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**Investigation and development of selective
polymeric liquid membranes for the optical
detection of NO₂ with chemical sensors**

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Cover illustration from top left to bottom right:

Spectral changes in absorbance of a membrane based on

μ -(oxo)bis(2,9,16,23-tetra-*tert*-butyl phthalocyaninatoiron(III)) with coordinated *p*-ethylpyridine due to exposure to NO_2

iron(II)-phthalocyanine with coordinated dibenzylamine due to exposure to NO_2

aquacyanocobalt(III)-cobyrinate and 2',4',5',7'-tetraiodofluorescein octadecyl ester due to exposure to NO_2

aquacyanocobalt(III)-cobyrinate and [11-[(1-butylpentyl)oxy]-11-oxoundecyl-4-{{9-(dimethylamino)-5*H*-benzo[*a*]phenoxazine-5-ylidene}amino}-benzenate] due to exposure to NO_2

iron(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecachloro-29*H*,31*H*-phthalocyanine with coordinated octadecylamine due to precipitation

iron(II)-phthalocyanine with coordinated octadecylamine after exposure to NO_2 (reverse reaction)

Per Cristina

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Summary

In the research of this thesis selective polymer membranes were developed for the optical detection of nitrogen dioxide. Two different principles were introduced for the selective measurement of NO_2 in the ppb-range.

Membranes based on an aquacyanocobalt(III)-cobyrrinate and a phenoxazine or a fluorescein derivative as chromoionophore showed a detection limit of 15 ppb. These polymer membranes did not show any cross-sensitivity to NO , CO and CO_2 in the ppm-range. The cross-sensitivity to SO_2 was found to come from an unspecific reaction which can be discriminated at dry conditions. As an explanation for the NO_2 -sensitivity, a reaction of NO_2 with the axial-coordinated H_2O -ligand of the cobyrinate was proposed. The resulting nitric and nitrous acid protonates the chromoionophore, which leads to its change in absorbance in the UV/VIS-region. Additionally, the nitrite binds to the cobyrinate. The proposed reaction mechanism was confirmed when the reaction products, nitrate and nitrite, were determined. Spectroscopic methods and the modification of the membrane composition provided further confirmation. Based on this reaction mechanism, a rate law was derived. It was shown that the theoretical model could describe the sensor response to different concentrations of NO_2 dependent on the amount of the cobyrinate within the membrane. A large variety of polymers and plasticizers were tested with respect to their sensitivity, reversibility and stability, to find ways of improving the membrane stability.

Optical micro gas sensors, consisting of photodiodes and a light emitting diode, were produced with the NO_2 -sensitive membranes. Within an industrial project it was shown that when fire detectors are equipped with these NO_2 -sensors, they generate considerably fewer false alarms.

As a second principle for the optical detection of NO_2 , phthalocyanine complexes dissolved in polymer membranes were introduced. The main focus was put on the development of a detection principle based on a ligand exchange reaction of NO_2 with axial-coordinated N-donor ligands of iron(II)-phthalocyanine. In this reaction the absorbance of the so-called

Q band of the iron phthalocyanine complex decreased. This change in intensity at 650 - 670 nm was used as the measurement signal of the sensor membrane. The N-donor ligands investigated were either nitrogen-containing polymers, or amines and pyridines, which act simultaneously as plasticizers. With the second approach it was possible to selectively measure NO_2 in the range of ppb. No cross-sensitivity was observed to NO , CO , CO_2 and SO_2 with concentrations in the ppm-range. Substitution at the macrocycle with alkoxy and especially with alkyl groups led to an improved solubility of the phthalocyanines within the plasticized polymer membrane. Even so, a precipitation of the metal complex within the polymer layer was observed, leading to a decolourisation of the membrane after 3 months.

The application of phthalocyanines in polymer membranes opens up new possibilities for measuring NO_2 selectively with optical methods. With suitable methods of immobilization, the stability of the sensor membrane could be directly improved.

Zusammenfassung

In dieser Arbeit wurden selektive Polymermembranen für die optische Detektion von Stickstoffdioxid entwickelt. Dabei wurden zwei verschiedene Prinzipien zur selektiven Messung von NO_2 im ppb-Bereich eingeführt.

Membranen basierend auf einem Aquacyanocobalt(III)-cobyrintat und einem Phenoxazin- oder einem Fluorescein-Derivat als Chromoionophor wiesen eine Detektionslimite von 15 ppb auf. Diese Polymermembranen zeigten keine Kreuzsensitivität gegenüber NO , CO und CO_2 im ppm-Bereich auf. Es konnte gezeigt werden, dass die Querempfindlichkeit gegenüber SO_2 von einer unspezifischen Reaktion herrührt und unter trockenen Bedingungen diskriminiert werden kann. Als Erklärung für die NO_2 -Sensitivität wurde eine Reaktion von NO_2 mit dem axialen H_2O -Liganden vom Cobyrintat vorgeschlagen. Die dabei entstehende Salpeter- und Salpetrige Säure protonieren den Chromoionophor, welcher dabei seine Absorption im UV/VIS ändert. Zusätzlich folgt eine Bindung des entstandenen Nitrits an das Cobyrintat. Der vorgeschlagene Reaktionsmechanismus wurde erhärtet mit der Bestimmung der Reaktionsprodukte Nitrat und Nitrit, durch spektroskopische Untersuchungen und durch Modifikationen der Membranzusammensetzung. Basierend auf dem Reaktionsschema wurde ein Geschwindigkeitsgesetz aufgestellt. Es konnte gezeigt werden, dass das theoretische Model in der Lage ist, das Antwortverhalten der Membran auf unterschiedliche NO_2 -Konzentrationen zu beschreiben, in Abhängigkeit der eingesetzten Konzentration des Cobyrintates in der Membran. Im Hinblick auf eine Verbesserung der Membranstabilität wurde eine Reihe von Polymeren und Weichmachern untersucht, hinsichtlich ihres Einflusses auf Sensitivität, Reversibilität und Beständigkeit.

Optische Mikro-Gassensoren bestehend aus Photodioden und einer Leuchtdiode wurden mit den NO_2 -sensitiven Membranen hergestellt. Im Rahmen eines Industrieprojektes konnte gezeigt werden, dass

Brandmelder, welche mit diesen optischen NO₂-Sensoren ausgerüstet sind, erheblich weniger Fehlalarme erzeugen.

Als zweites Prinzip zur optischen Detektion von NO₂, wurden Polymermembranen mit gelösten Phthalocyaninkomplexen eingeführt. Der Schwerpunkt lag auf der Entwicklung eines Detektionsprinzips basierend auf einer Liganden-Austausch-Reaktion von an Eisen(II)phthalocyanin axial-koordinierten N-Donor-Liganden mit NO₂. Dabei nahm bei den Eisenphthalocyaninkomplexen die Absorption der sogenannten Q-Bande ab. Diese Intensitätsänderung im Bereich von 650 - 670 nm wurde als Messsignal der Sensormembranen erfasst. Als N-Donor-Liganden wurden entweder stickstoffhaltige Polymere oder Amine und Pyridine, welche zugleich als Weichmacher fungierten, verwendet. Mit letzterem Ansatz konnte NO₂ selektiv im ppb-Bereich gemessen werden. Es wurde keine Kreuzsensitivität gegenüber NO, CO, CO₂ und SO₂, bei Konzentrationen im ppm-Bereich, beobachtet. Durch Substitution am Macrocyclus mit Alkoxy- oder Alkyl-Gruppen, konnte vor allem mit letzteren die Löslichkeit des Phthalocyanins in weichgemachten Polymermembranen verbessert werden. Dennoch wurde ein Ausfallen der Metallkomplexe in der Polymerschicht beobachtet, was zu einer Entfärbung der Membran nach 3 Monaten führte.

Die Verwendung von Phthalocyaninen in Polymermembranen eröffnet eine weitere Möglichkeit, NO₂ optisch und selektiv zu detektieren. Geeignete Immobilisierungs-Methoden würden sich direkt auf die Beständigkeit der Sensormembran auswirken.

1

Introduction

Nitrogen dioxide (NO_2) is a major component of outdoor air pollution. It reacts on soot particles to form HNO_2 , which is known to contribute to global environmental problems such as photochemical smog, ozone formation, acid rain and the corrosion of metals [1]. This highly toxic gas certainly has an impact on public health in urban and industrialised population centres. Nitrogen oxides (NO_x) are emitted by petrol- and diesel-burning engines and by coal/oil furnaces. Released NO combines with atmospheric oxygen to form NO_2 . The Swiss Clean Air Act sets 15 ppb as the maximum yearly average and 40 ppb as the maximum concentration for a 24-hours exposure. Gas sensors for monitoring nitrogen dioxide in a variety of industrial processes have been commercially available for several years. But they measure in the ppm-range, which is too high for environmental applications. Recently, there has been an increasing interest in the development of chemical gas sensors capable of detecting NO_2 in the ppb-range. In the last two years (2000-2001) as many studies about NO_2 -sensors were published in "Sensors and Actuators B" as were published in this journal in the previous four years. The need for air quality monitoring has stimulated recent investigations in the field of toxic gas sensors.

Besides monitoring pollution, another reason for wanting to find ways of detecting NO_2 is that it could be useful in fire prevention. When a fire starts NO_2 is released and reaches a concentration in the ppb-range within the very first minutes of the fire. A sensor which is capable of measuring this could be used for fire detection. This was the main motivation for developing the optical sensors for NO_2 described in this thesis.

The aim of the research was to develop a sensor which exhibits a detection limit below 200 ppb, is high selective for NO_2 and has a low power

consumption (< 2 mW). If such a sensor and additional sensors, which react selectively to combustion gases, are included in a fire detector, false alarms, which are a major problem, can be excluded. The application of the sensor and the main problems of fire detection are discussed in detail in Chapter 3.

There are mainly two types of commercially available gas sensors used for the detection of NO_2 : semiconducting metal oxides and amperometric sensors.

Semiconducting Metal Oxides Sensors

The oldest semiconducting metal oxides sensors are tin oxide (SnO_2) gas sensors which have been commercially available since the end of the sixties (Figaro, Japan). The general mechanism for gas sensing is a change

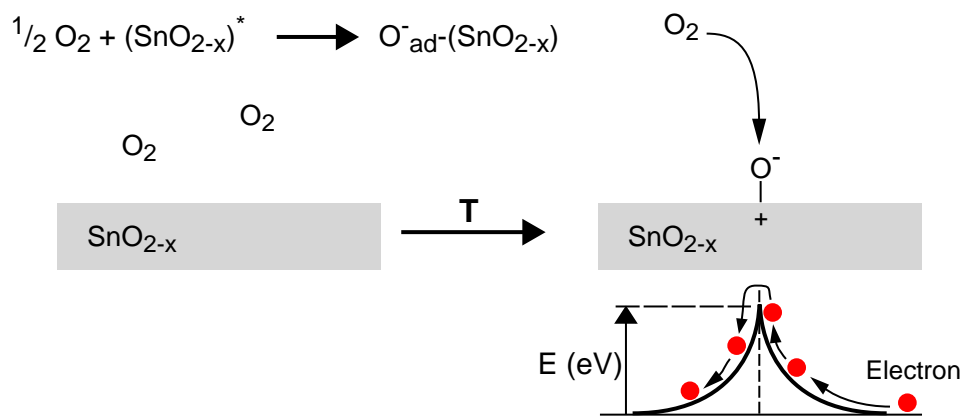


Figure 1. Initial state of heated semiconducting tin oxide layer at ambient air.

in the resistance (or conductance) of the sensor when it is exposed to an analyte relative to the sensor resistance in background air. The metal oxide layer, such as SnO_2 , ZnO and WO_3 , is heated to a temperature of $100 - 400$ $^\circ\text{C}$ in air so that oxygen is adsorbed on the surface with a negative charge (Figure 1). The donor electrons in the surface are transferred to the adsorbed oxygen, resulting in positive charges being left in a space charge layer. Thus, a surface potential is formed to serve as a potential barrier against electron flow. The electrical resistance of the sensor is attributed to this potential barrier. When the sensor is exposed to a reducing gas, the gas reacts with some adsorbed oxygen species (Figure 2). This leads to oxygen consumption, the return of electrons to the oxide grains, and a decrease in

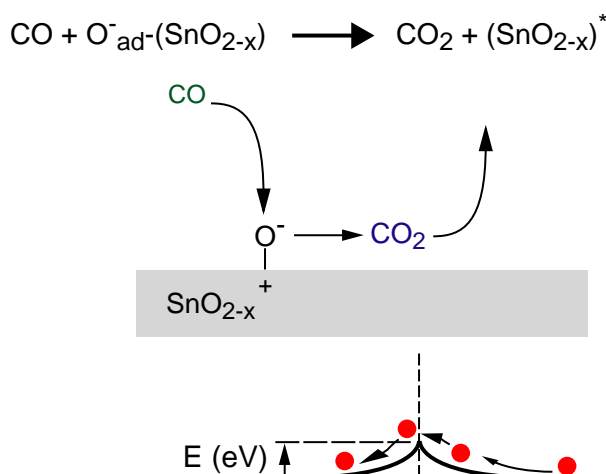


Figure 2. Reaction of a reducing gas like CO with surface adsorbed oxygen species.

the semiconductor resistance. When the metal oxide layer is exposed to an oxidizing gas such as NO_2 , the resistance increases as the gas chemisorbs as a negatively charged species to the semiconductor surface. The change in resistance is therefore due to the chemisorption of the oxidizing gas, assuming that the concentration of oxygen adsorbates remains constant.

Temperature is an important factor that affects the sensitivity of metal oxide sensors. Therefore, sensors are operated at temperatures up to 400°C to increase the reactivity of the semiconductor surfaces and to allow the desorption of reaction products.

The main disadvantage of semiconducting metal oxide sensors is they are not very selective. Their sensitivities to various gases can be enhanced by doping with metals. Metals promote the catalytic activity of the semiconductor surface with gases, leading to chemical sensitization. Typical doping metals, like Pt and Pd, have been shown to increase the sensitivity of tin oxide sensors to gases such as benzene and toluene [2].

For the detection of NO_2 it was found that WO_3 -layers are preferred over SnO_3 -layers because they discriminate interfering gases like CO and methane better [3]. But they can hardly distinguish between NO and NO_2 and it has to be expected that other gases will show a cross-sensitivity.

Since the detection principle of metal oxide sensors is based on the chemical adsorption and desorption of gases on the sensor's surface,

ambient temperature and humidity will affect sensitivity characteristics by changing the rate of chemical reaction.

A further disadvantage of metal oxide sensors is their high power consumption, which means they are not suitable for application in fire detectors.

In recent years other materials to be used in chemiresistors for NO₂-sensing have been investigated. Layers based on tellurium and on porous silicon have been shown to be sensitive to NO₂ at room temperature [4, 5]. Whereas with tellurium a sensitivity was only obtained in the ppm range, the more sensitive porous silicon layer showed a cross-sensitivity to humidity. Organic semiconductors like metal phthalocyanines have been extensively investigated for the detection of gases. For the detection of NO₂ and NO, mostly copper and lead phthalocyanines have been used, but titanyl phthalocyanine has also been tested [6-11]. With these materials chemiresistors were obtained which were able to measure NO₂ in the ppm-range. A higher sensitivity was achieved using a SAW-device, but it needed an operating temperature of 110 °C [12].

Amperometric Sensors

The principle behind amperometric sensors is the measurement of the current-potential relationship in an electrochemical cell where equilibrium is not established. The current is quantitatively related to the speed of the

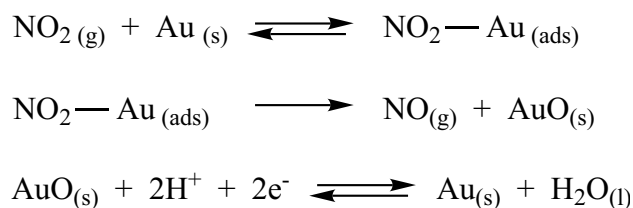


Figure 3. Electroreduction of NO₂ on a gold electrode of an amperometric sensor.

electrolytic process at the working electrode where the reference electrode's potential is constant. In amperometric gas sensors the analyte gas is oxidized or reduced at the working electrode at an applied potential which is adjusted for the target gas and allows a certain discrimination. The first amperometric gas sensors for NO₂ were based on the

electrochemical reduction at gold electrodes (Figure 3) [13, 14]. Since then solid polymeric electrolytes (SPE) like Nafion or poly(ethylene oxide) have been used with a gold minigrad pressed onto the SPE or with the gold chemically plated onto it [15]. By using SPE it was possible to miniaturize the devices and to operate them at room temperature.

The selectivity of an amperometric gas sensor can be improved by modifying the surfaces with metal layers, polymers, or applying semiselective filters exhibiting a certain pore size, charge and polarity. Commercially available amperometric sensors (Dräger, Germany) show a sensitivity for NO_2 in the ppm-range. But even more sensitive amperometric sensors would not be suitable for use in fire detectors due to their high price and power consumption.

Optical Sensors

Various attempts have been made to develop optical sensors for NO_2 . In an early work 3-aminophthalhydrazide (luminol) dissolved with a metal catalyst in a hydrogel was proposed as a chemiluminescent NO_2 -sensor [16]. But it exhibited a cross-sensitivity to atmospheric oxygen and the chemiluminescence reaction is irreversible. Irreversibility was also the main problem with a sensor based on the quenching of the photoluminescence of porous silicon with NO and NO_2 [17]. For Langmuir-Blodgett films of polyaniline it has been shown that the interaction with NO_2 can be monitored using surface plasmon resonance, [18] but the disadvantage was similar to that with chemiresistors based on an unspecific polymer layer, namely, cross-sensitivity and low sensitivity (ppm).

