

Radioluminescent sources for optical chemical sensors*

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Abstract: This paper reviews the concepts associated with chemical sensors. The important concepts are exemplified by a discussion of oxygen sensors.

INTRODUCTION

Traditionally, analytical chemistry is practised by collecting a representative sample from the system of interest and then submitting this sample to an appropriate analytical laboratory for quantitative analysis. Often, the result is returned to the operator after a significant period of time. Measurement turn-around times can be several minutes, hours, days or weeks depending on the capabilities of the laboratory and the needs of the operator. A current trend in analytical chemistry is to move away from the use of central laboratory facilities by placing dedicated analytical analyzers nearby the system of interest. In this scenario, the sample is collected, submitted to the analyzer, and the analytical information is provided on the spot. The primary impetus for dedicated analyzers is to provide the analytical information rapidly and accurately, thereby permitting direct feedback control of the process based on its dynamic chemical composition. It must be recognized, however, that the person handling the sample is frequently not trained in analytical measurements which requires a robust analyzer to minimize erroneous measurements.

Chemical sensors represent one mechanism for rapidly collecting the desired analytical information. A chemical sensor is a device that provides an electrical signal which is selectively related to the concentration of a particular chemical constituent within the system. Ideally, such a device can be positioned directly in the sample stream to provide continuous analytical information in a real-time manner. This information can be used to explore the system under investigation with the goal of understanding the chemical basis of the process. Once the chemistry of the process is understood, these sensors can provide the real-time chemical information necessary to control the chemistry of the process with the goal of optimizing function and maximizing quality.

Oxygen is an important component for many different processes. This simple diatomic molecule is critical for numerous combustion and oxidation reactions which explains its importance in industry, biology, and environmental science. The high reactivity of oxygen makes it necessary to control its concentration. Small amounts of oxygen can adversely affect some fermentation processes while nearly saturating levels are desirable for other cell cultivation processes. Regardless of the anaerobic or aerobic nature of the process, oxygen levels must be monitored to ensure a proper chemical environment. Optimum oxygen levels should be identified for most aerobic processes which motivates the implementation of oxygen sensing technology to provide the analytical information necessary to control oxygen levels in a dynamic and continuous fashion.

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Oxygen sensors

Dissolved oxygen levels are traditionally measured with a Clark oxygen electrode [1]. This electrochemical process involves the reduction of oxygen at a platinum cathode which is maintained at -0.6 V relative to a standard silver/silver chloride anode. A thin gas-permeable membrane separates these electrodes from the sample solution. Oxygen in the solution crosses the membrane, dissolves in an internal solution, diffuses to the cathode where the reduction takes place. The composition of the internal solution is designed to optimize the reduction reaction. Magnitude of the resulting cathodic current is directly proportional to the concentration of oxygen in the sample. A calibration line is typically used to relate the measured current to the actual sample concentration. Clark electrodes offer excellent selectivity and rapid response times which explains their popularity for short-term, continuous monitoring.

Potential limitations of the Clark electrode include the consumption of oxygen and the need for frequent recalibration. The reduction reaction inherent in the response mechanism of the Clark electrode requires the consumption of oxygen. In most cases, the amount of oxygen consumed is negligible and this potential drawback is inconsequential. In cases where the sample volume is low and/or the oxygen concentration is low, the consumption of oxygen can adversely affect the system under investigation. A more common problem with the Clark electrode is the instability of the calibration line and therefore the need for frequent recalibration. This problem stems from the fact that the magnitude of the cathodic current depends on the flux of oxygen to the electrode surface. Typically, Clark electrodes are design so that diffusion across the gas-permeable membrane is rate limiting, thereby controlling the flux of oxygen to the electrode surface. Membrane fouling and other interfacial processes can alter the rate of diffusion across the membrane, thereby altering the calibration function for the electrode. Accurate measurements demand frequent adjustment in the calibration function to account for such variations. Poor calibration stability limits the usefulness of Clark electrode technology for long-term, remote applications where unattended operation is desirable.

