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Optical sensor for sulfur dioxide based on fluorescence quenching

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Abstract

A series of potential indicator dyes is evaluated for use in the development of optical sensors for measuring sulfur dioxide in gaseous samples. Rhodamine B isothiocyanate is selected on the basis of relative sensitivity to dynamic quenching by sulfur dioxide and oxygen. A solid-state fluorometer is described for monitoring the sulfur dioxide induced fluorescence quenching of sensing membranes composed of silicone and rhodamine B isothiocyanate. A modulated blue LED is coupled with the lock-in detection of a photodiode detector to provide high signal-to-noise ratios. The limit of detection is $0.114 \pm 0.009\%$ for sulfur dioxide in a carrier stream of nitrogen gas. Selectivity measurements indicate no interference from several common gases (HCl, NH₃, NO, and CO₂). Oxygen alters the sensor response when comparing signals for sulfur dioxide in 0, 20 and 100% oxygen environments. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sulfur dioxide is a primary air pollutant. Major sources of environmental sulfur dioxide include power plants that burn high-sulfur coal, the paper and pulp industries, petroleum refineries, roasting of non-metallic ores, and the incineration of solid

waste, particularly hazardous and medical waste [1,2]. The toxicity of sulfur dioxide is well recognized. Concentrations of 5–10 ppm in air are recommended threshold limits for human exposure [3] and 2 ppm is the recommended limit for working environments [4]. In addition, sulfur dioxide contributes significantly to acid rain, thereby adversely affecting the biotic nature of both soil and water resources and eroding historic man-made structures [1].

Many analytical methods are reported for measuring sulfur dioxide either continuously or dis-

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creetly [5–13]. Chemical sensors are under development for sulfur dioxide with the goal of generating devices capable of real-time, remote monitoring. Examples of chemical sensors include: high-temperature solid electrolyte sensors that are capable of process gas control [14–16]; sensors based on changes in the dielectric properties of silicone membranes [17], and gas-sensing potentiometric electrodes with anion-selective internal sensing elements [18].

Optical sensors are reported for various gaseous species, including oxygen [19–22], carbon dioxide [23], ammonia [24], hydrogen sulfide [1] and sulfur dioxide [25–30]. Many of these sensors operate on the basis of fluorescence quenching where the target analyte decreases the luminescence of an immobilized indicator dye. Dynamic quenching is measured and related to analyte concentration through the well-known Stern-Volmer relationship [31]. Molecular oxygen quenches many of these dyes and, as such, represents a serious interference that must be removed before the analytical measurement [32–34]. The need to deoxygenate a sample prior to the measurement drastically reduces the utility of a method for real-time, remote analytical sensing.

We are interested in developing an optical chemical sensor for measuring sulfur dioxide emission in smokestacks during incineration of biomedical waste. The first step is to identify dyes that are strongly quenched by sulfur dioxide, yet unaffected by molecular oxygen. An evaluation of several candidate dyes identifies rhodamine B isothiocyanate as a prime candidate. Findings from our initial screening experiment are detailed in this report. In addition, the analytical response characteristics are established for the corresponding sulfur dioxide optical sensor. This sensor consists of a dedicated solid-state fluorometer coupled with the rhodamine B isothiocyanate indicator.

2. Experimental

2.1. Apparatus

Fluorescence spectra were collected by using a SLM Aminco SPF 500C spectrometer equipped

with a 250 watt xenon arc lamp. An OLIS (Bogart, GA) modified Cary 14 double beam spectrometer was used to collect all absorbance spectra. Fluorescence signals from sensing membranes were measured with either the SLM Aminco spectrometer or the custom built fluorometer described below.