The use of different dyes for coloration reactions in the detection of NO_2 has been proposed by various authors. If diazotizing reagents and naphthalene compounds, similar to the Saltzman reagents, are introduced into porous glass and exposed to NO_2 at humid conditions a diazocoupling reaction and a change in absorbance occur [19]. With the resulting glass chips the hourly change in the NO_2 concentration in ambient air can be shown, but the lifetime of the sensor is limited due to the irreversibility of the coupling reaction. A similar attempt was made with the Saltzman reagent combined with Acridine orange immobilized in silica sol-gel to obtain single-use fibres for fluorescence measurements [20]. In another

study, azobenzene chromophores immobilized in polysiloxane were found to change their absorbance upon exposure to 100 ppm NO₂ [21]. An optical sensor was developed based on bis(phthalocyaninato)titanium(IV) and shown to detect NO₂ in the ppm-range [22].

None of the optical sensors described above would, however, be suitable for application in a fire detector for the reasons given. What is needed is an optical device that combines a low-priced sensor with low power consumption. Additionally, it has to exhibit a detection limit below 200 ppb and a high selectivity for combustion gases.

The starting point of this thesis was an optical sensor membrane developed for selectively measuring nitrite in aqueous solutions [23]. This polymer membrane was developed by Caspar Demuth in our research group and was found to be sensitive to nitrogen oxides as well.

In the following chapters, it is shown how this sensor could be further developed and tested. Theoretical explanations of the membrane's mechanism are also proposed. The application in fire detectors is shown and the advantages are discussed. Additionally, a second principle for the optical detection of NO₂ based on polymer membranes is introduced.

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2

A Highly Sensitive NO₂-Selective Optode Membrane

T. Nezel, A. Fakler, G. Zhylyak, G. J. Mohr, U. E. Spichiger-Keller, Sensors and Actuators B, 70, (2000), 165-169

Abstract:

A new NO₂-sensitive polymeric optode membrane is introduced. It takes advantage of the reactivity of NO₂ with an aquacyanocobalt(III)-cobyrrinate derivative. The detection mechanism leads to a protonation of the Nile Blue derivative ETH 5418, which changes its visible spectrum thereby. The polymer layer also contains the aquacyanocobalt(III)-cobyrrinate derivative which significantly reduces the response time and improves the operational lifetime of the sensor compared to a blank membrane. No cross-sensitivity to NO, CO, CO₂ and only a small interference by SO₂ was observed.

A large variety of polymers and plasticizers were tested in order to achieve resistance to high temperature and to improve the lifetime of the sensor. Until now, the plasticized PVC membranes still remain the material of choice in view of a good compromise between stability, response time and solubility of components.

2.1. Introduction

Chemical gas sensors for volatile organic compounds (VOC) based on polymer films (so called "electronic noses") are usually lacking selectivity because only solubility interactions are responsible for signal changes [1]. However, for molecules such as NO_x, CO, CO₂, HCl, NH₃ etc., it should be possible to develop selective chemical sensors, especially when considering their individual chemical reactivity. Several optical sensors were investigated for ionic analytes such as nitrite, hydrogen carbonate, chloride and ammonium ions. However, it remains to be investigated to

what extent the working principle for ion sensors can also be transformed to gas sensors, and particularly whether it is possible to obtain a specific interaction between the analyte and a ligand.

Recently, we have introduced an optical sensor for nitrite which is based on polymer membranes containing an aquacyanocobalt(III)-cobyrrinate ligand and ETH 5418 as an optical transducer [2]. Solid state NO₂ gas sensors have been investigated by several authors [3-5]. Sensors based on the reduction of NO₂ on gold electrodes have been presented [6; 7] but they are working in the ppm-range. Relatively high detection limits are also observed for a surface acoustic wave (SAW) and a surface plasmon resonance (SPR) sensor [4; 8]. An SAW sensor based on crown ether substituted phthalocyanines with an enhanced sensitivity has recently been introduced [9].

In the present work, we have investigated whether an optical sensor for nitrite ion in aqueous solution can also be used for the reversible detection of nitrogen dioxide in the gas phase. In order to achieve resistance to high temperature and to improve the lifetime of the layer a large variety of polymers and plasticizers were tested. Since it is well known that PVC shows a radicalic decomposition [10], we investigated different alternative polymer materials. A major requirement for the present investigation was sufficient solubility of both the cobaltcobyrrinate and the chromoionophore in the polymer matrix. A second task was to avoid the use of plasticizers in order to simplify sensor production and improve the shelf lifetime.

In detail, we have investigated the effect of the polymer matrix on response time, reversibility and magnitude of signal changes. Furthermore, storage of membranes at elevated temperature has been identified as a vital parameter for the practical utility of optical sensor layers. Another important characteristic of the matrix is its apparent acidity, which has a main influence on the incorporated chromoionophore. Depending on the matrix, the chromoionophore exhibits a different degree of protonation which affects the response behavior and the dynamic range of the membrane.

2.2. Experimental

2.2.1 Chemicals and reagents

The NO₂-selective membrane (polymer layer) incorporates 0.5 to 10 weight% of a Co(III)-cobyrinate complex (aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrinate perchlorate, nitrite-ionophore I (Fluka Chemie AG, Buchs) or PEFA 10105, respectively, which works as a selective host compound. The nitrite ionophore I was resynthesized and modified (PEFA 10105) by Pentapharm AG, Basel. ETH 5418 ([11-[(1-butylpentyl)oxy]-11-oxoundecyl-4-[[9-(dimethylamino)-5*H*-benzo[*a*]phenoxazine-5-ylidene]amino]-benzenate]) was used in a concentration of usually 50 to 200 mol% relatively to the complexing agent. The following polymers and plasticizers were tested (Scientific Polymers, USA): poly(vinylchloride) (PVC), poly(4-methoxystyrene) (PMS), ethylvinylacetate (EVA), an aliphatic polyurethane (Tekoflex[®] EG 80 A from Thermedics Inc., Woburn, USA), polyvinylacetate (PVAC), polymethylmetacrylate (PMMA), cis- and cis/trans-polybutadiene (cis-PBD, cis/trans-PBD), poly(*p*-tert-butylstyrene) (PBS), an epoxy novolac resin (SU 8, from Shell, Birsfelden, CH) (Fig. 1). Plasticizer (Fluka Chemie AG, Buchs): 2-octyloxybenzotrile (CPOE), DOS (bis(2-ethylhexyl)sebacate), dibutylsebacate (DBS), tris(2-ethylhexyl)phosphate (TOP), tris(2-ethylhexyl)-trimellitate (TOTM) (Fig. 2).

2.2.2 Optode preparation and apparatus

The membranes were obtained using a spin-coating technique. Suitable solvents are tetrahydrofuran (THF), cyclopentanone and cyclohexanone. The membrane components were dissolved in freshly distilled solvent and 0.3 ml of this solution was injected onto a rotating glass plate of a spinning device [11]. The resulting layers show a thickness between 2 - 7 μm depending on the rotational speed and viscosity of the polymer mixture. The membrane-covered glass plates were mounted into a flow-through cell which was placed in a spectrophotometer (Specol 1100, Analytic Jena GmbH, D-07740 Jena). A gas stream with a flow rate of 200 ml/min was usually applied. 1 ppm NO₂ balanced in synthetic air (Carbagas, CH-8153

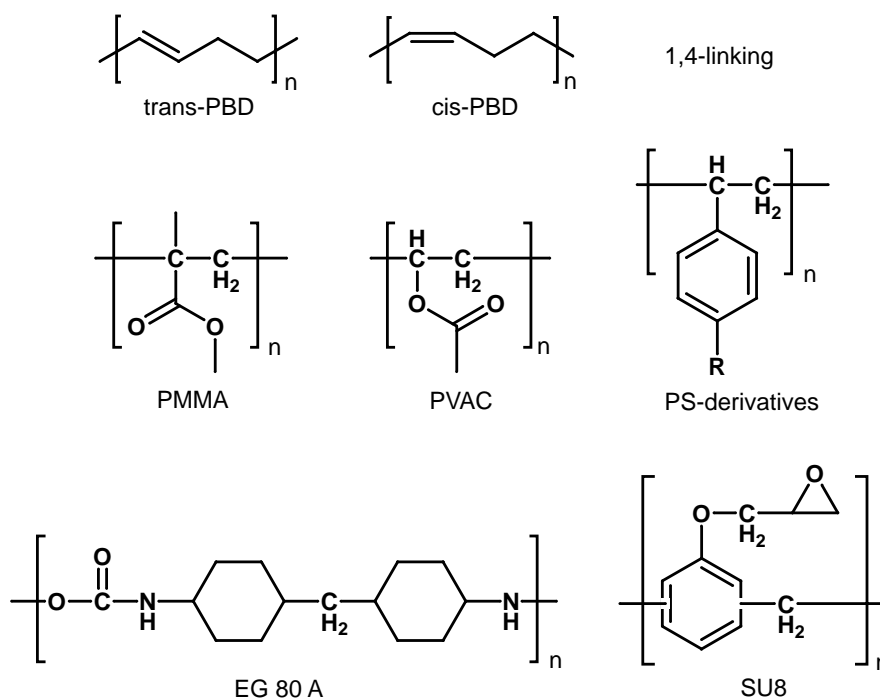


Figure 1. Investigated polymers.

Rümlang) was diluted with humidified synthetic air to give a relative humidity of 50%.

2.3. Results and Discussion

2.3.1 Sensor performance and effect of polymers

Figure 3 shows the response of membrane SU8-CPOE composed of ETH 5418, the cobyrinate, the epoxy polymer SU-8 and the plasticizer CPOE upon exposure to different concentrations of nitrogen dioxide. As the sensor response, the absorbance at 666 nm has been taken. Also shown is the reversibility of the optode after exposure to NO₂ has been suspended. The absence of artifacts indicates that no continuous enrichment of NO₂ takes place during the measurement. The response time t_{90} for 100 ppb nitrogen dioxide in the range of 30 - 40 minutes for forward response, and 1 - 2 days for full reversion of the response. However, the decisive fact is that already after two minutes a signal is achieved which clearly can be detected. The behavior of SU8-CPOE is comparable to sensor membranes based on plasticized PVC (PVC: plasticizer = 1:2) in terms of spectral

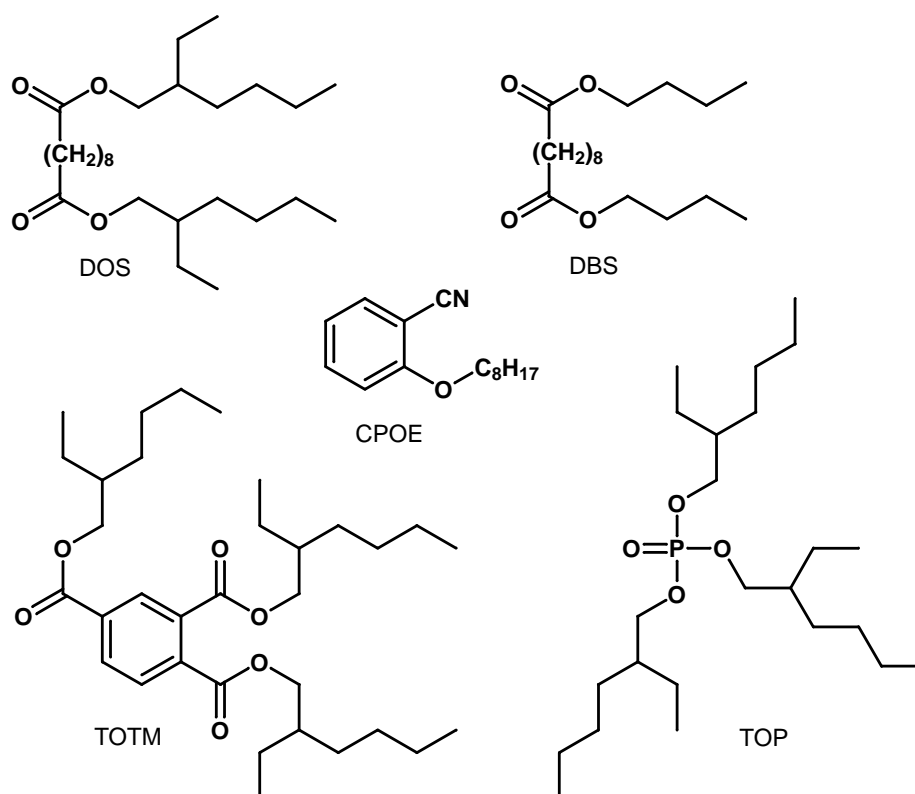


Figure 2. Investigated plasticizers.

characteristics, response and reversibility. PVC membranes plasticized by CPOE and DOS exhibit highest sensitivity to nitrogen dioxide followed by TOTM and DBS which give a sensitivity lowered by 20%. All other investigated polymers generally showed a significantly lower sensitivity than membranes based on SU8 or PVC. Polymethoxystyrene membranes only exhibited response to nitrogen dioxide when plasticized by CPOE or TOTM and were different to polybutylstyrene because only by using DBS and DOS significant signal changes were observed. Unsubstituted plasticized polystyrene, in contrast, gave no reversible response at all and the membranes exhibited only limited shelf-lifetime. However, their sensitivity was higher by a factor of two (with CPOE, DBS, DOS) compared to substituted polystyrenes. An unstable behavior similar to polystyrene was also encountered for EG80A as the polymer matrix, albeit with lower sensitivity, except in the case of CPOE which gave similar sensitivity. Membranes composed of PMMA were virtually insensitive to nitrogen dioxide with negligible signal changes in the case of DBS and TOTM as the plasticizers, whereas membranes based on PVAC were

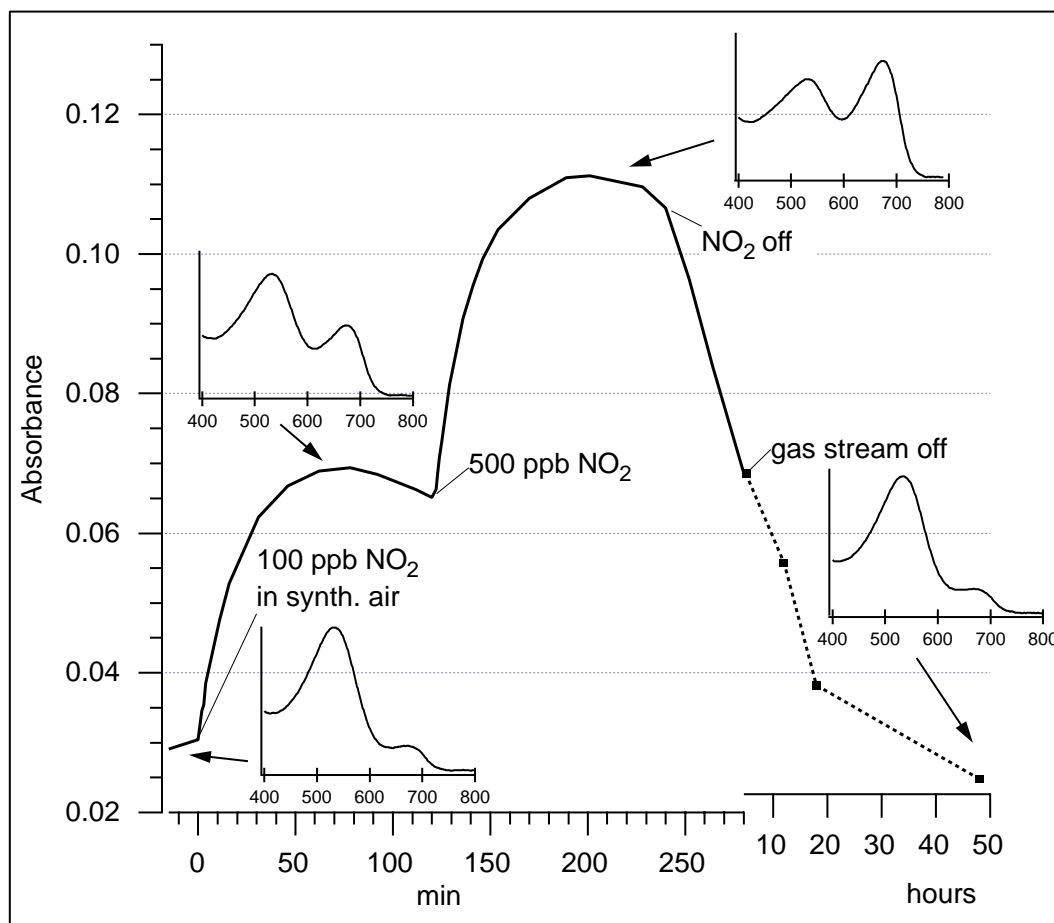


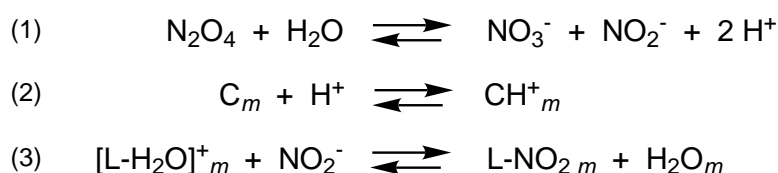
Figure 3. Response of a SU8-CPOE membrane to NO₂. Absorbance at 666 nm vs. time with spectral resolution at certain time steps.

completely insensitive to the analyte. Plasticized polybutadiene membranes gave small signal changes and showed phase separation upon storage. Of the polymers investigated, SU8 and EG80A gave signal changes without plasticizer, which, only in the case of SU8, was fully reversible.

