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Linear calibration function of luminescence quenching-based optical sensor for trace oxygen analysis†

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A mathematical response function derived from the Stern–Volmer equation was successfully applied to calibrate an optical oxygen (O_2) sensor using tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ditetrakis(4-chlorophenyl)borate adsorbed on silica gel as the O_2-sensitive material. The calibration of this optical sensor can be simply done by plotting the reciprocal of the luminescence intensity against the O_2 concentration ($1/I$ *vs.* $[O_2]$). A single air sample injection method combined with an exponential dilution technique produces O_2 standards at various concentrations. The modified Stern–Volmer plots demonstrate excellent agreement with the well known Stern–Volmer plot (I_0/I *vs.* $[O_2]$). The proposed method has the advantages of simple O_2 standard preparation and no I_0 data being needed for calibration. The response and recovery times of the optical O_2 sensor are less than 0.2 and 1 s, respectively. The limit of detection is 2.6–3.6 ppm v/v. The photostability of the O_2-sensitive material is good and there is no sign of photodegradation after 12 h of continuous use.

Life on earth relies on the presence of oxygen (O_2) and other gases in the atmosphere. The determination of O_2 concentration is important as O_2 is often involved in many chemical and biochemical reactions as reactants or products. Tremendous effort over the years has been devoted to the development of new ideas and techniques for the quantification of O_2. The Clark-type amperometric electrode, which is based on the electroreduction of O_2 on a polarised cathode, is one of the most commonly used O_2 sensors.[1] It is a moderately fast, simple and convenient technique. However, it suffers from several drawbacks, such as the flow dependence of the O_2 response, interferences from easily reducible species, such as hydrogen sulfide, relatively long response times and the tendency of the electrode to become poisoned by contaminants, including proteins and organics.

In order to overcome these drawbacks, optical sensors have been developed as an alternative approach for O_2 sensing. The advantages of these sensors are basically as follows: no O_2 consumption in the sensing process, no requirement for a reference electrode, inertness against sample flow rate and stirring speed and immunity to exterior electromagnetic field interference. The operating principles of these sensors are generally based on the dynamic quenching of the luminescence of an indicator by O_2. Ruthenium(II) complexes[2–12] are one of the most widely used O_2 indicators because they are efficiently quenched by molecular O_2 and they display favourable absorbances and emission wavelengths, large Stokes' shift and high photostability. These indicators have to be immobilised on a solid substrate before the actual performance of optical O_2 sensing. Adsorption of ruthenium(II) complexes on silica gel particles is an effective immobilisation technique for the fabrication of O_2 sensors.[13–16] Silica gel provides a useful solid substrate for dye immobilisation since it has high thermal stability, good photostability and optical transparency in the visible light region.

Traditionally, the calibration of luminescence quenching-based optical sensors is based on the Stern–Volmer equation:[17]

$$I_0/I = 1 + k_{SV}[O_2] \qquad (1)$$

where I_0 and I are the luminescence intensities in the absence and presence of O_2, respectively, and k_{SV} is the Stern–Volmer quenching constant. Plotting I_0/I against $[O_2]$ will give a linear calibration function for O_2. However, from this equation it is necessary to determine accurately the I_0 value beforehand and also a wide range of standard gases varying from low to high concentrations are needed to characterise fully the Stern–Volmer behaviour of a quenching-based optical sensor.

In this paper, we propose a response function by plotting the reciprocal of the luminescence intensity against the O_2 concentration ($1/I$ against $[O_2]$) for calibration of an optical O_2 sensor based on the luminescence quenching of tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ditetrakis(4-chlorophenyl)borate, $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$, adsorbed on silica gel packed in a flow cell. A single standard injection method combined with the exponential dilution technique is employed to generate O_2 standards at various concentrations. Using this response function, we demonstrate for the first time that not only a linear calibration plot of the response curve can be expected for luminescence quenching-based optical sensors, but also that the response curve will function well without prior knowledge of the I_0 value. This means that complicated instrumentation and standard O_2 gases are no longer required. The proposed method compares favourably with the typical Stern–Volmer plot for the O_2 sensor.

Experimental

Materials

For the preparation of oxygen-sensitive material, the following chemicals and solvents were used: acetone, diethyl ether, *N,N*-dimethylformamide, 4,7-diphenyl-1,10-phenanthroline, ethanol, ethylene glycol, ruthenium(III) chloride hydrate, sodium

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chloride, tetrahydrofuran (THF) and toluene from Aldrich (Milwaukee, WI, USA) and potassium tetrakis(4-chlorophenyl)borate from Fluka (Buchs, Switzerland). The dye ion pair, $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$, was synthesised according to a modified method.[18] All chemicals were used as received.

