An organopalladium-PVC membrane for sulphur dioxide optical sensing

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Abstract

The development of a sensing membrane for the determination of gaseous sulphur dioxide is described. An organopalladium complex, Pd₂(dpm)₂Cl₂ (dichloro-bis-(diphenylphosphine)-methane dipalladium I), was immobilised in a poly(vinyl chloride) thin film plasticised with ortho-nitrophenyloctylether (o-NPOE). Several membranes were prepared, using 20, 25 and 30% of PVC, 1, 5 and 8% of palladium complex and enough o-NPOE to make a total of 100 mg, which was dissolved in 1.0 mL of THF. The sensing membranes were obtained by manual deposition of 10, 15 and 20 μL of the solution onto cellulose acetate films, which were left to dry for 24 h and then stored in a desiccator sheltered from ambient light. The membrane was placed in an acrylic flow cell, in which the common end of a bifurcated optical fibre bundle was adapted and placed 1 mm from the membrane. Reflectance measurements were performed from 400 to 800 nm, after exposing the membrane to 0 to 500 ppmv of SO₂ in air, at a flow rate of 500 mL min⁻¹. The membrane composed of 20% PVC, 72% o-NPOE and 8% palladium complex showed the best performance and the film prepared from 20 μL of solution provided the highest signal (ca 160 mV upon exposure to 500 ppmv SO₂). Measurements made at 530 nm showed a linear response range up to 300 ppmv, with a detection limit of 3.5 ppmv. By employing a flow rate of 500 mL min⁻¹, response times (t₉₀%) of 3 and 2 min were obtained for reaction of the membrane with SO₂ and for reverse response upon exposure to dry nitrogen, respectively. Although the palladium complex also reacts with carbon monoxide in solution, this interference was not observed for concentrations up to 1000 ppmv of CO. The membrane showed a lifetime of ca. 2 months when stored in a desiccator.

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1. Introduction

Sulphur dioxide is the most common sulphur pollutant species in air. Sulphur oxides are produced when fuel containing sulphur (such as coal and oil) is burned, during metal smelting, by the paper industry, petroleum refining and by incineration of solid waste. Natural sources of sulphur oxides include swamps, oceans and volcanoes. The toxic effects of sulphur dioxide are well known, causing many respiratory problems. SO₂ is one of the major contributors to acid rain, which can cause acidification of soils and aquatic bodies, besides damaging vegetation. In addition, sulphur dioxide is the main precursor of aerosols and the main pollutant that impairs visibility [1,2]. Therefore, the monitoring of sulphur dioxide in air is of special importance for pollution control and efforts to develop methods of analysis and sensors to carry out this task are required.

Conventional methods for determination of sulphur dioxide in air are based on its collection in aqueous solution, followed of conversion to sulphite, which can be measured spectrophotometrically or electrochemically. For pollution control, however, sensors are frequently preferred, as they permit continuous, real-time monitoring. A variety of optical and electrochemical sensors have been proposed for sulphur dioxide determination. Among electrochemical sensors, those based on amperometric detection, which employs chemically modified electrodes, are probably the most popular [3–6]. Quartz crystal microbalances have been also emi...
ployed for developing SO$_2$ sensors, by using a selective coating on the surface of a piezoelectric crystal [7,8]. Despite their selectivity and detectability, these kinds of sensors are prone to electronic and electromagnetic interferences, which do not influence optical sensors.

Optical sensors for detection of gaseous species, such as ammonia [9], humidity [9,10], oxygen [11], carbon dioxide [12] and nitrogen oxides [13,14], have been frequently described in the literature. For determination of sulphur dioxide, as well as of sulphite, sensors based on absorbance [2,15,16], fluorescence quenching [17], chemiluminescence [18] and phosphorescence [19] have been proposed. Kurati and Pretsch [2] have developed plasticised PVC membranes based on a hydrogen ion-selective chromoionophores. Ordinary membranes respond only to humid SO$_2$, while those that additionally contain lipophilic alcohol or are made of hydroxylated PVC also respond to dry SO$_2$. Selectivity and sensitivity are enhanced by incorporating a lipophilic aldehyde into the membrane, although the response time is increased from 0.5 min to 10–20 min. Repeatability was evaluated by performing several absorbance measurements, providing a relative standard deviation better than 1.2%. Stangelmayer et al. [15] have described various sensing phases for determination of dissolved and gaseous SO$_2$ based on the immobilisation of lipophilic pH indicator ion pairs in silicone and phenyl substituted Ormosil. Membranes with response times lower than 1 min, presenting a detection limit of 1.0 $\times$ 10$^{-8}$ mol L$^{-1}$, with no cross-sensitivity to pH and CO$_2$, were prepared. Recently, Marcos et al. [16] proposed an optical sensor for sulphite based on polyaniline film chemically polymerised on a polyester support, which was subsequently covered by a silicone film. The sensor was not fully reversible, being useful for a few measurements in low-concentrate sulphite sample solutions ($<$0.5 mg L$^{-1}$), but presented a linear response from 0.025 to 1.50 mg L$^{-1}$, with a stabilisation time of 210 s. Razez et al. [17] have studied various indicator dyes which can be quenched by sulphur dioxide and not by oxygen. Rhodamine B isothiocyanate showed proper characteristics, providing a sensor with a response time of 30–60 s, a detection limit of 0.114 $\pm$ 0.009%, presenting no interference of HCl, NH$_3$, NO and CO$_2$. Lin et al. [18] have developed a chemiluminescent sensor for sulphite by employing tris(2,2'-bipyridyl)ruthenium(II) immobilised on the cationic ion-exchange resin Dowex 50W-X2, which was shown to be stable for at least 6 months, presenting a detection limit of 1.0 $\times$ 10$^{-7}$ mol L$^{-1}$. Papkovsky et al. [19] developed a phosphorescent probe based on a platinum(II) complex of coproporphyrin-I and bovine serum albumin immobilised on a Biodyne ABC membrane for detection of sulphite in solution, with a detection limit of 10 $\mu$mol L$^{-1}$.