When exposing the plasticized polymers to 60 ° - 80 °C for a period of 3 days, all sensor layers exhibited a significant decrease in signal magnitude, except in the case of PVC-DOS and PVC-DBS. The sensitivity of membranes based on PVC-CPOE, PVC-TOTM, PMS-CPOE, PMS-TOTM, PBS-DBS, PBS-DOS decreased by a factor of 2 and more, whereas the remaining membranes completely lost sensitivity to NO₂.

2.3.2 Response mechanism

Under standard conditions (1 bar, 298 K) NO_2 is found to 80% as the dimer N_2O_4 [12]. The heterogeneous reaction of NO_2 with the compounds of the membrane starts with its adsorption to the surface of the polymer layer. A solvent polymeric membrane can be described as a liquid phase where the active compounds are dissolved within the membrane. It is supposed that NO_2 adsorbed to or solvated within the polymer layer reacts with water of the membrane to give nitrate, nitrite and two protons (eq. 1).



This disproportion reaction is known to be very fast ($k = 8.4 (\pm 1.5) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [13]. The following two steps, protonation and binding of nitrite to the cobaltcobyrinate, $[\text{L}\cdot\text{H}_2\text{O}]^+$, involving charge compensation are the same as in the case of the nitrite membrane (eq. 2 and 3). The aquacyanocobaltcobyrinate enables the protonation of the chromoionophore, C, by loosing its competitive positive charge while binding nitrite, $\text{L}\cdot\text{NO}_2$. Simultaneously, it supplies the bulk membrane, m, with water for further reaction with NO_2 . The protonation of the chromoionophore results in an increase of its absorbance at 666 nm which can be measured quantitatively.

2.3.3 Enrichment of nitrogen dioxide in sensor layers for nitrite

The enrichment factor of a substance in a certain medium is defined as “the solubility of e.g. a gas in the polymer compared to the concentration of gas in air having the same volume as the polymer and under standard temperature and pressure” [14]. In the case of the NO_2 -sensitive polymer layer, several equilibria are involved in the overall distribution of NO_2 between air and membrane. The calculated "enrichment factor" is, to the best of our knowledge, higher than all published data [14]. Starting from a membrane volume of $0.45 \cdot 10^{-12} \text{ m}^3$, i.e. 0.45 nl, and an amount of $19 \cdot 10^{-12} \text{ Mol}$ of complexing agent or indicator per membrane $19 \cdot 10^{-12} \text{ Mol}$ or 874

pg NO₂ are extracted into the membrane, provided that it is in the state of saturation and the NO₂ concentration in the air amounts to 20 ppm (i.e. around 41 mg·m⁻³ or 0.89·10⁻³ Mol·m⁻³). This can easily be verified via the degree of protonation of the indicator, C, within the sensor membrane. Under these conditions an "enrichment factor" of 47'400 is observed.

2.3.4 Cluster analysis for polymer characterisation

The influence of single components on the membrane properties has been investigated and evaluated by cluster analysis (Fig. 4). The clustering was

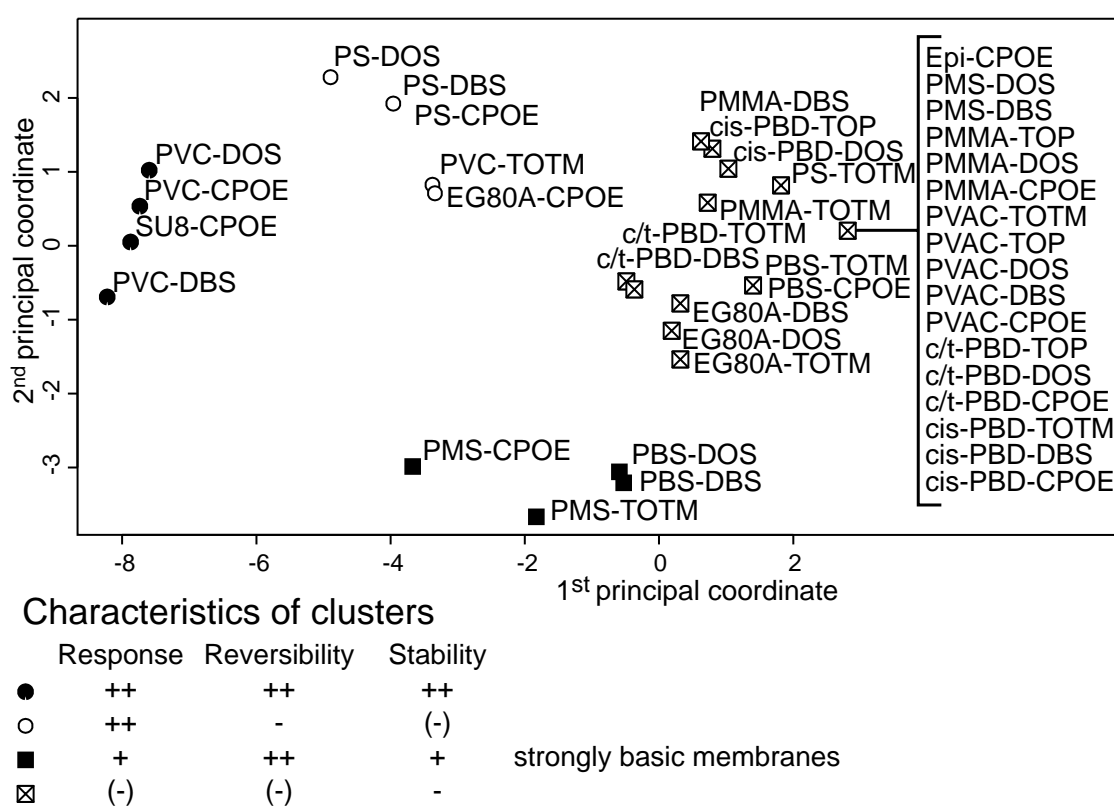


Figure 4. Graphical presentation of the cluster analysis in a metrical multi-dimensional scaling (MDS). MDS provides a two-dimensional view of the multidimensional data plot, which allows to recognize the separate clusters.

performed hierarchically by the single linkage method using the Euclidean distance. The variables were given by measured parameters which characterize sensitivity, reversibility, homogeneity of the membrane, the acidity of the dye in the membrane-phase and the stability of the spectra

respectively. These variables were standardized before calculating the clustering, i.e. they were shifted by the mean and divided by the standard deviation resulting in a mean of 0 and a standard deviation of 1 for the transformed data. By this procedure all the variables are equally weighted. Four clusters were set without any further criteria for the discrimination. The statistical software package used was S-Plus 4.5 Prof. Rel. 1.

The cluster analysis results in a clearly separated cluster of plasticized PVC-membranes which also contains the epoxy-polymer SU8 plasticized by CPOE. However, the latter unfortunately showed a dissatisfying mechanical stability during the stress tests (softening point 62 - 64 °C), while the PVC based polymer layers were of good durability at 65 °C. Another distinct cluster includes the membranes based on plasticized polystyrene, on PVC-TOTM and on EG80A-CPOE, which lack a satisfactory reversibility (polystyrene-membranes) and a sufficient mechanical stability. Another cluster consists of polymer layers based on PMS and PBS which increase the acidity of the indicator dye. The acidity (pK_a) of the dye in the membrane phase corresponds to the absorbance at the beginning of the measurement and the sensitivity to NO_2 . In the ideal case, the indicator dye is partially protonated. Thus, under NO_2 -Stress the detection limit is shifted along the sigmoidal response curve to a section of higher sensitivity. The remaining cluster collects all polymer-plasticizer combinations which do not lead to useful membranes.

It was found that membranes without plasticizer were practically useless or showed a decrease in sensitivity, even for soft polymers like polybutadiene. It was not possible to use parameters such as dielectric constant, lipophilicity and viscosity in order to further elucidate the sensing properties of the membranes.

Involving further parameters such as the melting point and glass point of the polymers and the dielectricity, lipophilicity, viscosity and the boiling point of the plasticizers into the statistical calculation did not change the classification.

2.4. Conclusions

The solvent polymeric optode membrane shows attractive characteristics for NO₂-sensing, such as high selectivity, a detection limit of approx. 50 ppb, a fast response time and good reversibility. Furthermore, an optical device based on this polymer membrane shows the advantage of low working temperature and low power consumption as compared with solid state NO₂ gas sensors. Therefore, up to now plasticized PVC membranes still remain the material of choice in view of a good compromise between stability, response time and solubility of components.

Acknowledgements

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3

Gas-Selective Optical Sensors for Fire Detectors

Tomas Nezel, Ursula E. Spichiger-Keller, Christian Ludin and Andreas Hensel, Chimia, 55, (2001), 725-731

Abstract:

At the Center for Chemical Sensors (CCS) of ETH-Zürich, gas-sensitive membranes have been developed during the last 3 years. In co-operation with Pentapharm AG, Basel, and Bosch Telecom GmbH, Frankfurt, it has led to the development of a world novelty, a gas-selective fire detector called MagicSens. Compared with conventional fire detectors this reacts specifically to combustible gases and considerably reduces thereby the false alarm ratio and the subsequent associated costs. Additionally, since combustible gases such as NO₂ are produced during the whole first phase of a fire, the fact that the membranes are very sensitive means the alarm time could be shortened. The signal transduction in the sensor can be produced with cheap optical items, such as LED and photodiodes. The new fire detector will, therefore, not be more expensive than a conventional one. The product is due to be launched on the market in the near future.

3.1. Introduction

For the analysis of volatile compounds, physico-chemical sensors can be used as alternatives to gas chromatographs (GC), ion mobility spectrometers (IMS) and quick tests based on test tubes such as those from Dräger [1]. Typical gas sensors are generally classified according to type of transducer into electrochemical, optical, calorimetric/thermal, gravimetric, magnetic sensors [2] and others, e.g. acoustic wave sensors [3]. The largest group of gas sensors belongs to the solid state sensors based on metal oxides and includes sensors using various transducers [4].

3.1.1 Micro sensors, sensor arrays and electronic noses

There is an increasing demand for micro sensors and sensor arrays for gas analysis. Applications include early recognition of cable fires, the protection of buildings and their inhabitants, monitoring industrial processes, checking products and their packaging, as well as medical applications such as monitoring blood gases and CO for premature babies. For well-defined applications, chemical sensors provide attractive solutions because they are economical, easy to use and small. Miniaturization, where single sensors have been combined in arrays to form, e.g. electronic noses, offers a further advantage.

Electronic noses either comprise relatively unspecific gas sensors which consist of metal oxide semiconductors [5], or contain specific types of transducers coated with polymer films or thin films of chemical compounds such as porphyrins [6] and phthalocyanines [7]. In the case of metal oxide semiconductors, the recognition process is based on the applied potential resulting from oxidation or reduction of the analyte relative to the adsorbed oxygen. In sensors coated with specific films, sorption of the analyte only changes the physical properties of the film [8]. Changes in the physico-chemical properties of the sensitive layer can be measured in terms of conductance, impedance, changes in visco-elasticity and density, mass enhancement, heat transfer or general changes in surface structure.

In addition, there are well-established gas sensors which exhibit a modest selectivity related to the applied potential consisting of amperometric devices [9]. They rely on an electrochemical reaction of the electroactive analyte in an internal buffer solution. Most of these sensors are complex to construct and their detection limit is too high for many applications, but an exception is described in [10].

3.1.2 Optical gas sensors

The number of optical gas sensors currently available is still small. The very first “optodes” were generally based on the incorporation of pH-sensitive dyes in polymer layers. On exposure to gases which are acidic, such as CO₂ and SO₂, or basic, such as NH₃, protonation and

deprotonation of the dyes occur, with a subsequent change in the absorption spectrum [11]. Later developments involved research on modifying the optical transducer principle, ranging from measurements of simple absorbance to assessments of luminescence resonance energy transfer [12]. However this type of “optode” still exhibited a poor selectivity.

In contrast, optical O₂-sensors based on the quenching of the luminescence of a ruthenium(II)-diimine dye by oxygen is an example of a very selective sensor [13]. These “optodes” were first described in 1968 by Bergman [14], who used them in physiological investigations.

Later, the specific complexation reactions of the target analyte with complexing agents were taken into account in order to enhance the selectivity of the sensors. In the group of W. Simon, selectivity together with optical transduction was achieved by combining a lipophilic pH indicator, a so-called chromoionophore, and an ionophore [15]. In this way, the information yielded from the host-guest interaction was transformed into an optical signal [16]. The chromoionophore changed its absorption spectrum due to an acid-base reaction with the target-gas molecule. In the case of a solvent polymeric NH₃-selective sensor, ammonium ions were formed by deprotonation of the chromoionophore. The NH₄⁺ ions were complexed by using ionophores with different stability constants and these reactions were used to determine the mass balance. The stability of the complex and the pK_a of the indicator together influenced the dynamic range of the optode [17].

In order to investigate the sensing principles for neutral analytes, their nucleophilic addition to trifluoroacetaniline derivatives, so-called reactands, was studied. Upon coupling such reactands to a chromophore, the conjugated system was elongated and the nucleophilic addition was followed by a broad hypsochromic spectral shift in the visible range. Optical sensors, incorporating chromoreactands in a plastified polymer film, responded with a reversible reaction either to alcohols [18], amines [19] or aldehydes [20]. The analyte concentrations in the gas phase and the related signals were correlated by means of optical spectroscopy [21]. A comparable reaction was investigated where a benzaldehyde derivative was added to enhance the selectivity of an SO₂-sensor [22].

The sensor array for fire detection was based on an optical sensor for NO_2 , which achieves its selectivity due to the reactivity of NO_2 with aquacyanocobalt(III)-cobyrrinate derivatives combined with a lipophilic pH-indicator dye incorporated into a solvent polymeric film. This “optode” enables measurements in the ppb range [23, 24]. On this basis a sensor for detecting combustion gases was obtained. In addition, an optical sensor, a NH_3 -selective optode, was developed for detecting NH_3 , a typical interfering gas. This sensor allows the discrimination of cigarette smoke, distinguishing it from any other combustion smoke, which means the number of false alarms can be reduced. At Bosch Telecom GmbH, a number of other sensors, e.g. for CO_2 and CO which are produced during combustion, have been tested. These sensors were provided by other research groups and are considered to be implemented in fire detectors [25].

3.1.3 Fire detectors with optical gas sensors

Current fire detection systems are designed to respond to the smoke or heat generated during smoldering and flaming combustion. Fire alarm sensors can be installed in various places under different conditions, but they should, of course, work properly and be failure-free. Smoke aerosols are commonly detected using stray-light sensors and ionization chambers. In reality, interfering particles like dust induce unintentional signals. Therefore about 20 % of alarms are false alarms (Frankfurt Airport [25]). Efforts to improve the sensors using intelligent algorithms have improved their reliability to such an extent that it takes 100 years, on average, for such a fire detector to produce one false alarm. Although this is an improvement, the number of detectors installed per object relativizes this figure. For instance, at Frankfurt Airport there are 65,000 fire detectors installed, and the fire brigade has to deal with more than 2,000 false alarms per year. This raises the costs, which could be largely avoided if more reliable fire detectors were constructed. If traditional fire detectors were additionally equipped with gas sensors, which react selectively to combustion gases such as CO, CO_2 , NO, NO_2 and H_2 , and do not react to ammonia or particles, it would be possible to avoid most false alarms. So far installing commercial gas sensors in conventional fire detectors has not been widely applied owing to the high power consumption of these

devices, their cross-sensitivity, short life-times and the high price of currently available gas sensors [25]. The power consumption for each detector must be limited to 2 mW because the whole system must be guaranteed to run for 72 h in order for an emergency power supply to cover the period of a power cut. For this reason, optical gas sensors, which have very low power consumptions and require low-priced components, such as photodiodes, LEDs and polymer layers, seems to be very promising.

For these reasons, the joint project of CCS, Pentapharm AG and Bosch Telecom GmbH has led to a leap in the technology of fire detection. It has developed a novel technology to selectively recognize combustion gases which has a low energy uptake (0.4 mW) and only moderate costs [26]. By combining these new sensors with conventional fire detectors, false alarms are as a matter of principle, excluded. Additionally the time taken to detect a fire has been reduced by up to 75 %. This is especially significant since a fire can spread to cover double the area every minute. Therefore, the chances of being successful in the market look extremely good.

The collaboration of CCS with Bosch Telecom GmbH started after CCS was awarded the "Technologie Standort Schweiz" prize in 1996 and had participated in the Hannover Fair in 1997.

3.2. Results and Discussion

If materials such as wood, cotton, polymers or organic solvents comparable to those used for test fires are burnt, a number of oxides are generated. In contrast to SO_2 , CO and CO_2 , NO and NO_2 are not primarily products of the burning materials. Instead they tend to be produced from the nitrogen and oxygen in air due to the rise in temperature in the burning zone. Open fires especially e.g. of ethanol, produce higher quantities of NO and NO_2 (up to 2 ppm) than smoldering fires of wood [25].

Gas monitoring is also concerned with interfering gases such as SO_2 and NH_3 . For SO_2 , long-term contact at room temperature, which may induce such damage as corrosion, is crucial, whereas for NH_3 it is primarily cigarette smoke which can be detected as an interferent for smoke detectors.

