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A Review of Dissolved Oxygen Concentration Measurement Methods for Biological Fermentations

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Abstract
Dissolved oxygen levels in biological processes depend on the biological, chemical, and physical properties of the process being monitored. The analysis of dissolved oxygen concentration is a key test for process control and optimization. A review of the measurement methods for dissolved oxygen concentrations will be presented in this paper. Included in this review are the chemical, volumetric, tubing, electrochemical electrode, and optode methods. Advantages and disadvantages of these methods are discussed and key considerations for their use are summarized.

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Dissolved Oxygen Concentration, Electrode, Galvanic Electrode, Optode, Polarographic Electrode, Time Constant, Tubing Method, Winkler Method

Disciplines
Biochemical and Biomolecular Engineering | Biomechanical Engineering

Comments

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A Review of Dissolved Oxygen Concentration Measurement Methods for Biological Fermentations

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Abstract. Dissolved oxygen levels in biological processes depend on the biological, chemical, and physical properties of the process being monitored. The analysis of dissolved oxygen concentration is a key test for process control and optimization. A review of the measurement methods for dissolved oxygen concentrations will be presented in this paper. Included in this review are the chemical, volumetric, tubing, electrochemical electrode, and optode methods. Advantages and disadvantages of these methods are discussed and key considerations for their use are summarized.

Keywords. Dissolved Oxygen Concentration, Electrode, Galvanic Electrode, Optode, Polarographic Electrode, Time Constant, Tubing Method, Winkler Method.
Introduction
The measurement of dissolved oxygen in aqueous solutions as a function of time is essential in calculating the oxygen mass transfer coefficient, a key factor in characterizing bioreactors. Because of the involvement of oxygen in the reactor dynamics, being able to monitor dissolved oxygen levels in the liquid is paramount for successful bioreactor operation. Over the last several decades many methods have been developed and used to measure and monitor dissolved oxygen concentrations, though in practice typically one of five general methods is employed. These methods include the chemical, volumetric, tubing, optodes, and electrochemical electrode method (Carroll, 1991; van Dam-Mieras et al., 1992). From a practical stand point each of these methods may be successfully employed to quantify dissolved oxygen concentrations in bioreactors; however, individual method limitations and process dynamics may limit an individual method’s application. In practice, the electrochemical electrode is the most widely used instrument to monitor dissolved oxygen concentrations; as such it is very important to understand its limitations and how it compares to the other methods.

Survey of the Non-Electrochemical Electrode Measurement Methods

Chemical Method

The chemical method, as its name implies, is an analytical procedure where a sample is taken from the reactor and the dissolved oxygen concentration is determined off-line by chemical titration. The most widely used chemical method is the Winkler method (iodometric method) developed by Lajos Winkler in 1888 (APHA Standards, 2005).

This method involves several steps which include: First, adding a divalent manganese solution followed by a strong alkali to a sample in a gas tight container; this causes the dissolved oxygen to oxidize an equivalent amount of manganese ions to hydroxide. Second, an acid is added to convert the hydroxide to iodine. Third, the solution is titrated with a thiosulfate solution in the presence of a starch indicator to determine the number of iodine molecules in solution. The number of measured iodine molecules is proportional to the number of dissolved oxygen molecules in the original sample. Equation (1) shows the relationship between the molecules of iodine and oxygen.

\[ 1 \text{ mole of } O_2 \rightarrow 4 \text{ moles of } \text{Mn(OH)}_3 \rightarrow 2 \text{ moles of } I_2 \]  

As with any analytical method, the success of the Winkler method is highly dependent upon how the sample is collected and prepared. Care must be taken during all steps of the analysis to ensure that oxygen is neither introduced nor lost from the sample. Furthermore, care must be taken to ensure that the sample is free of contaminants that may oxidize the iodide or reduce the iodine, which are problems commonly encountered with fermentation broths. Wilkin et al. (2001) claimed that the Winkler method was the most accurate and precise of all methods for determining dissolved oxygen concentrations, but that it is also the most challenging technique to master and the most time consuming. Hence the chemical method is often used to calibrate other instruments, such as the electrochemical electrodes that will be discussed later.