The present work reports the development of a sensing membrane for direct determination of gaseous sulphur dioxide by immobilising an organopalladium(II) complex in a plasticized poly(vinylchloride) thin film.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. High molar mass poly(vinylchloride) (PVC, Aldrich), ortho-nitrophenoxyctylether (o-NPOE, Fluka) and tetrahydrofuran (THF, Merck) were used as purchased. The Pd(I) complex, Pd$_2$(dpm)$_2$Cl$_2$, (dichloro-bis-(diphenylphosphino)-methane dipalladium-I), was synthesised as described by Gimenez and Alves [20]. Working gas standards were prepared by proper mixing of a 500 ppm, SO$_2$ standard (balanced in nitrogen) and high purity nitrogen (White Martins).

2.2. Preparation of the membranes

Stock solutions for casting the membranes were prepared by dissolving a total of 100 mg of membrane components (palladium complex, PVC and o-NPOE) in 1.0 ml of THF. Several membranes were prepared, using 20, 25 and 30% of PVC; 1, 5 and 8% of palladium complex and enough o-NPOE to make a total of 100 mg. The sensing membranes were obtained by manual deposition of 10, 15 and 20 $\mu$L of the solution onto cellulose acetate films, which were left to dry for 24 h and then stored in a desiccator sheltered from ambient light. For measurements, a membrane was placed in an acrylic flow cell, whose bottom was covered with a reflective aluminium foil to improve signal intensity.

2.3. Instrumentation

The instrumentation consisted of a radiometric source (Oriel 68830) with a halogen/tungsten lamp (12 V, 50 W), whose radiation was modulated at (190 $\pm$ 1) Hz by an optical chopper (Oriel 75,152) and focused onto one branch of a bifurcated optical fibre bundle (Oriel 77,565). The radiation light from the source was guided through the optical fibre to the flow cell, the reflected radiation was conducted by the other branch of the bundle and focused onto the entrance slit of a monochromator (Oriel 77,250). The radiation intensity was measured by a photomultiplier tube (Oriel 77,340), connected to a lock-in amplifier (Stanford Research Systems SR 510), synchronised with the chopper frequency. A microcomputer was employed to control the monochromator and the lock-in amplifier through an ACL-8111 parallel interface (Advantech) and a RS232 serial interface, respectively.

2.4. Flow set up and procedure

Two manual flow controllers (0–500 mL min$^{-1}$) were employed to mix the SO$_2$ standard gas (500 ppmv) and pure N$_2$ at different ratios for preparing standard mixtures from 0 to 500 ppmv of SO$_2$. PTFE tubing was used to construct the lines to mix the gases and to conduct the mixtures towards the flow cell. A total flow rate of 500 mL min$^{-1}$ was employed throughout.
Reflectance measurements were made from 400 to 800 nm, after exposing the sensing phase to the gas mixture for a pre-set interval of time.

3. Results and discussion

3.1. Sensing principle

The palladium complex structure contains reactive metal-metal bonds. The crystal structures of two of these complexes reveal that the two metal atoms are connected by direct single bonds. The coordination geometry about each metal is approximately planar but the two metal coordination planes are twisted, so that the dihedral angles between the planes are about 39° [21–23]. Sulphur dioxide and other molecules, such as carbon monoxide and isocyanides, insert into the metal-metal bond, moving the metal centres about 0.5 Å apart and breaking the formal metal-metal bond [22]. As a consequence, the optical properties of the complex are changed, which can be measured spectrophotometrically. This process is shown in Fig. 1, while Fig. 2 shows the spectra of the complex obtained in dichloromethane solution, after bubbling N₂ and 500 ppm SO₂. The molar absorption coefficients for the free complex and after reacting with SO₂ were estimated as 6600 (at 416 nm) and 3400 (at 509 nm) L mol⁻¹ cm⁻¹, respectively.