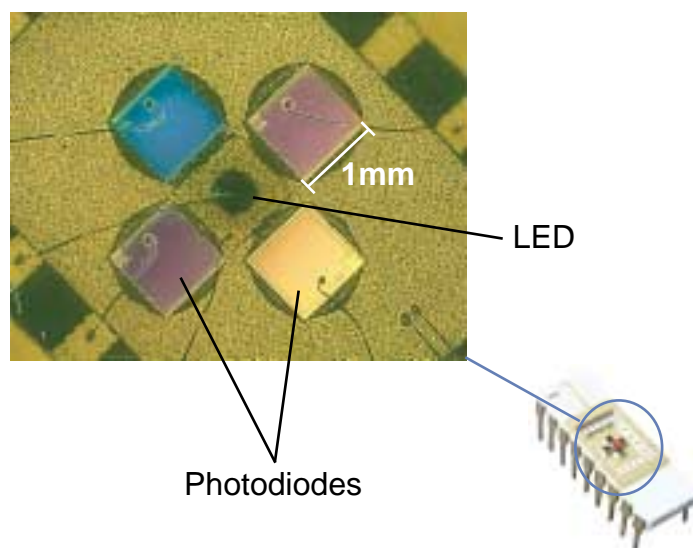


Figure 1. Optical chip used for gas sensing at CCS, consisting of an LED as the light source and 4 photodiodes as detectors. The photodiodes serve at the same time as substrates for the gas-sensitive polymer layers.

3.2.1 *Optical sensor chip*

For the research at CCS, optical chips have been used. These consist of photodiodes and an LED integrated onto a standard housing (Fig. 1). If gas-sensitive membranes are cast onto the photodiodes then they can be used as simple absorbance measurement devices for optode membranes. Four photodiodes surrounding a red LED allow to be monitored absorbance changes in the region around 660 nm simultaneously in up to four different membranes. Such a photodiode has edges 1 mm long. The planar arrangement facilitates the production as well as the casting, while the light intensity beside the LED is still high enough.

With this setup the responses of three different optode membranes selective to various (combustion) gases can be simultaneously recorded while keeping one photodiode as a reference.

3.2.2 *Influence of the cobaltcobyrinate on the sensor response*

In discussing the reactions above, it was suggested that a nitrite-sensitive membrane, such as the one introduced by C. Demuth [27] for measuring dissolved NO_2^- , may also be used in the gas phase. The nitrite-selective membrane showed exceptional selectivity (especially to nitrate and

chloride), a quick response time and a low detection limit at 10^{-5} M nitrite (0.24 mg l^{-1}). In the first experiments in a test set-up, this membrane was also shown to be very sensitive to nitrogen oxides generated by fires. Therefore further investigations were mainly based on the same composition of the solvent polymeric membrane. One membrane component, however, was omitted due to stability problems.

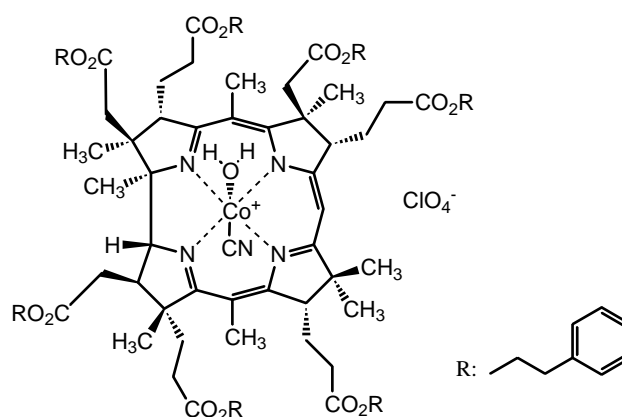


Figure 2. Structure of an aquacyanocobalt(III)-cobyrinate derivative as used for nitrite sensing, which was incorporated into the polymer layer.

The sensing scheme investigated in liquid samples is based on the coextraction of a nitrite and a proton from the sample phase. Thereby the nitrite ion is bound to aquacyanocobyrinate (L, ligand) (Fig. 2). A protonation of the chromoionophore (C) occurs, which leads to a change in its absorbance spectra and provides the optical signal in absorbance or transmission changes (Fig. 3a). The selectivity is introduced by complexation of NO_2^- to the metal complex. The binding of nitrite to the aquacyanocobyrinate can be studied with UV/VIS spectrophotometry since the absorption spectra of the nitrite-cyanocobyrinate complex shifts toward higher wave-lengths relative to the aquacyanocobyrinate. This effect can be referred to the exchange of the water molecule in the axial position with nitrite [27, 28]. Such a change in the spectra was not found in the experiments with humid NO_2 .

It is assumed that disproportionation of NO_2 , which is used as the analyte gas and is absorbed into the polymer layer, occurs with the water molecule of the aquacyanocobyrinate (L) (Fig. 2) to give nitric and nitrous acid. This induces a protonation of the chromoionophore (C) and results in an

increase in its absorbance at 666 nm (Fig. 3b). Absorbance is measured in transmission on the planar diode-sensor chip. The reaction rate of the sensor strongly depends on the amount of aquacyanocobyriinate within the membrane, whereas changes in humidity conditions have little influence on the response. Therefore, it is assumed that this species rather than dissolved water or humidity adsorbed at the surface of the film, is preferably the water source. The reaction is not completely reversible. The high acidity of nitric acid and the consequent nitrate enrichment seem to be the reason for this. However, the reaction mechanism with NO_2 has to be investigated further.

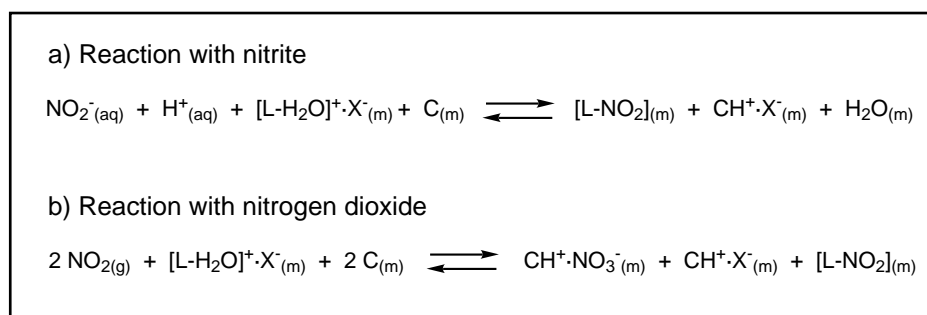


Figure 3. Reactions which occur in the membrane due to exposure a) to nitrite and b) hypothetically to NO_2 .

The sensor response is linear during the initial phase of the reaction and the slope strongly depends on the NO_2 -concentration. Therefore it is possible to obtain a dynamic range of 25 - 800 ppb NO_2 within the very first seconds (Fig. 4 and 5). The NO_2 -sensitive membrane was found not to show any cross-sensitivity to either NO or CO.

3.2.3 Enrichment factor, detection limit and nanotechnology

The enrichment factor of a substance in a certain medium is defined as “the solubility of e.g. a gas in the polymer compared to the concentration of gas in air having the same volume as the polymer and under standard temperature and pressure” [29]. The smallest concentration we could measure with our setup was 15 ppb (which corresponds to the admitted yearly average as determined in the Swiss clean air act). The membrane had a thickness of 25 μm and the concentration of the chromoionophore was $4.27 \cdot 10^{-3}$ M. 10 % of this amount was protonated after exposure to a

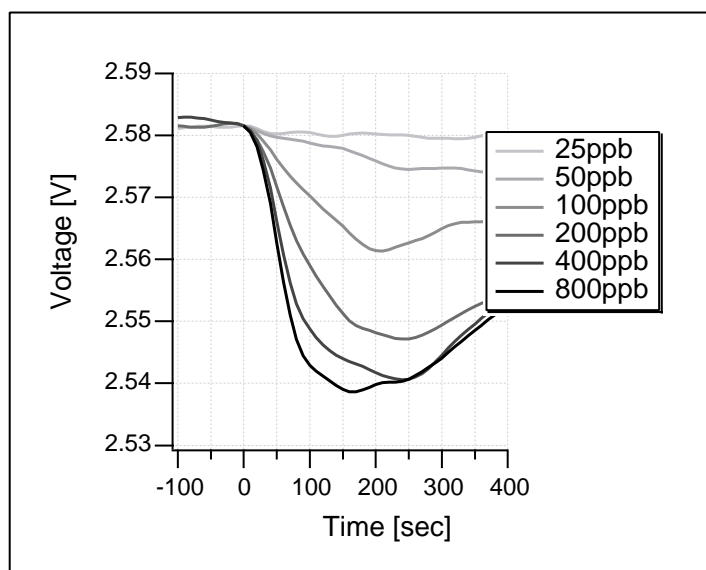


Figure 4. Response of the optical NO₂-Sensor in voltage [V] to 25 - 800 ppb NO₂ in air with 50 % relative humidity and a flow rate of 50 ml/min.

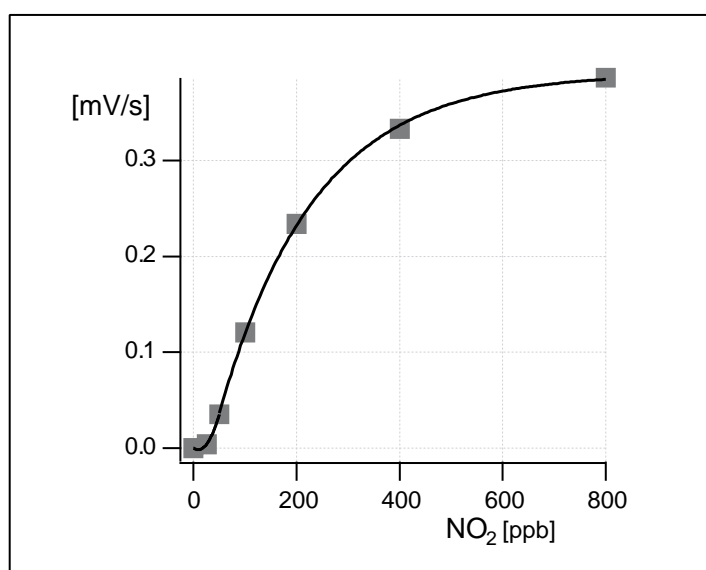


Figure 5. Slope of the sensor response to different NO₂-concentrations within the first minute of contact.

gas stream of 15 ppb NO₂ for 4 hours. This concentration of NO₂ corresponds to $6.7 \cdot 10^{-10}$ M in air. Compared with $4.27 \cdot 10^{-4}$ M of protonated chromoionophore as the reaction product or as the NO₂-concentration, which was extracted into the membrane, it gives an enrichment factor of $6.4 \cdot 10^5$ (Table). This extraordinarily high value

reflects the further reaction of the absorbed NO₂ whereby additional extraction of NO₂ from the gas sample into the membrane can occur. Therefore in this case the enrichment is not determined by the solubility of the analyte in the polymer layer, but rather by the equilibrium of the nitric and nitrous acid produced with water and the chromoionophore.

NO ₂ concentration outside:	30 µg / m ³	15 ppb
Amount of NO ₂ in a volume of 25 nl:	75·10 ⁻⁸ ng	9·10 ⁶ molecules
Extracted amount of NO ₂ :	0.48 ng	6·10 ¹² molecules
Sensitive compound within the membrane:	125 ng	6·10 ¹³ molecules

Table Calculated values for a membrane with a volume of 25 nl and a gas concentration of 15 ppb NO₂.

3.2.4 Flow-through systems and cross-sensitivity

Measurements in the batch mode omitting a flow-through system can lead to a depletion of the analyte in the sample phase. When we measured the NO₂-membranes in a desiccator and adjusted the initial concentration with an inlet of a known gas volume containing NO₂, we observed a heavy dependence on the size of the sensitive area. Thus, we had to take into account not concentrations but rather absolute quantities of analyte and sensitive membrane molecules.

However, for the sensor operating in a fire detector, the batch setup comes closer to real-life conditions than a flow-through system. Additionally, the influence on changes in humidity was much less pronounced in batch measurements. In the flow-through system a strong increase in absorbance was observed due to dry air. Measurements that were carried out in a desiccator with different humidity conditions, showed a negligible influence. There was a minor increase in absorbance due to increasing humidity. For membranes omitting the aquacyanocobaltcobyrinate, this cross-sensitivity was much more pronounced.

The discrimination of SO₂ is also referred to the activity of the aquacyanocobalt(III)-cobyrinate. With the batch setup the signal to NO₂ was determined to be 20 times higher than that to SO₂. Membranes where the metal complex was omitted showed a much higher sensitivity to SO₂.

These results were obtained with initial concentrations of 2 and 10 ppm SO_2 , compared to 0.5 and 1 ppm NO_2 . With both membranes the observed protonation of the chromoionophore caused by such high SO_2 -concentrations, was irreversible (12 ppb is the yearly average admitted by the Swiss Clean Air Act).

3.2.5 Integration in a fire detector

At Bosch Telecom, efforts to miniaturize the optical chip have led to a marketable silicon wafer which includes the whole optical setup within an area of only $1.5 * 1.5$ mm. The diameter of one optically sensitive area is then $300 \mu\text{m}$ (Fig. 6).

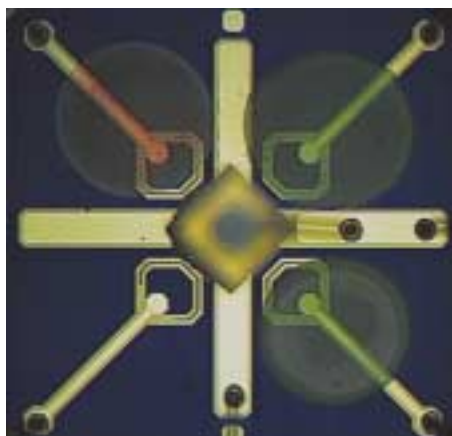


Figure 6. Prototype of an optical silicon wafer for gas sensing with an LED in the centre and with 3 photodiodes which are coated with polymeric membranes as used in fire detectors (Bosch Telecom GmbH).

Long-term measurements were performed to test the reproducibility and reversibility of the sensor response (Fig. 7).

Several measurements were carried out to obtain approval for the application of the NO_2 -sensor in fire detectors. To place a new fire detector on the market it has to pass various tests as laid down in the European norm EN 54. It was possible to demonstrate that the NO_2 -Sensor not only fulfils this requirement but also is even superior to optical reference systems in cases of smoldering combustion (Fig. 8 and 9). The NO_2 -concentration is between 40 ppb and 1.7 ppm, depending on the burning material.

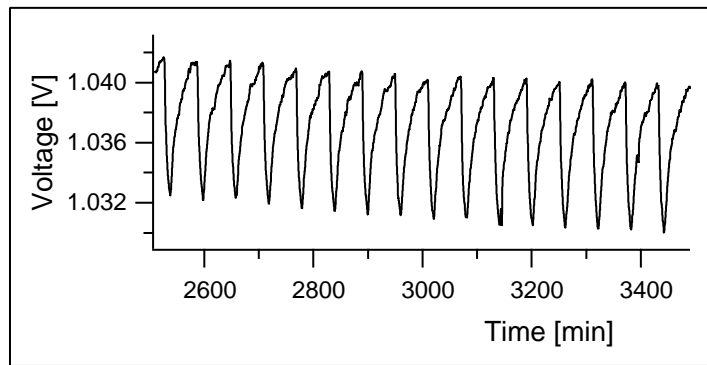


Figure 7. Reproducibility and reversibility of the NO₂-sensor response to 1 ppm NO₂.



Figure 8. One of the prescribed testfires: smoldering combustion of beech wood. When the fire stopped, the NO₂-concentration was 140 ppb.

NH₃ is released in measurable concentrations only when cigarettes and certain plastics are burnt. Thus, an NH₃-sensor like the one mentioned above could be used to discriminate cigarette smoke, which frequently gives rise to false alarms with stray light sensors.

The stability requirements for fire detectors are rigorous (European norm EN 54, part 5 and 7). For a gas sensor to be admitted to the market, an operational and shelf-lifetime of at least 2 years at temperatures up to 60 °C have to be demonstrated. Considerable efforts were made to reach this

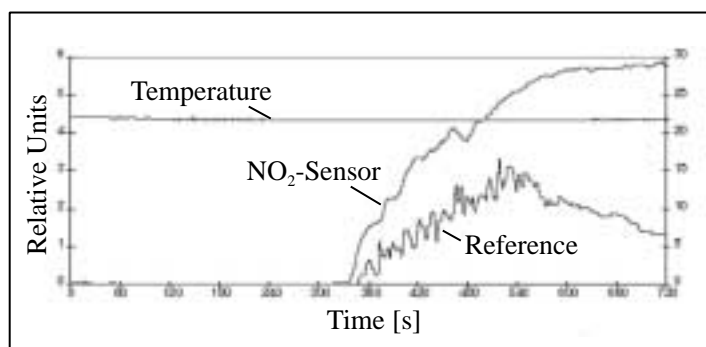


Figure 9. Measurements made during the smoldering combustion of beech wood with the NO₂-sensor, an optical smoke density measurement device (MIREX EC-911, Delta, DK) and a temperature sensor.

goal. Stress tests with NO₂-sensitive membranes have been performed exposing the polymer layers to temperatures ranging from -20 °C to 60 °C at a relative moisture content of 40% and 75% and to suspensions of bacteria and fungi, as a germ load stress test, for different lengths of time. Whereas the microorganisms had no influence on the membrane characteristics, a temperature of 60 °C led to a decomposition of the dye after already 14 days. Therefore new oxazine dyes were synthesized at CCS [30] and tested for their application in the NO₂-sensitive membrane. In addition, the influence of the matrix was taken into account and various polymers and plasticizers were screened in order to extend the lifetime [24]. Currently a novel approach to measuring NO₂ optically is being evaluated in cooperation with S.M. Zakeeruddin (group of M. Graetzel, EPFL). The focus is on incorporating metal phthalocyanines into polymer layers.

