Issues with ORP Measurements

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 composition of the water being tested.

Paradoxical measurement

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.

1. 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.
2. 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.
3. The composition of the surface 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 specification of ± 20 mV when in standards.

Inconsistency between different sensors

If you observe inconsistency between different sensors or experience ORP readings which seem unusual for the water being tested, the following steps are recommended to identify and/or correct the problem:

1. Make certain that the pH sensor is functioning properly. The reference electrode of the probe 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.
2. If the sensor performs well in the ORP standard, carry out the sequential cleaning process documented in ORP Electrode Maintenance.

Useful links

Website U.S. Geological Survey:

http://water.usgs.gov/owq/FieldManual/Chapter6/Archive/Section6.5.pdf

Website Van London-pHoenix Co:

http://www.vl-pc.com/tasks/render/file/?fileid=1081F85A-BB45-F901-019B8E7D430C3AE9

From:
http://www.consort.be/wiki/ - **Support website**

Permanent link:
http://www.consort.be/wiki/issues_with_orp_measurement?rev=1424332825

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