Four Ways Your DO Measurements Are Being Affected

By Patrick Higgins

Drum roll please.....the most significant variable for dissolved oxygen measurements is - **temperature**. Therefore, it is important to ensure the temperature sensor on the instrument is measuring correctly because temperature affects DO measurements in two ways.

Oxygen Solubility (mg/L)
14.6
12.8
11.3
10.2
9.2
8.6
0

Temperature and Diffusion

First, due to the increase or decrease in molecular activity, diffusion of oxygen through the membrane of an electrochemical probe or sensing element of an optical probe changes with temperature. The change in diffusion rate based on temperature can be up to approximately 4% per degree Celsius depending on the membrane material for steady-state electrochemical sensors, 1% per degree Celsius for Rapid Pulse sensors, and is approximately 1.5% per degree Celsius for optical sensors.

For example, if the temperature of a sample changes from $20 \,^{\circ}$ C to $15 \,^{\circ}$ C, the probe signal would decrease by varying rates depending on the sensor in use, giving a lower DO % saturation reading even though the % saturation of the water has not changed. Therefore, the sensor signal must be compensated for changes in temperature. This is done by adding a thermistor to the circuit of older, analog instruments. For newer, digital instruments, the software compensates for temperature changes with proprietary algorithms that use the temperature readings from the probe's thermistor.

Temperature and Oxygen Solubility in Water

The adjustment described so far only compensates for temperature's effect on the oxygen diffusion rate through a membrane or sensing element. In addition to this effect, temperature also affects the ability of water to dissolve oxygen. It is a scientific fact that the solubility of oxygen in water is directly proportional to temperature; see the <u>Oxygen Solubility Table</u>.

Warmer water cannot dissolve as much oxygen as colder water. For example, in an oxygen saturated sample of water at sea level (exposed to 760 mmHg of barometric pressure), the % saturation value will be 100% regardless of the temperature because it is fully saturated. However, the dissolved oxygen mg/L concentration will change with temperature because the solubility of oxygen in water changes with temperature. For instance, at 15°C water can dissolve 10.08 mg/L while 30°C water can only dissolve

7.56 mg/L of oxygen even though the % saturation value is 100% in both samples. Therefore, we must compensate the mg/L concentration reading per the temperature of the sample.

Both of these temperature effects are factored into the conversion of the probe signal to a mg/L concentration. For newer, digital instruments such as the optical <u>ProODO</u> and the traditional <u>Pro20</u>, the software compensates for both of these temperature-related factors after instrument calibration and during readings.

The temperature compensation for the % saturation reading is empirically derived, while the conversion from % saturation, temperature and salinity to a mg/L concentration is automatically carried out by the instrument's firmware using formulae available in Standard Methods for the Examination of Water and Wastewater. The calculation for converting % Saturation to mg/L and an example is provided below.

Determining DO mg/Lfrom % Saturation

The following explains how to convert % Saturation to mg/L (also referred to as ppm).

In order to perform this conversion, the <u>temperature</u> and <u>salinity</u> of the sample must be known. *This is the reason accurate temperautre values must be used in the calculation of mg/L values.*

Step one: Determine the % saturation, temperature, and salinity of the sample.

Step two: Multiply the % saturation reading by the value in appropriate column (depends on salinity) and row (depends on temperature) of the Oxygen Solubility Table.

Example:

Step one: Sample is measured to have: 80% DO saturation 0 ppt salinity at 20º C

Step two: Multiply .80 (which is the DO %) by 9.09 (value from oxygen solubility table at 0 salinity and 20° C) = 7.27 mg/L.

Result: 7.27 is the mg/L value that corresponds to an 80% DO Saturation reading of a sample with zero salinity at 20° C.

The second variable in our "What is Affecting Your Dissolved Oxygen Measurements" series that affects DO concentration is the **salinity** of the water sample. While the % saturation reading is not a function of the salinity (or dissolved solids content) of the water, the mg/L concentration changes significantly with salinity. As the salinity of water increases, its ability to dissolve oxygen decreases. For example, oxygen saturated freshwater with 0 ppt salinity at 25°C contains 8.26 mg/L of oxygen while oxygen saturated sea water (~36 ppt) at the same pressure and temperature contains only 6.72 mg/L of dissolved oxygen.

Thus, salinity (along with temperature) must be factored into the instrument's calculation of mg/L. This calculation is based on the % saturation reading, temperature reading, and the measured or entered salinity value using formulae found in Standard Methods for the Examination of Water and Wastewater.

Correcting for Salinity



The salinity value used by the instrument in the calculation of mg/L is obtained one of two ways, depending on the instrument being used. For YSI dissolved oxygen

instruments that also measure conductivity, the salinity value measured by the conductivity sensor is used for the mg/L calculation. Therefore, it is important to ensure the conductivity sensor is calibrated and reading accurately in order to obtain accurate DO mg/L readings.