The NH₃-sensitive membrane has been stable since the first experiments began in 1997 and therefore clearly fulfils the requirements for longevity. Therefore we are convinced that in the near future we will be able to equip fire detectors with a gas sensor array which detects gases like NO₂, NH₃, CO₂ and CO.

3.3. Conclusions

The fire detector introduced by Bosch Telecom containing the NO₂-sensitive membrane developed at CCS has many advantages over

conventional fire detectors. The main aim to reduce the number of false alarms can be fulfilled with the NO₂-selective sensor. Additionally, the recognition time could, in some cases, be decreased, depending on the burning material. From the scientific point of view, a new way of detecting gases with polymeric membranes has been launched.

3.4. Methods

3.4.1 Chemicals and reagents

The NO₂-selective membrane (polymer layer) incorporates 0.5 to 10 weight% of a Co(III)-cobyrinate complex (aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrinate perchlorate, nitrite-ionophore I (Fluka Chemie AG, Buchs) or PEFA 10105, which works as a selective host compound. The nitrite ionophore I was resynthesized and modified (PEFA 10105) by Pentapharm AG, Basel. ETH 5418 ([11-[(1-butylpentyl)oxy]-11-oxoundecyl-4-{{9-(dimethylamino)-5*H*-benzo[*a*]phenoxazine-5-ylidene}amino}-benzenate]) was usually used in a concentration of 50 to 200 mol% relative to the complexing agent. Poly(vinylchloride) (PVC) and DOS (bis(2-ethylhexyl)sebacate) as plasticizer (Fluka Chemie AG, Buchs) were used as the matrix.

3.4.2 Sensor coating

At CCS the membranes were obtained using a stainless steel capillary (Hamilton Bonaduz AG) connected to the valve of a dosimeter (Microlab 500, Hamilton Deutschland GmbH, Darmstadt, D). The membrane components were dissolved in freshly distilled cyclopentanone. 0.2 µl of this solution was injected onto the photodiode of the optical chip. After the evaporation of the solvent, the resulting layers were between 8 - 25 µm thick depending on the viscosity of the polymer mixture. The reproducibility of the coating was around 90% [31].

3.4.3 Measurement setup

A measurement setup to test gas sensors under various conditions was built at CCS. Dry synthetic air (quality 5.5, Sauerstoffwerk Lenzburg AG) was split in two lines before two mass flow controllers (MKS Instruments

Deutschland GmbH, München, D). One branch was humidified by guiding the air over the water surface in a 2-neck glass flask, thus avoiding the formation of water droplets. A relative humidity of up to 93% could be obtained. This was monitored with a hygrometer (Rotronic, Bassersdorf) located after the measurement cell. These two lines of synthetic air were merged to provide the desired carrier gas stream, which additional lines could be connected to. Mass flow controllers diluted 10 ppm NO₂ balanced in synthetic air (Carbagas, Rümlang) together with the interfering gases, which were mixed with the carrier gas stream to produce a gas flow in a variable range of 20 - 400 ml/min with 0.005 ppb - 3 ppm NO₂. Stainless steel or Teflon tubing was used throughout. A program based on LabView 5.1 was especially designed to operate the whole system and to collect and analyse the sensor data. A data acquisition (DAQ) multifunction card (Lab-PC-1200 from National Instruments, Ennetbaden) was used to connect an IBM PC 330 to self-made electronic control modules for the mass flow controllers and for the sensor chip.

The LED of the optical chip was driven with a sinus-modulated direct current at 10 kHz. Thus, the responses of the photodiodes, which were illuminated through the polymer membranes, had the same frequency. These signals were amplified and filtered with bandpass filters before passing to the DAQ card. Finally, the corresponding amplitudes were obtained from these alternating signals using a fast Fourier transformation implemented in the LabView program. With this self-developed module we were able to increase the signal-noise ratio by up to one order of magnitude compared with an LED operating in constant current mode [31].

To characterize the sensor responses to a fast exchange of gases, e.g. to enable kinetic measurements, a flow-through cell was designed with minimal volume and a constant cross-section along the flow-channel [13]. This meant that no flow dependency was observed and the real-time interaction of the polymer membrane with the gas sample could be investigated.

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4

Aquacyanocobalt(III)-Cobyrrinate as a Key Compound in NO₂-Sensitive Polymeric Liquid Membranes

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Abstract:

The reactions within a recently introduced NO₂-sensitive polymeric membrane based on aquacyanocobalt(III)-cobyrrinate are described. The detailed reaction mechanism was investigated in three ways: using UV/VIS-spectroscopy; determining the reaction products and investigating the influence of other gases. Additionally, the kinetic of the membrane reactions was studied. It could be shown that the membrane's high sensitivity and selectivity derives from the remarkable reaction of NO₂ with this cobyrrinate derivative which yields nitric and nitrous acid. This reaction can be transduced with a consecutive protonation of the included chromoionophore into an optical signal which allows the detection of NO₂ in the ppb-range.

4.1. Introduction

Recently an NO₂-sensitive polymeric optode membrane based on an aquacyanocobalt(III)-cobyrrinate derivative and a phenoxazine derivative has been introduced.¹ Optical micro-sensors based on this layer have been produced, characterized and shown to be suitable for application in fire detectors exhibiting a detection limit of 15 ppb NO₂.² It was proposed that the detection of NO₂ is based on the reaction of the analyte with the aquacyanocobyrrinate, which leads to the formation of nitric and nitrous acid. As a consequence the phenoxazine derivative, which acts as a chromoionophore, is protonated. Simultaneously, binding of nitrite to the

cobyrrinate was postulated as this occurs if such a membrane is used to detect nitrite.³

In this study the reaction mechanism which occurs within the NO₂-sensitive membrane was investigated in detail. Reactions occurring within the membrane were characterized by determining the reaction products and by modifying the contents and the quantities of the membrane compounds. Unfortunately, it was found, that during exposure of the membrane to NO₂, investigations with methods like NMR or ESR are experimentally very demanding. But in various experiments it was possible to obtain the necessary information with UV/VIS-spectroscopy due to the fact that both membrane compounds are optically active.

In sensor technology the interactions between the interfering species and the sensitive layer have to be studied to specify the selectivity. Unlike sensor schemes which are based only on unspecific acid/base reactions, the sensing scheme proposed here comprises a selective step. The interaction of SO₂ with the sensor membrane was investigated and compared with respect to the unique affinity of aquacyanocobalt(III)-cobyrrinate for nitrogen dioxide, to characterize the proposed reaction mechanism.

4.2. Experimental

4.2.1 Membrane Preparation and Reagents

The NO₂-selective liquid polymeric membrane used in this study incorporated 0.13 to 2 weight% of aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrrinate perchlorate (nitrite-ionophore I, Fluka Chemie AG, Buchs). The chromoionophores used were ETH 5418 ([11-[(1-butylpentyl)oxy]-11-oxoundecyl-4-{[9-(dimethylamino)-5*H*-benzo[*a*]phenoxazine-5-ylidene]amino}-benzenate]) and ETH 7058 (2',4',5',7'-tetraiodofluorescein octadecyl ester) in a concentration of 100 to 400 mol% relative to the cobalt complex. Poly(vinylchloride) (PVC) and DOS (bis(2-ethylhexyl)sebacate) as plasticizer (Fluka Chemie AG, Buchs) were used as the matrix in a ratio of 1:2.

ETH 7058 was synthesized from erythrosin extra bluish (Fluka) and 1-bromooctadecane (Fluka) and purified according to the procedure described in ⁴. A second purification step was added with flash chromatography (silica gel 60) using CH₂Cl₂ / acetone / triethylamine (20/5/1) as the eluent. The organic phase was extracted with 0.01 M HCl, washed three times with bidest. H₂O and dried over MgSO₄. After filtration and evaporation of the solvents the precipitate was dissolved in chloroform and converted into the potassium salt by exposure to 0.01 M KOH. Then the organic phase was dried with MgSO₄ and evaporated. The indicator salt obtained was dried at high vacuum.

The synthesis of ETH 5418 has been described in detail elsewhere.⁵ Dicyanocobalt(II)-cobyrrinate (nitrite-ionophore II), was obtained from Fluka and trihexadecylamine from ICN Pharmaceuticals Inc.. Gas mixtures of NO₂, NO, CO and SO₂ (class IV) were obtained from Carbagas (Rümlang), pure CO₂ (4.8) from Messer Griesheim GmbH (Krefeld, D) and synthetic air (quality 5.5) from Sauerstoffwerk Lenzburg AG.

For determining the reaction products and measuring the absorbance and fluorescence, the membrane layers were produced on glass substrates as described in.¹ For the measurements in the kinetic study the membranes solutions were injected onto the photodiodes of an optical chip.²

4.2.2 Apparatus

The absorbance measurements were performed on a Specol 1100 spectrophotometer (Analytic Jena GmbH, D-07740 Jena). The fluorescence measurements were performed on a Perkin Elmer LS 50 B spectrofluorimeter using a specially designed flow-through cell at 22 ± 2 °C.³ Membrane-covered glass plates layers or optical chips were fixed in the cell and a gas stream with a flow rate of 100 ml/min was applied. 10 ppm NO₂ balanced in synthetic air was diluted with a humidified carrier gas stream of synthetic air to adjust the desired NO₂-concentration as described in detail elsewhere.²

4.2.3 Determination of Nitrate and Nitrite

Membranes based on aquacyanocobyrrinate and varying amounts of ETH 5418 were cast onto glass substrates. Polymer layers with an area of 9.6 cm² and a thickness of around 6 μm were produced, obtaining a weight of around 6 mg. The relatively high quantity of sensitive material allowed measurable quantities of the reaction products to be detected. A measurement cell was used so that almost the whole area of a membrane layer with a diameter of 3.5 cm was exposed to NO₂. Because of the large volume of the cell lumen the gas exchange was very slow. Therefore a strong depletion of the sample phase occurred due to the large area of the membrane. The observed protonation degree of the chromoionophore at adjusted NO₂-concentrations was far below what it would be with a suitable setup like that which was used with the optical chip.

The membranes were exposed to NO₂ until the degree in protonation remained constant. The polymer layers were peeled off from the glass substrate and put in closed glass bottles with 0.5 ml bidest. water. After 12 h the quantity of one of the two extracted anions in 0.4 ml of the sample was determined. The proportion of nitrite in such an aqueous solution was spectroscopically determined with a diazo coupling reaction of 3-nitroaniline and N-(1-naphthyl)-ethylenediammonium dichloride.⁶ The reagents were obtained from Riedel-de-Haen/ Fluka (Buchs). The resulting absorbance of the azo dye was compared with a calibration curve which was linear in the range of 0.01 - 0.8 μg/ml. The aqueous solution did not contain all the nitrite because NO₂⁻ partly remained bound to the cobyrrinate in the membrane and some was evaporated as HNO₂ from the sample solution. Therefore membranes composed of cobyrrinate and ETH 5418 were prepared and treated with aqueous solutions with known amounts of nitrite without exposing them to NO₂. The quantity of the remaining dissolved nitrite was determined in exactly the same way. The quantity found was less by a factor of 2.9 (±0.9), which was used to correct the data. 2 - 4 membranes were used to obtain one correlation between the determined nitrite and the applied NO₂-concentration. The uncertainty of the mean values ranged from 8 - 31% with increasing quantities of nitrite. The amount of nitrate was determined using an enzymatic test kit from Boehringer Mannheim (Germany). The consumption of NADPH during the reduction of NO₃⁻ with nitrate reductase was monitored continuously

and fitted to obtain more accurate results. 2 membranes for the same NO_2 -concentration were used, and the highest deviation of the results was 6%. The membranes were afterwards dried at room temperature for several days and weighed to obtain the volume of each membrane and to calculate the original concentrations of the reaction products within the membranes.

4.3. Results and Discussion

4.3.1 Model of the Reaction Mechanism

Four reactions are proposed as the sensing mechanism of the NO_2 -sensitive membrane (Figure 1). The detection process begins with the

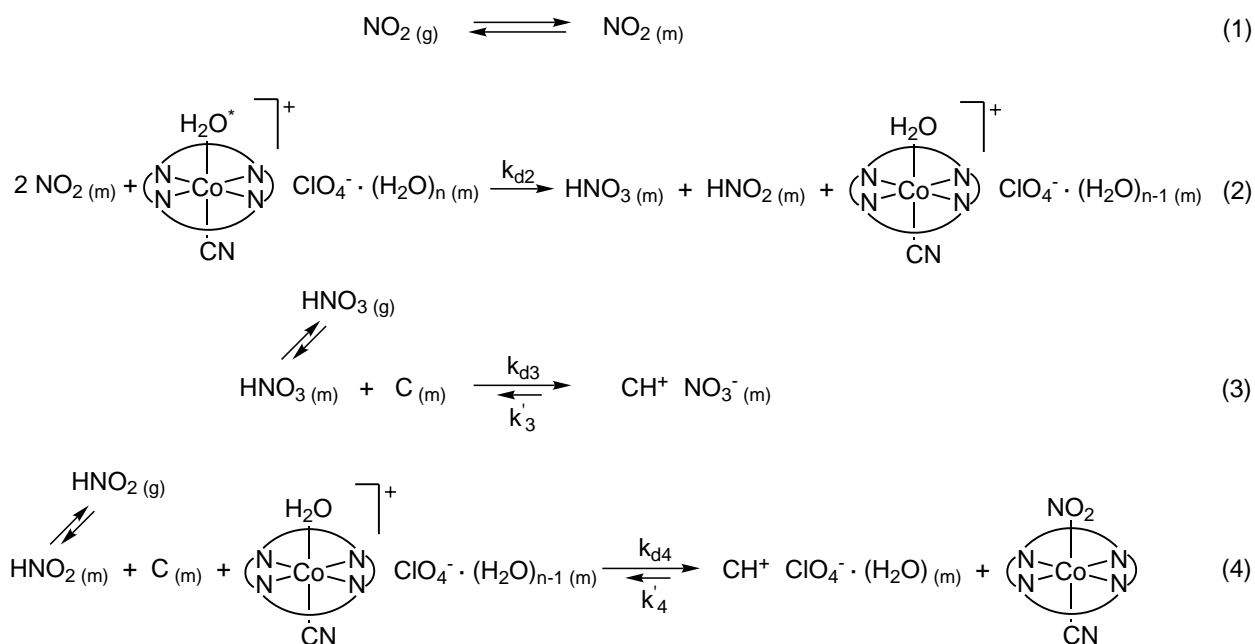


Figure 1. Reaction mechanism of the NO_2 -membrane: 1) Sorption of NO_2 into the membrane; 2) NO_2 reacts with the axial H_2O -ligand of the aquacyanocobyrinate to give nitric and nitrous acid; 3) and 4) Protonation of the chromoionophore C; in 4) simultaneous binding of the nitrite to the cobyrinate.

sorption of $\text{NO}_2(\text{g})$ into the polymer membrane (1). In a second step $\text{NO}_2(\text{m})$ reacts with the water molecule in the axial position of aquacyanocobalt(III)-cobyrinate perchlorate to form nitric and nitrous acid

(2). The reaction products do not remain at the cobalt centre, rather the axial position is assumed to be occupied immediately with a new water molecule from the outer sphere of the metal complex. In the third step of the reaction pathway nitric acid protonates the chromoionophore (C), which provides the optical signal (3). Under certain conditions HNO_2 protonates the chromoionophore, while nitrite is bound to the cobyrrinate to yield nitrocyanocobalt(II)-cobyrrinate (4).

The proposed mechanism was tested in a series of experiments. To examine the reaction of aquacyanocobyrrinate with NO_2 in reaction (2), measurements under different humidity conditions and with other gases such as SO_2 were performed. Additionally, when modifying the contents of the membrane the ability of other sources of H_2O to react with NO_2 were investigated. And finally, changes in the cobyrrinate were examined with UV/VIS-spectroscopy.

The reaction products in reaction (3) and (4), i.e. the nitrate and nitrite, were determined and correlated with the protonation of C. Whether a protonation of C occurs during NO_2 -sensing was investigated with UV/VIS-spectroscopy. Additionally, other chromoionophores were taken in account.

It was possible to identify the formation of the nitrocyanocobyrrinate in reaction (4) since the cobyrrinate is optically active. Observations were compared to those from the determination of nitrite.

Based on the conclusions from these experiments, a kinetic model was developed and a rate law proposed. The theoretical function obtained was compared with experimental data of the membrane response.

4.3.2 Selectivity, Cross-Sensitivity to SO_2 and the Influence of Humidity

Varying the thickness of the polymer layer showed that the recognition process is not restricted to the surface. Investigating reaction (2), a membrane containing the chromoionophore and a dicyanocobalt(II)-cobyrrinate instead of the aquacyano derivative was found not to be sensitive to NO_2 . This observation is ascribed to the missing water ligand. The source of water is the H_2O -molecule bound to the cobalt centre rather

than any unspecific water, which explains the high selectivity as will be shown in this section.