Other chemical methods such as the NADH oxidation and phenylhydrazine oxidation have been employed to determine dissolved oxygen content (van Dam-Mieras et al., 1992), but do to their
limited use, nothing more will be said of these methods. The use of chemical methods for systems that have rapidly changing dissolved oxygen content is limited because these methods are laborious, slow, and prone to error if done incorrectly.

**Volumetric Method**

The volumetric method is simple and robust in principle, but rather inaccurate in practice. This method relies on the chemical conversion of dissolved oxygen to carbon dioxide which is then driven out of solution. As the carbon dioxide is driven out of solution, it is collected and its volume determined at a known pressure and temperature. Then, using the ideal gas law and an elemental balance for the oxygen to carbon dioxide reaction, the oxygen concentration is determined. While simple in theory and nearly unaffected by other compounds in the sample, this method, like the chemical method, is slow and lacks the sensitivity needed for dynamic biological applications (van Dam-Mieras et al., 1992).

**Tubing Method**

The tubing method consists of using a very small diameter thin walled tube of semi-permeable material that is immersed in a fermentation broth (van Dam-Mieras et al., 1992; Turner and White, 1999). A slow stream of oxygen free carrier gas is pumped through the immersed tube, and allowed to absorb oxygen from the fermentation broth by diffusion. The concentration of oxygen in the exit gas stream is then measured using a gas analyzer or electrode. Variations of this method include using a liquid instead of a gas as the sweeping fluid, however when this is done the oxygen concentration must be measured with an electrode or an optode (Towe et al., 1996). This method is strongly influenced by the tubing type, length, diameter, carrier gas flow rate, wall thickness, temperature, and the mixing characteristics within the reactor vessel. Due to the many factors that may influence the operation of this method, extensive calibration is required. The tubing method has been shown to have response times of two to ten minutes (Turner and White, 1999). However, despite the long response times and the need for extensive calibration, this method can be very accurate, robust, and withstand repeated sterilization cycles. This method also may be used to measure other dissolved gas concentrations such as hydrogen, carbon dioxide, carbon monoxide, and nitrogen to name a few.

**Optode Method**

A recent development for the measurement of gaseous and dissolved oxygen has been the introduction of the photometric transducer or optode (Koeneke et al., 1999). Many types of optodes exist, of these the fluorescence quenching optode is the most widely used for oxygen measurements (Turner and White, 1999).

Optodes for oxygen sensing are constructed using an immobilized fluorophore (a special dye) attached directly to the end of an optic fiber. The fluorophore, when excited by a reference light wave, will emit another light wave having a different wavelength with an intensity that depends on the quencher concentration. Thus when the quencher is oxygen, the intensity of the emitted light is proportional to the dissolved oxygen concentration.

These relatively new sensors show great promise as they can be used in very harsh environments, do not consume oxygen, are very small, are very sensitive to oxygen concentration changes, and are not prone to time response issues common to other methods (Zuber and Findlay, 1965;
Terasaka et al., 1998; Koenke et al., 1999; Turner and White, 1999; Kohls and Scheper, 2000; Glazer et al., 2004). However, a few drawbacks like ambient light interactions and photo bleaching are currently preventing their widespread use.

Survey of the Electrochemical Electrode Method

In 1950, Leland Clark developed the membrane coated dissolved oxygen electrodes that have become one of the most important process instruments for aerobic fermentations. Normally, the membrane used with these electrodes is only gas permeable and impermeable to most ions, such as those used in the electrolyte solution. Thus these electrodes do not disturb the biological process. For this reason, and the fact that dissolved oxygen electrodes are relatively easy to use, they are very popular and widely used in industry. Today most all oxygen electrodes can be classified as either polarographic or galvanic.

Both of these electrodes are based upon the reduction of oxygen at the cathode, which is negatively polarized with respect to the anode. While these electrodes are similar in construction and operation, the main difference between the two is the source of the needed polarization voltage. Polarographic electrodes are typically charged with a negative voltage of 0.75 volts by an external source, while galvanic electrodes utilize a negative 0.75 volt potential caused by the use of dissimilar metals.

It is important to note that both the polarographic and galvanic electrodes measure the oxygen partial pressure of the medium in which they are placed (Doran, 1995). So when an electrode is placed in a liquid, it does not measure dissolved oxygen, but rather the dissolved oxygen partial pressure which is proportional to oxygen tension in the fluid. It is necessary to know the oxygen solubility, pressure, and temperature of the fluid medium in order to determine the exact dissolved oxygen concentration.

