Dissolved Oxygen Sensors

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Dissolved Oxygen

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Introduction
Dissolved oxygen (DO) is an essential measurement parameter in aerobic bioreactors. The growth of all cells is heavily dependent on DO because it acts as a terminal electron acceptor in aerobic respiration. However, if excessive amount of DO is added to the process, it may limit the growth of the culture and promote undesirable organisms. Consequently, the measurement of DO is critical to effective operation of systems. Today, a variety of sensors are available in the market, each with its own advantages and disadvantages.

**Dissolved Oxygen**

Dissolved oxygen is a physical distribution of oxygen molecules in water. Oxygen does not react with water, but mixes with it. There are two main sources of DO in water: atmosphere and photosynthesis. [2]

Ambient air contains about 20% oxygen and is essential for breathing, also for fish and other aquatic organism. Dissolved oxygen is the amount of free oxygen in water suitable for the breathing purpose. If there is not enough oxygen, it is lethal to fish: the oxygen level below 2 mg/l is deadly and the amount between 2 and 5 mg/l affects fish health.

Also dissolved oxygen data or BOD (biological oxygen demand) is needed to determine effluent water quality. It is a common environmental procedure to determine the amount of microorganisms in a sample. This measurement is used in wastewater treatment, food manufacturing and filtration facilities where this quantity is important for the process and final product. “High concentrations of DO predict that oxygen uptake by microorganisms is low along with the required break down of nutrient sources in the medium” [1].

**Types of DO sensors**

There are two main types of dissolved oxygen sensors: optical (luminescent) and Clark electrochemical (membrane covered electrode or amperometric). These main types have subtypes, slightly differing from each other, see figure 1.
**Figure 1.** Diagram of sensor types. Source: [6]

Different sensor types suit some applications better than the others. These properties will be discussed later on the page, meanwhile the applications can be found from Figure 2.
Figure 2. Best applications for different types of sensors. Source: [6]

**Optical Sensors**

Optical sensing of oxygen is based on the measurement of the red fluorescence of a dye/indicator illuminated with a modulated blue light as shown in Figure 3.

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Membrane Material</th>
<th>Best Application (in general)</th>
</tr>
</thead>
</table>
| Optical            | Sensing element with diffusion layer           | • Deep water profiling  
|                    |                                                 | • Shallow water where stirring is difficult  
|                    |                                                 | • Low flow applications  
|                    |                                                 | • Samples that are small in volume  
|                    |                                                 | • Samples with hydrogen sulfide  
|                    |                                                 | • Continuous long-term deployments with the ROX sensor  
| Galvanic or Polarographic | 1.25 mil PE            | Sampling applications that require the fastest response time  
| Galvanic or Polarographic | 2.0 mil PE            | Sampling applications that require a lower flow dependence  

Figure 3. Principal of oxygen detection using fluorescent dye. Source: A comparison of amperometric and optical dissolved oxygen sensors in power and industrial water applications

The probe emits a blue light of the proper wavelength that causes the dye in the sensing element to luminesce or glow red. Oxygen constantly diffuses through the paint layer, affecting the luminescence of the sensing layer. The amount of oxygen passing through to the sensing layer is inversely proportional to the lifetime of the luminescence in the sensing layer.

The sensor measures the lifetime of the dye’s (sensing layer’s) luminescence, caused by the presence of oxygen, with a photodiode (light detector) in the probe. To increase the accuracy and stability of the measurement the reading is compared to a reference. The lifetime of the luminescence from excitation by the red light acts as the reference (“the sensor emits a red light that is reflected by the dye layer back to the photodiode in the sensor” [6]), so the lifetime of luminescence of the blue light is compared to it, and the stable oxygen concentration is calculated by the probe.

The oxygen concentration is determined with the Stern-Volmer equation that sets the relationship between luminescence lifetime (intensity) and oxygen concentration see Figure 4.
Figure 4. Stern-Volmer equation. Source: [6]

The most significant advantage of an optical dissolved oxygen sensor is low maintenance cost and the possibility of less frequent calibration. Other advantages and disadvantages can be found from Figure 5.
Electrochemical Sensors

Electrochemical DO electrodes are divided into two separate types: polarographic and galvanic. These electrodes are constructed with an anode and a cathode submerged in an electrolyte solution. An oxygen-permeable membrane is used to confine the cathode. When the cathode is polarized with a constant voltage, dissolved oxygen molecules diffusing through the membrane is reduced at the cathode. Then, an electrical signal produced by the cathode travels to the anode and then to the instrument. The oxygen tension versus the electrode current can be calibrated since the diffusive flux is a function of the partial pressure of oxygen in the flow\textsuperscript{[3]}.