2.2. Chemicals, reagents and hardware

The following fluorescent dyes were purchased from the indicated supplier: (1) rhodamine B isothiocyanate (Sigma Chemical, St. Louis, MO); (2) pyrene isothiocyanate (Molecular Probes, Eugene, OR); (3) perylene (Fluka, Ronkonkoma, NY); (4) 2-ethoxynaphthalene (Pfaltz and Bauer, Waterbury, CT); and (5) 1-aminoanthroquinone (Pfaltz and Bauer, Waterbury, CT). All solvents were obtained from common suppliers. Oxygen (99.8%), nitrogen (99.9%), sulfur dioxide (99.9%), hydrogen chloride (99%), ammonia (99.99%), nitric oxide (99%) and carbon dioxide (99.98%) were purchased from Air Products and Chemicals (Allentown, PA). All commercially obtained chemicals were used as received without further purification. Type I, reagent grade water was obtained by passing house distilled water through a Milli-Q three-house purification unit.

Hardware components for the solid-state fluorometer were purchased from common suppliers. Interference and dichroic filters were purchased from Edmond Scientific (Barrington, NJ), blue LED's were obtained from Nichia (Japan) and the VTP-1250 photodiode detector was purchased from GE&E (St. Louis, MO). In general, individual circuit elements were obtained from Newark Electronics (Chicago, IL), although the OPA 121K operational amplifiers were from Insight Electronics (Milwaukee, WI). The model 506 Protek digital multi-meter was from Cole Palmer (Vernon Hill, IL) and the Omnibook 5500CS computer was from Hewlett Packard (Wilmington, DE).

2.3. Procedures

2.3.1. Sensing membranes

1-Aminoanthraquinone, 2-ethoxynaphthalene, and perylene were immobilized in silicone mem-

branes by the procedure of Sharma and Wolfbeis [29]. Membranes with rhodamine B isothiocyanate and pyrene isothiocyanate were prepared from a casting solution prepared by first dispensing the dye in the silicone prepolymer, followed by adding toluene and mixing until the solution appeared homogeneous. In all cases, membranes were formed by dispensing a volume of casting solution onto the cleaned surface of a glass microscope slide. Solvent was allowed to evaporate under ambient conditions to produce sensing membrane layers with thicknesses on the order of 200 microns.

2.3.2. Membrane characterization

Glass slides with membranes were positioned along the diagonal inside a disposable polystyrene fluorescence cuvette. A two-hole rubber stopper was securely fitted into the top of the cuvette. Small glass tubes were placed in each hole to provide an inlet and outlet for flowing gases. For measurements taken with the SLM spectrofluorometer, the cuvette was mounted within the conventional cell holder which permitted surface fluorescence measurements from the sensing layer. For measurements taken with the custom fluorometer, the cuvette was mounted in a similar fashion as indicated schematically in Fig. 1.

Sensing membranes were characterized by monitoring the surface fluorescence as a function of time while exposing the immobilized fluorophore to different concentrations of selected gases. The required gas concentrations were obtained by mixing appropriate levels of the test gas with a nitrogen carrier gas. A Manostat 36-541-055 flow meter (New York, NY) was used to supply the correct amount of test gas to the nitrogen supply.

3. Results and discussion

Our development of a selective gas sensor for sulfur dioxide was carried out in two steps. First, a series of potential indicator dyes was screened with the goal of finding a dye that responds selectively for sulfur dioxide over oxygen. Results

from this screening experiment indicate that rhodamine B isothiocyanate is suitable for sulfur dioxide measurements. Secondly, the analytical response characteristics of membranes with rhodamine B isothiocyanate were established with the solid-state fluorometer described above.

3.1. Indicator screening

Seven unique indicator layers were evaluated as potential sensing chemistries for the selective measurement of sulfur dioxide over oxygen in gaseous samples. Five of these layers were composed of a single indicator, while two layers were composed of binary mixtures of indicators. Table 1 provides a listing of the tested indicator dyes along with the excitation and emission wavelengths used to monitor their luminescence. The excitation wavelengths correspond to absorbance wavelength maxima, which were taken directly from absorbance spectra. The emission wavelengths were taken from emission spectra collected with the SLM Aminco spectrofluorometer.