Unlike common metal oxide and amperometric NO₂-sensors, the polymer membrane does not show any cross-sensitivity to NO or CO. It was found that no interference occurs with these two gases up to an investigated concentration of 100 ppm. It is more likely that there will be an interaction with similar acidic gases like SO₂ and CO₂, depending on the ability of these gases to react with H₂O. Additionally, the pK_A of the produced acid will strongly influence the protonation degree of the chromoionophore. CO₂ is known to dissociate only to 0.2% in water, which indicates its unreactivity. The real pK_{A1} value of carbonic acid is 3.88 and much higher than that of nitric acid.⁷ Indeed, no cross-sensitivity to CO₂ was observed at concentrations as high as 10 vol.-%. In the case of SO₂ protonation of the chromoionophore (ETH 5418) was observed at 50% relative humidity. The signal obtained at 2 ppm SO₂ was 4.2 times smaller than that with NO₂ (Figure 2).

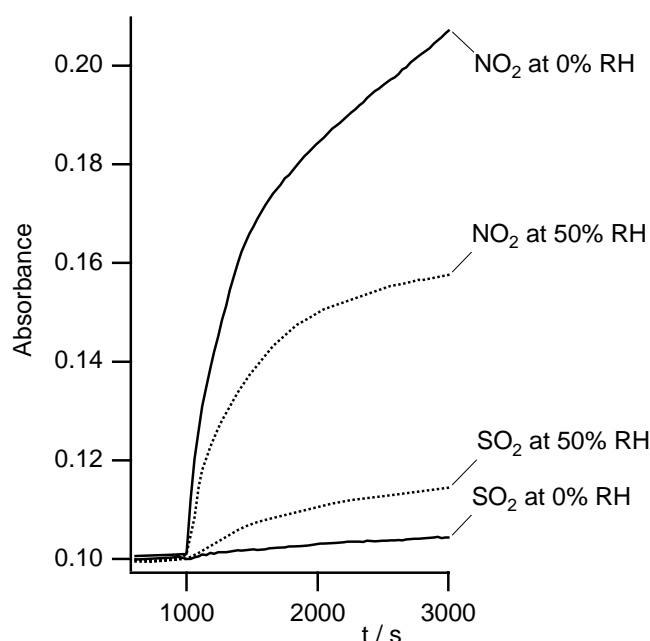


Figure 2. Changes in absorbance of the membrane based on aquacyanocobyrinate and ETH 5418 due to 2 ppm of SO₂ and of NO₂ at relative humidities of 0% and 50%.

When performing measurements under dry conditions ($RH < 1\%$), nearly no signal arising from SO_2 was observed, unlike with NO_2 . Measurements covering the whole range from 0 - 100% relative humidity showed that, with the NO_2 -sensitive membrane, the signal due to SO_2 decreases with decreasing humidity. This observation suggests that SO_2 reacts rather with humidity than with the aquacyanocobyrrinate to form the acid for the protonation of C. To test this theory membranes were made with potassium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (KTTFPB) in the presence of C, instead of aquacyanocobyrrinate perchlorate to preserve ionic sites and exposed to SO_2 . Consistently at 50% relative humidity the same degree of protonation was obtained, again with no signal under dry conditions.

The humidity of the carrier gas stream affects the sensitivity to NO_2 in the opposite direction. The protonation obtained is significantly higher than that at 50% or 100% relative humidity, especially under very dry conditions ($< 30\%$ RH). Investigations of membranes containing only the aquacyanocobyrrinate showed spectral changes in the metal complex when the humidity was decreased from 30% to 0%. It is assumed that, under these conditions, the major fraction of immobilized water is evaporated from the membrane, which then affects the spectrum of the cobyrinate. These changes are very fast and completely reversible as would be expected for solvatochromism of the cobyrinate in a polymeric membrane. For comparison, spectra of the cobyrinate obtained with either ethanol as a protic solvent or dichloromethane as an aprotic solvent exhibit very similar differences. As can be seen in Figure 2, the response to NO_2 under dry conditions is faster and yields a higher degree of protonation. It is assumed that water molecules within the polymer matrix hinder the protonation of C by the produced acids. Additionally, the acids are more acidic the less they are diluted with membrane water.

These investigations have shown that NO_2 reacts preferably with the H_2O of the aquacyanocobyrrinate rather than with membrane water, and it is this reaction which enhances the sensitivity of the membrane for NO_2 over SO_2 . To investigate if only water from the outer sphere of the cobyrinate reacted and if other sources of water could be used in this reaction, the metal complex was replaced with other compounds containing a hydration shell. It was not possible to obtain similar results to those with the

aquacyanocobyrinate when membranes containing the very hygroscopic KTTFPB and C were used. Nor was it possible with membranes containing a salt of tetraoctyl ammonium and Phenol Red, which is known to react with CO₂ to produce bicarbonate.⁸ Especially in the case of the CO₂-sensitive membrane, where we assume that the acidic gas reacts with the hydration sphere of the salt to form the acid underpins with its insensitivity to NO₂ the high affinity of NO₂ for the axial H₂O ligand of the cobyrinate.

With other interfering gases volatile acids have to be considered because the chromoionophore acts as a pH-indicator within the membrane. Their cross-sensitivity will therefore depend on their solubility within the polymer matrix.

4.3.3 Protonation of Chromoionophores due to NO₂

The protonation of the chromoionophore and its changes in transmission is the reaction which provides the final optical signal. The spectral changes were monitored with UV/VIS spectroscopy while exposing the membrane to NO₂ and trifluoroacetic acid alternately. The decrease in absorbance at 523 nm and the increase at 666 nm with an isosbestic point at 573 nm, proofed that a protonation of ETH 5418 occurred. Independent of whether NO₂ or trifluoroacetic acid was used the same changes in absorbance were observed.

Using ETH 5418 as the chromoionophore with long exposure periods to NO₂ or at high concentrations of NO₂, the absorbance of the protonated species started to decrease after it had reached its maximum. Simultaneously, a new absorbance band at a lower wavelength of 540 nm appeared. It is assumed that, under such conditions, a nitrosation occurs at the amino or imino group of the phenoxazine derivative.⁹ Similar observations were also made with other Nile Blue derivatives like ETH^T6000.¹⁰ Therefore, the use of a different type of chromoionophore, an erythrosin derivative, was considered. 2',4',5',7'-tetraiodofluorescein octadecyl ester (ETH 7058) was synthesized and converted to a potassium salt to obtain its basic form. Hence it represents a different type of chromoionophore, which is negatively charged in its deprotonated form and neutral if protonated (C⁻/CH). The basicity of ETH 7058 in 2-

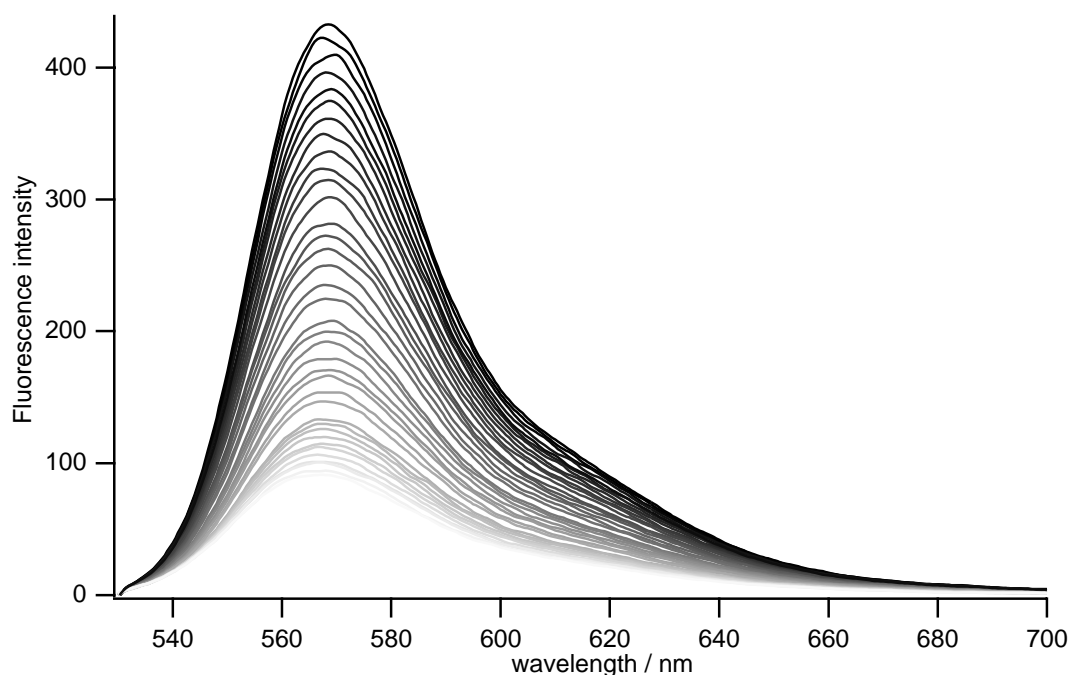


Figure 3. Fluorescence spectra of the NO_2 -sensitive optode membrane containing ETH 7058. A decrease in fluorescence intensity is observed when exposed to 500 ppb NO_2 . The emission spectra were recorded with the excitation wavelength set to 520 nm.

propanol/ H_2O -solution was determined to be 1.5 orders of magnitude lower than ETH 5418. Absorbance measurements were performed with NO_2 -sensitive membranes containing ETH 7058 as chromoionophore. They showed the same response to NO_2 as membranes with the Nile Blue derivative. Additionally, a decomposition or bleaching was not observed. In contrast with the phenoxazine derivative, its absorbance at $\lambda_{\text{max}} = 549$ nm decreases due to protonation with a simultaneous decrease in fluorescence at 568 nm. As shown in Figure 3, the fluorescence decreases due to the protonation of the chromoionophore when exposed to NO_2 . The forward and reverse response showed the same time constant as in the absorbance mode. Thus no artefacts were observed. For some sensor applications the measurement of fluorescence intensity has an advantage over transmission mode. With ETH 7058 it was shown that the uses of the NO_2 -sensitive membrane described here are not restricted to phenoxazine derivatives but it can handle completely different chromoionophores. This means it is possible to monitor the optical signal at any wavelength using an appropriate chromoionophore.

4.3.4 Determination of Reaction Products

According to the reaction scheme presented above, it should be possible to determine the products formed (i.e. nitrate and nitrite) in eq (3) and (4) shortly after exposure to NO_2 before the reverse reactions take place and gaseous acids are formed, as indicated in Figure 1.

To determine the amount of nitrate and nitrite produced due to NO_2 , exposed membranes were peeled off from the glass substrate and immersed in closed glass bottles containing bidest. water. The quantity of ions extracted in the aqueous solution was determined spectroscopically using an enzymatic test for nitrate and a diazo coupling reaction for nitrite (see experimental section). In the quantitative evaluation, the evaporation of $\text{HNO}_{2(\text{g})}$ from the sample solution and the complexation of nitrite was taken in account. Membranes with a stoichiometry of 2 : 1 of chromoionophore : cobyrrinate were produced and exposed to different NO_2 -concentrations in air while measuring the absorbance spectra. This allowed the relation between the acids formed and the protonation degree of the chromoionophore to be established. Because of the necessarily high membrane volumes in this experiment, relatively high NO_2 -concentrations had to be applied to achieve a protonation (see experimental section). Therefore these experiments should not be compared directly with measurements obtained with the optical chip.

As one would expect from the reaction scheme, the amount of nitrate determined increases with increasing NO_2 -concentration (Figure 4). More surprising is the generally large quantity of nitrate compared with the protonation degree of the chromoionophore. Almost all the protonation (98%) could be explained by the reaction with HNO_3 . Additionally, membranes with the cobyrrinate but without the chromoionophore contained about 5 times less nitrate than these were the chromoionophore was included under the same conditions. Thus reaction (2) takes place regardless of whether there is a basic compound for a further reaction. This leads to a slight accumulation of HNO_3 . Nitrate was found to be partly able to evaporate as $\text{HNO}_{3(\text{g})}$ from the membrane as proposed for the reverse reaction (Figure 1 (3)). This derived from experiments with membranes where the time before they were immersed in water was extended and less nitrate was determined. Unfortunately the ion pair in (3)

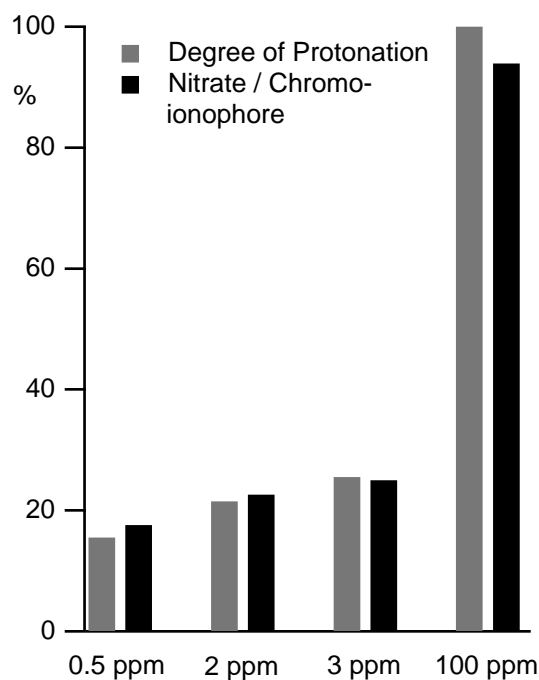


Figure 4. Quantity of nitrate produced within the membrane due to different concentrations of nitrogen dioxide. For all measurements the protonation of the chromoionophore could be only due to nitric acid as deduced from the amount of nitrate, which is represented in a ratio to the total amount of chromoionophore.

disfavors the reversibility significantly compared with membranes without the chromoionophore.

The quantity of nitrite determined also depended on the applied NO₂-concentration (Figure 5). More nitrite was found with increasing NO₂ until the final protonation degree of the chromoionophore was 20%. But with higher concentrations of NO₂ the nitrite determined started to decrease. In membranes which show a protonation degree higher than 40%, the amount of nitrite is several times smaller than the amount of nitrate. As mentioned, we believe this is due to the different acidities of the two acids which compete for the protonation of the same chromoionophore but exhibit different rate constants. HNO₂ can easily evaporate out of the membrane, as confirmed by lengthening the time period before the membrane was immersed in water to extract nitrite. To demonstrate how the formation of nitrite depends on the NO₂-concentration applied, numerical simulations were performed. The simulation program consisted of a set of differential

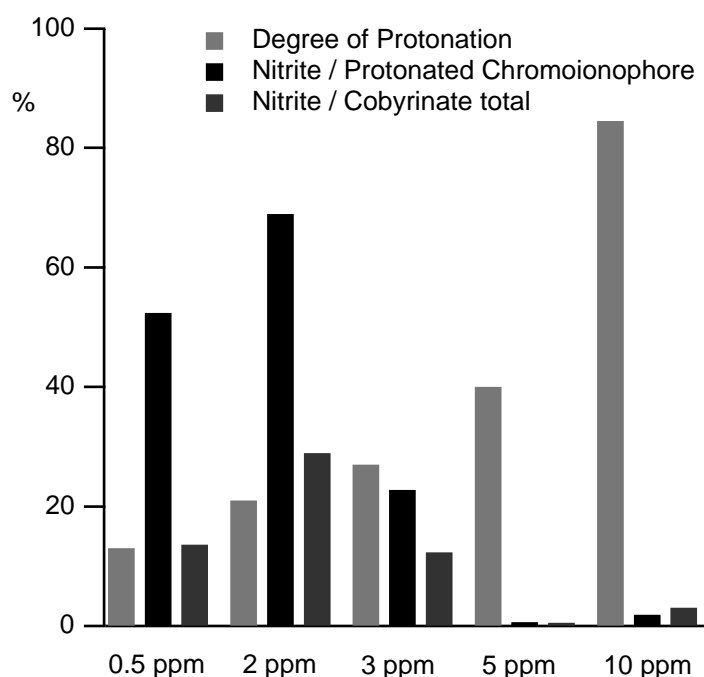


Figure 5. Quantity of nitrite produced within the membrane due to different concentrations of nitrogen dioxide. At concentrations higher than 3 ppm the protonation of the chromoionophore is not even partly due to nitrous acid. The amount of nitrite is shown in ratio to the protonated chromoionophore.

equations describing the concentration changes in each species involved in the reactions (2)- (4). Maintaining the relation $k_{d2} > k_{d3} > k_{d4}$, the same trend in nitrite formation was found. At low concentrations of NO_2 , nitrite and more nitrate were produced. With an increase in the NO_2 -concentration, the formation of anions increased. If a certain NO_2 -concentration was exceeded, the initial slope of the nitrite formation began to level off due to the fast decrease in available unprotonated chromoionophore, caused by reaction (3). At more increased NO_2 -concentrations this slope approached zero and therefore no nitrite was produced.

In the samples with the highest amount of nitrite, the protonation of the chromoionophore could have been raised to 50% due to nitrous acid. The results obtained from the nitrite and nitrate analysis also showed that generally higher concentrations of acids are produced than would actually be expected on protonation of the chromoionophore. This shows that, with

long-term exposures to NO_2 the membrane matrix becomes highly acidic, due especially to HNO_3 . This greatly affects how readily the chromoionophore in the membrane subsequently deprotonates, which is the reverse response of the sensor membrane.

