Dissolved Oxygen Info

Dissolved Oxygen (DO) is the term used for the measurement of the amount of oxygen present in a unit volume of water. Although dissolved oxygen (DO) is usually displayed as %, mg/L or ppm, DO sensors do not measure the actual amount of oxygen in water, but instead measure the partial pressure of oxygen in water, which is dependant on both salinity, pressure and temperature. The amount of dissolved oxygen (DO) that can be present in a given volume of water is primarily a function of three factors: the atmospheric pressure at the water-air interface; the temperature of the water; the amount of other dissolved substances (e.g., salts, sugars, or other gases) present in the water.

Environmental Impact

Dissolved oxygen is consumed in the water by respiration and decomposition. It is replenished mainly by the atmosphere and photosynthesis. Water temperature is a key factor in the regulation of water's oxygen level. Warm water contains a lower oxygen concentration than cold water. If DO concentrations get too high, though the dissolved oxygen can become toxic to plant and animal life.

Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/L, aquatic life is put under stress. The lower the concentration, the greater the stress. Oxygen levels that remain below 1-2 mg/L for a few hours can result in large loss of aquatic life.

Applications

Dissolved oxygen measurements are used to monitor processes where oxygen content affects reaction rates, process efficiency, or environmental conditions:

- Aquariums
- Aquaculture / Fish Farming
- Bio-reactions / BOD
- Environmental testing (lakes, streams, oceans)
- Water / Wastewater treatment
- Wine production

Biochemical Oxygen Demand (BOD)

The BOD test is typically perfomed in wastewater treatment plants, where it is important to understand the amount of oxygen that microorganisms consume from the water when they break down organic matter. This test allows the plant to determine the effectiveness of their water treatment, or the amount of pollution that still exists. By measuring the amount of oxygen dissolved in samples at the beginning and end of a specified incubation period, the relative oxygen requirements of wastewaters, effluents, and polluted waters can be determined. You can calculate BOD by measuring DO at time 1 (T_1) and subtracting the DO at time 2 (T_2); multiple that number by the final volume (V_F) and dividing that number by the initial sample volume (V):

$$\text{BOD (mg/L)} = (T_1 - T_2)V_F/V$$

Pressure Compensation

DO readings must take into consideration any differences between the sample and calibration pressures. The pressure values must, in turn, account for elevation above sea level and/or overpressure in a vessel. Any significant process pressure variations will lead to DO measurement errors. The pressure dependence of the dissolved oxygen concentration in water can be understood by considering Dalton's law of partial pressures. This law states that if different gases are mixed in a confined space of constant volume at a set temperature, then each gas will exert the same pressure as if it alone occupied this space. The pressure of the mixture as a whole is the sum of the partial pressures of each of the gases comprising the mixture:

$$P_T = p_1 + p_2 + p_3 \ldots$$

Dalton's law simply states that the partial pressure of each gas component in a mixture is what the pressure of that gas component would be if all other gases present in the mixture suddenly vanished, without changing the temperature of the gas remaining. When Dalton's law is combined with the ideal gas law, the partial pressure of each gas in a mixture is proportional to the number of molecules of that gas in the mixture. It is also important to note that the concentration of dissolved oxygen follows Henry's law: i.e., it is linearly proportional to the total pressure. In accordance with Henry's law, the molar concentration of dissolved oxygen in water can be calculated from the partial pressure as:

$$x_{O2} = K_{O2}\,P_{O2}$$

where x_{O2} is the molar concentration of oxygen in mol/L, K_{O2} is Henry's constant (1.28×10^{-3} mol/L-atm @ 25°C) and p_{O2} is the partial pressure of oxygen in atm. Henry's constant will vary with the process temperature. Henry's law simply states that the solubility of a gas in a liquid is directly proportional to the pressure of that gas above the liquid. As the pressure of the air above the aqueous solution is increased, more oxygen will become dissolved in the solution, and the DO concentration will increase.

