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Optical sensors for dissolved sulfur dioxide

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Abstract Colorimetric sensing membranes for the determination of sulfur dioxide were developed and characterized. These films can be used for sensing trace amounts of sulfur dioxide both in the gas phase and in aqueous solutions. Lipophilic pH indicator ion pairs were immobilized in hydrophobic gas-permeable silicone and phenyl substituted ormosil. On exposure to SO₂ the films undergo a visually detectable color change from blue to yellow. No cross-sensitivity to pH and CO₂ was observed. Response times depend on the thickness of the sensing membranes, the indicator concentration in the film as well as on the respective SO₂ concentration. Membranes with response times of < 1 min (t_{90}) were developed. The sensitivity to sulfur dioxide depends on the pK_a of the indicator. An increase in the pK_a results in a lower detection limit. The new optical SO₂ sensors are chemically and mechanically stable and are easy to manufacture. The storage stability of the membranes is at least 7 months if stored in the dark.

Introduction

Sulfur dioxide is a widely used reagent for food preservation. It is an effective preservative against yeast in fruit juice, dried fruit and wine. Free sulfur dioxide is useful for maintaining wine quality but its content decreases due to binding reactions with carbonyl compounds. A periodic addition of sulfur dioxide to wine is essential to maintain an appropriate concentration of free sulfur dioxide during fermentation and storage. A simple tool for continuous control of free SO₂ is necessary to optimize such kind of process.

Sulfur dioxide can be detected via spectrometric [1–9] or electrochemical methods [10–16], mass-sensitive sen-

sors [17] or gas chromatography [18]. In literature optical sensors based on luminescence-quenching were described [19, 20]. Solid state SO₂ electrodes have been described as well [21].

In this work highly sensitive colorimetric films for sensing of dissolved and gaseous SO₂ are presented. The new materials are useful to develop SO₂ optodes as well as test strips for the rapid estimation of the SO₂ content in wine, beverages and foods.

Experimental

Chemicals and reagents. Tridodecylmethylammonium chloride (TDMA-Cl), tetraoctylammonium chloride (TOA-Cl), cetyltrimethylammonium chloride (CTA-Cl), tetraoctylammonium hydroxide (TOA-OH), and phenyltriethoxysilane were from Fluka (Buchs, Switzerland). Bromothymol blue as sodium salt (BTB), bromocresol purple as sodium salt (BCP) and bromophenol blue as sodium salt (BPB) were from Aldrich (Steinheim, Germany). The silicone prepolymers Elastosil N10 and silicone A07 were from Wacker (München, Germany). Sulfur dioxide in nitrogen gas (250 mg m⁻³ SO₂) was from Linde AG (Regensburg, Germany). All buffer components and sodium salts of the respective anions were from Merck (Darmstadt, Germany). A polyester foil (125 µm, Goodfellow, Cambridge, UK) was used as support for the sensing films.

Preparation of the ion pairs. CTA and TDMA salts of the sulfonphthalein dyes were prepared by dissolving 500 µmol of the sodium salt of the respective indicator in 40 mL of distilled water. Diluted HCl (0.1 M) was added to protonate the indicators (color change from blue to orange). 500 µmol CTA-Cl (dissolved in 10 mL of water) or TDMA-Cl (dissolved in 10 ml of acetone) were added to the indicator solution. The ion pairs formed were extracted with dichloromethane. The solvent was removed from the combined organic extracts under vacuum, and the residue was dried in a desiccator over NaOH.

Preparation of the ormosil. For preparation of the ormosil 25 mL of phenyltriethoxysilane were dissolved in 25 mL of ethanol. Then 5.5 mL of 0.15 M HCl were added and the mixture was stirred in a water bath for 2.5 h (60 °C). The solution was pored into 200 mL of cold water. A honey-like prepolymer was formed at the bottom and was separated from the water phase. The prepolymer was dried at 200 °C for 1 h. The glassy material is soluble in chloroform, toluene and other organic solvents.

