



Measuring ORP on YSI 6-Series Sondes: Tips, Cautions and Limitations

Introduction and Basic Theory

As described in *Standard Methods for the Examination of Water and Wastewater* (Section 2580 B.), ORP is a potentiometric measurement in which the potential (or tendency) of the medium for electron transfer is sensed by an inert metal electrode and read relative to a reference electrode that is immersed in the same medium. This determination can also be referred to as a “redox” measurement (combination of REDuction and OXidation). For most multiparameter monitoring systems, the inert metal electrode is a button or ring made of platinum and the reference electrode is the same one associated with the pH sensor, usually Ag/AgCl. The readout of the sensor is a voltage (relative to the reference electrode), with positive values (e.g., +300 mV vs. Ag/AgCl) indicating an oxidizing environment (ability to accept electrons) and negative values (e.g. -300 mV) indicating a reducing environment (ability to furnish electrons).

The determination of ORP is particularly worthwhile in water which contains a relatively high concentration of a redox-active species, e.g., the salts of many metals (Fe^{2+} , Fe^{3+}) and strong oxidizing (chlorine) and reducing (sulfite ion) agents. Thus, ORP can sometimes be utilized to track the metallic pollution in ground or surface water or to determine the chlorine content of wastewater effluent. However, ORP is a nonspecific measurement, i.e., the measured potential is reflective of a combination of the effects of all the dissolved species in the medium. Because of this factor, the measurement of ORP in relatively clean environmental water (ground, surface, estuarine, and marine) has only limited utility unless a predominant redox-active species is known to be present. Users should thus be careful not to “over-interpret” ORP data unless specific information about the site is known.

ORP vs. Eh: Calibration of ORP Sensors

Many users of YSI 6-series sondes that make field or laboratory redox measurements have questions about the difference between ORP and Eh. In essence, the two parameters are the same in that both quantify the potential of the medium to transfer electrons -- the difference is the reference electrode (and thus the voltage offset) against which the potential of the platinum sensor is reported. Eh is defined as a voltage reading vs. the Standard Hydrogen Electrode (SHE), while ORP is a much less specific term in which the measurement can be made relative to any

practical or theoretical reference electrode, such as Ag/AgCl, calomel, or SHE. Generally, it is not easy to use the SHE in laboratory or field measurements and thus redox readings are made using either the Ag/AgCl or calomel reference electrodes, with Ag/AgCl being more popular in multiparameter water quality instrumentation. Thus, Eh is usually not determined directly. However, the voltages obtained as ORP readings vs. non-SHE electrodes can easily be converted into Eh values by two mechanisms:

- Adding (or subtracting) an offset voltage to the ORP readings obtained vs. a practical reference electrode to account for the fixed difference between the SHE and the other reference system. The offset voltage can easily be obtained for several practical reference electrodes in Table 2580: II of the section of *Standard Methods* on ORP. For example, the potential of Zobell solution vs. the Ag/AgCl reference electrode using 4 M KCl is +228 mV while the same solution read vs. the SHE is +428 mV. Therefore to convert ORP readings taken under these conditions to Eh, simply add 200 mV to the ORP voltage. For example, ORP readings of +150 and -172 mV translate to Eh values of +350 and +28 mV, respectively.
- Using the instrument software to automatically add the offset voltage to the ORP readings as they are displayed or logged. This method is implemented during calibration of the ORP sensor in YSI 6-series sondes. For example, when calibrating an instrument with Zobell solution that has an ORP reading of 228 versus the YSI reference electrode, enter 428 mV at the calibration prompt instead of 228. After the calibration is confirmed, 200 mV (the difference between Ag/AgCl and SHE reference electrodes) will automatically be added to all displayed and logged ORP values, effectively converting them to Eh with no further correction needed. The software in YSI 6-series sondes is likely to interpret the entry of the higher voltage value as an “out of range” calibration error and provide a warning to this effect. As long as the user is knowledgeable about the procedure, the error can be “overridden” with no ill effects.

Effect of Temperature

The temperature of the water for which ORP is being determined will affect the voltage output of the sensor. This factor definitely needs to be taken into account for calibration and should be considered when reporting field ORP values.

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For calibration, the following table can be used when using Zobell solution, the YSI-recommended standard. Thus, if the Zobell calibration standard is at 15° C instead of 25° C, enter 241 mV at the calibration prompt instead of 228 mV (the 25° C value which is commonly quoted).

| Temperature, C | Zobell Solution Value, mV vs. Ag/AgCl (4 M KCl) |
|----------------|--|
| -5 | 267.0 |
| 0 | 260.5 |
| 5 | 254.0 |
| 10 | 247.5 |
| 15 | 241.0 |
| 20 | 234.5 |
| 25 | 228.0 |
| 30 | 221.5 |
| 35 | 215.0 |
| 40 | 208.5 |
| 45 | 202.0 |
| 50 | 195.5 |

The user may be able to locate similar temperature-dependence data in the literature for other ORP standards such as Light's Solution and quinhydrone standards in pH buffers.