Temperature Compensation

The temperature dependence of the dissolved oxygen concentration results from changes in the solubility of oxygen in water with temperature: i.e., the solubility is greater in cold water than in warm water. The oxygen is then caged by water molecules, which weakly pin it in place. A simple perspective on solubility of oxygen in water is that when the water is colder, the water molecules

Dissolved Oxygen Saturation Table in mg/L

Temp. (°C)	Salinity (parts per thousand)					
	0	9	18.1	27.1	36.1	45.2
0	14.62	13.73	12.89	12.10	11.36	10.66
10	11.29	10.66	10.06	9.49	8.96	8.45
20	9.09	8.62	8.17	7.75	7.35	6.96
25	8.26	7.85	7.46	7.08	6.72	6.39
30	7.56	7.19	6.85	6.51	6.20	5.90
40	6.41	6.12	5.84	5.58	5.32	5.08

Solubility of solutes as a function of temperature (mg of solutes per liter of water)

Solute	Temperature (°C)					
	0	20	40	60	80	100
O_2	69	43	31	14		
CO_2	3,350	1,690	970	580		
NaCl	357,000	360,000	366,000	373,000	384,000	398,000
KCl	276,000	340,000	400,000	455,000	511,000	567,000

move less, and the oxygen remains trapped in the aqueous solution. The temperature dependence of oxygen solubility is often calculated as a function of vapor pressure. Other dissolved substances will affect the ability of oxygen to dissolve in water at the same temperature and pressure, because there is less "room" for the oxygen in the water(oxygen is less water soluble than most salts) whose solubility increases with temperature. See the tables at the bottom of the previous page for additional information.

Galvanic & Polarographic Sensors

If the electrode materials are selected such that the difference in potential between the cathode and the anode is -0.5 Volts or greater, an external potential is not required, and the system is called galvanic. If an external voltage must be applied to the sensor, the system is called polarographic.

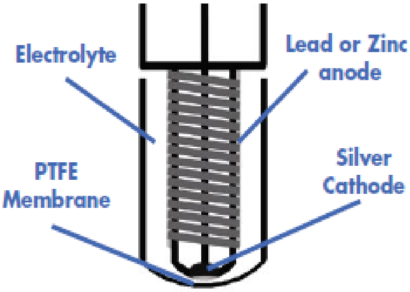
The major difference between the galvanic and polarographic sensors is in the choice of anode materials, which determines their suitability for applications. Galvanic sensor electrodes are generally made from lead or zinc, so the sensor is self-polarizing, i.e. the voltage is generated in the sensor by the electrodes themselves, comparable to the process in a battery. Polarographic electrodes, however, are often made using silver, which requires a voltage in order to activate the oxygen permeation process.

Galvanic Sensors

The galvanic sensor converts the oxygen concentration into a voltage (via a sacrificial anode) that is proportional to the amount of DO. Therefore, the sensor has an absolute zero, namely, when no DO is present, the sensor will read "zero" to within the limit of the electronics. In general, galvanic sensors are more stable and accurate at low DO levels, and can operate for extended periods of time without electrolyte or membrane replacement.

Galvanic DO sensors consist of two electrodes, an anode and cathode which are both immersed in electrolyte (contained inside the sensor body). The electrodes provide a high enough potential for the reduction and oxidation of oxygen. This means that there is no need to provide an external potential or "polarize" the electrodes. An oxygen permeable membrane separates the anode and cathode from the solution being measured. Oxygen diffuses across this membrane and interacts with the anode and cathode to produce an electrical current. The current between the anode and cathode passes across a resistor that changes output with temperature in order to produce an output voltage (typically in millivolts). For the same oxygen pressure, higher operating temperatures will increase the amount of oxygen diffusion into the sensor due to increased membrane permeability, thus resulting in more current. For accurate DO measurements, a separate and independent (often integrated) temperature sensor is used to measure the temperature and directly compensate for the membrane permeability changes. The sensor output voltage is then converted to ppm, %, or mg/L of DO.