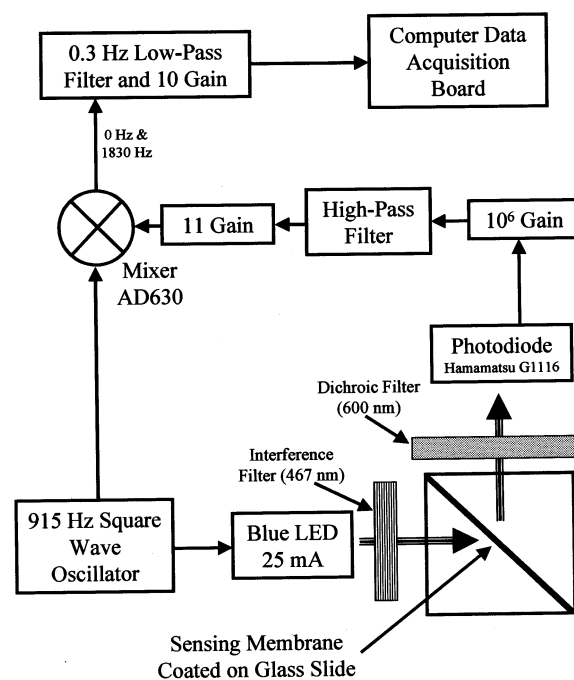


Fig. 1. Schematic representation of the solid-state fluorometer system, showing the sample holder configuration and a block diagram of the optic and electronic operation.

Table 1
Indicator layers and wavelengths for luminescence measurements

Indicator	Excitation wavelength (nm)	Emission wavelength (nm)
Pyrene isothiocyanate	435	510
Rhodamine B isothiocyanate	466	607
Perylene	433	497
1-Aminoanthraquinone	479	594
2-Ethoxynaphthalene	300	356
Perylene and 1-aminoanthraquinone	419	464
Perylene and 2-ethoxynaphthalene	407	465

The selected indicator dyes were initially screened by comparing the degree of fluorescence quenching measured for sulfur dioxide and oxygen. These screening measurements were performed in the SLM Aminco spectrofluorometer and the surface fluorescence intensity was recorded continuously as a function of time. Initially, a baseline fluorescence reading was recorded by exposing the test membrane to a carrier stream of pure nitrogen. The membrane was then exposed sequentially to higher percentages of sulfur dioxide in the nitrogen carrier stream and the steady-state fluorescence signals were recorded at each step. The gas stream was switched back to pure nitrogen and a second baseline signal was recorded. Similarly, the test membrane was exposed sequentially to higher levels of oxygen in the nitrogen carrier stream. For sulfur dioxide, membranes were exposed to five concentration levels between the range of 0.3–6%. Concentration levels of oxygen were greater and ranged between 20 and 100%.

The resulting intensity values were plotted in a typical Stern-Volmer manner ($(I_0/I - 1)$ versus percentage of the test gas). Linear regression analysis was used to compute the slopes (or Stern-Volmer constants) for these individual plots. Magnitude of the resulting Stern-Volmer con-

stants for sulfur dioxide and oxygen were taken as a measure of the relative sensitivity of the immobilized dye to sulfur dioxide and oxygen, respectively. The measured Stern-Volmer constants are tabulated in Table 2 for each of the tested indicator layers.

Sulfur dioxide quenched the fluorescence of each indicator layer. The highest degree of sulfur dioxide quenching was recorded for the combined mixture of perylene and 1-aminoanthraquinone. Unfortunately, the luminescence from this indicator layer was also quenched by oxygen, albeit to a much lesser extent. In fact, all the indicator layers that contained perylene responded to oxygen by essentially the same amount. Only layers composed of pyrene isothiocyanate, rhodamine B isothiocyanate, and 1-aminoanthraquinone demonstrate no response to oxygen under our experimental conditions. Of these, rhodamine B isothiocyanate possesses the highest sensitivity to sulfur dioxide. In addition, response and recovery times were rapid for the rhodamine B isothiocyanate layer and the preliminary Stern-Volmer plots were linear ($r^2 = 0.995$). The limit of detection was estimated as $0.52 \pm 0.02\%$ ($S/N = 3$) from these plots. For this reason, all subsequent experiments were performed with rhodamine B isothiocyanate.