For YSI dissolved oxygen instruments that do not have a conductivity sensor, the salinity value of the sample must be manually entered by the end user. See the salinity guide below for a list of typical salinity values for various types of water.

Salinity Guide - Average salinity by water type

Water Type	Average Salinity
Fresh Water	<0.5 ppt*
Brackish Water	0.5 to 30 ppt
Sea Water	33 to 37 ppt
Saline Water	30 to 50 ppt
Brine	>50 ppt

*Salinity is a unitless measurement determined from conductivity and temperature readings according to the Practical Salinity Scale which can be found in <u>Standard Methods for the Examination of Water and</u> <u>Wastewater</u>. Historically, salinity values determined via the Practical Salinity Scale were given the designation "ppt" because these values were very close to those determined by the previously used method where the mass of dissolved salts in a given mass of water (parts per thousand) were reported. Today, ppt is commonly replaced by psu (Practical Salinity Units) as the preferred unit to describe salinity calculated by the Practical Salinity Scale; however, these values are equivalent since they are determined by the same method.

When sampling water of varying salinity, for example in brackish waters such as estuaries or coastal wetlands, it is recommended that you use a dissolved oxygen instrument that also measures conductivity for highest data accuracy. A dissolved oxygen instrument that also has a conductivity sensor will use the real-time salinity readings from the conductivity sensor for every mg/L calculation (such as the <u>Pro2030</u>). This will make sampling easier since it will not be necessary to manually change the correction factor at each sampling new site.

It's important to keep in mind, when calibrating a DO meter, if you have to manually input the salinity value to input the value of the water you will be measuring. If you have a conductivity sensor in conjunction with the DO sensor, make sure the conductivity is calibrated properly in order to compensate for the correct salinity value.

Another factor with regard to potential affects in your dissolved oxygen calibration and measurement is **barometric pressure**.

You might want to grab a coffee, or a beer, we're going to get into some math right away here. Let's do this!

Barometric pressure affects the pressure of oxygen in a sample of air or water. For example, the percentage of oxygen in air is always 21%, but the actual pressure of oxygen varies with changes in barometric pressure. At sea level, the pressure of oxygen is 160 mmHg (.21 x 760 mmHg).

In a fully aerated sample, under these conditions, the % saturation measured by a sensor would be 100% (160/160 x 100%). If the temperature of the sample is 25°C, the instrument would calculate the dissolved oxygen concentration as 8.26 mg/L based on the <u>Oxygen Solubility table</u>. As the sample is moved up in altitude and kept air-saturated, the barometric pressure would decrease and so would the pressure of

oxygen in the sample. At 1126 ft of elevation, the pressure of oxygen would be 153 mmHg (.21 x 730 mmHg) and the % saturation relative to sea level read by the probe would be 95.6% (153/160 x 100%) in the fully aerated sample. If the temperature of the sample is 25°C, the instrument would calculate a dissolved oxygen concentration of 7.92 mg/L or 96% of 8.26 based on the Oxygen Solubility table.

Pressure		Altitude		Calibration Value	
Inches Hg	mm Hg	kPa	Feet	Meters	Percent Saturation
30.23	768	102.3	-276	-84	101
29.92	760	101.3	0	0	100
29.61	752	100.3	278	85	99
29.33	745	99.3	558	170	98
29.02	727	70.0	011	254	97
28.74	730	97.3	1126	343	96

The effect of barometric pressure is overcome by proper sensor calibration. Barometric pressure is used in the majority of dissolved oxygen sensor calibrations as described in the Calibration section of <u>The</u> <u>Dissolved Oxygen Handbook</u> since it determines the absolute pressure of oxygen in a sample of air or water at the time of calibration and it is this pressure which is measured by all oxygen sensors. When calibrating oxygen sensors, the sensor's output is set to this known pressure of oxygen. If the sensor output changes after calibration, then the instrument would calculate a % saturation based on a simple linear regression calculation.

Thus, as long as the system does not drift, the sensor's output can always be used to define the oxygen pressure in any medium after performing a proper calibration and the use of the barometric pressure (or altitude) at the time of calibration is the key factor in setting the proper calibration coefficient. Therefore, it is not necessary to correct for changes in barometric pressure after performing a proper calibration in order to obtain accurate readings in the field. OK, we're going to say this one again - seriously - we're repeating it and underlining it. It is not necessary to correct for changes in barometric pressure after performing a proper calibration in order to obtain accurate readings in the field.

Summary

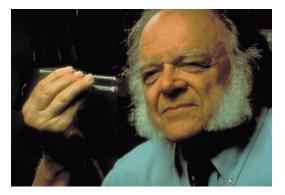
In summary, as barometric pressure changes due to a change in altitude or local weather front, the pressure of oxygen changes. However, there is never any reason to compensate for this change if a proper calibration has already been performed and the sensor has not drifted. As always, YSI recommends a proper daily calibration of your DO meter or, at the very least, a quick check to see if the DO % value is reading within +/-2% of what it should read at your altitude/barometric pressure.

