Oxidation-Reduction Potential (ORP)

Oxidation Reduction Potential (ORP) is a measure of the oxidizing or reducing tendency of a liquid. The ORP measured for a solution is dependent on the activity (related to concentration) and nature of chemical species present, the temperature, the pH, and the electrode used. Because of the large number of potentially oxidizing or reducing species and the complex chemical equilibria in natural waters and wastewaters, it is difficult to relate the ORP of these systems directly to chemical concentrations. Nevertheless, because oxidation-reduction reactions are so important in biological systems as well affecting corrosion and other properties of aqueous solutions, ORP measurement is often useful in characterizing water samples.

The ORP electrode is usually a platinum electrode, although gold and graphite electrodes are sometimes used. The important characteristics of the ORP electrode are inertness and an ability to either supply or absorb electrons as required. Adsorption onto the Platinum ORP electrode of materials from solutions previously tested can cause incorrect readings. The Platinum surface should always be brightly polished.

The Standard Hydrogen Electrode (SHE; sometimes called the Normal Hydrogen Electrode, NHE) is the reference electrode used in tables of standard reduction potentials, but it is fragile and impractical for routine laboratory and field use. Instead, Calomel and Silver-Silver Chloride electrodes are commonly used as reference electrodes in ORP determination. The choice of electrode (including filling solution) has a pronounced effect on the ORP reading (See Table 1). A redox electrode incorporating a Silver-Silver Chloride reference electrode with 4 M KCl filling solution is used for ORP determinations at RICCA CHEMICAL COMPANY. The ORP values measured with other reference electrodes can be converted to Eh values relative to the SHE by using the same electrode system to measure the ORP value of a solution whose theoretical Eh value is known (all at the same temperature). The Eh value for the sample is then obtained by adding the difference between the theoretical (Eh) and measured values for the standard to the measured value for the sample. Based on the data in Table 1, 200 mV would be added to experimental ORP values obtained at 25°C using the Ag/AgCl electrode with 4 M KCl filling solution to obtain Eh values relative to the SHE at 25°C.

Table 1. Potential of the Platinum Electrode at 25°C for Different Reference Electrodes for Light's Solution (0.1 M Fe^{2+} / 0.1 M Fe^{3+}), RICCA Cat. No. 4330.

Reference Electrode	Filling Solution	ORP, mV
Calomel (Mercury/Mercuric Chloride)	saturated KCl	+430
Silver/Silver Chloride	1.00 M KCl	+439
Silver/Silver Chloride	4.00 M KCl	+475
Silver/Silver Chloride	saturated KCl	+476
Standard Hydrogen Electrode	--	+675

The ORP of most chemical systems is strongly affected by pH, even if Hydrogen or Hydroxide ions do not appear to be involved in the redox reaction. In general, ORP tends to decrease with increasing pH.

Temperature also has an effect on ORP, both directly (temperature is a term in the Nernst equation, used to calculate oxidation-reduction potentials) and indirectly, by causing changes in pH, activities, or E^o. Because the magnitude and even direction of temperature dependence is different for different chemical systems, automatic temperature compensation, as done for pH and conductivity measurements, is not practical for ORP measurements. To minimize temperature effects, adjust solutions to 25°C for ORP measurement.

It is not possible to calibrate ORP electrodes over a range of redox potentials, as is done for pH electrodes. Instead, the electrode response is checked by measuring standard solutions whose potentials are known for the electrodes being used. RICCA CHEMICAL COMPANY manufactures the following standard solutions according to published (APHA, ASTM) formulations:

Ricca Cat. No.	Solution Name	ORP (Pt electrode, Ag/AgCl reference, 4 M KCl filling solution)
4330	Light's Solution	+475 mV
6595	Redox Standard Solution, Iodide-Triiodide	+220 mV
9880	ZoBell's Solution	+228 mV

Other ORP standards are available on a custom basis. All custom ORP standards will be referenced to the electrode system above unless otherwise specified.