Table 2
Stern-Volmer constants for the screened indicator dyes

Indicator	Stern-Volmer constant for sulfur dioxide ($\%^{-1}$)	Stern-Volmer constant for oxygen ($\%^{-1}$)
Pyrene isothiocyanate	0.100	0.000
Rhodamine B isothiocyanate	0.186	0.000
Perylene	0.250	0.007
1-Aminoanthraquinone	0.130	0.000
2-Ethoxynaphthalene	0.063	0.006
Perylene and 1-aminoanthraquinone	0.330	0.005
Perylene and 2-ethoxynaphthalene	0.250	0.005

3.2. Solid-state fluorometer

A solid-state fluorometer was built to facilitate data collection from the sensing membranes. This fluorometer is modeled after that reported by Hauser [35,36] and contains a modulated light emitting diode (LED) source and a solid-state photodiode detector. The schematic diagram in Fig. 1 illustrates the basic optical arrangement and general measurement configuration. In this design, the excitation radiation illuminates a portion of the sensing membrane by striking at a 45° angle relative to the membrane surface. The emitted luminescence is then detected 90° relative to the excitation beam. A 467 nm interference filter isolates the excitation radiation and a 600 nm dichroic filter isolates the emitted radiation before detection. This dichroic filter is attached directly to the detector housing to minimize stray source radiation from being detected. The source is a high intensity (1000 mcd) blue LED and the detector element is a Hamamatsu (G-1116) photodiode.

The basic circuitry to drive both the excitation and detection optics is taken from the work described by Hauser [35,36]. In our system, the LED source is modulated at a frequency of 915 Hz by using an LMC555 timer to generate a square-wave signal at 915 Hz. Output of the LMC555 drives a NPN transistor (2N3904) to switch the LED on and off. In addition, the LMC555 output is used as a reference signal for the multiplier circuit (AD630). Fluorescence from the sulfur dioxide sensitive membrane is detected by a photodiode and amplified by a transimpedance amplifier with a gain of 100 million. The signal is high pass filtered to remove any d.c. bias and amplified by an additional factor of eleven. The amplified signal is input into the AD630 where mixing occurs. The output of the AD630 provides signals at twice the input signal (1830 Hz) and d.c. A 0.3 Hz low-pass filter with a gain of ten provides the final output signal.

During normal operation, the fluorescence signal is continuously recorded as a function of time while gaseous samples are passed across the test membrane. The voltage is recorded by a Protek digital multi-meter interfaced with an Omnibook

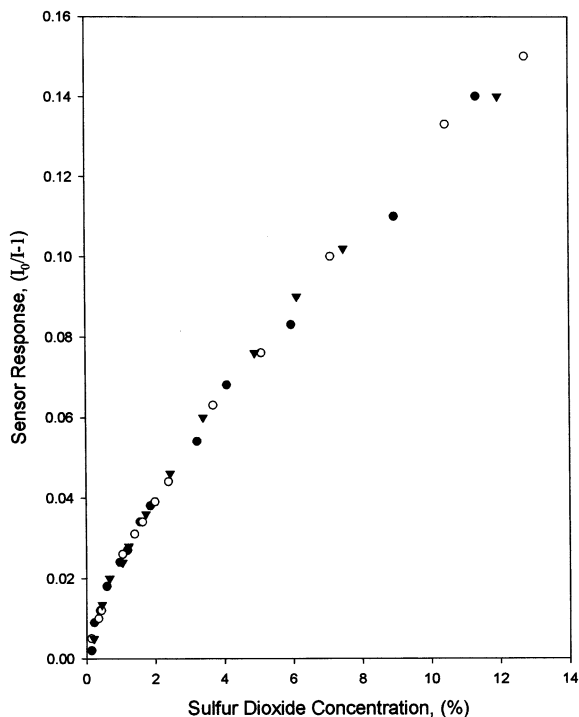


Fig. 2. Cumulative response curves for three sequential sensor responses to sulfur dioxide showing data for trial 1 (solid circles); trial 2 (open circles) and trial 3 (triangles).

portable computer. A typical signal-to-noise ratio (SNR) for the instrument was 6000 under baseline conditions. This SNR value corresponds to typical signal of 3.704 ± 0.0006 volts (mean ± 1 standard deviation) with pure nitrogen as the carrier gas.