Note: If DO% Local is being measured with a YSI <u>6-series sonde</u> or <u>556</u> it may be necessary to recalibrate the instrument after extreme changes in barometric pressure or altitude in order to keep the DO% Local value at 100% in a fully saturated environment. This is not a requirement if only mg/L values are being recorded since these values will remain accurate without recalibrating Local DO %. If reporting DO% Local with newer instruments such as the <u>Professional Plus</u>, <u>ProODO</u>, or <u>Pro20</u>, it is not necessary to recalibrate after a significant barometric pressure change in order to report an accurate DO% Local since these instruments have an on-board barometer that is read by the instrument continuously.

A subsequent blog post will delve into the issue of using barometric pressure for dissolved oxygen calibrations.

There are many factors that can affect your dissolved oxygen meter measurements. In this series, we are focusing on the affects from temperature, salinity, barometric pressure and **flow dependence**.

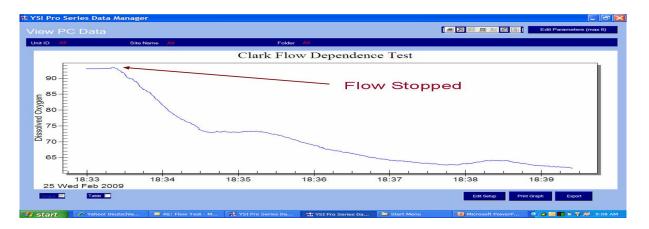
Steady-state electrochemical sensors, Clark (Dr. Leland Clark pictured at the right) polarographic and galvanic, consume oxygen during measurement and therefore require sample movement or the readings will be artificially low. This is commonly referred to as flow dependence since the sensor is dependent on flow or water movement across the membrane in order to obtain accurate readings.



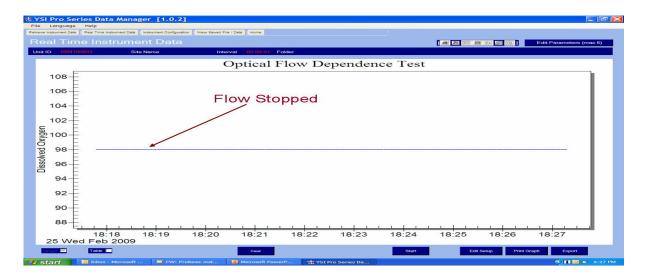
Optical sensors (<u>ProODO</u>, <u>EXO</u>), however, use a nonconsumptive method for dissolved oxygen measurements resulting in a sensing method with zero flow dependence

or stirring requirement. However, YSI scientists have confirmed response times on optical sensors can be improved with flow. Accuracy doesn't change - just the amount of time to get to a reading which may be an advantage in the laboratory measuring many BODs.

The graphs below illustrate this advantage of the optical sensor. The first is a graph of data measured with a steady-state polarographic sensor in an air-saturated water sample where adequate sample movement was provided by a mechanical stir bar. When the stirring mechanism was turned off, the readings began to fall resulting in artificially low dissolved oxygen measurements.

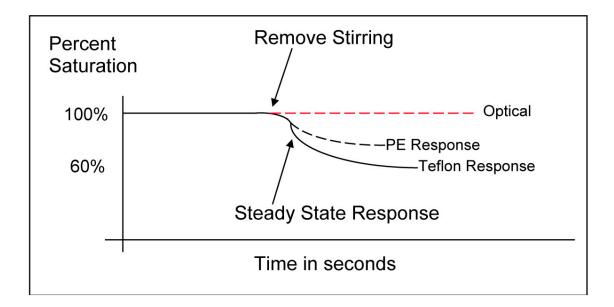


The second is a graph of data measured with an optical sensor in the same air-saturated water sample where sample movement was provided by a stir bar. When the stirring mechanism was turned off for the optical measurements, the readings remained constant and accurate proving the optical sensor is not dependent on flow. This is a considerable advantage of the optical sensor especially for low flow applications or applications where probe stirring or sample movement is difficult such as down well.



For steady-state electrochemical sensors, the membrane material and thickness dictates the degree of the sensor's flow dependence. For example, polyethylene membranes, frequently notated as PE, require less movement or flow then traditional Polytetrafluoroethylene (you know it as a more common name but we're not allowed to use it) membranes as illustrated by the graph below.

In this graph, three different sensors were placed in fully aerated water with a stir bar. Once the stirring was ceased, the steady-state electrochemical readings began to fall. Notice how the Polytetrafluoroethylene covered sensor fell further and more rapidly then the PE covered sensor.



The stirring dependence of each sensor and membrane type, along with the recommended stirring rates, is listed in the <u>Membrane Comparison Guide</u>.