$[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ adsorbed on silica gel was synthesised using the following procedure. A 10 g amount of silica gel 60 (Merck, Darmstadt, Germany) was stirred with 10 cm^3 of a 0.1 mol dm^{-3} ethanolic solution of $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ overnight. The solid residue of $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ adsorbed on silica gel was filtered and washed successively with THF, diethyl ether, acetone, ethanol and water in order to remove excess and unadsorbed $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ dye ion pair. The solid residue was heated in an oven at 100 °C for 5 h to evaporate the solvents. The dry $[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ adsorbed on silica gel was then kept in a desiccator for further use.

Instrumentation

$[Ru(dpp)_3][(4\text{-}Clph)_4B]_2$ adsorbed on silica gel was packed in a laboratory-made flow cell[19] and placed securely in a spectrofluorimeter containing a lamp power supply (Model LPS-220), a xenon lamp (Model A1010) and a photomultiplier detection system (Model 710), from Photon Technology International (London, Ontario, Canada). Different concentrations of O_2 standards from an exponential dilution flask (Fig. 1) were injected into the flow cell. All fluorescence measurements were made at room temperature (23 °C) and atmospheric pressure.

Flow injection system

Fig. 1 illustrates the flow injection of an air sample into the flow cell. A stream of argon (Ar) carrier gas at a flow rate of 110 $cm^3\ min^{-1}$ was continuously supplied to the flow injection system. An open air (20.95% v/v) sample (0.2–0.5 cm^3) was injected into the exponential dilution flask (135 cm^3) with a Hamilton gas-tight syringe (Supelco, Bellefonte, PA, USA) through a rubber stopper. The injected air sample was then drawn into the flow cell by the Ar carrier gas. Employing this experimental arrangement, an initial concentration, C_0, in the flask is exponentially diluted according to the expression[20,21]

$$C = C_0 \exp(-Ft/V) \qquad (2)$$

where C is the concentration at time t, F is the volumetric flow rate of the Ar carrier gas, V is the effective volume of the exponential dilution flask and t is the time after introducing the air sample. Obviously, this equation relates C to t exponentially. Recording t we can obtain the concentration of O_2 reaching the flow cell at time t.

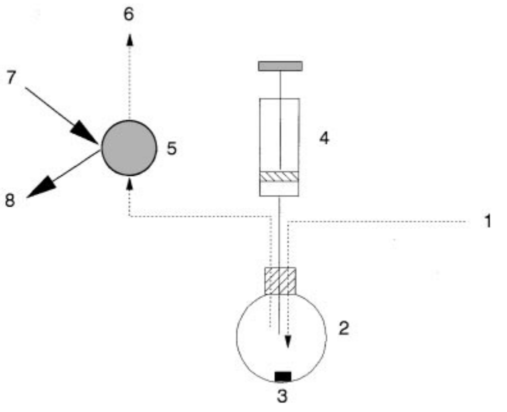

Fig. 1 Experimental set-up for calibration of the oxygen sensor. (1) Ar carrier gas; (2) exponential dilution flask; (3) magnetic stirrer; (4) injection syringe; (5) flow cell situated in spectrofluorimeter; (6) gas vent; (7) excitation light beam; (8) emission light beam. The dotted line shows the flow path of the Ar carrier gas.

Results and discussion

The Ru(II) complex adsorbed on silica gel shows a very strong and stable pink emission when excited by blue light and it is efficiently quenched by molecular O_2. The luminescence material displays strong emission at 604 nm when it is excited at 468 nm. Fig. 2 shows the typical response curve of the O_2 sensor when it is exposed to different volumes of injected air sample. Different air sample volumes cause different degrees of luminescence quenching on the O_2 sensor. It is found that the luminescence intensity drops sharply at first and exponentially recovers its intensity as the O_2 molecules continue to be carried away from the flow cell by the Ar carrier gas. This flow injection system gave rise to the formation of an O_2 sample plug which reached the flow cell with the exponential decay concentration profile illustrated in eqn. (2). Recording t, the concentration of O_2 gas reaching the flow cell at time t can be conveniently obtained.