The oxygen-reduction reaction at the cathode can be presented as:

\[
O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \\
H_2O_2 + 2e^- \rightarrow 2OH^- 
\]

As in the case for the polarographic electrodes, a voltage is applied externally while an internal potential is generated as in the galvanic electrodes.
**Figure 6.** An illustration of an electrochemical sensor. Source: [6]

**Working Principle - Amperometry**

Amperometry is a technique used to detect ions in a solution based on electrical current produced by electrochemical reaction of an electro-active species.

A reduction reaction will occur when a suitable potential is applied to the electrode: \( \text{ox} + \text{ne}^- \rightarrow \text{red} \)

Where \( \text{ox} \) is the oxidized species, \( \text{red} \) is reduced species, \( n \) is the number of electrons transferred and \( e^- \) is an electron.

A concentration gradient of \( \text{ox} \) caused by its depletion at the electrode surface leads to mass transport by diffusion. This leads to a flux of \( \text{ox} \), \( J_{\text{ox}} \) (mol/m²s) that related to the reduction current, \( i_{\text{red}} \), through the electrode with an area \( A \) according to Faraday’s law [5]:

\[
i_{\text{red}} = - \frac{n \times F \times A \times J_{\text{ox}}}{n \times F \times A} = -i_{\text{red}}/n \times F \times A
\]

Where:

- \( i_{\text{red}} \) = reducing current (A)
- \( J_{\text{ox}} \) = flux of dissolved oxygen (mol/m²s)
- \( n \) = number of moles (mol)
- \( F \) = Faraday’s constant
A = surface area of the electrode (m²)

The electrical current is now proportional to the amount of DO transported by the electrode. The driving force for $J_{ox}$ is the concentration gradient ($C/x$) of ox near the electrode. Fick’s first law of diffusion is used to relate the original concentration of ox to the measured current [5]:

$$i_{red} = -nJ_{ox}AxF = nxFxAxDxC/x$$

Where:

D = diffusion coefficient (m²/s)

$C/x =$ concentration gradient ($x = 0 => C = 0$; the concentration of ox at the electrode drops to 0)

A few assumptions are made in order to obtain a simple expression for the gradient.

1. The slope of the gradient is linear,
2. The thickness of the layer (s) is fixed.
3. The concentration of ox drops to zero. $x = 0$, $C = 0$.

The equation above becomes:

$$i_{red} = nxFxAxDx C/s$$

**Polarographic Electrode**

A typical polarographic electrode consists of a silver anode, a gold or platinum cathode and an electrolyte solution (KCl or AgCl). In order to create a sensor, a constant voltage of 0.8 volts is applied to the probe, and a digital meter is installed to read the DO response measured by the sensor [6].
Figure 7. A simplified diagram of a polarographic sensor. Source: [6]

Limitations

- Warm-up time for this type is approximately 10 minutes. Wrong readings will occur if measurements are made when the required amount of time has not been attained.

- Chloride ions in the electrolyte will be eventually consumed resulting in gradual drift in the electrode signal. The electrolyte must be replaced.

- Since the electrode consumes oxygen, readings are affected by flow across the sensor tip. Thus enough flow rate at the membrane (or sample renewal rate) must be ensured for accurate results.

Advantages

- Fast response time therefore best suited where fastest response time is necessary or for huge amount of measurements.

Galvanic Electrode
A typical galvanic electrode consists of a zinc or lead anode, a gold or silver cathode and an electrolyte solution (KCl or KBr). The principle of the galvanic sensor is that it uses 2 different types of metal and the difference in them with the electrolyte results in an electromotive voltage. This electromotive voltage is around 0.8 V which is enough to operate the sensor. Therefore the biggest advantage of the galvanic sensor is that there is no need for outside voltage source and there is no warm-up time.

Figure 8. A simplified diagram of a galvanic sensor and circuit. Source: [6]

Limitations

- The sensor continuously consumes the anode, even when turned off. Therefore the lifetime of the sensor is much shorter than of the polarographic sensor and the warranty is usually for 6 months only [2].

- Since the electrode consumes oxygen, readings are affected by flow across the sensor tip. Thus enough flow rate at the membrane (or sample renewal rate) must be ensured for accurate results.