3.3. Solid-state sulfur dioxide sensor

Sulfur dioxide sensors were constructed by placing membranes with rhodamine B isothiocyanate in the custom-built fluorometer described above. Typical sensor response curves for sulfur dioxide are illustrated in Fig. 2. This figure shows computed responses for three sequential calibrations over a sulfur dioxide concentration range from 0.01 to 12.8%. Computed values correspond to the typical Stern-Volmer transformation (response = $I_0/I - 1$) where I_0 and I correspond to the measured steady-state intensities in the absence and presence of the quenching agent, re-

spectively. As the data in Fig. 2 demonstrate, this transformation of the data results in a non-linear curve with greater sensitivity at lower sulfur dioxide concentrations. Such non-linearity is common for optical sensors based on fluorescence quenching when the indicator is entrapped within a polymeric membrane [37–39]. Heterogeneity within the membrane matrix is thought to be responsible for such responses. Nevertheless, responses to sulfur dioxide are both sensitive and reproducible with rhodamine B isothiocyanate entrapped within silicone.

A portion of the data in Fig. 2 was used to estimate the limit of detection for this sensing configuration. Responses at low concentrations of sulfur dioxide are essentially linear. As such, the limit of detection was estimated from the pseudo-linear region from 0 to 0.67% sulfur dioxide. Responses from the three data sets were combined for this purpose. Linear regression analysis over this region for the combined data points indicates an r^2 value of 0.9545 along with a slope of $3.079 (\pm 0.002) \times 10^{-20} \%^{-1}$ and a y -intercept of $-6.2 (\pm 9.6) \times 10^{-4}$. The corresponding limit of detection (SNR = 3) is $0.114 (\pm 0.009) \%$.

Time-dependent response properties are presented in Fig. 3. This figure shows a series of raw data presented in a signal versus time format. In this experiment, the sensor is initially exposed to blank carrier gas. A brief initialization period is required to obtain a steady-state baseline signal. After an initial steady-state signal is achieved, sulfur dioxide is added to the nitrogen carrier stream to a final concentration of 0.28% while the response is monitored. After a steady-state signal is achieved, the level of sulfur dioxide is increased to 0.43%, and so on as indicated by the concentration values presented above the arrows in Fig. 3. The sensor response is continually recorded as sequentially higher sulfur dioxide levels are introduced. After the response to 10.94% sulfur dioxide, the sensing membrane is exposed to pure nitrogen carrier gas and the baseline intensity (I_0) is measured. Finally, responses are presented while cycling the carrier gas from high to low sulfur dioxide levels.

The data in Fig. 3 demonstrate rapid response and recovery times for the rhodamine B isothio-

cyanate membranes. For both increases and decreases in the sulfur dioxide levels, steady-state responses were generally available within 30–60 s. In addition, the reproducibility of the baseline signal is illustrated by the data in this figure.

Selectivity of the rhodamine B isothiocyanate membrane was characterized in two ways. First, the membrane was exposed to varying levels of potentially interfering gases while monitoring sensor luminescence. Gases tested in this manner include hydrogen chloride, ammonia, nitric oxide and carbon dioxide. No changes in the luminescence signal of the rhodamine B isothiocyanate layer were noted for any of these gases. Hydrogen chloride, ammonia and nitric oxide were tested individually at levels up to 1%. Carbon dioxide was tested up to 12.4%. Again, none of these gases interferes with the signal.