The O_2 sensor data can be linearised by starting with the Stern–Volmer equation and rearranging the equation as follows:

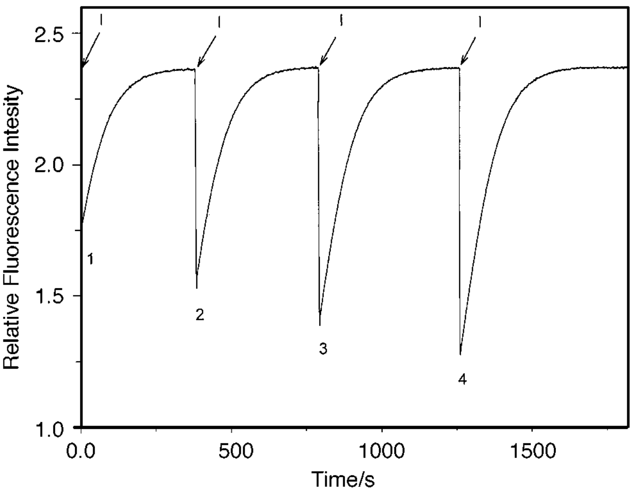

Fig. 2 Typical response curves of the oxygen sensor at excitation/emission wavelengths of 468/604 nm when subjected to various volumes of air sample injection. (I) Injection point; (1) 0.2; (2) 0.3; (3) 0.4; (4) 0.5 cm^3.

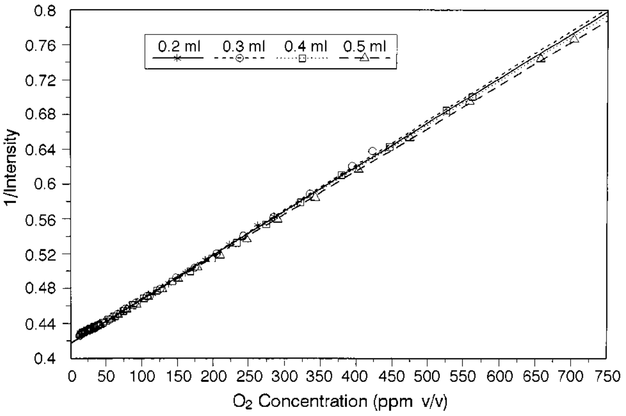

Fig. 3 Calibration plots for the oxygen sensor at various volumes of air sample injection.

$$I_0/I = 1 + k_{SV}\,[O_2]$$

$$1/I = 1/I_0 + (k_{SV}/I_0)\,[O_2] \qquad (3)$$

A linear calibration plot can now be generated by using the above equation and plotting the reciprocal of the luminescence intensity against the O_2 concentration, $1/I$ *versus* $[O_2]$. The corresponding linear plots are presented in Fig. 3 and the resulting regression coefficients are listed in Table 1 along with the computed r^2 values and the k_{SV} values. The results demonstrate the excellent linearity of this modified Stern–Volmer equation without recording the I_0 value. There was not much difference in the calibration curves on injecting air samples with volumes varying from 0.2 to 0.5 cm^3. The limit of detection is low. It was determined from eqn. (3) as the O_2 concentration which produced an analytical signal equal to three times the standard deviation of $1/I$ at zero value and was found to be 2.6–3.6 ppm v/v.

In order to validate eqn. (3), the most widely used Stern–Volmer [eqn. (1)] was also employed to calibrate the optical O_2 sensor. The relative luminescence intensity ratios I_0/I were plotted against the O_2 concentration and the results are displayed in Fig. 4. The statistical results of the calibration curves are given in Table 2. The Stern–Volmer quenching constants, k_{SV}, obtained from the calibration curves using eqns. (1) and (3) show excellent agreement. The advantages of the proposed method are that a single O_2 standard from the open air is adequate to calibrate the O_2 sensor and there is no need to prepare and use various standard O_2 gases. The I_0 value is not essential for calibration. In addition, the optical O_2 sensor developed is very sensitive to trace amounts of O_2 gas even at ppm levels.

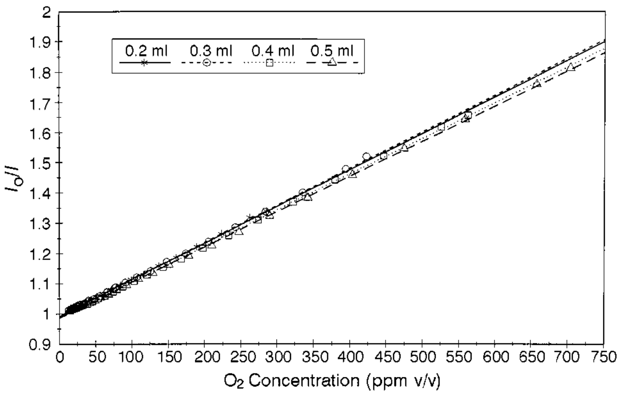

Fig. 4 Stern–Volmer plots for the oxygen sensor at various volumes of air sample injection.