Advantages

- No warm up time, it can be set immediately after turn-off
- The electrolyte is never used up; in theory it can be used forever.
- Fast response time.
Measuring dissolved oxygen with either sensor type

Neither electrochemical nor optical dissolved oxygen sensors do not measure the concentration of dissolved oxygen in mg/L or ppm (parts per million which is equivalent to mg/L). Instead, they measure the pressure of oxygen that is dissolved in the sample. To interpret the readings from the measurement, the pressure of the dissolved oxygen is expressed as DO %-saturation. The instrument converts the dissolved oxygen pressure value from the sensor to %-saturation by dividing the sensor output in mmHg by 160*** (the pressure of oxygen in air at 760 mmHg) and then multiplying by 100. For example, a measured oxygen pressure of 150 mmHg would be displayed by a sensor as 93.8 %-saturation (150 /160 * 100). [6]

***The pressure of oxygen at sea level is 160 mmHg because oxygen is about 21% of the earth’s atmosphere and 21% of 760 (average sea level barometric pressure) is about 160 mmHg.

The fact that the sensor measures the pressure instead of the concentration for dissolved oxygen can be illustrated by two water samples: one of fresh water and the other of sea water. The sample of fresh water can dissolve more oxygen than a sample of sea water at the same temperature and at the same altitude (or under the same barometric pressure). However, the sensor’s output signal is identical in both samples since the oxygen pressure is identical in both media. See Figure 9 for an example.

![DO Sensors Measure % Saturation](image)

If two samples, one of fresh water and one of sea water, are fully saturated with oxygen the dissolved oxygen concentration will be:

- Fresh water at 25°C = 8.26 mg/L
- Sea water (36 ppt) at 25°C = 6.27 mg/L

However, the signal output from either sensor type will be identical in two samples. Since both are 100% saturated, % saturation (or oxygen pressure) is what both sensors are measuring.

Figure 9. DO sensors measure %-saturation. Source: [6]

Variables that affect DO measurements
There are several parameters that affect the DO measurement accuracy and reliability, they are temperature, salinity, atmospheric (barometric) pressure and flow (stirring). Temperature, salinity and pressure are discussed below.

**Temperature**

Temperature is the most significant variable for the measurement accuracy. Therefore, it should be ensured that the temperature sensor on the probe is working correctly. Temperature can influence the DO measurement in two ways [6]:

- Diffusion of oxygen through the membrane (electrochemical) or sensing element (optical) on the probe increases/decreases with higher/lower temperature due to change in molecular activity (up to 4% difference per °C). With digital sensors, the effect of temperature can be compensated with software, as the temperature is known; with analog sensors, compensation is done by adding a thermistor (a temperature-sensitive resistor) into the circuit. [6]
- Ability of water to dissolve oxygen is directly proportional to temperature. Warmer water dissolves less oxygen than colder water. Consequently, with same saturation rate, warmer water contains less oxygen in absolute terms. The absolute (mg/L) concentration must be therefore compensated according to the temperature of the sample. [6]

**Salinity**

Similarly with temperature, increasing water salinity decreases its ability to dissolve oxygen. Some of the DO sensors measure also conductivity, and the value is used for calculating salinity and, based on that, oxygen concentration. If built-in conductivity sensor is available, it is important to ensure that it is calibrated and working correctly. If the conductivity is measured with separate sensor, the salinity value must be entered by the user. [6]

**Pressure**

As mentioned earlier, DO sensors measure the dissolved oxygen pressure in the water (or air), not the absolute concentration. This pressure depends not only on the oxygen concentration, but also on the atmospheric (barometric) pressure, which varies according to elevation and weather. The atmospheric pressure is not, however, needed to be known to obtain correct concentration values. Proper calibration of the sensor is enough to ensure proper measurements.

When the sensor is calibrated, known atmospheric pressure is used. After calibration, the measurements are correct, even though the pressure would change. [6]

Some of the DO sensors do the pressure compensations automatically; see for example Hanna Instruments's model HI 98186. [4]

**Calibration**

Electrochemical sensors are more prone to drift and require more frequent calibrations than optical sensors. In principle, steady-state galvanic and polarographic sensors need calibration daily when in use. If the measurements, however, are reliable also with less frequent calibrations, calibration frequency can be reduced. [6]
Optical sensors are more stable than traditional electrochemical sensors. It has been shown that optical sensors can hold their calibration for months. It is still recommended to calibrate the sensor regularly to obtain most correct measurements. The calibration is done by measuring known sample and comparing the measured value to the known real value. [6]

Three main methods for calibrating DO sensor are

- Winkler titration (See, for example [link](http://web.colby.edu/colbyatsea/2011/02/11/winkler-titrations-measuring-dissolved-oxygen/))
- Air-saturated water (See, for example [link](http://water.usgs.gov/owq/FieldManual/Chapter6/Archive/Section6.2.pdf))
- Water-saturated air (Hanna Instruments's video of calibration: [link](http://www.youtube.com/watch?v=sxI_PS7b8XI))

**Cleaning and Maintenance**

The membrane of the sensors is sensitive to contamination which caused by inappropriate cleaning. Contamination affects the reading (usually lowering the reading) when measuring small DO amount due to the damage on the membrane surface for the diffusion of oxygen. The attempt to deal with the contamination by rinsing it with water is not sufficient enough. Acids such as acetic or citric acid (concentration of 5~10% by weight) are preferable for cleaning the membrane. It should draw attention from avoid using strong mechanical treatment of the membrane during all cleaning activities because its thickness is easily destroyed. Also, it is not appropriate to clean the sensor by using ultrasonic water bath which may cause the coating of the anodes to peel off. In addition, it is best to use a soft paper towel instead.