3.2. Study of the membrane composition

The membrane characteristics were evaluated by varying the concentrations of their constituents (polymer and plasticiser) as well as the concentration of the palladium complex, aiming at obtaining the best response. For the preparation of the solutions, from which the membranes are cast, the solids components (PVC and palladium complex) were first dissolved in the THF solvent, before the addition of the α-NPOE. Different from the usual procedure, in which all components are mixed together before adding THF solvent, in the present work it was necessary to add the plasticiser at the end, because the Pd(I) complex dissolves preferably into α-NPOE, causing a phase separation if it was added before THF. As a consequence, heterogeneous membranes was obtained, in which the sensing reagent was mostly dispersed in the plasticiser. High molecular mass PVC (>100,000) was tested as the immobilisation matrix due to its adequate mechanical properties [24].

The first membrane studied was based on the procedure proposed by Wang and Meyerhoff [25] and 20/3.15 solution containing 30% PVC, 69% of α-NPOE and 1% palladium complex were employed. This membrane did not react with standard SO₂ mixtures, only with the pure gas. This fact can be probably attributed to the low solubility of SO₂ in the membrane, although the concentration of the plasticiser was close to those usually employed. In addition, due to the low concentration of the Pd(I) complex in the PVC matrix, the intensity of the reflected radiation was very low. Therefore, different compositions of the membrane were tested, increasing the concentrations of the organometallic complex and of the plasticiser (with the consequent decrease in the PVC concentration). By increasing the concentration of the Pd(I) complex, the difference between the signals generated by the membrane under N₂ and SO₂ atmospheres is increased, leading to a more sensitive sensing phase. Fig. 3 summarises the behaviour of the membrane as a function of its composition. The spectra are shown as the difference between the signals obtained after exposing the membrane to nitrogen (used as reference) and to sulphur dioxide. Although the maximum difference in solution occurs around 510 nm (Fig. 2), when the Pd complex is immobilised in PVC, there is a shift to longer wavelength and the maximum difference between the intensities of the spectra occurs around 530 nm. As can be seen in Fig. 3a, more intense signals are obtained by using 8%
Fig. 3. Reflectance spectra of the Pd_2(dpm)_2Cl_2 complex immobilised in PVC matrix containing (a) 30% PVC and (b) 8% Pd(I) complex after exposure to 500 ppmv SO_2.

Pd_2(dpm)_2Cl_2, which is the maximum concentration allowed due to the solubility of the complex in the cocktail mixture. These spectra were obtained with membranes constituted by 30% PVC and different concentrations of α-NPOE (75 and 72% for membranes prepared with 5 and 8% of Pd complex, respectively). Fig. 3b shows the effect of the concentrations of PVC and α-NPOE on the signal generated by membranes prepared with 8% Pd(I) complex. The solubility of SO_2 in the membrane is increased as the concentration of PVC is decreased, therefore the most intense signal was obtained by using 20% of PVC and 72% of α-NPOE. It is important to note that the reflectance maximum is shift to longer wavelengths as the concentration of α-NPOE is increased, demonstrating that the medium in which the SO_2 gas is dissolved also affect the energy of the electronic transition, as well as the immobilisation of the complex.

Once the best composition of the membrane was defined, the volume of solution deposited onto the cellulose acetate support to cast the sensing phase film was varied (10, 15 and 20 μL). As shown in Fig. 4, the thickest membrane (prepared with 20 μL) provided the most intense signal, and it was then employed throughout the remainder of the work, even though it presented the longest response time.

3.3. Sensor performance

Fig. 5 shows the analytical signals, measured at 530 nm, obtained when the membrane was exposed to SO_2 gas standards flowing at 500 mL min^{-1}. The membrane presented a reversible behaviour, with a response time (t_{90%}) of 3 min for reaction and 2 min for reverse response upon exposure to dry nitrogen. The sensor showed a linear response range up to 300 ppmv of SO_2, with a detection limit 3.5 ppmv (calculated as 3σ_{blank}/slope). An analytical curve from 0–300 ppmv SO_2 ($r^2 = 0.994$) is shown in Fig. 6, also demonstrating the precision obtained in the measurements. Although the palladium complex also reacts with carbon monoxide in CH_2Cl_2 solution, this interference was not observed for concentrations up to 1000 ppmv of CO, which can be explained based on the permeability of the PVC membrane to these gaseous
species. Finally, the membrane showed a lifetime of ca. 2 months when stored in a desiccator.

4. Conclusion

The present work describes a simple and reproducible method for preparation of PVC membranes using a palladium complex. This membrane shows great potential to be used for SO\textsubscript{2} monitoring in a polluted environment. The best results were obtained with a membrane whose composition was 8% Pd(I) complex, 20% PVC and 72% o-NPOE (w/w), cast from 20 \mu L of THF solution. The membrane presented a good performance, with a detection limit of 3.5 ppm, The interference of CO, which reacts with Pd\textsubscript{2}(dpmp\textsubscript{2})Cl\textsubscript{2} in solution, was avoided. Experiments have been carried out in our laboratory demonstrating that the membrane can respond to carbon monoxide if higher concentration of plasticiser is used, which might lead to a sensor for simultaneous determination of these species.

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