An important observation was that no nitrite was found in membranes without chromoionophore, independent of the NO_2 -concentration applied. Unlike to nitric acid, HNO_2 does not remain or does not dissociate in the polymer matrix if it cannot react with the chromoionophore. Instead it evaporates with the applied gas stream. This result is in agreement with the observations made during the spectroscopic investigations of aquacyanocobyrrinate within the membrane, as shown in the next section (see 4.3.5).

The determination of the anions produced within the membrane has shown that, at all applied NO_2 -concentrations the amount of nitrate is higher than the amount of nitrite. It should be noted that reaction (3) is clearly more dominant than reaction (4) the higher the NO_2 -concentration is.

4.3.5 Spectroscopic Investigations of Aquacyanocobyrrinate

The aquacyanocobalt(III)-cobyrrinate perchlorate is itself optically active in the UV/VIS region, but its molar absorption coefficient is smaller by a factor of 3 than that of the Nile Blue derivative. If polymeric membranes are produced that contain a relatively high amount of 2.7 wt.-% of only the cobyrrinate, the changes in absorbance of the metal complex due to interaction with gases can be investigated. When such a membrane was exposed to concentrations of up to 100 ppm NO_2 , no changes in the UV/VIS spectrum could be observed. As shown above with the determination of nitrate (4.3.4), reaction (2) does occur in such a membrane. The missing spectral change is in agreement with the assumption that water is supplied very fast to the axial position of the cobyrrinate. This experiment also shows that the nitrogen dioxide itself is not bound to the cobyrrinate.

In membranes containing only the cobyrrinate, nitrate was determined but no nitrite was found (see 4.3.4). Aquacyanocobyrrinate is known to bind nitrite and its visible spectrum shifts to higher wavelengths due to the exchange of the H_2O -ligand in the axial position with an electron donor like nitrite.^{3, 11} A possible explanation is that the produced HNO_2 does not

dissociate if a base (like ETH 5418) is missing within the membrane but rather it evaporates out of the polymer layer. Therefore membranes were produced containing a lipophilic amine as a substitute for the chromoionophore to simulate the complete NO_2 -membrane with basic sites but without a Nile Blue derivative, which would hide the VIS-spectrum of the cobyrinate. Because of the ability of amines to coordinate to various metal centres, the amine used was trihexadecylamine, which is sterically hindered so that it cannot bind itself in the neutral form to the cobyrinate.

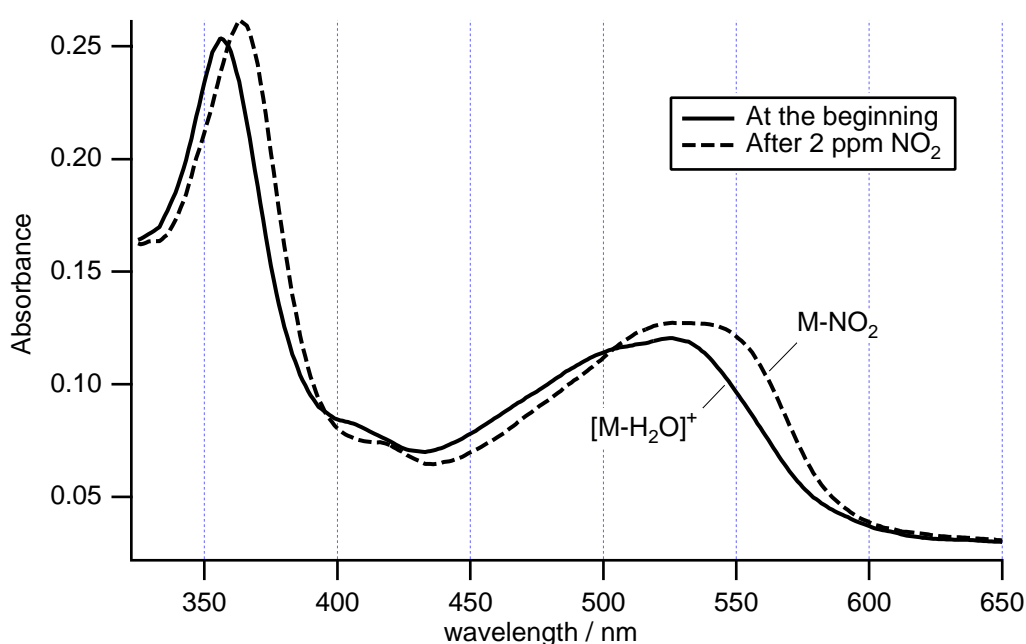


Figure 6. Absorbance spectra of aquacyanocobyrinate within a PVC/DOS-membrane containing trihexadecylamine as a base (solid line), after exposure to 2 ppm NO_2 , indicating the formation of nitrocyanocobyrinate (dotted line).

In fact, with such a membrane a shift of the cobyrinate to higher wavelengths could be observed at NO_2 -concentrations of 2 ppm and lower (Figure 6), indicating the binding of nitrite and the formation of nitrocyanocobalt(II)-cobyrinate $[\text{M}-\text{NO}_2]$. The same spectral changes were observed with a membrane containing only the cobyrinate on exposure to an aqueous nitrite solution. In addition to the determination of nitrite, this experiment shows that reaction (4) does occur during NO_2 -sensing.

An important observation was that, at the same NO_2 -concentration, the spectral changes took longer than in the membrane containing the chromoionophore, instead of the lipophilic amine, and measuring the spectral changes of the chromoionophore. This is not an effect of the different basicities because the pK_A -value for C was 9 in a PVC/DOS membrane and estimated to be 6.8 in water.⁵ Therefore it is even lower than with tertiary amines, which have a pK_A of 10-11 in aqueous solutions. We expect that within the membrane, this value will be higher rather than lower. This supports the assumption that reaction (4) is slower than reaction (3), and that the protonation occurs mostly as a result of nitric acid and not nitrous acid.

The binding of nitrite was found to be only partly reversible, which would explain the observed decrease in sensitivity when a membrane is exposed to NO_2 several times. This could be avoided using a chromoionophore with a lower pK_A -value to suppress reaction (4). Thus the chromoionophore would be protonated only due to HNO_3 , and HNO_2 would not dissociate. But with such a membrane a decrease in sensitivity must be expected.

4.3.6 Kinetic Analysis

To test the reliability of the reaction model proposed above, a rate law was derived and compared with real measurements. An important task for such measurements is to prevent a depletion of the sample phase along the sensitive surface. Otherwise the reaction rate obtained would tend to depend on the flow of the gas stream rather than on processes within the membrane. Using a special measurement cell¹² with a constant cross-section of 1.8 mm^2 , the gas stream had a velocity of 0.93 m/s above the sensitive layer while applying a carrier gas stream of 100 ml/min . Additionally, the area of the sensitive membrane was kept small at 1 mm^2 . Under these conditions, no flow dependency of the applied gas stream was observed, which means that the NO_2 reached an equilibrium between the sample phase and the membrane phase. In such a case, the distribution of an analyte between the gas phase and the sorbent phase is given by its partition coefficient (here K_1).¹³

Considering the processes within the solvent polymeric membrane, it has to be assumed that not one of the chemical reactions in the membrane is itself the rate-determining step. Rather this is determined by the diffusion of a compound involved in this reaction. For reactions (2) and (3), it is likely that nitric acid rather than gaseous nitrogen dioxide will be the diffusion-controlling species. In this discussion the less pronounced reaction (4) will be ignored for the sake of simplicity. The rate-determining step is therefore reaction (3). The experimental condition where there is no dependence on the gas flow means, therefore, that the rate of formation in reaction (2) is higher or equal to the rate of formation in reaction (3). This was found to be the case with a wide range of NO_2 -concentrations where the flow rate was kept constant, only at very low concentrations of NO_2 was the extraction of gaseous NO_2 into the membrane phase the rate-determining step (1). Using C as an abbreviation for chromoionophore, the rate law is:

$$-\frac{d}{dt}[\text{C}] = k_{d3} \cdot [\text{HNO}_3][\text{C}] - k'_3 \cdot [\text{CH}^+\text{NO}_3^-] \quad (5)$$

k_{d3} is not the rate constant of the protonation itself, but the rate constant of the formation of the preceding encounter pair as this is a diffusion-controlled process. The concentration of HNO_3 is assumed to be given by a fast pre-equilibrium determined by the formation of HNO_3 in reaction (2) and the evaporation of HNO_3 from the membrane. Evidence for these processes were found when determining nitrate using membranes without chromoionophore. Only a limited amount of nitrate was found and it seems that nitric acid must have evaporated. The slower reaction (3) will not affect the maintenance of this pre-equilibrium and eq (5) can be expressed with $[\text{HNO}_3] = K_{\text{HNO}_3} \cdot [\text{NO}_2][\text{M-H}_2\text{O}]_0^n$ as:

$$-\frac{d}{dt}[\text{C}] = k_{d3} \cdot [\text{C}][\text{NO}_2][\text{M-H}_2\text{O}]_0^n K_{\text{HNO}_3} - k'_3 \cdot [\text{CH}^+\text{NO}_3^-] \quad (6)$$

The concentration of the aquacyanocobyrinate ($\text{M-H}_2\text{O}$) is kept constant (indicated with the subscript 0) because the migration of an H_2O -molecule from the outer sphere to the axial position is faster than any diffusion processes. The binding of nitrite leading to nitrocyanocobyrinate is ignored within this approximation. The superscript n indicates the reaction

order in M-H₂O. The constant terms can be summarized in one rate constant:

$$-\frac{d}{dt}[C] = k \cdot [C][\text{NO}_2] - k' \cdot [\text{CH}^+] \quad (7)$$

with an overall rate constant $k = k_{d3} \cdot [\text{M-H}_2\text{O}]_0^n \cdot K_{\text{HNO}_3}$ and k' for the reverse reaction. NO₂ remains constant when the measurement is carried out in a flow-through system. With $[\text{CH}^+] = [\text{C}]_{\text{tot}} - [\text{C}]$ and $k' = k/K$, eq 7 can be expressed as:

$$-\frac{d}{dt}[C] = k \cdot [C][[\text{NO}_2]]_0 - \frac{k}{K} \cdot [\text{C}]_{\text{tot}} + \frac{k}{K} \cdot [C] \quad (8)$$

Summarizing the terms for [C] gives:

$$-\frac{d}{dt}[C] = k \cdot \left([\text{NO}_2]_0 + K^{-1}\right)[C] - \frac{k}{K} \cdot [\text{C}]_{\text{tot}} \quad (9)$$

This rate law is an ordinary differential equation of the form:

$$\frac{d}{dt}[C] = -a \cdot [C] + b \quad (10)$$

with $a = k \cdot ([\text{NO}_2]_0 + K^{-1})$ and $b = k/K \cdot [\text{C}]_{\text{tot}}$.

Separating the variables and integration gives the solution for [C] as a time dependent function:

$$[C] = \left([\text{C}]_0 - \frac{b}{a}\right) \cdot e^{-at} + \frac{b}{a} \quad (11)$$

As t tends to infinity, the concentration of C leads to a final value not equal to zero but to b/a , or $[\text{C}]_{\text{tot}} / (K \cdot [\text{NO}_2]_0 + 1)$, because the reverse reaction was taken in account in the rate law. Therefore [C] depends on the applied NO₂-concentration and the equilibrium constant K as it would be expected of a sensor membrane.

The half-life method is the usual way to validate an integrated rate law and to determine the rate constant. A slightly different way was, however, chosen because the final value of [C] is not below $1/2 \cdot [\text{C}]_0$ at all applied NO₂-concentrations. For the measurements the time t_{50} was determined as

where $[\text{CH}^+](t)$ corresponds to half of the final CH^+ -concentration at $t = \infty$. The appropriate expression for equation (11) in terms of $[\text{CH}^+]$ can be obtained with the relations: $[\text{CH}^+] = [\text{C}]_{\text{tot}} - [\text{C}]$ and $[\text{C}]_0 = [\text{C}]_{\text{tot}} - [\text{CH}^+]_0$. At time t_{50} the following condition is fulfilled:

$$\frac{[\text{CH}^+]_{t_{50}}}{[\text{CH}^+]_{t_{\infty}}} = \frac{1}{2} = \frac{[\text{C}]_{\text{tot}} - \left([\text{C}]_{\text{tot}} - [\text{CH}^+]_0 - \frac{b}{a}\right) \cdot e^{-at_{50}} - \frac{b}{a}}{[\text{C}]_{\text{tot}} - \frac{b}{a}} \quad (12)$$

If the initial concentration $[\text{CH}^+]_0$ is zero, eq 12 becomes:

$$\frac{1}{2} = e^{-at_{50}} \quad (13)$$

The expression for t_{50} follows directly from this and is:

$$t_{50} = \ln 2 \cdot \frac{1}{a} = \frac{\ln 2}{k} \cdot \frac{1}{[\text{NO}_2]_0 + K^{-1}} \quad (14)$$

If all the assumptions made above are valid, the t_{50} -values obtained from the measurements should be in a straight line if plotted against $1/[\text{NO}_2]_0$. Additionally, an applied linear fit has to cross the x-axis at negative values because of the term K^{-1} . If the reverse reaction is ignored, this term would not appear in eq 14 and the fit function would have to pass the zero point of the graph.

Measurements were carried out with NO_2 -sensitive membranes containing $4.22 \cdot 10^{-3}$ M of C (ETH 5418) and M- H_2O at 25 °C. The layers were cast onto the photodiodes of an optical chip and exposed to various concentrations of NO_2 . As shown in Figure 7, the t_{50} -values obtained match the requirements described above and show the validity of the derived rate law. If the rate law had been derived under the assumption that diffusion of nitrogen dioxide (reaction (2) and not (3)) is the rate determining step, equation (14) would not contain a term for the NO_2 -concentration. Under that assumption, the expression obtained for t_{50} would be a constant, e.g. $t_{50} = \ln(2) \cdot K/k_3$, and independent of the NO_2 -concentration applied.

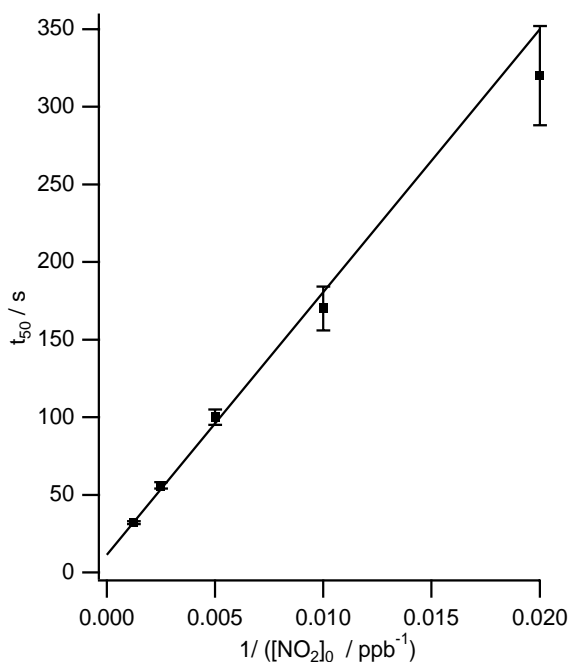


Figure 7. Membrane response in terms of t_{50} -values depend on the applied NO_2 -concentrations from 800 - 50 ppb.

The slope of the linear fit over the data points gives the overall rate constant k . Additionally, the method of initial rates was applied to obtain k by determining the initial rate for the first 30 seconds and ignoring the reverse reaction (eq 6). But for concentrations of 100 ppb NO_2 and less the initial rates were too low, indicating that the extraction of gaseous NO_2 into the membrane phase was the determining step. These concentrations were therefore ignored. For each NO_2 -concentration, measurements were performed with three membranes. The value of k determined in this study was $(3.1 \pm 0.3) \cdot 10^5 \text{ ppb}^{-1} \text{ s}^{-1}$, or $(7.5 \pm 0.7) \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ respectively.