Alternatively, dissolved oxygen can be measured optically based upon dynamic fluorescence quenching of an immobilized indicator dye [2–6]. Optical oxygen sensors consist of an indicator layer immobilized at the surface of an optical transduction scheme. The indicator layer contains an oxygen sensitive fluorophore. The optical transducer supplies the incident light required to excite the fluorophore and detects the subsequent luminescence. The magnitude of the luminescence is related to the concentration of dissolved oxygen according to the following Stern–Volmer relationship:

$$\frac{I_0}{I} = 1 + K_{SV} \cdot [O_2] \quad (1)$$

where I_0 and I represent the luminescence intensity in the absence and presence of the quenching agent (oxygen in this case), respectively, K_{SV} corresponds to the Stern–Volmer proportionality constant, and $[O_2]$ is the dissolved oxygen concentration in the sample. The Stern–Volmer constant equals the product of the bimolecular collision rate constant (k_q) and the fluorescence lifetime of the fluorophore in the absence of the quenching agent (τ_F°). Basically, the rate of radiative relaxation competes with the energy transfer rate between the excited fluorophore and the quencher. For dynamic quenching, the rate of energy transfer to the quencher is controlled by the rate of bimolecular collisions. In practice, longer fluorescence lifetimes provide greater sensitivity to the quenching agent. Various organo-ruthenium (II) complexes are frequently used as the indicator dye for measuring dissolved oxygen. Such dyes provide excellent selectivity for oxygen, a large Stokes shift, and reasonable photo and thermal stability.

Light sources for chemical sensors

The type of light source used to excite the fluorophore is a critical design consideration. Convention light sources used for this purpose include tungsten filament lamps, arc lamps, lasers and light emitting diodes (LEDs). It is generally recognized that brighter light sources are preferred because higher radiant powers for the excitation light produces larger luminescence signals. It is also true that variations in the source output are principally responsible for the noise levels of such measurements. Lock-in amplification is often used to minimize such noise, thereby enhancing the measurement signal-to-noise ratio (SNR). In addition, high radiant powers frequently accelerate photo-decomposition pathways of the immobilized

indicator dyes which adversely affects sensor performance. In some cases, analytical measurements can be made based on fluorescence lifetimes which avoids the negative aspects of degrading indicator during sensor operation.

We have evaluated radioluminescent (RL) light sources for chemical sensor applications. RL-sources are self-powered units where light is generated from the radiative relaxation of a solid-state phosphor which is initially excited by beta particles from a trapped radioactive nuclide. The primary advantage of a RL source stems from the low noise of the emitted radiation. We have found that the low radiant powers associated with RL sources can be countered by their low noise operation, thereby providing high SNRs and low limits of detection [7].

A novel RL-source based oxygen sensor configuration is described in this paper. A commercially available, tritium-powered RL source is used in conjunction with a ruthenium-based indicator layer to measure dissolved oxygen in aqueous samples. The response properties and analytical features of this sensor configuration are evaluated in terms of potential measurements in wastewater samples where oxygenation is critical.

EXPERIMENTAL

Ruthenium complex

(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) chloride ($\text{Ru}(\text{dpp})_3$) was used as the oxygen sensitive indicator dye throughout this work. This compound was prepared by the procedure described by Lin *et al.* [8]. The crude $\text{Ru}(\text{dpp})_3$ product was recrystallized, washed with water and then dried at 100 °C for one hour. The final product was stored at room temperature in a light protected desiccator.

Membrane chemistry

The membrane casting solution contained $\text{Ru}(\text{dpp})_3$, titanium oxide and a silicone adhesive mixed together in a methylene chloride solvent. The ruthenium solution was prepared by dissolving 0.0049 g of $\text{Ru}(\text{dpp})_3$ in 4 mL of methylene chloride. The casting solution was prepared by mixing 0.3 mL of this ruthenium solution with 0.15 g of the silicone adhesive and 0.025 g of titanium oxide. The silicone adhesive was a clear, acetic acid-releasing one component adhesive produced by Dow Corning and sold for general household use. The titanium oxide was purchased from Aldrich Chemical Co. as +99.9% pure particles with diameters of 5 μm or less. Membrane layers were formed by flowing approximately 20 μL of this casting solution through a 2-cm length of the capillary tube (1.5 mm internal diameter). Afterwards, ambient air was passed through the tube continuously for 15 min to solidify the membrane.