Polarographic Electrodes

Polarographic electrodes usually contain a platinum or gold cathode, a silver/silver chloride anode, and a potassium chloride electrolyte. Figure 1a shows a schematic representation of a polarographic electrode. When the anode of the electrode is polarize by an external power supply, the following reactions take place at the surface of the electrode (Linek et al., 1985; van Dam-Mieras et al., 1992; Turner and White, 1999):

\[
\begin{align*}
\text{cathode:} & \quad O_2 + 2H_2O + e^- \rightarrow H_2O_2 + 2OH^- \\
& \quad H_2O_2 + 2e^- \rightarrow 2OH^- \\
\text{anode:} & \quad Ag + Cl^- \rightarrow AgCl + e^- \\
\text{overall:} & \quad 4Ag + O_2 + 2H_2O + 4Cl^- \rightarrow 4AgCl + 4OH^- 
\end{align*}
\]
The potassium chloride electrolyte solution between the membrane and probe tip provides the chloride ion needed for the above reactions. Since chloride ions are consumed over time with this type of probe, it is necessary to periodically replace the electrolyte solution. Due to the reactions that take place at the electrode surface, a voltage dependant current is created that can be related to the oxygen partial pressure as shown in the polarogram (current vs. voltage diagram) in Figure 2. The rate at which the current producing reaction takes place at the electrode surface in the plateau region shown in Figure 2 is limited by the diffusion rate of dissolved oxygen through the membrane and electrolyte, as schematically shown in Figure 3 (Linek et al., 1985; Linek, 1988; van Dam-Mieras et al., 1992). Since these reactions are very quick, the diffusion rate is a function of the bulk fluid oxygen concentration. As shown in Figure 2, when the correct polarization voltage is selected for a particular electrode, the current output is linear with respect to dissolved oxygen concentration. Care must be taken to ensure that the voltage is not too high to prevent the formation of hydrogen peroxide due to water electrolysis as this will increase the current generation. On the other hand, if the voltage is too low, the current response will be nonlinear. Care must also be taken to ensure that the reaction at the electrode is sufficiently fast to prevent the built up of hydrogen peroxide that may promote hydrogen peroxide diffusion from the electrode tip. If hydrogen peroxide diffuses away, the electrode reaction stoichiometry will be altered. Likewise, it has been shown that the accumulation of OH\(^-\) ions also retards the probe reaction rates (Linek et al., 1985). Thus, it can be concluded that a careful balance must be achieved to ensure proper electrode operation, however, on a positive note, this balance is easy to achieve and maintain in practice.
Figure 2: Typical polarographic electrode polarogram, adopted from Lee and Tsao (1979).

Figure 3: The typical oxygen transport path encounter at an electrode tip.

**Galvanic Probes**

In contrast to the polarographic electrode, a galvanic probe utilizes an anode of zinc, lead, or cadmium and a cathode of silver or gold, where a silver cathode and lead anode are the most common (Linek et al., 1985). Figure 1b shows a schematic representation of a typical galvanic probe. The electrochemical reactions that take place at the probe surface are (Linek et al., 1985; van Dam-Mieras et al., 1992; Turner and White, 1999):

\[
\begin{align*}
\text{cathode:} & \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
\text{anode:} & \quad Pb \rightarrow Pb^{2+} + 2e^- \\
\text{overall:} & \quad 2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2
\end{align*}
\]

Like the polarographic probe, the galvanic probe is constrained by the rate limiting step of oxygen diffusion across the probe membrane. Thus, the current output of the probe is linearly related to the dissolved oxygen concentration in the bulk fluid.