The photostability of the O_2-sensitive material is extremely good. There was no sign of photodegradation when it was irradiated at 468 nm using a xenon lamp which was set at 70 W for 12 h. The luminescence intensity was stable throughout 12 h of exposure to excitation light. The long-term stability of the optical sensor is good since the analytical performance of the optical sensor did not show any change over a period of 6 months storage in a dry box. The typical response curves of the optical O_2 sensor at excitation and emission wavelengths of 468 and 604 nm, respectively, on exposure to different concentrations of gaseous O_2 are displayed in Fig. 5. The response time of the optical O_2 sensor is less than 0.2 s on going from 0.0 to 21% v/v O_2 and the recovery time is less than 1 s on reversing from 21 to 0.0% v/v O_2.

Conclusion

A modified Stern–Volmer equation combined with a single O_2 standard from the open air has been successfully applied to calibrate an O_2 sensor composed of tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ditetrakis(4-chlorophenyl)borate adsorbed on silica gel, which is capable of monitoring O_2 continuously. The ruthenium(II) complex adsorbed on silica gel possesses high photochemical stability and is not leached out by washing with organic solvents or aqueous solutions.[22] The

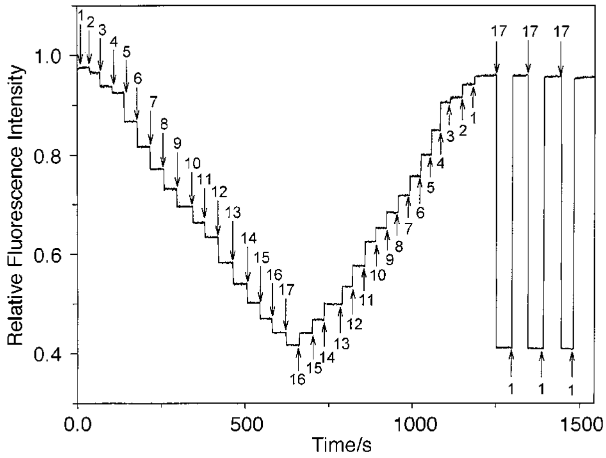

Fig. 5 Typical response curves of the oxygen sensor at excitation/emission wavelengths of 468/604 nm on exposure to different concentrations of gaseous oxygen standards. (1) 0.00; (2) 0.42; (3) 0.84; (4) 1.05; (5); 2.10; (6) 3.15; (7) 4.20; (8) 5.25; (9) 6.30; (10) 7.35; (11) 8.40; (12) 10.5; (13) 12.6; (14) 14.7; (15) 16.8; (16) 18.9; (17) 21.0% v/v.

Table 1 Linear regression analysis results for the oxygen sensor at various volumes of air sample injection using the modified Stern–Volmer eqn. (3)

Air injection volume (cm^3)	Slope × 10^{-4} (ppm^{-1})	*y*-intercept	r^2	*n*	k_{SV} × 10^{-4} (ppm^{-1})
0.2	5.084 ± 0.035	0.4169 ± 0.0004	0.9992	20	12.19 ± 0.10
0.3	5.133 ± 0.031	0.4171 ± 0.0006	0.9993	22	12.31 ± 0.09
0.4	5.023 ± 0.024	0.4178 ± 0.0006	0.9995	24	12.02 ± 0.07
0.5	4.936 ± 0.019	0.4178 ± 0.0005	0.9996	26	11.81 ± 0.06

Table 2 Linear regression analysis results for the oxygen sensor at various volumes of air sample injection using the Stern–Volmer eqn. (1)

Air injection volume (cm^3)	Slope × 10^{-4} (ppm^{-1})	*y*-intercept	r^2	*n*	k_{SV} × 10^{-4} (ppm^{-1})
0.2	12.11 ± 0.082	0.9927 ± 0.0011	0.9992	20	12.11 ± 0.08
0.3	12.21 ± 0.075	0.9923 ± 0.0014	0.9993	22	12.21 ± 0.08
0.4	11.87 ± 0.057	0.9876 ± 0.0013	0.9995	24	11.87 ± 0.06
0.5	11.67 ± 0.046	0.9880 ± 0.0013	0.9996	26	11.67 ± 0.05

sensor shows high photostability and a long lifetime. It does not show hysteresis, as shown in Fig. 5. The optical sensor should also be able to be easily adapted for remote measurements by using fibre optics in future developments.

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