Dedicated to the memory of Professor Dr. Robert Kellner

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Table 1 Compositions of the cocktails used for making sensing membranes

Membrane number	Thickness ^a [μm]	Indicator	Matrix type [mg]	Solvent [μL]	Dye molality [mmol kg ⁻¹]	Base-to-indicator ratio ^b
M1	40	BTB-CTA	A 07 silicone 500	CHCl ₃ 500	2	6.7
M2	40	BTB-TDMA	A 07 silicone 500	toluene 500	4	3.4
M3	20	BTB-TDMA	ormosil ^c 500	toluene 500	4	3.4
M4	100	BCP-CTA	N 10 silicone 500	CHCl ₃ 500	4	1.7
M5	100	BCP-CTA	A 07 silicone 500	CHCl ₃ 500	2	3.4
M6	20	BPB-CTA	A07 silicone 500	toluene 500	1	no base

^a before solvent evaporation and curing of the membrane

^b TOAH was used as the base in all cases

^c prepolymerized phenyltriethoxysilane

Cocktail and membrane preparation. The compositions of the sensing membranes are described (in terms of their molalities and the base-to-indicator ratios) in Table 1. The molality is defined as the amount of indicator ion-pair per kilogram of matrix material. Toluene or chloroform were used to dissolve the indicator ion-pair, the silicone prepolymer or the ormosil. In case of BTB and BCP, TOA-OH was added to the indicator/polymer solution to stabilize the indicators in the deprotonated form. Membranes containing BPB were prepared without TOA-OH. The indicator concentration in the sensing membranes varied from 1 to 4 mmol kg⁻¹, and the TOA-OH/indicator ratio from 1 to 7. The mixtures were cast onto a polyester film in a thickness of 20 to 100 μm. The final thickness of the cured films varied from 10 to 40 μm. The films were cured in humid air at room temperature for at least 48 h. They were stored in a desiccator to protect them from acidification by volatile acids like HCl. The sensing membranes were blue and transparent and showed no inhomogeneities.

Preparation of sulfur dioxide solutions. Solutions with a defined SO₂ content were prepared by dissolving sodium hydrogensulfite in a Sørensen citrate buffer. The buffers were prepared by diluting 21.0 g citric acid and 8 g of sodium hydroxide in 1000 mL of distilled water and adjusting the pH with 0.1 M HCl.

Concentrations of free SO₂ were calculated using the following equation:

$$[\text{SO}_2] = 10^{(\text{pK}_a - \text{pH})} \cdot [\text{HSO}_3^-]$$

The pK_a of H₂S₂O₃ is 1.8 at T = 25 °C.

1 mg L⁻¹ (1 ppm) corresponds to 1.56 · 10⁻⁵ mol L⁻¹ SO₂.

The buffer solution was purged with nitrogen for at least 2 h to remove dissolved oxygen before sodium sulfite was added. SO₂ standard solutions were freshly prepared before each measurement and used within 4 h to avoid errors caused by sulfate formation.

Instrumentation for optical measurements. Absorption measurements were performed with a spectrophotometer (Perkin Elmer, Lambda 14 P). The membrane was fixed in a flow-through cell with a volume of 62 μL. Calibration solutions were passed through the flow-through cell at a flow rate of 1.5 mL min⁻¹. For measurements in the gas phase defined SO₂ concentrations were adjusted with a gas blender (Scott Speciality Gases, P.N. 52-31B-4-44) mixing nitrogen and diluted SO₂ (250 mg m⁻³ SO₂ in nitrogen). All measurements were performed at room temperature.

Results and discussion

Selection of polymer matrix. Due to its high permeability for gases, silicone is the preferred matrix material for optical gas sensors. It guarantees short response times and a high sensitivity. In addition, silicone is impermeable to

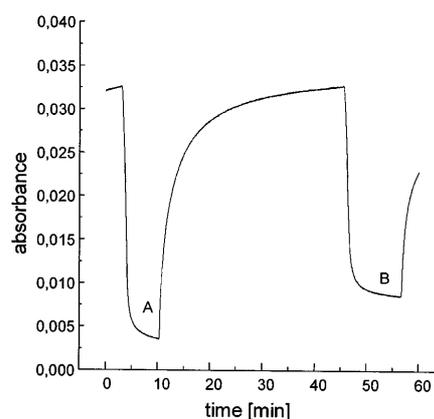


Fig. 1 Response of sensing membrane M3 to dry sulfur dioxide in nitrogen gas mixture with a concentration of 250 mg m⁻³ SO₂ (A) and 125 mg m⁻³ SO₂ (B)

ionic species, including protons or heavy metals and acts as a barrier to potentially interfering species. Therefore, the sensor membrane is not affected by changes in pH or ionic strength of the sample solution. Good optical transparency and no significant swelling in water are other important criteria. Silicone is chemically inert and shows good adhesion to polyester and glass.