**Electrochemical Electrode Application**

Despite their fundamental differences, both electrochemical electrodes operate on the same basic principles, where the electrode behavior may be predicted using an appropriate model to account for electrode dynamics (Lee and Tsao, 1979): A schematic representation of the one and three
layer models are shown in Figure 4. The one layer model is an over simplification of actual conditions, but it is very useful for steady state conditions where neglecting boundary layer affects is acceptable. However, in application, this is rarely the case and the three layer model should be used. This model accounts for the effects of the electrolyte and stagnant boundary layer as shown in Figure 4b (Aiba et al., 1968; Lee and Tsao, 1979; Sobotka et al., 1982). While the three layer model is more suited to quantifying the electrode response to transient conditions, it only provides the foundation for determining the electrode response constant due to the many factors listed in the literature that may affect it. Electrode design aspects like membrane type, membrane thickness, cathode surface area, electrolyte, and electrode style all profoundly affect the behavior of the electrode response to oxygen partial pressure. Likewise, bulk fluid properties such as fluid type, viscosity, temperature, total pressure, oxygen partial pressure, fluid velocity, and solid loading can also affect electrode dynamics.

Although the one layer model is an over simplification of actual conditions, its application to the case where the oxygen partial pressure is allowed to change with time illustrates how electrode properties affect transient dissolved oxygen measurements. Fick’s second law is needed to describe the unsteady state diffusion in the membrane, which shows that the diffusion coefficient of the membrane directly determines how fast an electrode will respond to a step change in the oxygen partial pressure (Aiba et al., 1968; Lee and Tsao, 1979; Sobotka et al., 1982). Lee and Tsao (1979) showed mathematically that the electrode time response (τ_e), for the one layer model, depends on the electrode time constant defined as follows:

$$\tau_e = \frac{\pi^2 D_m}{d_m^2}$$

(4)

where \(D_m\) is the membrane diffusion constant and \(d_m\) is the membrane thickness. A large \(\tau_e\) results in a fast probe response, which means that the membrane is either very thin or it has a high \(D_m\). On the other hand, a small \(\tau_e\) indicates that the membrane is impermeable to oxygen or that the membrane is too thick. Since electrode stability relies on membrane controlled diffusion, a compromise between electrode response and stability is required.
Due to the complexity involved in estimating the electrode time constant, most opt to measure the electrode response time to a step change in the oxygen partial pressure. Typically, the electrode response time is defined as the time it takes the electrode to indicate 63% of the total change in dissolved oxygen concentration (Sobotka et al., 1982; Vardar and Lilly, 1982; Doran, 1995; Tribe et al., 1995). There are several experimental procedures described in the literature for obtaining the $\tau_e$ to stepwise concentration changes (Linek et al., 1985). Regardless of the procedure used to find $\tau_e$, care must be taken to ensure that the hydrodynamic conditions around the electrode during the time response test closely resemble those of the process in which the probe will be used, and that the step change is as rapid as possible.

Most oxygen measuring electrodes used in biological processes have response times that range from 3 to 100 seconds (Van't Riet and Tramper, 1991; Gaddis, 1999), which may result in the need to correct oxygen concentration data depending on the reactor dynamics. Many models have been developed to correct for $\tau_e$ and are discussed in great detail in the literature (Lee and Tsao, 1979; Linek et al., 1979; Linek et al., 1981; Ruchti et al., 1981; Sobotka et al., 1982; Vardar and Lilly, 1982; Lee and Luk, 1983; Linek et al., 1984; Linek et al., 1985; Linek, 1988; Chang et al., 1989; Chisti, 1989; Kim and Chang, 1989; Linek et al., 1989; Linek et al., 1991; Van't Riet and Tramper, 1991; Linek et al., 1992; Tribe et al., 1995; Gaddis, 1999; Tobajas and Garcia-Calvo, 2000; Freitas and Teixeira, 2001; Lopez et al., 2006). Lee and Luk (1983) and Sobotka et al. (1982) provide a good review of these model corrections.

Van’t Riet (1979) and Gaddis (1999) suggest that if $\tau_e$ is less than three seconds, then dissolved oxygen concentrations can be accurately measured without model correction. However, Van’t Riet (1979) cautioned that this is really only true for steady state conditions and for conditions where oxygen concentration changes are much slower than $\tau_e$. For all other cases, some form of data transformation must be considered. Hence, the use of electrochemical electrodes to accurately measure dissolved oxygen concentrations can be complicated due to internal instrument dynamics as well as system dynamics. Thus, as implied by Tribe et al. (1995) and others (Lee and Tsao, 1979; Keitel and Onken, 1981; Sobotka et al., 1982; Lee and Luk, 1983; Linek et al., 1985), the proper selection of an electrode and method for evaluating its signal will greatly impact the accuracy of the experimental results. To achieve reasonably accurate results, $\tau_e < 1/k_{La}$ is recommended as problems occur when this is not the case (Van't Riet and Tramper, 1991; Lopez et al., 2006). Thus, in practice there are three conditions of interest (Gaddis, 1999):

1. $\tau_e << 1/k_{La}$: In this range, the response time of the electrode is much smaller than the dynamic oxygen concentration change in the reactor and the electrode is suitable for monitoring changes in oxygen concentration with small error.

