Oxidation Reduction Potential: Understanding a Challenging Measurement

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Theory

Oxidation Reduction Potential (ORP or Redox Potential) measures an aqueous system's capacity to either release or accept electrons from chemical reactions. When a system tends to accept electrons, it is an oxidizing system. When it tends to release electrons, it is a reducing system. A system's reduction potential may change upon introduction of a new species or when the concentration of an existing species changes.

ORP values are used much like pH values to determine water quality. Just as pH values indicate a system's relative state for receiving or donating hydrogen ions, ORP values characterize a system's relative state for gaining or losing electrons. ORP values are affected by all oxidizing and reducing agents, not just acids and bases that influence pH measurement.

From a water treatment perspective, ORP measurements are used often to control disinfection with chlorine or chlorine dioxide in cooling towers, swimming pools, potable water supplies, and other water analysis applications. For example, studies have shown that the life span of bacteria in water is strongly dependent on the ORP value. In wastewater, ORP measurement is used frequently to control treatment processes that employ biological treatment solutions for removing contaminants.

The ORP (Redox) Sensor

ORP sensor operation works similarly to that of a standard pH sensor. A two-electrode system makes a potentiometric measurement. The ORP electrode serves as an electron donor or electron acceptor, depending upon the test solution. A reference electrode supplies a constant stable output for comparison. Electrical contact is made with the solution using a saturated potassium chloride (KCl) solution.

Platinum is normally used as an indicating sensor and the potential is measured against a reference electrode, usually Ag/AgCl. Other noble metals can also be used, such as gold or silver. For additional information about the ORP sensor and its theory of operation, please consult the Hach Application Note *Introduction to Oxidation Reduction Potential Measurement*.

Challenges Observed in ORP (Redox) Measurements

Although the electrode design and reference system is similar to a traditional pH electrode, ORP measurements cannot be characterized as similar. While a pH electrode is selective for the hydrogen ion concentration in a solution, the ORP sensor provides a response according to the sum of oxidation-reduction reactions occurring in a sample; i.e. redox potential is a composite parameter of all ions and molecules taking part in the redox reaction. The ORP sensor is a non-selective electrode and is not specific for any one element or chemical species. Additionally, the design and condition of the sensor itself can influence the measurement value or response provided by the electrode. The following conditions can influence the measurement value (mV) generated by the electrode:

- Reference potential versus the Standard Hydrogen Electrode (SHE). The reference potential vs. the SHE may be different for different types of electrodes. Typically this difference can be determined by knowing the type and molarity of the reference electrolyte and the temperature of the measurement. For instance, the Hach IntelliCAL™ ORP probe with a 3M KCl-Ag/AgCl reference has a potential of 210 mV @ 25°C vs. the SHE. For other values, see Table 2 in the Hach Application Note *Introduction to Oxidation Reduction Potential Measurement*. When comparing values from different electrodes, the difference in the reference system and reference potential should be considered.

Continued on next page.

- Surface of the platinum sensor. Most electrodes selected for use in water analysis use a platinum sensing element. Redox potential should be measured when the electron activity of the sample and sensor surface reaches equilibrium. This equilibrium is highly dependent on material and surface of the electrode and the sample matrix. Therefore, the surface of the platinum plays a critical role in response of the electrode, as noted in the Ingold paper, *Redox Measurement; Principles and Problems*. A surface that is rough or uneven will adsorb more oxygen and form an oxidized layer on the platinum, affecting electrode response. The platinum sensor found on Hach IntelliCAL electrodes is finely polished to eliminate this variability. Even with a new sensor, it is difficult to determine the purity and state of the platinum surface found on differing electrode types and between manufacturers. This fact can contribute to the variability often observed in electrode response. Hach recommends regular cleaning and maintenance of the ORP sensor to minimize these differences.
- Oxidation state or passivation of the platinum sensor. As discussed above, it is common for a monomolecular oxide layer to form on the sensor surface, especially when routine measurements in oxidizing solutions are made. This oxidation, as well as the age of the electrode will affect its response. It is important to maintain the electrode properly to minimize this affect, and regularly check the performance of the electrode with a chemical standard with known mV potential. The Troubleshooting section of the *Hach IntelliCAL ORP Electrode User Instructions* provides instructions on proper maintenance steps that will improve electrode response and eliminate variability contributed by oxidation of the sensor material.
- Interferences in the sample matrix. *Standard Methods for the Examination of Water and Wastewater* (SM 2580 B., 2005) notes that interferences can contaminate the electrode surface, salt bridge, or electrolyte and can lead to drift, poor response, and incorrect potentials. Interferences can come from organics, sulphides, and bromide and can increase in severity over the life of the electrode. Proper cleaning, refilling, and maintenance of the electrode are recommended for minimizing the potential for electrode contamination.

Due to one or more of the conditions above, it is likely that two ORP electrodes will not provide the same measurement result in similar samples. The factors above can influence the response and measured potential (in mV) of the sensor. Differences observed in laboratory and in-plant sampling can be as small as several milliVolts or greater than 50 mV. Treatment application and sample type can also influence electrode variability and response time. Controlled laboratory evaluations of several electrode types and their response have been conducted and can be observed in the following charts.

Important note: Electrode performance should be periodically checked over the useful life of the electrode using an ORP standard such as ZoBell's solution or Light's solution. This important indicator will provide assurance that the electrode is responding accurately. For additional information about verifying performance in standard solutions, refer to the Hach Application Note *Introduction to Oxidation Reduction Potential Measurement*.