Temperature will also clearly have an effect on field readings, but, in this case, the variation is usually not definable since the temperature effect depends on the dissolved species responsible for the ORP reading, and these species are usually not known exactly for environmental water. For this reason, ORP readings on YSI 6-series sondes are **not** temperature compensated in any manner. The user must remember that ORP variation in field water could be due to temperature changes rather than analyte compensation. Usually, however, gross changes in ORP (>100 mV) are not due to the effect of temperature.

Confirming ORP Response

Unlike pH, YSI 6-series sondes only allow a single point calibration for ORP, i.e., an offset adjustment as described above. This is almost always adequate if the ORP sensor has been maintained properly. However, some users like to confirm that their ORP system tracks changes in ORP correctly, in the same way that a pH sensor responds to immersion in pH 7 and pH 10 buffers.

To check the "slope" and response characteristics of the ORP sensor, YSI recommends that the user purchase item number B125 (ORP Calibration Kit) from the manufacturer of one of our ORP sensors:

Sensorex
Tel. +1 714 895 4344
Fax. +1 714 894 4839
Email. info@sensorex.com
Web. www.sensorex.com

The kit contains solid quinhydrone which, when added to the supplied buffers, yields two solutions with well-defined, but different, ORP values.

Problems with ORP Sensors

Although based on relatively simple theory, ORP is, unfortunately, also a measurement that can show more problems than other water quality sensors with regard to consistency between different instruments and overall accuracy. In addition, these issues are further complicated in that their extent is likely to depend on both the condition of the sensor and the makeup of the water being tested. The most common problem reported with regard to ORP determination in environmental water is that readings from various instruments (sometimes with exactly the same sensor type and electronics) differ by a significant margin (50-100 mV) even though the sensors are in the same container of water. To make the problem more perplexing, all of the sensors show identical readings in an ORP standard such as Zobell solution. The exact explanation for this paradox is sometimes elusive, but there are at least three possible reasons for its occurrence.

- First, ORP sensors can show a slow response in environmental water if the platinum button of the probe has been contaminated with extraneous material. Common contaminants include hard water deposits, oil/grease, or other organic matter. If the platinum electrodes in the above example are variably contaminated, then some of them (the more contaminated) will be likely to approach potentiometric equilibrium slower. Under this scenario, if left long enough all the sensors would read the same. However, it might take days for the contaminated sensors to reach their final value, and, therefore, they appear in the time frame of a sampling experiment (< 1 hour), to be different. Naturally, if the electrode contaminant is redox-active, either in itself or because it contains redox-active impurities, the reading from that sensor will exhibit erroneous readings that may never change unless the contaminant is removed.

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- Second, in clean environmental water, there may be very few redox-active species present, and those that are present may be in very low concentration. In many cases, the concentration can be so low that the redox influence of the species is effectively below the detection limit of the method. Under these conditions, the readings will have questionable meaning and could show this type of variation described above. Note that the ORP reading variance associated by this scenario is likely to be exacerbated if any of the electrodes is also contaminated as described above.
- Third, the makeup of the surface composition of the electrode may not be ideal for the measurement in the medium under investigation. While “platinum” ORP electrodes are primarily composed of the metal itself (in a neutral state), it is well known that the surface of the electrode (where the redox action takes place) is coated to varying extents with a molecular layer of platinum oxide (PtO). The Pt/PtO ratio can change over time, depending on the medium in which the probe is stored, and thus the surface of the electrode actually possesses its own potential that can be variable. If this surface potential is similar to the ORP potential of the medium, then electrode response can be sluggish. The cleaning procedure recommended later in this document will result in a surface characterized by a low Pt/PtO ratio and one that possesses a very positive potential. This should be suitable for most environmental measurements.

The fact that similar or identical ORP sensors read differently in environmental water yet the same in Zobell solution is due to the fact that the concentration of redox-active species (ferricyanide/ferrocyanide for Zobell) is much greater in the standards. This higher concentration usually “swamps out” the inconsistencies related to detection limit problems (caused by low amounts of redox-active species) and response time issues (caused by electrode contamination), thus all sensors respond rapidly and read within the YSI specification of +/- 20 mV when in standards.