The optical isolation layer was constructed in a similar manner with a casting solution composed of 0.1 g of Elastosil N-198, RTV black silicone suspended in 0.3 mL toluene. This black silicone was a gift from Wacker Silicone Corporation (Adrian, MI). After passing 20 μL of the black silicone casting solution through the treated capillary tube (i.e. tubes with the ruthenium layer), the membrane layers were allowed to cure overnight under ambient conditions. Fresh membranes were flushed thoroughly with water before use to remove any residual components.

Sensor construction

Figure 1 provides a schematic diagram of the RL oxygen sensor used in this work. This sensor is designed for measuring dissolved oxygen in flowing solutions. The sample flows through a glass capillary tube which has been treated to contain the ruthenium complex. Two layers are coated on the inner wall of the glass capillary. A thin layer of silicone is placed immediately adjacent to the glass wall. This gas-permeable layer contains the ruthenium complex and is approximately 25 μm thick. A thinner outer layer of blackened silicone is deposited onto this inner ruthenium-containing layer as a means to optically isolate this inner layer from the sample solution. This outer layer is approximately 10 μm thick.

The optics required to monitor the ruthenium luminescence are located outside the glass capillary. The RL light source is positioned immediately adjacent to the outer surface of the capillary and held in place

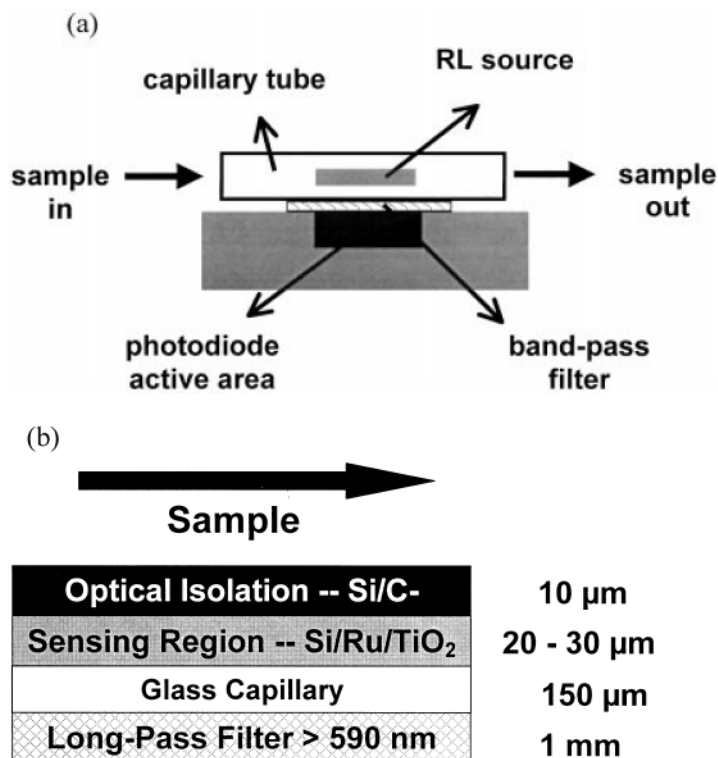


Fig. 1 Schematic diagram showing the basic configuration of the RL-oxygen sensor (a) and the membrane layers involved in the optical sensing scheme (b).

with epoxy. The RL source used in these experiments was purchased from MB-Microtec (North Tonawanda, NY). These sources emit blue light centered at 450 nm. They contain 3 mCi of tritium gas which is contained within a small, sealed borosilicate glass tube with a diameter of 0.7 mm and a length of 2.5 mm. The capillary-tube and RL-source unit is placed on the surface of a bandpass filter and secured with epoxy. This bandpass filter has a maximum transmission of 64% at 602 nm with a bandwidth of 90 nm (FWHM). This whole unit sits on the window of a silicon-photodiode detector (Hamamatsu HC 210-3314, Bridgewater, NJ). Voltage from the detector was amplified with a dedicated circuit and the resulting signal was monitored with a common laboratory multimeter and recorded on a strip chart recorder.