Figure 1. Average measurement value and precision of Hach IntelliCAL and other ORP electrodes in drinking water. Measurements conducted under controlled laboratory conditions on treated drinking water samples using new electrodes. Measurement value (mV) equals the average of three electrodes evaluated per electrode type. Error bars above and below the measured value are equal to one standard devation.

Comparison of ORP Electrode Potentials and Precision in Drinking Water Samples

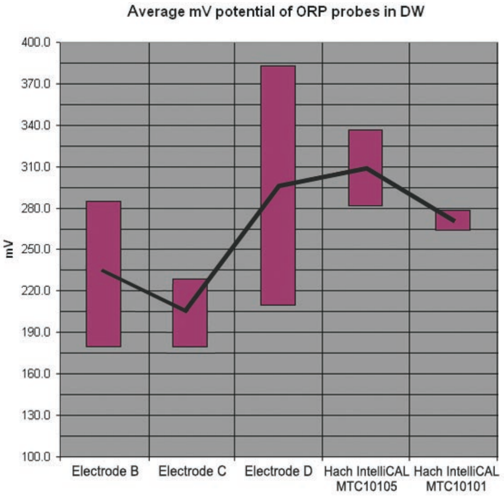

Figure 2. Average measurement value and precision of Hach IntelliCAL and other ORP electrodes in wastewater. Measurements conducted under controlled laboratory conditions on treated wastewater samples using new electrodes. Measurement value (mV) equals the average of three electrodes evaluated per electrode type. Error bars above and below the measured value are equal to one standard devation.

Comparison of ORP Electrode Potentials and Precision in Wastewater Samples

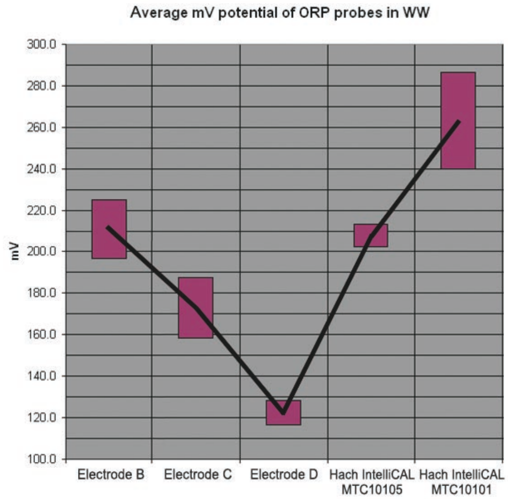

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Figure 3. Average stabilization time of Hach IntelliCAL and other ORP electrodes in treated drinking water samples. After initial measurement, electrodes were conditioned for 24 hours in sample. Measurements were then made again in fresh sample.

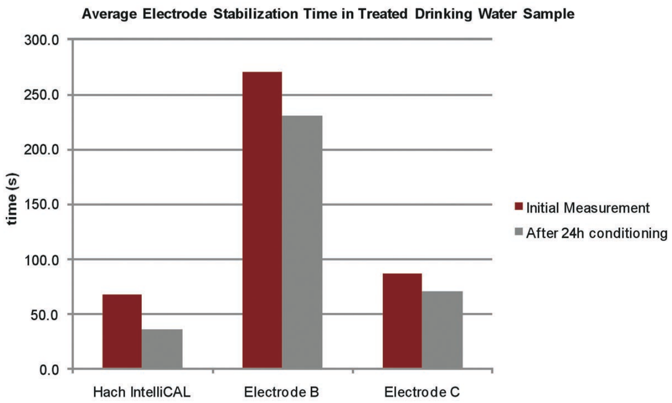
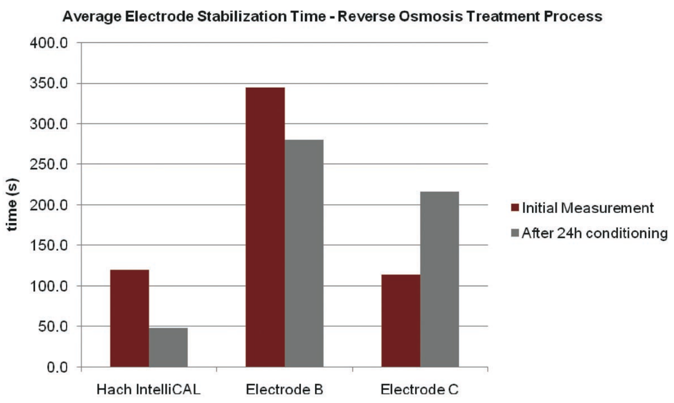


Figure 4. Average stabilization time of Hach IntelliCAL and other ORP electrodes in samples taken from a Reverse Osmosis treatment process. After initial measurement, electrodes were conditioned for 24 hours in sample. Measurements were then made again in fresh sample.



Summary

As described, ORP (Redox) is a complex measurement and should not be compared to the more straight-forward pH measurement. The oxidation state and surface chemistry on the platinum sensor can significantly influence the response over the useful life of ORP electrodes. These same factors can make it difficult to compare measurement values from different electrode types or manufacturers. For this reason, it is important to understand the influences on the measurement and proper maintenance and troubleshooting procedures, and periodically check the response of the electrode using an ORP standard solution.

References

American Public Health Association, American Water Works Association, Water Environment Federation (2005) *Standard Methods for the Examination of Water & Wastewater,* 21st ed.; Washington, DC

Bühler, H., Baumann, R., (1982) *Redox Measurement, Principles and Problems*; Zürich

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Lit. No. 2070
J9 Printed in U.S.A.

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