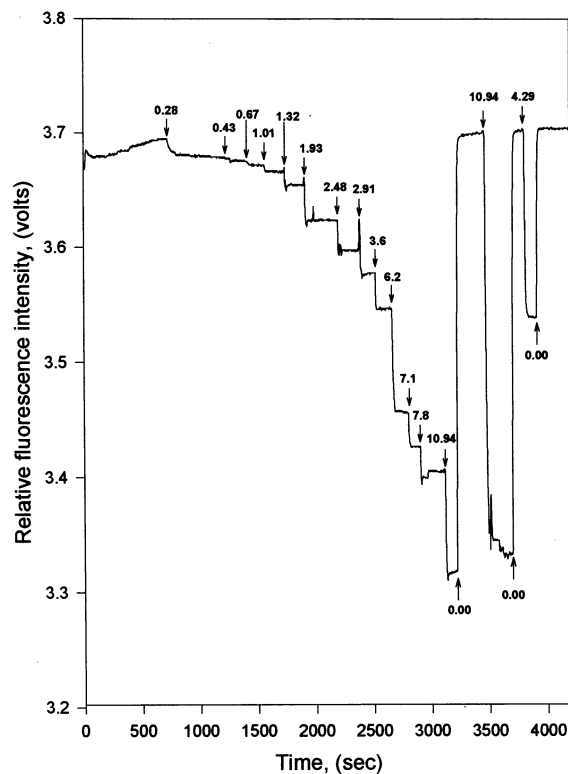


Fig. 3. Time profile showing dynamic response to different levels of sulfur dioxide. Arrows indicate point when the sulfur dioxide level was changed and the value associated with the arrow indicates the resulting level of sulfur dioxide in the nitrogen carrier gas.

Sensor selectivity was also tested by monitoring the sensor response to various levels of sulfur dioxide in the presence of oxygen. Responses to sulfur dioxide were recorded with air (20% oxygen) and 100% oxygen as the carrier gas and these responses were compared to those obtained with a pure nitrogen carrier gas. Although oxygen did not significantly quench the fluorescence in our initial screening experiment, subsequent results reveal a substantial effect by oxygen. Significantly lower responses are observed for a given sulfur dioxide level in the presence of oxygen. The extent of this interference can be judged by comparing Stern-Volmer constants computed for sulfur dioxide in the presence of 0, 20, and 100% oxygen in the carrier gas. Again, Stern-Volmer constants were computed over the pseudo-linear region from 0 to 1% sulfur dioxide, as discussed and identified above. The resulting values are 0.031 ± 0.002 ; 0.024 ± 0.003 and $0.022 \pm 0.007\%^{-1}$ for 0, 20 and 100% oxygen in the carrier stream, respectively. These values indicate a significantly lower response in the presence of oxygen. No significant differences are indicated, however, between responses in 20 and 100% oxygen. These results suggest that the proposed sulfur dioxide sensors must be calibrated in the presence of the expected level of oxygen to avoid systematic errors. These findings also suggest that measurement accuracy is relatively insensitive to small differences in ambient oxygen levels (i.e. no difference between 20 and 100% oxygen). This second point may be critical, as oxygen-independent calibrations may be possible over a well-defined oxygen concentration range.

4. Conclusions

Results from experiments described in this paper illustrate the feasibility of measuring sulfur dioxide levels in gaseous samples by fluorescence quenching. Membrane layers composed of rhodamine B isothiocyanate provide strong responses to sulfur dioxide even in the presence of high levels of molecular oxygen. The estimated limit of detection for sulfur dioxide is $0.114 \pm 0.009\%$. This level of performance is achieved by com-

bining rhodamine B isothiocyanate membranes with a dedicated solid-state fluorometer.

