Oxygen sensor via the quenching of room-temperature phosphorescence of perdeuterated phenanthrene adsorbed on Whatman 1PS filter paper

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Abstract

Perdeuterated phenanthrene (d-phen) exhibits strong room-temperature phosphorescence (RTP) when adsorbed on Whatman 1PS filter paper. An oxygen sensor was developed that depends on oxygen quenching of RTP intensity of adsorbed d-phen. The system designed employed a continuous flow of nitrogen or nitrogen–air onto the adsorbed phosphor. The sensor is simple to prepare and needs no elaborate fabrication procedure, but did show a somewhat drifting baseline for successive determinations of oxygen. Nevertheless, very good reproducibility was achieved with the RTP quenching data by measuring the RTP intensities just before and at the end of each oxygen determination. The calibration plots gave a nonlinear relationship over the entire range of oxygen (0–21%). However, a linear range was obtained up to 1.10% oxygen. A detection limit of 0.09% oxygen in dry nitrogen was acquired. Also, carbon dioxide was found to have a minimal effect on the RTP quenching. Thus, oxygen could be measured accurately in relatively large amounts of carbon dioxide. The performance of the oxygen sensor was evaluated by comparing data obtained with a commercial electrochemical trace oxygen analyzer. Also, additional information on the quenching phenomena for this system was obtained from the RTP lifetime data acquired at various oxygen contents. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorescence; Oxygen; Quenching

1. Introduction

There is considerable interest in the development of novel and sensitive oxygen sensors [1–5], and numerous oxygen sensors have been developed based on fluorescence detection [2,4,5]. However, very few oxygen sensors have been described that stem from solid-matrix room-temperature phosphorescence (RTP). Wolfbeis [6] has reviewed earlier work where RTP was used for oxygen sensing. Charlesworth [7] reported the details of a RTP method to monitor oxygen concentrations in a gas stream using camphorquinone as the phosphor. He was able to determine oxygen in the range of 0.1–25%. Liu et al. [8] evaluated immobilized room-temperature phosphorescent metal chelates as sensing materials for oxygen. They were able to develop an oxygen transducer based on the RTP quenching of Al-ferron...
Garcia et al. [9] showed that Erythrosin B gives a strong RTP signal when adsorbed on non-ionic resins or when encapsulated in silicone films. Oxygen transducers based on RTP quenching of the immobilized erythrosin B were evaluated by the previous authors. In addition, phosphorescent complexes of porphyrin ketones have been employed in oxygen sensing [10]. In particular, platinum(II) octaethylporphrine ketone was dissolved on a polystyrene layer to give an oxygen-sensitive film. A detection limit of 1.5 hPa was obtained for oxygen. In later work, Hartmann and Trettnak [11] studied the effects of polymer matrices on calibration functions of luminescent oxygen sensors that were based on porphyrin ketone complexes. Also, Lee and Okura [12] developed an oxygen sensor which depended on the RTP quenching of platinum octaethylporphrine in polymer films. Recently, Alava-Moreno et al. [13] reported on oxygen sensing by the RTP quenching of some lead 8-hydroxyquinoline complexes. The sensors developed were shown to be useful for the determination of dissolved oxygen in tap water.

In this work, a very simple solid-matrix RTP method was developed for sensing oxygen in which the phosphor, perdeuterated phenanthrene (d-phen), adsorbed on Whatman 1PS paper acted as the sensor. Several analytical figures of merit were obtained for the sensor and detailed consideration was given to the experimental conditions for obtaining RTP.

2. Experimental

2.1. Instrumentation

Spex Fluorolog 2 and Perkin Elmer LS50B spectrofluorimeters were used to obtain the solid-matrix RTP intensity and RTP lifetime ($\tau_p$) data of d-phen adsorbed on Whatman 1PS and No.1 filter papers.

