

Introduction to Oxidation Reduction Potential 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.



Sensors

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. The electrode behavior is defined by the Nernst equation:

$$E = E_0 - \frac{R \cdot T}{n \cdot F} \ln \frac{C_{ox}}{C_{red}}$$

WHERE:

- E = measured potential (mV) between the platinum and the reference electrode
- E₀ = measured potential (mV) between the platinum and the reference electrode at a concentration of C_{ox} = C_{red}
- R = Universal gas constant (R = 8.314 J mol⁻¹ K⁻¹)
- T = Temperature in K (Kelvin), where T (K) = 273.15 + t°C and t is the temperature of the measured solution
- F = Faraday constant (96485 C mol⁻¹)
- n = electrical charge of the ion
- C_{ox} = oxidant concentration in moles/L
- C_{red} = reductant concentration in moles/L.

Platinum is normally used as the 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.

Since the ORP potential is temperature dependent, temperature must also be recorded with every measurement in order to permit comparison of the two ORP values. Typically there is no automatic temperature compensation available in most commercial ORP meters.

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ORP measurements are often pH dependent. For example, chlorine exists in solutions as hypochlorous acid (HOCl), and depending on the pH, the HOCl can provide more or less free chlorine. At lower pH values, more chlorine is formed.

ORP measurement readings occur slowly compared to pH measurements. While a pH value can be obtained within seconds, a stable ORP value can take up to several minutes, if not hours, to reach the final equilibrium due to the type of reactions and their reaction rates. The ORP measurement behavior is strongly influenced by the platinum surface condition. For example, a new, unconditioned ORP electrode will show different values than an ORP electrode that has been conditioned and considered in use.

NOTE: Most natural waters contain many species that are involved in the redox process, making it more difficult to calculate ORP with the Nernst equation. All redox species do, however, reach equilibrium. A standard solution of known redox potential for a particular ORP electrode is used to calibrate the ORP sensor. The ORP sensor can then give a calibrated response in mV when placed in a sample.

The result of the redox measurement can be given as ORP or as “Eh.” The Eh value refers to the SHE (Standard Hydrogen Electrode) also known as Normal Hydrogen Electrode (NHE), which is used to compare values between different ORP probe types. Normally, only the absolute ORP mV value is recorded in order to see relative changes over time; Eh is then an unnecessary calculation.

Example: If using an Ag/AgCl reference electrode with 3M electrolyte solution, a measured redox potential of +150 mV calculates to $E_h = +360$ mV, just by adding 210 mV for the potential shift from Ag/AgCl to SHE (@ 25°C). For details, see Table 2.

Calibration/Check Standards

There are several redox standard solutions available, the most common of which are:

- ZoBell's Solution
- Light's Solution
- Quinhydrone Solutions

NOTE: The following mV readings at 20°C are given for an Ag/AgCl reference electrode with a 3M KCl filling solution.

Solution Preparation Instructions

ZoBell's Solution

Soluble 2.64 g $K_4[Fe(CN)_6] \cdot 3 H_2O$ and 2.06 g $K_3[Fe(CN)_6] \cdot H_2O$ under stirring in 500 mL buffer pH 7.00 at 25°C. After approximately 15 minutes of stirring, the solution is ready to use.

Potential @ 20°C = +228.5 mV ±5 mV

Light's Solution

Soluble 1.861 g $Fe(NH_4)_2(SO_4)_2 \cdot 6 H_2O$ and 2.411 g $Fe NH_4(SO_4)_2 \cdot 12 H_2O$ under stirring in 500 mL 1 M H_2SO_4 at 25°C. After approximately 15 minutes of stirring, the solution is ready to use.

Potential @ 20°C = + 462.4 mV ±5 mV

Quinhydrone Solutions

Solution A: Add 3 g Quinhydrone to 500 ml buffer pH 4.01 and stir for 15 minutes. Un-dissolved Quinhydrone powder must be present. If necessary, add Quinhydrone powder.

