# Dissolved Oxygen Background

All aquatic life depends on the availability of dissolved oxygen (DO) in water. While terrestrial organisms live in an atmosphere composed of approximately 20% oxygen, aquatic organisms must work with considerably less oxygen. The solubility of oxygen in fresh water ranges from 14.6 mg/L at 0 ^{o}C to approximately 7.0 mg/L at 35 ^{o}C under one atmosphere of pressure. The dissolved oxygen concentration in water is governed by Henry's law, which is an equilibrium relationship between the partial pressure of oxygen in the atmosphere and the concentration of oxygen in the water. Additional factors influencing the concentration of oxygen in water are the barometric pressure of the atmosphere (and therefore elevation above sea level), the salt content, and the temperature of the water. A table of aqueous oxygen saturation levels (in mg/L) as a function of temperature is given in this module. Respiration can greatly reduce dissolved oxygen in natural water bodies, microbial respiration, the most significant of these processes results from the degradation of organic waste.

Two methods are commonly used to determine the concentration of dissolved oxygen in water samples: the Winkler Titration (iodometric method) and the membrane electrode technique. Details on each of these methods can be found in Standard Methods (1995) and Chemistry for Environmental Engineering (1978). The idiometric method will be discussed first.

The iodometric method, the more accurate of the two, determines the dissolved oxygen concentration through a series of oxidation-reduction reactions. First Mn^{2+}(as $MnSO_4$) is added to a 250 mL sample. Next the Alkali-iodide reagent (KI in NaOH) is added. Under these caustic conditions, any present oxygen will oxidize the Mn^{2+} to

Mn^{4+}, which precipitates as a brown hydrated oxide. This reaction is relatively slow and the solution must be shaken several ties to complete the reaction. The following equations represent this reaction:

$$2Mn^{2+} + 4OH^- \longrightarrow 2MnO_2 + 2H_2O$$

And
$$2Mn(OH)_2 \longrightarrow 2MnO_2 + 2H_2O$$
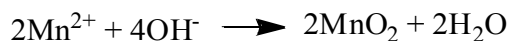
After the MnO_2 precipitate settles to the bottom of the flask, sulfuric acid is added to make the solution acidic. Under these low pH conditions, the MnO_2 oxidizes the I^- to free I_2 through the following reaction

$$MnO_2 + 2I^- + 4H^+ \longrightarrow Mn^{2+} + I_2 + H_2O$$
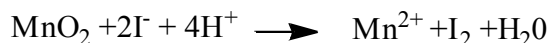
Now the sample is ready for titration with sodium thiosulfate ($Na_2S_2O_3{:}5H_2O$). In this reaction thiosulfate ion is quantitatively added in order to convert the I_2 back to I^-. Because the amount of I_2 present at this stage in the procedure is directly related to the amount of Oxygen present in the original sample, we can use this volume to find the original dissolved oxygen concentration. This reaction can be represented by

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

The titration is complete when all of the I_2 has been converted to I^-. The endpoint of this titration can be determined through potentiometry or by using calorimetric indicators. The most common indicator is starch which turns from deep blue to clear.

The dissolved oxygen concentration can be determined using the following equation that reflects the series of reduction-oxidation reactions in the equations given above.

$$O_2 \text{ conc. (mg/L)} = \frac{[(\text{Volume } S_2O_3^{2-})(\text{Conc. } S_2O_3^{2-})]\left(\frac{I_2}{S_2O_3^{2-}}\right)\left(\frac{MnO_2}{I_2}\right)\left(\frac{O_2}{2\ MnO_2}\right)\left(\frac{32\ g\ O_2}{mol\ O_2}\right)\left(\frac{1000\ mg}{1\ g}\right)}{\text{Volume of original sample}}$$

Several modifications of the Winkler method have been developed to overcome interferences in the method. The most common modification, which uses azide, effectively removes interference from nitrite, which is commonly present in water samples from biologically treated wastewater effluents and incubated biochemical oxygen demand samples. Nitrite interferes by converting I^- to I_2, thus overestimating the dissolved oxygen in the sample. This is illustrated in the following equations:

$$2NO_2^- + 2I^- + 4H^+ \longrightarrow I_2 + N_2O_2 + 2H_2O$$

And $\qquad N_2O_2 + 1/2\ O_2 + H_{20} \longrightarrow 2NO_2^- + 2H^+$
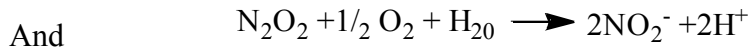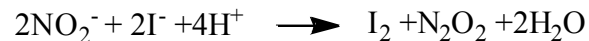
Note that the in the second reaction N_2O_2 is oxidized by oxygen, which enters the sample during the titration procedure, and is converted to NO_2^-, establishing a cyclic reaction that can lead to erroneously high results. Nitrite contamination thus results in a final concentration far in excess of the amounts that would be expected.

Nitrite interference can be easily overcome through the addition of sodium azide (NaN_3). Azide is usually added with the alkali- KI reagent, and when the sulfuric acid is added, it results in the removal of NO_2^-, as shown in the following reaction series:

$$NaN_3 + H^+ \longrightarrow HN_3 + Na^+$$

$$HN_3 + NO_2^- + H^+ \longrightarrow N_2 + N_2O + H_2O$$
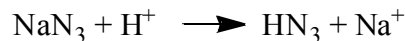
Other methods can also be used to remove the ferrous iron (the permanganate modification), ferric iron (potassium fluoride modification), and suspended solids (alum flocculation modification). The electrode method offers several advantages over the

titration method, including speed, elimination or minimization of interferences, field compatibility, continuous monitoring and *in situ* measurement. However, there is some loss in accuracy. Modern electrodes rely on a selectively permeable membrane, which allows dissolved oxygen to enter the measurement cell, thus eliminating most interferences. The calibration and measurement is relatively simple and a direct readout of the oxygen concentration is usually given. Refer to Sawyer and McCarty (1978) for the operation of the electrodes.

References:

Sawyer, C.N. and McCarty, P.L.. Chemistry for Environmental Engineering (3rd ed), McGraw-Hill Book Company, New York, 1978.