If you observe inconsistency between different sensors or experience ORP readings which seem unusual for the water being tested with your YSI 6-series multiparameter instrument, YSI recommends the following steps to identify and/or correct the problem:

First, make certain that the pH sensor is functioning properly. The reference electrode of the sonde is common to both pH and ORP sensors and, therefore, if both pH and ORP sensors are malfunctioning this is likely to be the source of the problem. Reference electrode problems usually appear as either total failure or as a slow response in both pH and ORP readings. If

a reference electrode problem is suspected, test the ORP sensor in a standard and make certain that it is within 20-30 mV of the predicted value. If reference electrode performance is indicated, clean the sensor according to the instructions shown below and then retest.

Second, if the sensor performs well in the ORP standard, remove the probe from the sonde and carry out the sequential cleaning process documented in the next section.

ORP Electrode Cleaning

The following procedure will result in removal of many common contaminants from the platinum ORP electrode. Fouling of the electrode can, however, be deployment-specific, and some contaminants from polluted water may not be dissolved by this method. The use of other solvents and reagents may be possible, but they must be selected carefully so as not to damage the reference electrode or pH glass of the combination sensors nor to leach or dissolve the CPVC body of the probe itself. Consult YSI Customer Service before using cleaning methods other than those documented below.

YSI recommends that the user perform the cleaning/reconditioning operation in the order indicated. Performance can be rechecked at the conclusion of each major section (A, B, and C) and the cleaning discontinued if, at that point, the performance problem has been corrected.

Procedure A

1. Soak the probe for 10-15 minutes in clean water containing a few drops of commercial dishwashing liquid.
2. Wipe the platinum button or ring by rubbing with a cotton swab soaked in the cleaning solution. CAUTION: For 6565 probes, be certain not to damage the glass bulb of the combination sensor during this process.
3. Rinse the probe in clean water, wipe with a cotton swab saturated with clean water, and then re-rinse with clean water.

Procedure B

1. Soak the probe for 20-30 minutes in one molar (1 M) hydrochloric acid (HCl). This reagent can be purchased from most laboratory supply dealers. Be sure to follow the safety instructions supplied with the reagent.
2. Wipe the platinum button by rubbing with a cotton swab soaked in the acid. CAUTION: For 6565 probes, be certain not to damage the glass bulb of the combination sensor during this process.
3. Rinse the probe in clean water, wipe with a cotton swab saturated with clean water, then rerinse with clean water.

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Procedure C

1. Soak the probe for approximately 1-2 hours in a 1 to 1 dilution of commercially available chlorine bleach.
2. Rinse the probe with clean water and then soak for at least 1 hour in clean water to remove residual bleach from the reference junction. **CAUTION:** If removal of the chlorine bleach is incomplete, this cleaning reagent can seep into either your calibration standards or measurement media and cause erroneous ORP readings until it is dissipated. Always err on the side of caution in the chlorine bleach removal. Soaking the probe in clean water for periods of time longer than 1 hour can do no harm, however, lesser soaking times can cause problems.
3. Dry the sonde port and probe connector with compressed air and apply a very thin coat of O-ring lubricant to all O-rings before re-installation of the probe. After the probe is reinstalled, place the sensors in Zobell solution and make certain that observed ORP readings stabilize within a few minutes and remain stable for 15-20 minutes.

Typical ORP Data in Standards and Freshwater

| Probe # | Zobell Reading | | |
|---------|----------------|--------|---------------|
| | Initial | 1 hour | After Testing |
| 1 | 228 | 228 | 233 |
| 2 | 227 | 226 | 227 |
| 3 | 227 | 227 | 228 |
| 4 | 224 | 224 | 228 |
| 5 | 227 | 227 | 228 |

Table 1. ORP sensor performance in Zobell Solution.

Experiments have been performed at YSI to demonstrate the typical performance of YSI ORP sensors in both standards and in freshwater. Five (5) new 6565 sensors were taken from stock and placed directly into Zobell solution at 22° C. As shown in Table 1 below, all sensors read within 4 mV of each other. The sensors were left in the Zobell solution for 1 hour and the values recorded again. Finally, the sensors were retested in Zobell solution after the entire regimen of testing described below was completed. The values were basically unchanged, demonstrating the stability of the sensor in redox buffer.

The sensors were then rinsed and soaked in DI water and then transferred to tap water that had been diluted with deionized water to a specific conductance of 290 uS/cm and saturated with air. The ORP readings were recorded 1 minute after transfer and then again after 2.5 hours in the low-to-medium conductivity water. Note that all readings are fairly close at 1

minute, with probe 5 showing a somewhat more positive reading. Note also that the discrepancy between probe 5 and the others increased slightly after longer-term exposure to the water sample. Cleaning the ORP platinum sensor of probe 5 with clean water and a cotton swab resulted in a decrease of the reading to 207

| Probe # | ORP Reading | |
|---------|-------------|-----------|
| | 1 minute | 2.5 hours |
| 1 | 138 | 178 |
| 2 | 143 | 161 |
| 3 | 132 | 177 |
| 4 | 135 | 169 |
| 5 | 166 | 221 |

Table 2. ORP sensor performance in 290 uS/cm natural water.

mV -- significantly closer to the other sensors. Finally, note that all readings increased by an average of about 40 mV after longer-term exposure to the natural water. This stabilization pattern, along with some variation in probe readings, is likely to occur with all ORP sensors when used in environmental water samples. The difference in behavior between Zobell solution and the water sample is striking and demonstrates that a lower accuracy specification must be tolerated in natural water samples than in buffers. (Note that the YSI accuracy specification of +/- 20 mV refers to readings taken in redox standards.) See Table 2 for the data described in this experiment.