Potential @ 20°C = + 265.1 mV ±5 mV

Solution B: Add 3 g Quinhydrone to 500 mL buffer pH 7.00 and stir for 15 minutes. There must be an excess of undissolved Quinhydrone powder. If necessary, add Quinhydrone powder.

Potential @ 20°C = + 87.4 mV ±5 mV

Electrode Calibration

Using a Hach HQd meter, select the ORP standard with the correct value vs. temperature. Rinse the probe with DI (Deionized) water then dip it into the selected ORP standard solution. Wait until the signal stabilizes. Take a reading. There can be a deviation from the theoretical ORP value for that standard at that temperature. This offset (discussed in the next section) should be stored for future sample readings.

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**Typical mV readings in ORP standard solutions at different temperatures
(Reference Ag/AgCl 3M KCl)**

Temperature °C	ZoBell's Solution		Temperature °C	Quinhydrone in pH 7.00
10	243.5		10	95.4
15	236.0		15	92.9
20	228.5		20	87.4
25	221.1		25	81.5
Temperature °C	Light's Solution		Temperature °C	Quinhydrone in pH 4.01
10	447.4		10	268.4
15	453.2		15	267.6
20	462.4		20	265.1
25	469.3		25	261.3

Table 1: mV Readings in ORP Standards

Acceptance Criteria for Calibration

For accurate sample measurements, check the ORP electrode performance against an ORP standard solution. The difference between the standard mV potential and the measured mV potential is called the offset. As long as the reference electrode is working properly, the ORP standard potential should be within ± 10 mV for ORP probes in routine use, at a defined temperature. If desired, this offset may be subtracted from the sample mV readings. The Hach HQd Meter Series and IntelliCAL™ Probes automatically subtract this offset during sample measurement.

With use over time, and depending on the type of sample, the platinum disk or ring may become coated with chemical and/or biological layers, which may cause a shift in potential (30-50 mV). Cleaning the probe periodically is therefore necessary.

Electrode Cleaning

If ORP measurements indicate a shift in potential over time, increased stabilization times or instable readings, electrode cleaning is recommended. Conduct cleaning with minimal sensor surface impact, starting with standard cleaning and if this does not help, aggressive cleaning (see instructions below). Be careful with your probe: Avoid aggressive and over frequent cleaning as it may be destructive and lead to ORP probe replacement.

Standard Cleaning Procedures:

- A.** Soak the probe for 10-15 minutes in fresh tap water that contains a few drops of a commercial detergent such as dishwashing soap. Additionally, wipe the Pt surface with a cotton cloth, but take care not to damage any part of the probe. Afterwards, rinse with fresh tap water.
- B.** Soak the probe for 15 minutes in 0.1 M hydrochloric acid (HCl). Following safety instructions, wipe the Pt surface with a cotton cloth or swab. Afterwards, rinse with fresh tap water.

Aggressive Cleaning Procedures:

- C:** Soak only the platinum element (not the reference junctions) for 1-2 hours in a 50:50 dilution of commercial chlorine bleach.

NOTE: Make sure that the diaphragm (ceramic pin or open junction etc.) is NOT in the chlorine bleach.

Afterwards, rinse with fresh tap water and soak the probe for 1-2 hours in tap water to dilute the remaining bleach. It might be necessary to repeat the rinsing to remove all bleach from the probe; otherwise, the results of the calibration and sample measurement may be false due to the chlorine bleach.

- D:** Polish the Pt surface with an abrasive paper of 600 grid or higher, or use an extra fine grinding paste and polish with a cotton cloth. Then soak the probe for 10 minutes in 1 M hydrochloric acid (HCl) and rinse thoroughly with fresh tap water.

To achieve the best, most reproducible results, let the probe rest for several hours. After following the cleaning procedures described above (B,C,D), soak the ORP probe in the reference electrolyte solution overnight, then rinse with DI water and calibrate. The offset in an ORP standard should be a maximum of ± 20 mV.