RESULTS AND DISCUSSION

Sensor operation

The RL-oxygen sensor shown schematically in Fig. 1 is designed to measure dissolved oxygen in a flow through manner. As noted above, the sensing chemistry is located within a thin silicone polymer layer coated along the inner wall of a capillary tube. Two silicone layers are needed. The sensing layer is located immediately adjacent to the capillary wall. This layer contains the ruthenium complex and is approximately 25 μm thick. This sensing layer is separated from the solution by a thin ($\approx 10 \mu\text{m}$) optical isolation layer composed of silicone impregnated with carbon-black. The purpose of this outer layer is to restrict the optical measurement to the sensing layer. As the sample flows past the sensing region, dissolved oxygen diffuses through these layers and quenches the fluorescence of the immobilized ruthenium complex. A commercially available tritium-powered RL light source is mounted along the outer wall of the capillary tube. This source is selected to provide the blue light needed to excite ruthenium. Light emitted from this source is centered at 450 nm which exactly matches the excitation frequency for ruthenium. The capillary tube, source unit is positioned on a thin long-pass filter designed to pass the ruthenium luminescence while blocking the excitation radiation. A 590-nm long-pass filter is

used to pass the ruthenium luminescence which is centered at 610 nm. A standard solid-state, silicon photo-diode detector is used to measure the fluorescence. The low radiant powers of the RL source result in low signals which require high amplifier gain and electronic filtering. Once fully constructed, the measured sensor signal is high in the absence of oxygen which corresponds to unquenched fluorescence (I_0). The addition of oxygen to the sample solution causes a decrease in the detector signal (I) as a result of dynamic quenching.

Basic response properties

Figure 2a shows a typical sensor response as a function of dissolved oxygen concentration. As described before, this relationship is nonlinear owing to heterogeneity within the polymer matrix and the combination of stray light and nonquenchable luminescence from the ruthenium complex [9]. Several transformations are available to linearize these data [2,4,6,9,10], such as the one used to obtain the plot shown in Fig. 2b. In this case, the data were transformed according to Equation 2 where I_{NQ} represents the intensity of light detected which cannot be quenched by oxygen. I_{NQ} includes any ruthenium luminescence that is not quenchable by oxygen and any stray radiation in the system.