The sensors were then cleaned using the 1 M HCl treatment described above, soaked in DI water to remove all acid traces, and then placed back into the 290 uS/cm natural water sample. ORP readings were taken 5 minutes after placing the probes in the water. The calibration of the sensors was then checked in Zobell solution the probes returned to the natural water sample, and the readings recorded after 5 minutes. Results are shown in Table 3.

| Probe # | Water Sample 5 minutes post cleaning | Zobell Solution Calibration check | Water Sample 5 minutes post cal check |
|---------|--|---|---|
| 1 | 195 | 233 | 186 |
| 2 | 188 | 227 | 183 |
| 3 | 214 | 228 | 184 |
| 4 | 197 | 228 | 184 |
| 5 | 280 | 228 | 230 |

Table 3. ORP sensor performance in 290 uS/cm natural water after cleaning sensors with 1 M HCl.

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Note the following from the data in Table 3:

- The results in the natural water sample are about the same after the cleaning as before -- probe #5 is still significantly higher than the other 4 that are fairly tightly bunched.
- Even after multiple exposures to standards, the natural water sample, and 1 M HCl, the probes (including probe #5) all read effectively the same in Zobell solution.
- Although the effect is relatively minor, the water sample readings are somewhat dependent on the previous reagent to which the probes were exposed. Note that the results are more consistent and slightly lower overall after the probes had been in Zobell solution (column 3) than after they had been in 1 M HCl (column 1).

Most users would consider the performance of probes 1-4 in natural water acceptable in terms of their consistency with one another, but might wonder why probe 5 always seems to read somewhat more positive than the other sensors except in Zobell solution where it has the same reading. Although difficult to prove, the difference is most likely due to a different Pt/PtO ratio on the surface of probe 5. Consistent with this hypothesis, the final experiments indicate that probe 5 responds to ORP changes and that its ORP reading in natural water becomes closer to those of the other four sensors after longer-term exposure to this medium.

In the final testing, the probes were placed in a sodium sulfite solution, a reducing environment that should produce a decrease in the ORP readings. As shown in Table 4, this effect was indeed observed. The probes were then carefully cleaned and returned to the natural water sample for 18 hours and then the ORP values recorded to conclude the test protocol. These final values are found in Table 4.

| Probe # | Sodium Sulfite Solution, after 5 minute exposure | Natural Water, after 18 hour exposure |
|---------|--|---------------------------------------|
| 1 | 135 | 196 |
| 2 | 125 | 174 |
| 3 | 140 | 207 |
| 4 | 120 | 195 |
| 5 | 95 | 218 |

Table 4. ORP sensor performance in sodium sulfite solution and after long-term exposure to natural water.

YSI would consider Probe 5 as an acceptable sensor for use with our 6-series sondes for the following reasons even though it reads an average of 50 mV different from the other sensors tested:

- The sensor responds quickly and shows the proper reading in Zobell solution;
- The sensor's reading in natural water is not radically different (>100 mV) from the other sensors and becomes closer after extended exposure to this medium;
- The sensor tracks changes in ORP properly.

Summary

The determination of ORP in environmental water can provide valuable insight into the sample as long as there is a significant concentration of a redox-active species present. However, in the absence of these species, ORP can be a significantly less exact measurement than for most other sensors found in YSI 6-series sondes. The inexactness is usually due to contamination of the electrode surface (either physically or chemically), but can also be due to the lack or low concentration of redox active agent in the environmental water.

The quoted accuracy specification for the YSI ORP sensor (+/- 20 mV) refers to redox- standards, such as Zobell solution, and not to environmental water of variable, and usually unknown, content. In many cases, the +/- 20 mV specification will be met in natural water, but it cannot be guaranteed.

Periodic maintenance of your YSI ORP sensor (6032 or 6565) will increase your field consistency and accuracy, but may not overcome all problems.

The value of ORP in determining the content of environmental water is greatly enhanced if the user has some knowledge or history of the site.

For additional information please contact

YSI Environmental

Tel. +1 937 767 7241

US 800 897 4151

Fax +1 937 767 1058

Email. environmental@ysi.com

Web. www.ysi.com