Regeneration of the sensor is required when the function responds has dropped remarkably when calibration. This is caused by the depletion of electrolyte solution when the membrane is damaged or contaminated. To maintain the sensor, exchanging the electrolyte solution and membrane head and cleaning the electrodes are needed.

In general, electrode maintenance should only be necessary about once per year for steady-state polarographic sensors and about once every 3 months for steady-state galvanic sensors. Do not perform the following maintenance procedures just because a sensor ‘looks’ dirty. Only perform the following procedures if the instrument will not calibrate or if the readings are unstable and a regular membrane change did not correct either of these problems. [6]

The following points should be emphasized when carrying out the cleaning and maintenance process [1].

- The sensor must be disconnected from the meter. When the sensor is connected and submerged in the cleaning solution, no chemical reaction takes place between the solution and the oxidized reference electrode surface; instead, the cleaning solution may become electrolyzed!
- Use the cleaning or electrolyte solution suitable for the particular sensor as stated in the operating manual! A solution that is suitable for silver electrodes cannot regenerate lead electrodes!
• Only the gold cathode should be polished; the counter electrode is merely wiped clean with a soft cloth to wipe away easily removable salt deposits! A spotty coating after regeneration of the lead or silver electrodes does not impair measurements!
• When polishing the gold electrode, only use the moistened EID abrasive film that has a special grain that polishes and do not scratch!
• It is also recommended to use a new membrane head since the used membrane cannot necessarily guarantee that the membrane fits correctly against the gold cathode which is ensured by a spacing lattice on the inside of the membrane. Baggy clothing doesn't fit either!

Note:

• The spacing lattice is clearly visible when the membrane head is held up against the light.
• Always re-calibrate an instrument after changing a membrane.

Applications

Here are several examples of the application when using a dissolved oxygen sensors.

A. Foods and Beverages
Many foodstuffs are packed in conditions where require a low or controlled oxygen level. Dissolved oxygen levels in drinks, such as beer, should be kept in specific range. Practice of adding oxygen under pressure to bottled water to make oxygenated water has become more common. These dissolved oxygen measurements required dissolved oxygen probes that can be cleaned at elevated temperatures without being removed from the application.

B. Aquaculture (Fish Farming)
Dissolved oxygen sensors, such as multi-channel dissolved oxygen meters, are needed for fish farmers. It is essential to have such instrument to measure and control the dissolved oxygen level in the water body. Dissolved oxygen monitoring and logger are encompassing alert units with both high dissolved oxygen alarm and low dissolved oxygen alarm.

C. Sea cages
Since it is difficult to control the dissolved oxygen content of the sea, dissolved oxygen measurement is very important because the feed uptake and dissolved oxygen levels are interconnected. Intensive feeding after fish have experienced low dissolved oxygen levels can not only be a waste of food, but can actually harm the fish. The measurement of dissolved oxygen levels enables feed to be dosed optimally and, if relayed to the shore can warn that the cage should be moved if extremely low dissolved oxygen levels should occur.

D. Waste Water Treatment
Waste water treatment is critical in these years. It is no longer enough just to filter the water and dump it into the sea directly. The larger part of the waste is mainly organic, and this must treated in sludge tanks to break it down for further filtration. Sludge tank dissolved oxygen measurement and control is kept. Flow measurement, such as suspended solids measurement, sludge blanket detection, conductivity measurement, nitrate measurement and phosphate measurement utilizing the DO sensors are also all used to enable the efficient and effective cleaning of waste water.

E. Safety Monitoring
DO sensors can be utilized for safety monitoring such as oxygen detection in flammable gas and oxygen monitoring in ambient air. Blanket gas is often used where flammable substances occur. Blanket
gas is gas that cannot burn or sustain fire, i.e. it does not contain oxygen. Volumetric oxygen measurement is carried out both on the blanket gas and the surrounding air, the latter for worker safety. Special versions of the dissolved oxygen electrodes are approved for use in potentially dangerous atmospheres, i.e. in classified areas.

Market and Sell

You can find different DO sensors with price in the link for the two companies below. In general, optical sensors are much more expensive than electrochemical sensors.

Company:

- Hanna Instruments
- Fondriest Environmental

References


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