Galvanic Diagram

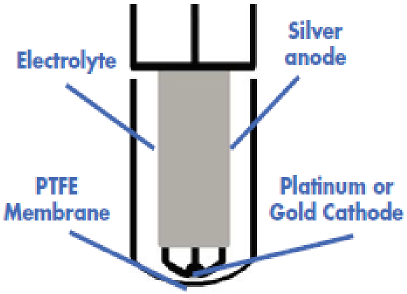


Polarographic Sensors

Polarographic sensors exploit an amperometric technique using a Clark cell, so named after Leland C. Clark. In polarographic sensors, the anode and cathode are immersed in an electrolyte, into which oxygen permeates through a membrane. It differs from a galvanic sensor in that the anode must be polarized, after which a current flows in the sensor. At zero dissolved oxygen, the sensor has an offset for which the readout electronics must be compensated, and which changes as the sensor ages. Furthermore, as the oxygen permeable membrane ages, the operating characteristics of the sensor also change. Polarographic sensors must be charged or polarized during use and carefully calibrated prior to each bioprocess run for maximum accuracy.

In the polarographic (or Clark) cell shown, a cathode of a noble metal (platinum or gold) is made negative by 0.6 to 0.8 Volts with respect to a suitable reference anode (Ag/AgCl electrode in a neutral KCl), so that any oxygen dissolved in the liquid is reduced at the surface of the noble metal cathode. The anode/cathode pair causes current to flow in direct proportion to the amount of oxygen entering the system. The magnitude of the current thus gives us a direct measure of the amount of oxygen entering the probe. Because the oxygen entering the probe is chemically consumed, the partial pressure of oxygen in the electrolyte tends toward zero. Therefore, a partial pressure gradient exists across the membrane and the rate of oxygen entering the probe is a function of the partial pressure of oxygen in the air or water being measured. The gradient helps continually drive new oxygen molecules across the membrane and into the electrolyte. As the negative voltage applied to the noble metal cathode is increased, the current will initially increase but eventually saturates. In this plateau region, the reaction of oxygen at the cathode is so fast that the rate of reaction is limited by the diffusion of oxygen to the cathode surface. Further increases in the negative bias voltage will eventually reach a point where the current output of the electrode increases rapidly due to other reactions, mainly the reduction of water to hydrogen. Ease of use, linearity, and calibration dictates biasing the electrodes such that it operates on the plateau. If a fixed voltage in the plateau region (for example, - 0.7V) is applied to the cathode, the current output of the electrode can be linearly calibrated to the dissolved oxygen. A fixed voltage between -0.6 and -0.8 V is usually selected as the polarization voltage when using Ag/AgCl as the reference electrode. The current produced by the cell is proportional to the oxygen partial pressure and closely approximates the activity of oxygen. As the oxygen is consumed by the Clark cell cathode, a pressure gradient is created across the membrane. The result is a constant rate of oxygen diffusion across the membrane which is proportional to the partial pressure of O2 in the water. The membrane, which is very often a fluoropolymer (e.g.: Teflon, PTFE), is oxygen permeable, but by design is not permeable to other dissolved solids/ions (or many gases) that might be present in solution. Consider the detailed oxygen reduction reaction for a Clark cell constructed using Ag/AgCl and gold electrodes, and using aqueous KCl as the electrolyte. In order for the oxygen to undergo reduction, a potential between 400 to 1200 mV must be present; a voltage of 700 mV is typically applied to the cell from an external source (your meter or controller). The total reaction that occurs can be broken down into the reactions occurring at each electrode:

Polarographic Diagram



- Cathode (Reduction):
  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- Anode (Oxidation):
  $4Ag + 4Cl^- - 4e^- \rightarrow AgCl$

The overall reaction that occurs is summarized in equation 5:

- Overall:

$$4Ag + O_2 + 2H_2O + 4Cl^- \rightarrow 4AgCl + 4OH^-$$

From the overall equation, it can be seen that every time an oxygen molecule is reduced, 4 electrons are generated and the cathode is "depolarized". These electrons lead to a current that is related to the partial pressure of the dissolved oxygen, and that can be found by accounting for all the aforementioned effects. The current can be calculated from:

$$i_d = [\ 4\ F\ P_m\ (t)\ A\ p_{O_2}\ ] / \ d$$

where Faraday's constant, F, is 9.64 x 10^4 C/mol, Pm(t) is the permeability of the membrane (which is a function of temperature), A is the surface area of the noble metal electrode, p_{O_2} is the partial pressure of oxygen, and d is the thickness of the membrane. Typical currents i_d are on the order of 0-0.4 mAmps.