2.2. Reagents

Absolute ethanol was purified by distillation. Perdeuterated phenanthrene ($D_{10}$) (99.5 atom % D, MSD Isotopes, Montreal, Canada) was used as received. Cylinders of nitrogen (ultrahigh purity), compressed air (U.S.P.) and carbon dioxide (U.S.P.) were purchased from United States Welding, Denver, CO. Oxiclear was obtained from Labclear, Oakland, CA. Whatman No.1 and 1PS filter paper circles were developed in ethanol to collect impurities at one end.

2.3. Measurements

A 1 µg sample of d-phen in ethanol–water (90:10) was spotted onto a Whatman No.1 or 1PS filter paper circle of 6.4 mm diameter. The sample was dried at 110°C for 30 min. A sample holder was made from a rectangular teflon block which fit tightly inside a 1-cm fluorescence cell. As shown in Fig. 1, holes were made in the teflon block which permitted gas to flow in and out of the 1-cm$^2$ fluorescence cell. As indicated in the Fig. 1, a section of teflon was cut from the teflon block, and a circular depression was made in the flat part of the teflon that remained after the removal of the section of the teflon. Four pieces of blank filter paper were placed in the depression, and then the piece of filter paper with the d-phen was placed on top of the blank filter paper samples. The sample holder was inserted into the quartz cell and wrapped at the top with parafilm to prevent entry of ambient air. In the Spex spectrofluorimeter, the following phosphorimetric parameters were used to get the maximum RTP intensity from the sample: excitation and emission maxima of 287 and 498 nm, respectively; delay time of 10 ms and zero time between flashes; 10 flashes per data point; a window of 100 ms was chosen to obtain a strong RTP intensity.

2.4. Gas flow manifold and measurements

As shown in Fig. 1, nitrogen or carbon dioxide gases were passed through Drierite and Oxiclear to remove traces of moisture and oxygen, respectively. Compressed air was passed through Drierite to minimize its moisture content. An environment with various concentrations of oxygen was maintained in the cell by varying the relative flow rates of nitrogen, compressed air, or...
carbon dioxide. A mass flow meter/controller (Model 201, Porter, Hatfield, PA) was used to control and measure the flow rate of each gas. Tygon tubing of 1/4" inner diameter was employed to carry the gases, and two-way brass valves (Whitey) were used to select the gas or gas mixture that would flow to the sample. The gas flow over the sample was maintained at a constant flow rate of 200 ml min$^{-1}$ for both nitrogen and nitrogen–air mixtures with or without carbon dioxide. The oxygen concentration (% v/v) was calculated by dividing the flow rate of air by the sum of flow rates of nitrogen and air, and considering that pure air has 20.95% oxygen. All the RTP measurements were made at 23 ± 1°C.

Initially, nitrogen was passed into the sample cell for 15 min to cool it to room temperature after drying the filter paper sample. Then, either nitrogen, a nitrogen–air, or nitrogen–air–carbon dioxide mixture was allowed to flow through the sample holder for about 7–9 min at each percentage of oxygen. The solid-matrix RTP intensity data were acquired with the phosphorimeter collecting data for 25 s under optimized conditions. The recovery time for the sensor was 7.5 min. For the RTP lifetime measurements, nitrogen and nitrogen–air mixtures were passed successively over the sample for 5 min before collecting a decay curve. RTP decay data were processed for a single exponential decay, which resulted in a correlation coefficient value of 0.991, or greater, in an environment of pure air and 0.997 or greater in the nitrogen atmosphere.

A Teledyne (Model 316RB) trace oxygen analyzer was first calibrated with compressed air at the recommended flow rate of 2 scfh (944 ml min$^{-1}$), and then the analyzer in the instrument was flushed with ultrahigh purity nitrogen for 1 h to remove traces of oxygen. Each nitrogen–air mixture was passed into the analyzer at a flow rate of 200 ml min$^{-1}$ for 15 min. This much time was allowed for the oxygen in the nitrogen–air mixture to reach a steady state of diffusion to the electrochemical fuel cell of the analyzer because this flow rate was less than the flow rate recommended by the instrument manufacturer. The analyzer showed a constant analog reading after 5 min for all the gas mixtures studied. The oxygen contents of these mixtures, calculated from the relative flow rates of gases, showed essentially a perfect linear relationship with the values obtained from the Teledyne analyzer.
3. Results and discussion