References

- [1] G.T. Miller Jr, Living in the Environment, Wadsworth Publishing Co, Belmont, CA, 1992.
- [2] B.L. Walker, C.D. Copper, J. Air Waste Manag. Assoc. 6 (1992) 784.
- [3] R.C. Weast (Ed.), Handbook of Chemistry and Physics, 55th edn., CRC Press, Cleveland, OH, 1975, p. D-90.
- [4] N.I. Sax, R. Lewis, Hazardous Chemical Desk Reference, Van Nostrand Publishers, New York, 1987.
- [5] J. Janak, Z. Vecera, Microchim. Acta 3 (1990) 29.
- [6] S.A. Al-Tamrarh, V. Townshend, A. Wheatley, Analyst 112 (1987) 883.
- [7] T.A. Arowolo, M.S. Cresser, Talanta 39 (1990) 1471.
- [8] J.P. Lodge, Methods of Air Sampling and Analysis, Lewis Publishers, New York, NY, 1989.
- [9] P.W. West, G.C. Gaeke, Anal. Chem. 28 (1956) 1816.
- [10] R.V. Nauman, P.W. West, F. Tron, G.C. Gaeke Jr, Anal. Chem. 32 (1960) 1307.
- [11] F.P. Scaringelli, B.E. Saltzman, S.A. Frey, Anal. Chem. 39 (1967) 1709.
- [12] G. Schiavon, G. Zotti, R. Toniolo, G. Bonempelli, Analyst 116 (1991) 797.
- [13] M.S. Black, R.P. Herbst, D.R. Hichcock, Anal. Chem. 50 (1978) 848.
- [14] J.M. Skaef, A.A. Dubreuil, Sensors and Actuators 10B (1993) 161.
- [15] Y. Yan, Y. Shimizu, N. Miura, N. Yamazoe, Chem. Lett. (1992) 635.
- [16] T. Maruyama, Mat. Sci. Eng. 146A (1991) 81.
- [17] H.-E. Enders, L.D. Mickle, C. Kosslinger, S. Dors, F. Hutter, Sensors and Actuators 6B (1992) 285.
- [18] M.E. Meyerhoff, D.M. Pranita, H.S. Kim, N.A. Chanio-takis, S.B. Park, ACS Symposium Series 403, Chemical Sensors and Microinstrumentation, 1989, pp. 26–43.
- [19] M.E. Cox, B. Dunn, SPIE 576 (1985) 60.
- [20] J.R. Bacon, J.N. Demas, Anal. Chem. 59 (1987) 278.
- [21] A. Sharma, O.S. Wolfbeis, Appl. Spectro. 42 (1988) 609.
- [22] C.A. Parker, W.T. Rees, Analyst 85 (1960) 587.
- [23] G. Orellana, M.C. Moreno-Bondi, E. Segova, D. Marazuela, Anal. Chem. 64 (1992) 2210.
- [24] A. Sharma, A. Zulfiquar, I. Higgins, SPIE 1637 (1992) 107.
- [25] M. Kuratli, E. Pretsch, Anal. Chem. 66 (1994) 85.
- [26] R.L. Cook, R.C. Macduff, A.F. Sammells, Anal. Chim. Acta 226 (1989) 153.
- [27] A. Sharma, O.S. Wolfbeis, Spectrochim. Acta B (1987) 1417.
- [28] A. Sharma, O.S. Wolfbeis, Anal. Chim. Acta 208 (1989) 53.
- [29] A. Sharma, O.S. Wolfbeis, SPIE 990 (1989) 8.
- [30] A. Sharma, A. Zulfiquar, D. McStay, SPIE 1637 (1992) 280.

- [31] J.D. Ingle Jr, S.R. Crouch, *Spectrochemical Analysis*, Chapter 12, Prentice Hall, Englewood Cliffs, NJ, 1988.
- [32] M.E. Rollie, C.N. Ho, I.M. Warner, *Anal. Chem.* 55 (1983) 2445.
- [33] M.E. Rollie, G. Patonay, I.M. Warner, *Anal. Chem.* 59 (1987) 180.
- [34] S. Matsuzawa, A. Wakisaka, M. Tamura, *Anal. Chem.* 62 (1990) 2654.
- [35] P.C. Hauser, S.S.S. Tau, *Analyst* 118 (1993) 991.
- [36] P.C. Hauser, C.L.C. Liang, B. Muller, *Meas. Sci. Technol.* 6 (1995) 1081.
- [37] E.R. Carraway, J.N. Demas, B.A. DeGraff, *Anal. Chem.* 63 (1991) 332.
- [38] J.N. Demas, B.A. DeGraff, *SPIE* 1981 (1992) 2.
- [39] J.N. Demas, B.A. DeGraff, W. Xu, *Anal. Chem.* 67 (1995) 1377.