$$\frac{I_0 - I_{NQ}}{I - I_{NQ}} = 1 + K_{SV} \cdot [O_2] \quad (2)$$

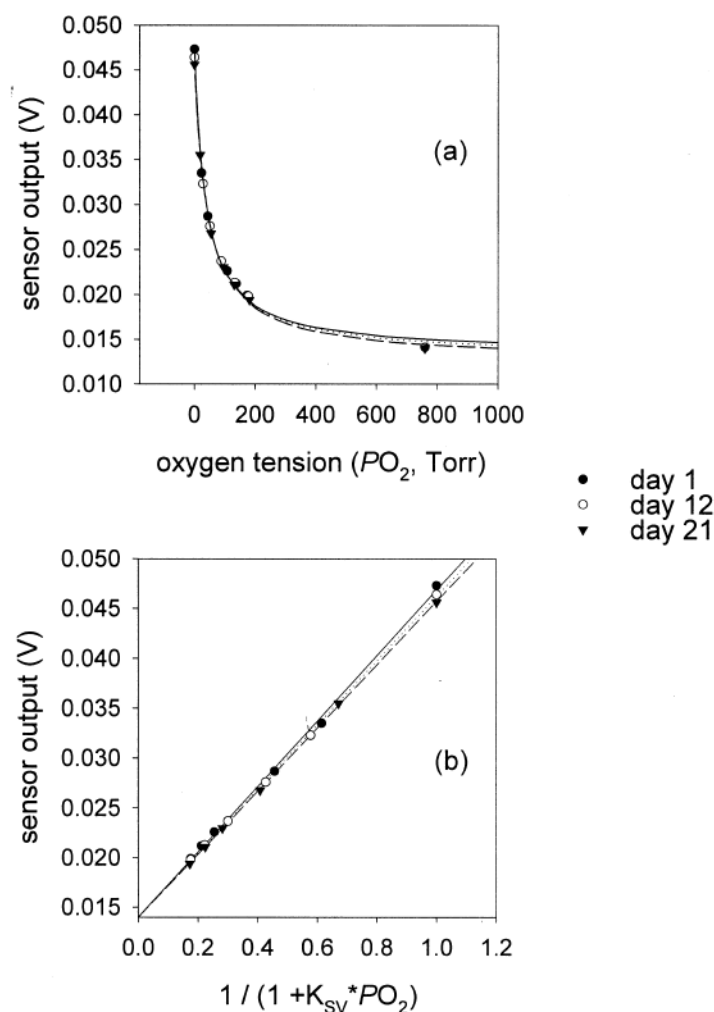


Fig. 2 Raw signal as a function of dissolved oxygen concentration (a) and linear calibration curve following data transformation according to Equation 2 in the text (b).

The nonlinear nature of the sensor response creates a situation where the sensitivity is not uniform across oxygen concentrations. For fluorescence quenching measurements, the highest level of sensitivity is achieved at low concentrations where the magnitude of signal change is greatest for a given change in oxygen concentration. Sensitivity begins to roll-off at higher oxygen levels. Near 100% air saturation, which is most relevant for many environmental and biological systems, the RL-oxygen sensor can distinguish differences of 30 p.p.b. (6 mmHg) in dissolved oxygen levels. The limit of detection is 5 p.p.b. (0.1 mmHg).

Dynamic response properties are critical for accurate *in situ* measurements where analyte concentrations vary as a function of time. Ideally, the sensor response is instantaneous, thereby providing a accurate measure of the dynamic process. Response times of our RL-oxygen sensor are limited by the time required for the oxygen to equilibrate within the indicator layer. Thicker layers result in longer response times. Response times are approximately three minutes for RL-oxygen sensors with an overall polymer layer thickness (indicator layer plus optical isolation layer) of 30–35 μm .

A critical feature of this oxygen sensing technology is the ability to operate for extended times without the need for recalibration. Calibration stability was established in an experiment where the sensor was used to measure oxygen levels over a 21-day test period. In this experiment, the RL-O₂ sensor was calibrated on day 1 and then solutions with different oxygen levels were measured daily over the course of the experiment without recalibrating the sensor. The measured oxygen values matched the actual values over the entire period. The computed standard error is only 2.8% for predictions across all samples. Moreover, no obvious systematic bias is evident in the corresponding correlation plot (data not shown). A detailed analysis of measurement residuals, however, reveals of slight positive bias in predicted values which can be corrected by using a daily, one-point calibration. Repeated use of these RL-oxygen sensors confirms the stability and robustness of the calibration models. This level of performance is attributed to the stability of the RL-light source and the lack of photobleaching provided by the low radiant powers of these sources.

Membrane stability in wastewater

The treatment of wastewater is a critical aspect of environmental control. This multistep process involves: (i) filtering the water to remove large debris; (ii) exposure to a primary clarifier to permit large particles to settle; (iii) addition of sludge to digest the organic impurities; (iv) aeration of the sludge-water mixture to supply sufficient oxygen for the bio-organisms in the sludge; (v) exposure to a secondary clarifier to permit settling of the sludge treated water; and (vi) addition of chlorine before releasing the water back into the environment. Oxygen levels are critical and must be measured to ensure efficient sludge metabolism and waste removal. Clark electrodes are prone to membrane fouling under these conditions. As a result, frequent electrode calibrations are required and prolonged unattended operation is not possible.

The extent to which the indicator membrane of the RL-oxygen sensor is affected by the components within sludge-containing wastewater was evaluated by submerging several such membranes at the exit stream of the second aeration base at the southern Iowa City Wastewater Treatment Facilities. Membranes were held approximately 2 feet below the water surface. Membranes were removed after 7 and 18 days of exposure to this highly polluted water. Immediately after removal, membranes were gently rinsed with distilled water and placed within a fluorometer for analysis.