3.1. Choice of solid matrix and phosphor

Filter paper is one of the most widely used solid-matrices for obtaining room-temperature fluorescence (RTF) and RTP from adsorbed organic compounds. The ability to obtain RTP from numerous types of organic compounds, low limits of detection, small sample size, and relative ease of sample application are some of the factors responsible for its popularity [14,15]. Recent studies have shown that Whatman 1PS filter paper has several advantages for obtaining RTF and RTP signals compared to Whatman No. 1 filter paper [16–18]. According to the technical information available from the manufacturer, the 1PS filter paper has been impregnated with a heat cured coating of silicone and a proprietary tin complex [19]. This coating imparts stability and hydrophobic character to the 1PS filter paper. The 1PS filter paper is normally employed in the separation of aqueous and organic phases. However, when a small drop of a phosphor in ethanol:water (1:1) was spotted onto the 1PS filter paper, it formed a tiny droplet that spread very little on the filter paper surface [17]. As the solvent evaporated, the phosphor was adsorbed on a very small area of the filter paper. The localization of phosphor to a small area on the 1PS paper, in contrast to diffusion of the sample with Whatman No. 1 filter paper, is largely responsible for an increase in the sensitivity of solid-matrix RTP [17]. It is quite likely that the tin complex in the filter paper also exerts a heavy-atom effect to enhance the RTP from phosphors [17].

In a search for a suitable phosphor in this study, the following compounds were first tested on Whatman No. 1 filter paper for their potential to give strong RTP: acriflavine, benzo[f]quinoline hydrobromide, 9-bromoanthracene, 6-bromocoumarin-3-carboxylic acid, 9-bromophenanthrene, bromophenol blue, bromotriphenylethylene, coumarin-3-carboxylic acid, decacyclene, eosin B (spirit soluble), eosin B, fluoranthene, β-naphthoflavone, potassium 1-bromonaphthyl sulfate, phenanthrene, d-phen, and triphenylene. Of these compounds, d-phen, followed by triphenylene, were found to have the strongest RTP emissions and long RTP lifetimes. In this work, d-phen was chosen because it gave not only a strong RTP signal, but it also gave the maximum RTP quenching for a given oxygen content with the phosphor adsorbed on 1PS filter paper. Recently, Ramasamy and Hurtubise [20] reported a detailed comparison of the solid-matrix luminescence properties of d-phen and phenanthrene adsorbed on several solid matrices. For example, they showed that d-phen gave a RTP lifetime of 9.7 s on Whatman No.1 filter paper.

3.2. Oxygen quenching of RTP signals

Fig. 2 shows a typical quenching pattern of the RTP intensity of d-phen adsorbed on Whatman 1PS filter paper for sequential flows of nitrogen and nitrogen–air at numerous oxygen contents. The duration of the measurement of the RTP signal was found to be important in getting reproducible results. In this study, average RTP values were obtained over a 25 s time period. For a given oxygen content, a shorter measurement period resulted in lower RTP values, and therefore, lower sensitivity. By using a fixed measurement time, very accurate results were obtained. An important observation about the quenching results in Fig. 2 is that the RTP intensity in the presence of nitrogen remained essentially steady before oxygen was introduced into the system, but decreased after successive nitrogen–air flows. However, the decrease in these RTP values did not affect the accuracy of the method because equal increments of time were used between each oxygen measurement.

Continuous passing of nitrogen for more than 1 h over the phosphor, after the phosphor had been exposed to several percentages of oxygen, did not restore the original RTP intensity. Also, the RTP intensity, after the introduction of oxygen, changed somewhat with time as indicated in Fig. 2. Thus, it was necessary to measure the RTP after a fixed time period. The changes in RTP did not greatly affect the accuracy and precision of the oxygen determinations as discussed in the next section. The RTP intensity versus time plot in Fig. 2 shows RTP signals over a wide time frame.
Fig. 2. RTP intensity versus time plot for several percentages of oxygen passed sequentially into the experimental system.

