

Calibrating ORP Measurement Systems

Background

Like pH, Conductivity/TDS, and other electrochemical measurements, Oxidation-Reduction Potential (ORP) or Redox measurements are based on displaying the response of a specialized electrode in a solution. Like pH electrodes, each ORP electrode has unique characteristics that cause variability in the signal the electrodes send to the meter. Both the offset and slope characteristics of the pH electrode must be compensated by calibration to the meter in order to obtain accurate readings. ORP electrodes and measurements present different problems.

The major concern lies with the offset characteristics of the ORP electrode. The slope characteristics of ORP electrodes are less variable than pH electrodes since the ORP sensors are made of noble (more or less non-reactive) metals such as Platinum or Gold, and do not change very much with use. Response times (which is sometimes confused with slope) of these sensors can vary greatly depending on the surface area, size and construction, and how clean the sensor is.

For most ORP applications, the absolute accuracy is far less important than the speed and relative changes measured in the system. Many procedures and specifications call for target ORP values with tolerances of ± 25 mV, or ± 50 mV, or they specify changes in ORP such as a 400 mV drop in the value with a target end point value. Since ORP has a variety of uses with methods that have their own specialized target readings or reading changes that are based on experience, we cannot elaborate on these in detail. It is sufficient to say the precision required for pH and other electrochemical measurements typically does not apply for ORP, and so calibration for ORP electrodes and meters is not common.

Calibration Solutions for ORP

Some reputed ORP solutions are available in the market. Careful evaluation of these reveals they are not calibration solutions, they are described as checking solutions. Also, these solutions typically have very wide tolerances, ± 35 mV or more, for the actual values one can expect when checking their ORP. Combine this with the fact that the solution's ORP will change substantially with time and with each change in temperature, these solutions are practically useless except to check if the electrode gives any form of response to ORP. This is a relative minor benefit compared to the extreme toxicity of most ORP solutions. Alternatives to this are recommended and are available.

There are some procedures offered in the market which involve a two-point check of ORP. The user can make up these solutions fresh, which gives better reliability for the expected ORP values than the off-the-shelf solutions described above, though no specific accuracy or values can be given. In these procedures, the desired result is to take readings that are expected to have a specified differential value with tolerances of ± 10 mV possible. If your ORP readings have a differential close to this specified value, the electrode and meter system are considered to be in working order.

As an alternative to either of these methods we recommend the use of household bleach (FOLLOW THE SAFE HANDLING INSTRUCTIONS ON THE LABEL) and water. For a quick check whether your ORP measurement system is working properly, simply take a reading of your tap water (this will typically be a value well below 200 mV) and then take a reading of the same tap water adding an equal volume of bleach. In both tests you will need to allow the electrode to stabilize at a reading which may take up to 30 minutes. When the bleaches added you should get a much higher reading (up to 800 mV is possible through lower values, 300 to 600 mV, are typical).

If the readings remain close to the readings for the tap water only, there is some problem with the ORP measurement system (i.e. the electrode sensing metal is dirty/coated or reference junction is clogged). If your test of the bleach and water mixture gives the higher readings, the ORP measurement system is working.

ORP Offset Adjustment and Relative mV

Most Eutech's instruments (except the CyberScan pH20) used for ORP measurements offer push button mV offset adjustments and Relative mV adjustments, which are essentially the same function. These allow an offset adjustment to be input to the meter to compensate for the only ORP electrode variable that can cause measurement variability; the electrode offset. The offset adjustment is not meant to enhance accuracy, but to make readings comparable to some reference.

A reference for ORP is a measurement using another measurement system and a sample of the liquid to be measured. Often an ORP measurement method and target values have some protocol established using an ORP electrode and meter. When the electrode is replaced, electrode offset differences between the old electrode and the new one will cause differences in the readings that are not errors, but do add some confusion.

If for example, your method calls for a target value of 310 mV which was defined with your previous electrode and meter system, the new electrode and meter system may read 325 mV in the same liquid. Using the offset adjustment or Relative mV adjustment on Eutech's ORPScan or pH/mV meter respectively, this 15 mV difference can be eliminating the confusion. Then when the other readings occur, they can be found to be compatible to those from the old electrode and meter system.