2. $\tau_e \approx 1/k_{La}$: In this range, the response time is of the same order of magnitude as the reactor response time and considerable errors may be encountered when calculating overall mass transfer coefficients. However, since this case is commonly encountered, models have been developed that can account for some of this error.

3. $\tau_e >> 1/k_{La}$: In this range, the response time is much larger than that of the reactor and the use of electrodes to monitor changes in oxygen concentration is not suitable.

To illustrate the importance of correctly accounting for $\tau_e$ in dynamic systems, two of the models discussed by Sobotka et al. (1982) for estimating $k_{La}$ values from dissolved oxygen data will be
compared for three operating conditions that represent the first two conditions listed above. Model A shown in Equation (5) neglects electrode dynamics and assumes that there is ideal mixing and insignificant gas phase concentration changes. Model B shown in Equation (6) again assumes that there is ideal mixing and insignificant gas phase concentrations while accounting for electrode dynamics by assuming that the electrode response is a first order lag function.

Model A: \[ \frac{C^* - C_L}{C^* - C_0} = \exp\left(-k_{La} \cdot t\right) \]  

Model B: \[ \frac{C^* - C_L}{C^* - C_0} = \frac{\left(e^{-k_{La} \cdot t} - k_{La} \cdot \tau_e \cdot e^{-t/\tau_e}\right)}{\left(1 - k_{La} \cdot \tau_e\right)} \]  

where \(C_0\) is the initial dissolved oxygen concentration at \(t = 0\), \(C^*\) is the final dissolved oxygen concentration at \(t = \infty\), and \(C_L\) is the dissolved oxygen concentration at time \(t\).

The first condition considered is where \(\tau_e\) and \(1/k_{La}\) equal 2.3 and 120.5 seconds, respectively (Figure 5). Figure 5 shows when \(\tau_e << 1/k_{La}\), there is no real difference in how Models A and B represent the experimental data. In fact, the two \(k_{La}\) values obtained by each of the models differ only by 0.1% (Table 1). This result is as expected and shows that when \(\tau_e\) is sufficiently smaller than \(1/k_{La}\), it is acceptable to use an electrochemical electrode to measure changes in dissolved oxygen concentrations.

![Graph showing comparison between Models A and B for \(\tau_e << 1/k_{La}\).](image)

**Figure 5:** Comparison of the experimental data to Models A and B for \(\tau_e << 1/k_{La}\).

Table 1: Model A and B \(k_{La}\) estimates for the three experimental conditions where \(\tau_e\) ranges from \(\tau_e << 1/k_{La}\) to \(\tau_e \approx 1/k_{La}\).
The second condition of interest is where $\tau_e$ and $1/k_{La}$ equal 2.3 and 9.5 seconds, respectively (Figure 6). As $\tau_e$ approaches $1/k_{La}$ there begins to be a noticeable difference in the model representation shown in Figure 6 and the $k_{La}$ values calculated using Models A and B (Table 1). In this case, the difference in estimated $k_{La}$ values is 12.6%, representing an increase in error of over a 100 times compared to the previous condition. Hence Model A, which does not account for electrode dynamics, lacks the ability to correctly estimate $k_{La}$ values for systems with rapidly changing oxygen concentrations relative to the electrode time constant.

![Figure 6: Comparison of the experimental data to Models A and B for $\tau_e < 1/k_{La}$.

The third condition where $\tau_e$ and $1/k_{La}$ equal 2.3 and 5.8 seconds, respectively, is shown in Figure 7. Like before as $\tau_e$ continues to approach $1/k_{La}$ the ability of Model A to correctly estimate $k_{La}$ continues to diminish. In this case, the difference between $k_{La}$ for the two models is now 23.3% (Table 1), which is twice as big as before showing that the error associated with using Model A to estimate $k_{La}$ increase rapidly as $\tau_e$ nears $1/k_{La}$. Figure 7 also shows that Model B, which has a term to account for electrode dynamics, begins to incompletely model the experimental data. This indicates that even models like Model B are limited in their ability to completely account for electrode dynamics as the difference between $\tau_e$ and $1/k_{La}$ becomes small.
Figure 7: Comparison of the experimental data to Models A and B for $\tau_e \approx 1/k_{La}$.