Thus, the phosphor was exposed to several oxygen levels over this time period. For a typical RTP measurement with an unknown sample, the phosphorimeter would be on for a 25 s period to measure the RTP of the sample after the gaseous mixture was passed over the sample for a fixed time period (7–9 min). In addition, a calibration curve most likely would be prepared from much fewer percentages of oxygen compared to the ones in Fig. 2.

3.3. Analytical figures of merit

Since the baseline changed for successive oxygen determinations, the $P_0$ values for each oxygen quenching measurement were obtained in the presence of dry nitrogen just before each oxygen determination. The RTP signal ($P$) during the quenching step was measured as described in the previous section. Fig. 3 shows a typical Stern–Volmer plot for the oxygen quenching of the RTP of d-phen adsorbed on 1PS filter paper (average of three runs). The calibration plot over the entire range of percent oxygen investigated (0–21% oxygen) followed a nonlinear relationship. However, a linear range was obtained from 0 to 1.10% oxygen with a linear correlation coefficient of 0.995 (Fig. 3). The limit of detection (LOD) using the 0–1.10% oxygen range was 0.09% oxygen. The LOD was calculated from the equation, LOD = 3 (standard deviation of the blank)/(slope of the calibration plot). The RTP quenching values, ($P_0/P$), were reproducible with 95% confidence limits of ± 0.01, ± 0.22, and ± 0.57 at 0.21, 3.00 and 21.00% oxygen levels, respectively. Also, six successive determinations of 0.54% oxygen showed a 95% confidence interval of ± 0.007 for $P_0/P$ (a relative standard deviation of 0.6%).

Whatman 1PS filter paper samples without any phosphor adsorbed showed a very weak RTP quenching pattern for the range of oxygen percentages shown in Fig. 2 compared to the quenching pattern observed for d-phen. To account for the contribution from the blank signals, the blank $P_0$ and $P$ values from Whatman 1PS paper were subtracted from the corresponding d-phen $P_0$ and $P$ values. The blank corrected RTP values were used in another calibration plot. The overall
shape and the linear range of the calibration plot did not change compared to plots without blank subtraction. Generally, the phosphor signals for the phosphor adsorbed on 1PS paper were 43 times greater than the RTP background signals of the 1PS paper from 0.10 to 21% oxygen. By using each $P_0/P$ value without blank subtraction and the corresponding $P_0/P$ value with blank subtraction in the range of 0.10–1.10% oxygen, the average percentage error was calculated as 0.84%. In the range of 1.70–21.0% oxygen, the average percentage error for $P_0/P$ without blank subtraction was 3.78%. Thus, for highly accurate results, it would be necessary to correct the $P_0$ and $P$ values for d-phen with the corresponding $P_0$ and $P$ values from blank Whatman 1PS filter paper. Also, the ratio of the slopes for plots of $P_0/P$ vs. %O$_2$ from 0 to 1.10% O$_2$ without and with blank subtraction was 1.09. For the ranges of 0–1.70% O$_2$ and 0–2.33% O$_2$, the ratios of slopes without and with blank subtraction were 1.09 and 1.10, respectively. If there were no effect due to the blank, then the ratio of slopes would be 1.00. This is so because the blank phosphorescence signals would be quenched to different extents with increasing % O$_2$.

3.4. Baseline change

Whatman 1PS filter paper was exposed to polychromatic UV radiation from a 450 W xenon lamp for 1 h to photochemically decompose the phosphorescent impurities so as to minimize the phosphorescence background signals [15]. However, d-phen adsorbed on the UV treated 1PS filter paper gave a calibration plot and linear range similar to the non-UV treated filter paper sample. Thus, there was no major advantage to using the UV-treated 1PS filter paper. Also, samples of the phosphor adsorbed on 1PS filter paper, after oxygen quenching, were reheated and cooled in nitrogen. However, the RTP intensity prior to exposure to oxygen was not restored. The exact reason for this has not been established. However, different samples of phosphor spotted on 1PS filter paper and heated to 110°C for 30, 45, and 60 min gave similar phosphorescence lifetime ($\tau_p$) values after 15 min cooling in a nitrogen atmo-
sphere. Thus, moisture was absent in the filter paper matrix after drying, otherwise it could have been another potential source for the change in the baseline.