If the calibration is not satisfactory, or the offset is > 50 mV, replace the ORP probe.

Measurement in Various Applications

Typically, probes should be calibrated to verify performance. An ORP standard should be used to determine the actual mV offset value for correction of measurement values. Take several readings in the same ORP standard to verify the final result.

Calculate the offset with the following formula:

$$E_{\text{offset}} = E_{\text{standard}} - E_{\text{measured}} \text{ [mV]}$$

Add the mV offset to all sample results to adjust for the actual ORP probe performance. If necessary, also add the mV value for the reference system used to get the reference mV value for SHE (standard hydrogen electrode).

$$E_{\text{SHE}} = E_{\text{offset}} + E_{\text{reference}} + E_{\text{measured}} \text{ [mV]}$$

Ag/AgCl potential [mV] Filling solution [M] vs. Temperature [°C]				
mol/l	15	20	25	30
0.1	286	287	289	290
1	236	236	236	237
3	211	210	210	210
3.5	207	207	206	206
4	203	203	203	203
sat.	188	188	187	187

Table 2: Ag/AgCl reference potentials vs. SHE

NOTE: Unlike conductivity (a similar situation applies to pH), there is no automatic temperature compensation for ORP sample measurements. For ORP measurements, the temperature of the sample must always be recorded for further reference. Some samples may also require recording the actual pH value, because some Redox couples are pH dependent.

Hach's HQd Meter Series allows calculation of the offset from an ORP standard measurement (ORP calibration) and stores the actual offset. This offset is then subtracted from each sample mV reading automatically.

Drinking Water

Drinking Water (DW) can be of very low ionic strength (e.g. 80 to 200 μS), causing problems with stabilization time and final readings. After ORP probe calibration, rinse the probe with some of the DW sample and transfer it into a new beaker filled with the DW sample. Wait at least 15 minutes for the first reading and then check every 5 minutes for stability. Depending on the temperature (lower values take longer), and on the conductivity (lower values take longer), it might take several hours to get a final reading. Most pH/ORP meters offer a stability function with adjustable or pre-defined stability criteria. Refer to the *IntelliCAL User Instructions* for specific stability criteria information.

Surface Water

Typical surface water (SW) has a conductivity value exceeding 600 $\mu\text{S}/\text{cm}$, sometimes even in the mS/cm range. ORP measurement can be performed immediately following calibration. Because rivers, reservoirs and wells contain sufficient ORP active species, the measurement should be stable within 5 or 6 minutes.

Rinse the probe after each measurement with tap water to remove any biological films from the Pt surface. This will help keep the Pt surface ready for measurement.

Wastewater

The composition of Wastewater (WW) characteristically contains sufficient ionic strength, temperatures below 20°C, and a composition of chemical and biological contaminants. Depending on the location in the Wastewater Treatment Plant (WWTP)—influent, aeration basin, nitrification/denitrification, effluent—samples can show different ORP values.

While the influent often comes with ORP readings around -200 mV, the WW stream changes the ORP to positive values of around +50 mV due to oxidation of the reducing species.

ORP [mV]	Process
-280...-150	Development of methane
-200...+100	Reduction of sulfate
+180...+400	Reduction of iron
+220...+500	Reduction of manganese
+300...+600	Reduction of nitrate

Table 3: Typical ORP values of WW in a WWTP

ORP readings can be disturbed by air bubbles (aeration), floating particles, biological layers, etc. Therefore, it is essential for continuous ORP control to be based on measurement in the same location, at the same depth and under reproducible conditions. It may be faster to conduct a grab sample vs. waiting on a stable reading inside the basin or stream.

After each WW measurement the probe needs to be cleaned first with DI water, then detergent solution, followed by a final rinse with DI water. Wipe the surface dry with a soft cloth and keep the probe in the recommended storage solution between measurements. This procedure will assure a long probe lifetime along with reproducible and accurate results.



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