Hence the use of the electrochemical electrode method to measure dissolved oxygen concentrations for dynamic systems is nearly error free as long as the appropriate relationship between $\tau_e$ and $1/k_{La}$ is maintained. Likewise the electrochemical electrode method is very good at accurately measuring dissolved oxygen concentrations in steady state conditions.

Conclusion

Five common methods for measuring dissolved oxygen concentrations in bioreactors were presented and briefly discussed. Table 2 shows a summary of the advantages and disadvantages alluded to for each of these methods. While the chemical method and volumetric methods can be used to acquire reasonable measurement results, they cannot be used online and are therefore useless in applications that require real-time process monitoring. On the other hand, the tubing, optode, and electrochemical electrode methods can be used online to provide real-time dissolved oxygen measurements; however, each of these methods is limited in its applicability due to their inherent shortcomings (Table 2). Thus, a compromise has to be made between accuracy, usability, cost, etc. when selecting an appropriate measurement method for monitoring dissolved oxygen concentrations.
Table 2: Dissolved oxygen measurement method disadvantage and advantage summary.

<table>
<thead>
<tr>
<th>Measurement Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Method</td>
<td>Accurate for steady state conditions</td>
<td>Offline chemical titration</td>
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<tr>
<td></td>
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<td>Sensitive to contaminants</td>
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<td></td>
<td></td>
<td>Slow</td>
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<td></td>
<td></td>
<td>Laborious</td>
</tr>
<tr>
<td>Volumetric Method</td>
<td>Simple</td>
<td>Offline chemical reaction</td>
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<tr>
<td></td>
<td></td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inaccurate and insensitive</td>
</tr>
<tr>
<td>Tubing Method</td>
<td>Very accurate</td>
<td>Requires expensive gas analyzers</td>
</tr>
<tr>
<td></td>
<td>Robust</td>
<td>Hard to calibrate</td>
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<tr>
<td></td>
<td>Online measurement</td>
<td>Slow response times</td>
</tr>
<tr>
<td></td>
<td>Can withstand repeated sterilization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Can measure other gas species</td>
<td></td>
</tr>
<tr>
<td>Optode Method</td>
<td>Very fast response time</td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td>Online measurement</td>
<td>Sensitive to ambient light</td>
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<td></td>
<td>Robust</td>
<td>Photo bleaching</td>
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<td></td>
<td>Sensitive</td>
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<td></td>
<td>Small</td>
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<tr>
<td></td>
<td>Sterilizable</td>
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<tr>
<td>Electrochemical</td>
<td>Relatively inexpensive</td>
<td>Moderate to slow response time</td>
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<tr>
<td>Electrode Method</td>
<td>Easy to use</td>
<td>Requires repeated calibration</td>
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<tr>
<td></td>
<td>Online measurement</td>
<td>Complex electrode dynamics</td>
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<tr>
<td></td>
<td>Sterilizable</td>
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<tr>
<td></td>
<td>Sensitive</td>
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References


Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>C_o</td>
<td>Steady state liquid phase molar concentration at t = 0</td>
<td>(µM)</td>
</tr>
<tr>
<td>C_L</td>
<td>Liquid phase molar concentration</td>
<td>(µM)</td>
</tr>
<tr>
<td>C_*</td>
<td>Steady state liquid phase molar concentration at t = infinity</td>
<td>(µM)</td>
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<tr>
<td>d_m</td>
<td>Oxygen electrode membrane thickness</td>
<td>(mm)</td>
</tr>
<tr>
<td>D_m</td>
<td>Oxygen electrode membrane diffusivity</td>
<td>(cm² s⁻¹)</td>
</tr>
<tr>
<td>k_La</td>
<td>Overall volumetric mass transfer coefficient based on liquid film</td>
<td>(s⁻¹)</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>(s)</td>
</tr>
</tbody>
</table>
$\tau_e$  Oxygen electrode time constant  (s)