The baseline decrease that occurred with time (Fig. 2) happened after quenching, whether the sample was continuously exposed to the exciting radiation or exposed only during the RTP measurement. The previous result suggests that little photodecomposition of the phosphor occurred while the sample was exposed to the exciting radiation. This was supported by the fact that no decrease in RTF intensity was observed when d-phen in ethanol was subjected to the repeated cycle of quenching with air and regeneration with nitrogen.

3.5. Effects of moisture and carbon dioxide on the quenching of RTP

Moist nitrogen and moist air were found to cause significant quenching of the RTP intensity of d-phen adsorbed on 1PS filter paper. This was most likely due to the breaking of hydrogen bonds in the cellulose network of the filter paper by moisture and thus causing the phosphor to be held less rigidly in the matrix [14,15]. It is well known that moisture can quench RTP.

Carbon dioxide in the presence of nitrogen and air had little effect on the quenching of the RTP of the phosphor. For instance, 10–95% carbon dioxide (v/v) in nitrogen–air mixtures with 1.05% oxygen caused an error of only 0.6–4% for the RTP quenching measurements. Similarly, for 5.24 and 10.45% oxygen in air with 10–75% carbon dioxide and 10–50% carbon dioxide produced an error of 2–3% and 2–5%, respectively. Thus, oxygen can be determined in the presence of a wide range of carbon dioxide concentrations with a relatively small error in the determination.

3.6. Comparison of RTP results with Teledyne trace oxygen analyzer

The percent oxygen of five nitrogen–air mixtures ranging from 0.21 to 1.05% were obtained with a Teledyne trace oxygen analyzer and compared to the percent oxygen obtained from the

RTP quenching method. Table 1 compares the data from the two methods. As indicated in Table 1, the percent oxygen obtained by the RTP method gave values that were much closer to the accepted values of oxygen. The accepted values were calculated as described in the Section 2. In fact, the results from the Teledyne system were all lower compared to the corresponding values obtained by RTP. The data in Table 1 show that the RTP method is very reliable.

3.7. RTP lifetime before and during oxygen quenching

The phosphorescence lifetime (τ_p) values of d-phen adsorbed on Whatman 1PS filter paper were obtained. The τ_p values were measured after a 5 min equilibration period for each nitrogen–air mixture, and the τ_p values were acquired before each oxygen quenching measurement by passing nitrogen through the cell for a 5 min time period between the measurement steps. Fig. 4 illustrates the change of τ_p/τ_p values with oxygen content. As indicated, the τ_p/τ_p plot showed a nonlinear relationship over the entire percent oxygen range. Because the plot was not linear, a simple diffusion controlled oxygen quenching mechanism was not occurring over the range of % oxygen investigated. For all the different oxygen contents studied, the P/0 values were considerably greater than the τ_p/τ_p values. Thus, P/0 was used in the determination of the percentage oxygen. Studies are continuing to develop a detailed understanding of the RTP quenching mechanism of oxygen with d-phen adsorbed on 1PS paper.

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<th>RTP method (% oxygen)</th>
<th>Teledyne analyzer (% oxygen)</th>
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4. Conclusion

A solid-matrix RTP oxygen sensor was developed that is inexpensive and easy to use. The basis of the sensor is the oxygen quenching of the RTP of a phosphor adsorbed on filter paper. It is a simple matter to prepare the sensor. One adsorbs the phosphor on filter paper, dries the filter paper with the adsorbed phosphor, and then the dried paper is placed in a spectrofluorometric cell. Oxygen can be determined over a wide range, the reproducibility and accuracy of the sensor were very good, and the limit of detection for oxygen was very low (0.09%). One disadvantage of the sensor is that the RTP of the phosphor is sensitive to moisture, but if moisture is minimized very accurate data can be obtained from the sensor. However, a major advantage of the sensor would be for the determination of oxygen in samples that contain large amounts of carbon dioxide.

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