Figure 3 shows the results of our analysis where the response to oxygen is plotted for two identical sensor membranes submerged in this exit steam for 0, 7, and 18 days. No significant changes are evident in either the response sensitivity (calibration slope) or limit of detection. Likewise, response times are not significantly different after exposure. The only differences observed correspond to slight shifts in the response lines which are likely caused by an inability to reproducibly position the membrane in our fluorometer during the analysis. Upon removing the membranes from the wastewater, the membranes appear clear which indicates minimal adsorption or growth of microbes during exposure.

CONCLUSIONS

The results described above indicate a sensing layer composed of silicone, TiO₂, and Ru(dpp)₃ is well

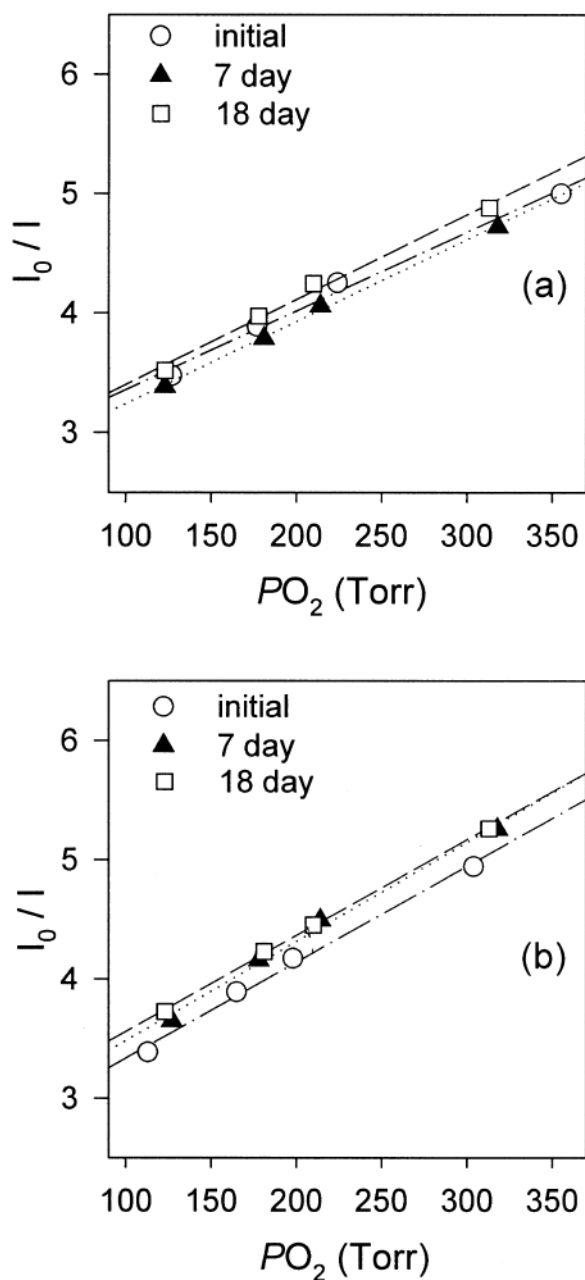


Fig. 3 Dynamic quenching from oxygen for two identical membranes exposed to raw, aerated wastewater for 0 days (circles), 7 days (triangles) and 18 days (squares). Responses are not corrected for nonquenchable light according to Equation 2.

suited for monitoring dissolved oxygen in wastewater streams. Such layers are easy to fabricate, provide high fluorescence signals, offer excellent stability and exhibit antifouling activity. In addition, the stability provided by the RL source and the self-powered nature of these sources suggest that this RL-oxygen sensing technology is capable of performing long-term, unattended measurements. The proposed RL-oxygen sensors offer a reliable means for continuously monitoring dissolved oxygen in aqueous samples. Remote, long-term monitoring is particularly noteworthy with potential applications in wastewater treatment plants, depth profiling during oceanographic investigations, and onboard spacecraft to ensure adequate environmental conditions.

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