute a redox couple. The equation shows how the two elements of the couple are related by the gain or loss of an electron:

$$Fe^{+3} + e^- = Fe^{+2}$$
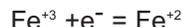
If an inert metal electrode is placed in a solution of Fe^{+3} and Fe^{+2}, an electrical potential (the ORP) develops at the electrode. The Nernst equation describes the relationship between ORP and the concentrations of Fe^{+3} and Fe^{+2}:

$$E = E° - \frac{2.303\ RT}{nF} \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

E is the measured ORP, Eo is the standard state ORP (the ORP when the concentrations of Fe^{+2} and Fe^{+3} are unity), T is temperature in Kelvin, n is the number of electrons transferred (one in the pre-sent case), and R and F are constants. The brackets represent the molar concentrations of the ions. Plotting ORP against log{$[Fe^{+2}]/[Fe^{+3}]$} gives a straight line with intercept Eo and slope

-2.303RT/nF. At 25ºC and for n = 1, the slope is

-59.16 mV/decade.

If ORP is measured at two different ratios of $[Fe^{+2}]$ to $[Fe^{+3}]$ and plotted as described above, the points will define a straight line. The line can then be used as a calibration curve to convert a measured ORP a concentration ratio. However, the calibration line is valid only for the redox couple used to define it. Only in this very limited application will a two-point ORP calibration be possible.

GENERAL CASE FOR TWO-POINT CALBRATION (WHY IT DOES NOT MAKE SENSE)

Now consider the question of a two-point calibration for an ORP sensor that is not intended to measure a specific redox couple. There are two issues to consider. What two ORP standards should be chosen, and what property of the solutions should be plotted on the x-axis to produce a calibration line?

The first part of the question is easy. Most common ORP standard are listed in the table above.

The Nernst equation for Light's solution at 25ºC is:

$$E = E°_{Light} - \frac{59.16}{n} \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

The Nernst equation for ZoBell's solution at 25ºC is:

$$E = E°_{ZoBell} - \frac{59.16}{n} \log \frac{[Fe(CN)_6^{-4}]}{[Fe(CN)_6^{-3}]}$$

In both equations, the number of electrons transferred (n) equals 1.

The next question, what to plot on the x-axis, is more difficult to answer. For a straight line plot of the Nernst equation, the x-axis must be the logarithm of the concentration ratio with the reduced form of the couple in the numerator and the oxidized form in the denominator. The resulting plot—an attempt to do a two point ORP calibration is shown below.
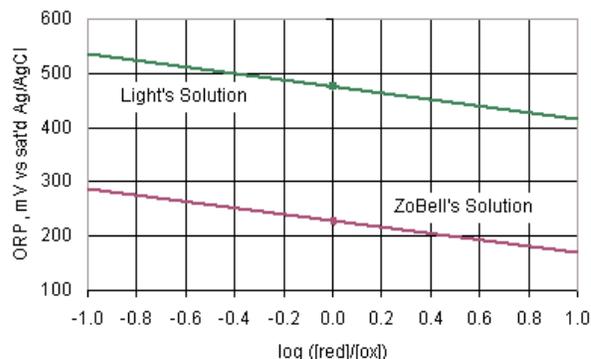
The dots are the ORP of Light's and ZoBell's solutions, and the lines are the graphs of the Nernst equation for the two standards. The x-value is zero for each standard solution because each contains equimolar concentrations of the oxidized and reduced forms of the couple (log 1 = 0).

The graph shows why a two-point ORP calibration is not possible. The calibration solutions are entirely different chemical systems. Each calibration point lies on a unique line, which is the Nernst equation for the redox couple constituting the standard. Because the concentration ratios involve different chemicals, they cannot be linked in a common calibration curve.

SUMMARY

ORP sensor is generally calibrated at one-point. It provides sufficient accuracy for ORP measurements, ±10 mV. The range of the ORP can be checked at multiple points with various available standards. However, adjustments for the slope and offset are not recommended because it does not provide more accuracy that single point calibration. In fact, it can create problems. The true two-point calibration is possible in rare case of tightly controlled conditions when the only redox couple is present in a solution and its chemistry is known.

INSTRUMENTATION

Model 1056 Analyzer

- MULTI-PARAMETER INSTRUMENT – single or dual input. Any combination of pH/ORP/ISE, Resistivity/Conductivity, Chlorine, Oxygen, Ozone, Turbidity, Flow.

- LARGE DISPLAY – easy-to-read process measurements.

- SEVEN LANGUAGES: English, French, German, Italian, Spanish, Portuguese, and Chinese.

- HART AND PROFIBUS DP Digital Communications.

PERpH-X pH/ORP Sensors

- HIGH TEMPERATURE DESIGN Increases sensor life when used in elevated temperature applications.

- FAST, ACCURATE & STABLE.

- RUGGED & VERSATILE RYTON CONSTRUCTION.

- LONG LASTING REBUILDABLE REFERENCE can be customized with different chemical formulations.

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