Troubleshooting Tips

- When using a polarographic style probe, connect it to your meter and allow the probe at least 15 to 30 minutes or polarization time before calibrating or measuring.
- To ensure that the membrane has no air bubbles in the electrolyte solution, the ASI membrane caps are designed to release all air while the module is being installed.
- Do not allow any air bubbles to be trapped on the membrane surface, as it will read an air bubble as an oxygen-saturated sample.
- Calibrate your electrode at temperatures close to the sample temperature, even when using a meter with automatic temperature compensation (ATC).
- Always calibrate your DO electrode dry using air as the 100% test point
- Membranes wear out, you should replace the membrane as needed.
- Short your galvanic elecctrode when not in use with a shorting cap [provided with

Galvanic versus Polarographic Electrodes

	GALVANIC DO Sensor	POLAROGRAPHIC DO Sensor
Polarization	Self-polarizing (they create their own voltage or potential, much like a battery)	Requires a voltage to be applied to make these electrodes work (meter output)
Anode	Lead or Zinc (Zinc is RoHS and less hazardous option and may also be longer lived due to lower hydroxide ion development in electrolyte)	Silver
Cathode	Silver	Gold or Platinum
Electrolyte	Potassium Chloride (KCl) / Custom	Potassium Chloride (KCl)
Membrane	PTFE	PTFE
Output (typical)	Depends on meter's current to voltage converter, but typically 0-0.4mA (0-40mV)	Depends on meter, but typically 0-0.4mA
Range	0-200% saturation (0.5-20ppm typically)	0-200% saturation (0.5-20ppm typically)
Calibration	100% done in air or humidity chamber, zero with oxygen scavenger in solution	100% done in air or humidity chamber, zero with oxygen scavenger in solution
Accuracy	Dependent on meter software but typically 0.1 mg/L DO or ±2% (whichever is greater)	Dependent on meter software but typically 0.1 mg/L DO or ±2% (whichever is greater)
Influencing Factors	Pressure, Temperature, Salinity, membrane thickness – these are typically accounted for with meter measurement software or nomograph data	Pressure, Temperature, Salinity, membrane thickness – these are typically accounted for with meter measurement software or nomograph data
Expected life	Typical 2-3 years, but can be as long as 5-years if shorting cap is used and design has large electrolyte reservoir.	Typical 2-3 years.
Advantages	• Robust, accurate measurement for many general purpose measurements • Standard Methods (4500-O) • Low maintenance • Fast start-up time • Sulfide poisoning reduced (silver cathode has net negative charge so sulfide cannot poison it) – this makes it a better choice in dirty water samples (WW) • Non-replaceable membrane cap design (for ease of use) is feasible since electrolyte is not consumed	• Well documented, popular sensor technology • Standard Methods (4500-O) • Affordable, common design • Oftentimes smaller form factor makes it easier to use in some samples • Required design factor for replaceable membranes (to refresh electrolyte) are preferred in dirty water samples
Disadvantages	• A shorting cap MUST be used when the sensor is not measuring. If the shorting cap is not used, the probe will consume the electrolyte and the anode/cathode system and it cannot be refurbished. • Larger size required to make electrolyte reservoir and anode/cathode system long-lasting • Dedicated meter requirement (cannot interchange with polarographic probes) • May be higher cost due to larger size and manufacturing requirements	• The sensor must be charged or polarized before being calibrated or used to measure. This involves 15-30 minutes of meter on-time with the probe connected (this may drain meter battery) • Sulfide poisoning can occur in dirty water samples due to silver anode (positive charge attracts sulfide • Electrolyte solution needs to be refreshed often since the polarographic reaction produces hydroxide ions at the cathode, which increases the pH of the electrolyte • May need more frequent calibration due to electrolyte activity causing zero shift • Dedicated meter requirement (cannot interchange with galvanic probes)