As alternative matrix a soluble phenyl substituted sol gel (ormosil) was evaluated. Due to its porous structure the ormosil has a high gas permeability. In addition, the solubility of the lipophilic ion pairs in the ormosils is even higher than in silicone (up to 30 mM). With the ormosil, it was possible to manufacture very thin and mechanically stable films (10 μm). They showed fast response times (M3, Fig. 1). The membranes were hard, transparent and showed no inhomogeneities. The ormosil offers a good alternative to silicone as matrix. Presently this matrix material is investigated in detail.

Selection of indicators. Sulfonphthalein dyes were selected as the most suitable indicators for sulfur dioxide sensing, since they undergo a well detectable color change from blue to yellow in case of protonation (Fig. 2). They are commercially available with pK_a values from 3.8 to

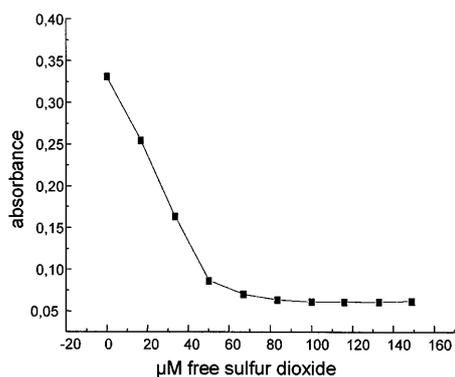


Fig. 4 Calibration curve of membrane M2 for SO₂ in a 0.1 M citrate buffer solution of pH 3.8

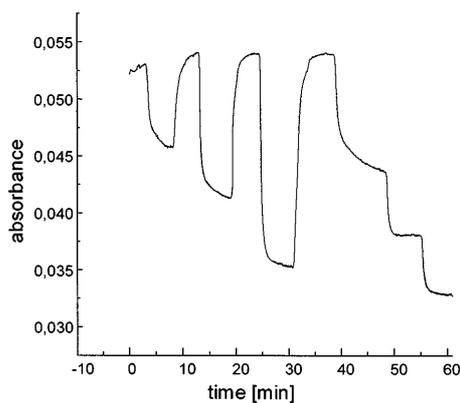


Fig. 5 Response of conditioned membrane M6 towards 5, 25 and 50 mg L⁻¹ SO₂ dissolved in a phosphate buffer of pH 5.8. Membrane was conditioned for 2 h in a 0.1 M phosphate buffer of pH 5.8 before measurement

The storage stability of the membranes (M1-M6) was at least 7 months if protected from acidification by volatile acids.

The combined exposure of the sensing films to sulfur dioxide and oxygen at the same time destroys the sensors. In this case the sensors do not react reversibly. If molecular oxygen is present, the hydrogen sulfite formed in the sensing film is oxidized to sulfate. Sulfate is a non-volatile counterion and is accumulated in the membrane. It binds all free cationic counterions in the sensing films which are essential to stabilize the deprotonated form of the pH indicator. As a consequence, deprotonation of the

indicator is not possible any more. Therefore, the sensing films can only be used to monitor sulfur dioxide in anoxic systems. The sensors were fully reversible if measurements were performed in the aqueous phase, since the high excess of HSO₃⁻ reduces all oxygen. Reversible gas phase SO₂ monitoring in air is impossible with the new sensors. Only if nitrogen was used as carrier gas a reversible response was observed.

Highly sensitive colorimetric SO₂ sensors useful for test strips to estimate the content of dissolved free SO₂ in beverages were developed. Depending on the SO₂ concentration, the test strips undergo a visually well detectable irreversible color change from blue via green to yellow when dipped into the probe. In presence of oxygen SO₂ is bound irreversibly within the sensing film due to the fast oxidation of the HSO₃⁻ to sulfate.

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