For the aqueous-phase reaction of NO_2 , Park and Lee have determined the rate constant to be $(8.4 \pm 1.5) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$.¹⁴ In the case of the polymeric liquid membrane, the obtained overall rate is determined by the diffusion of the acids produced. It is assumed that the reaction of the encounter pair NO_2 and $\text{M-H}_2\text{O}$ is even higher than that of the aqueous-phase reaction. A catalytic effect of the cobalt-centre is considered, similar to the heterogeneous hydrolysis of NO_2 at surfaces as reported in the field of atmospheric chemistry.¹⁵⁻¹⁷ Therefore a shorter sensor response could be obtained by improving the diffusion of the nitric (and nitrous) acid with a

more suitable membrane matrix. Indeed, varying polymers and plasticizers had an effect on the response time of the sensor.¹

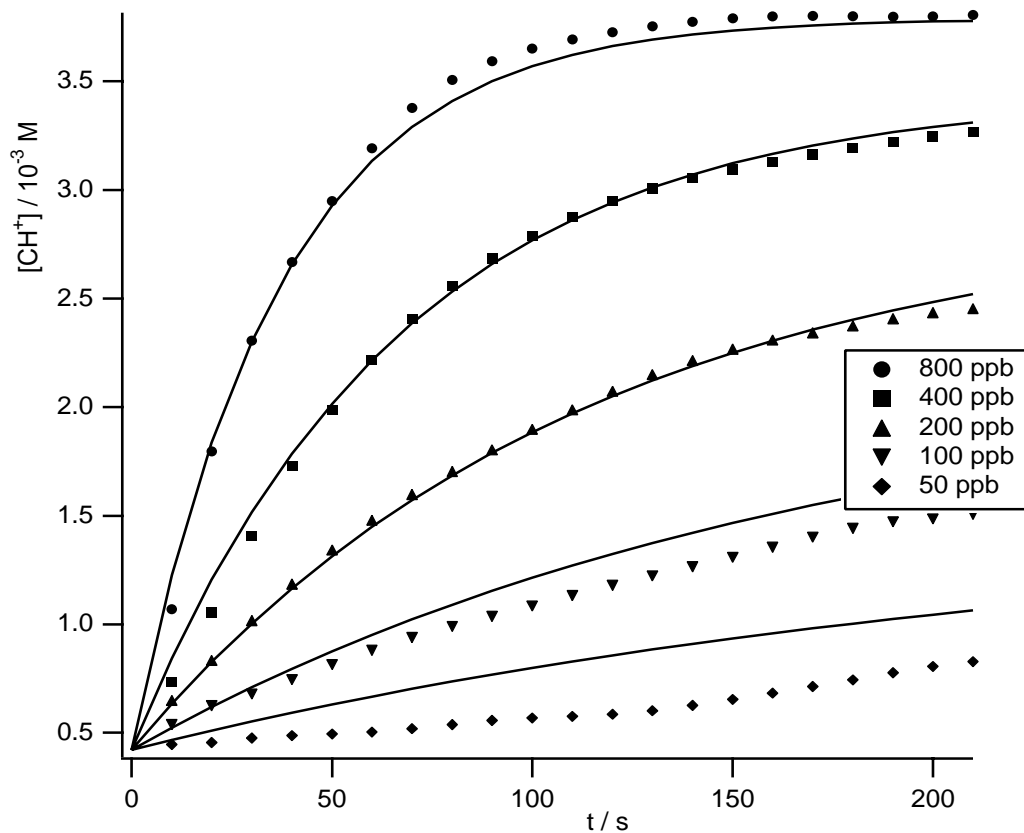


Figure 8. Membrane response to various concentrations of NO_2 . Individual points are experimental results (average of 3 measurements), and the solid lines are calculated using the integrated rate law (eq 11) and the rate constant reported in this study.

With the integrated rate law (eq 11) and $k = 7.5 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ it was possible to describe the sensor response at several NO_2 -concentrations as shown in Figure 8. For K the value $2.7 \cdot 10^8 \text{ M}^{-1}$ was found to fit the data points best. The sensor response starts with a concentration of CH^+ at $4.2 \cdot 10^{-4} \text{ M}$, which corresponds to an initial degree of chromoionophore protonation of 10%, as found after membrane preparation. For nearly all NO_2 -concentrations there was good agreement between the theoretical function and the experimental data, which indicates the validity of the kinetic model proposed in this study. At 100 ppb and lower concentrations the membrane response is below the calculated results, which can probably be attributed to the fact that the condition specified at the beginning of this

section is not fulfilled anymore and the extraction of $\text{NO}_{2(g)}$ into the polymer layer (1) becomes the rate determining step. Correlations between the calculated and experimental differ with increasing time due to the binding of nitrite to the cobyrinate, which is not included in this approach. Thus the amount of available $\text{M-H}_2\text{O}$ continuously decreases, which leads to a lower signal than that calculated with a constant amount of $\text{M-H}_2\text{O}$. This is more pronounced with longer response times, i.e. the more nitrous acid is produced.

In the determined overall rate constant $k = k_{d3} \cdot [\text{M-H}_2\text{O}]_0^n \cdot K_{\text{HNO}_3}$, the concentration of $\text{M-H}_2\text{O}$ is included as a constant. The next step was to verify if this is valid for any concentration of the cobyrinate, especially when the concentration is lower than that of the chromoionophore. Then the reaction order n in the cobyrinate was determined. Measurements were carried out with an optical chip consisting of 4 photodiodes which were covered with the polymeric membranes. In this way four different membranes could be simultaneously exposed under the same conditions to NO_2 . The layers contain different quantities of aquacyanocobyrrinate using 1:1, 1:0.5, 1:0.25, 1:0 stoichiometry of C : $\text{M-H}_2\text{O}$. The membrane without cobyrinate was kept as a reference. These membranes were exposed to

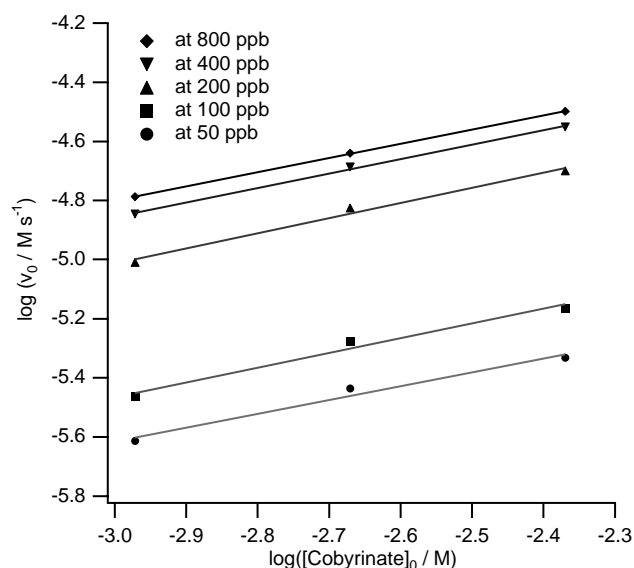


Figure 9. Determination of the reaction order in Aquacyanocobyrrinate with the method of initial rates. The slope of the logarithm of the initial rate against the logarithm of the concentration is 0.49 ± 0.01 , which gives the reaction order in the cobyrinate.

several different concentrations of NO_2 to see if n remains constant and the derived model is consistent. Additionally, with this approach, it was possible to verify that the reaction order in NO_2 is first order. The logarithms of the initial rates against the logarithms of the concentrations of M- H_2O result in straight lines with slope n , as shown in Figure 9. Over the range from 50 till 800 ppb the slope was found to be 0.49 ± 0.1 . Therefore, the reaction order in aquacyanocobyrinate is assigned to be half. When the logarithms of the initial rates were plotted against the logarithms of the concentrations of NO_2 , it was found that the reaction is first order in NO_2 at all the concentrations of M- H_2O investigated. Thus the reaction orders obtained in NO_2 and M- H_2O reflect the reaction stoichiometry: $2 \text{NO}_2 + \text{M-H}_2\text{O} = \text{products}$. But, it is thought that probably 2 water molecules of the cobyrinate are involved in this reaction and thus the reaction order in H_2O itself, is one. Laboratory studies have reported that the heterogeneous reaction of NO_2 with surface-adsorbed H_2O is first order in both NO_2 and H_2O .¹⁸

To compare these measurements with the calculated values, the term for $k = k_{d3} \cdot [\text{M-H}_2\text{O}]_0^n \cdot K_{\text{HNO}_3}$ (eq 7) has to be set at $k = 1.16 \cdot 10^7 \cdot [\text{M-H}_2\text{O}]_0^{1/2}$. The obtained constant $1.16 \cdot 10^7 = k_{d3} \cdot K_{\text{HNO}_3}$ derives from the value for k as determined above at a concentration of $4.22 \cdot 10^{-3}$ M of M- H_2O . The response of these membranes at 400 ppb NO_2 fits the calculated values during the first 100 seconds, as shown in Figure 10. Afterwards the supply of water starts to determine the reaction rate. This means the assumption that $[\text{M-H}_2\text{O}]$ is constant no longer applies and water has to be supplied by the bulk membrane, rather than from the depleted outer-sphere of the metal complex. The final protonation degree of these membranes reflects the fact that one molecule of aquacyanocobyrinate can react several times with NO_2 while the chromoionophore protonates.

The derived rate law in this study is consistent with the reaction mechanism proposed for the NO_2 -sensitive membrane based on aquacyanocobyrinate. The rate law describes the sensor response well at the beginning of the response while only reaction (2) and (3) are considered. This conforms with findings from the determination of reaction products which have shown the dominance of reaction (3) over (4).

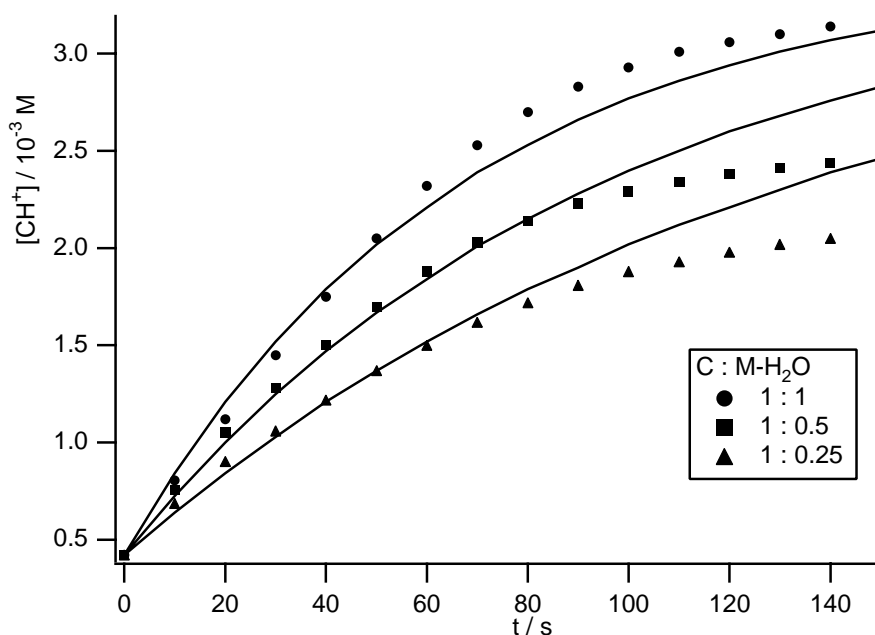


Figure 10. Responses of membranes to 400 ppb NO_2 , containing equimolar, half and quarter amounts of $\text{M-H}_2\text{O}$ relative to the chromoionophore. Solid lines are calculated with eq 11 including the amount of cobyrinate and its reaction order of $1/2$.

4.4. Conclusions

It has been possible to show, through determining the reaction products, studies with different membrane compositions and investigations with SO_2 , that the sensitivity and selectivity of the NO_2 -sensitive membrane described here derive from the unique reaction of NO_2 with the H_2O of the aquacyanocobalt(III)-cobyrrinate in which nitric and nitrous acid are formed. It was found that either the axial position is immediately occupied with a new water molecule from the outer-sphere of the metal complex or a second H_2O -molecule nearby reacts with NO_2 and the coordinated H_2O plays an active role as a catalyst. This finding is based on spectral investigations of membranes containing the cobyrinate alone (without chromoionophore), where no changes in the UV/VIS-spectrum could be observed due to exposure to NO_2 (shown in section 4.3.5), while reaction (2) did occur as it is derived from the determination of reaction products (section 4.3.4). It was shown that the source of water is the H_2O -molecule bound to the cobalt centre rather than any unspecific water (section 4.3.2).

However, it is quite possible that the axial H₂O-ligand is not the only water molecule involved in this reaction. In a theoretical study based on density functional theory calculations, it was shown that, in homogeneous gas-phase hydrolysis, there are two or more water molecules involved.¹⁹ Another finding of that study was that the hydrolysis occurs with the monomer of nitrogen dioxide, because with N₂O₄ the reaction is always endothermic. This theoretical result is in agreement with the proposal made here that the aquacyanocobyrinate reacts with two monomers of nitrogen dioxide and not with the dimer. This conclusion draws on the known fact that, when measuring nitrogen dioxide in concentrations of ppb and ppm, the monomer is the dominating species and the concentration of the dimer N₂O₄ is negligible.

The optical signal obtained with the NO₂-sensitive membrane is caused mainly by the protonation of the chromoionophore with HNO₃ and to a lesser extent with HNO₂. Due to the high acidity of nitric acid ($pK_A = -1.4$), this reaction is more dominant than the protonation with nitrous acid ($pK_A = 3.3$). It was found that at high concentrations of NO₂ the protonation occurs mostly due to nitric acid, as was shown in section 4.3.4. Numerical simulations demonstrated that at higher NO₂-concentrations, the turn-over of the faster reaction (3) becomes high enough to consume almost all unprotonated chromoionophore (C). Thus less C remains for the slower reaction (4). Under these conditions most of the HNO₂ formed evaporates from the membrane. Therefore no nitrite remains within the membrane, as was the case when determining the reaction products. The derived rate law was found to be sufficient to describe the sensor response within the first time period, if only reaction (2) and (3) and not (4) are considered.

The protonation with HNO₂ and the simultaneous binding of nitrite occurs at low concentrations of NO₂ with long exposure times. It was shown that nitrocyanocobalt(II)-cobyrrinate is formed only if a basic species like the chromoionophore is involved (section 4.3.4 and 4.3.5).

It was also shown that the optical signal derives from a protonation of the chromoionophore with the acids formed and that nitrosation can occur as a side reaction while using phenoxazine derivatives. It was possible to

describe the optical signal as dependent on the NO₂-concentration applied with a rate law which is consistent with the proposed mechanism.

Unlike with metal oxide semiconductor layers, the principle described here shows the advantages of a specific reaction to obtain a high selectivity. Additionally, with a consecutive second reaction, a transduction is possible so that optical sensor schemes, which are favoured in many applications, may be used.

Acknowledgements

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5 Additional Experiments with the Membrane Based on Aquacyanocobyrinate

5.1. Investigations with ATR IR of the NO₂-Sensitive Membrane

Various spectroscopic methods were used to investigate the sensing principle of the NO₂-sensitive membrane based on aquacyanocobalt(III)-cobyrinate and a chromoionophore, such as ETH 5418. With infrared (IR) spectroscopy, a sample composed of several chemical compounds can be investigated, and the changes due to its interactions with the analyte can be studied. However, infrared spectroscopy is not as sensitive a method as NMR. When investigating a sensor membrane, changes in the layer must be monitored on-line at room temperature during the sensing process. A useful technique for this task is Attenuated Total Reflection Fourier Transform Infrared (ATR FT-IR) spectroscopy. The principle of Attenuated Total Reflection relies on light which is trapped by total reflection inside a waveguide of a high refractive index. Absorption takes place only in a very thin layer outside the waveguide due to the so-called evanescent field. If the waveguide is covered with the polymer membrane, a setup is obtained where the sensitive layer can be freely accessed by the sample on one side and the IR-spectrum can be simultaneously recorded with the spectrometer on the opposite side. Therefore, changes within the membrane due to exposure to NO₂ or any other gas can be monitored with FT-IR spectroscopy.

The penetration depth, dp , of the evanescent wave into the cast membrane can be calculated according to:

$$d_p = \frac{\lambda / \hat{n}_1}{2\pi \sqrt{(\sin \theta_1)^2 - (\hat{n}_2 / \hat{n}_1)^2}} \quad (1)$$

where λ is the wavelength of the IR-beam, \hat{n}_1 and \hat{n}_2 are the complex refractive indices of the waveguide and the polymer layer, respectively, and θ_1 is the angle with which light is coupled into the waveguide [1]. Thus the penetration depth depends on the wavelength. The wavelength investigated ranges from 3500 till 700 cm^{-1} , and the corresponding depths form 0.6 till 3 μm . This implies that the intensities of the absorption bands at higher wavelengths compared with those at lower wavelengths are overemphasized in contrast to a transmission measurement. The polymer layer produced was thicker than 10 μm and, therefore, the evanescent field did not leave the membrane.

Experimental

A zinc selenide crystal ($n = 2.3$) was used as a waveguide in which the IR-beam was reflected 6 times. The FT-IR-measurements were carried out with the Excalibur FTS 3000 spectrometer from BioRad. Membrane cocktails of 20 mg PVC and 15 mg DOS dissolved in 0.6 ml THF containing 0, 1 and 12 wt.-% aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrrinate perchlorate were prepared. The fraction of cobyrrinate usually used for UV/VIS-spectroscopy of a NO_2 -sensitive optode membrane is 1 wt.-%. In order to be able to distinguish the absorption bands ascribed to the cobyrrinate from the bands of the IR-spectrum induced by other membrane components, the concentration of the metal complex was increased to 12 wt.-%.

The membrane cocktail was applied as a film-coating layer to the surface of one side of the waveguide. The ATR crystal was fixed into the measurement cell of the IR-device and the light beam was coupled into the waveguide, with an incident angle of 30° , providing 6 reflections. The measurement cell was connected with the tubing of the gas measurement station to allow a controlled flushing with NO_2 .

To obtain a reference spectrum of the cobyrinate, a solution of the metal complex in THF was dropped onto the crystal, allowed to dry completely and measured. A reference spectrum of a pure PVC/DOS membrane was also recorded. Membranes containing the cobyrinate were flushed with a gas stream of synthetic air, while NO₂ was mixed in under controlled conditions.

Results and Discussion

The IR-spectrum of the PVC/DOS-membrane, containing 12 wt.-% of the cobyrinate, is shown in Figure 1. Two single bands at 1500 and 1580 cm⁻¹ are assigned to the metal complex, as can be deduced from the reference spectra in the upper part of Figure 1. The wavenumbers at 1580 and 1500 cm⁻¹ indicate an aromatic system, and these bands are tentatively attributed to the phenol groups of the cobyrinate. The strong band at 1720 cm⁻¹ is typical for C=O_{st} in ester groups. It is mainly attributed to the fact that the plasticizer adds to the absorption of the cobyrinic acid ester. No spectral changes could be observed due to exposure to NO₂. At the bottom of Figure 1, a difference spectrum of IR-spectra is shown before and after the membrane was treated with 100 ppm NO₂.

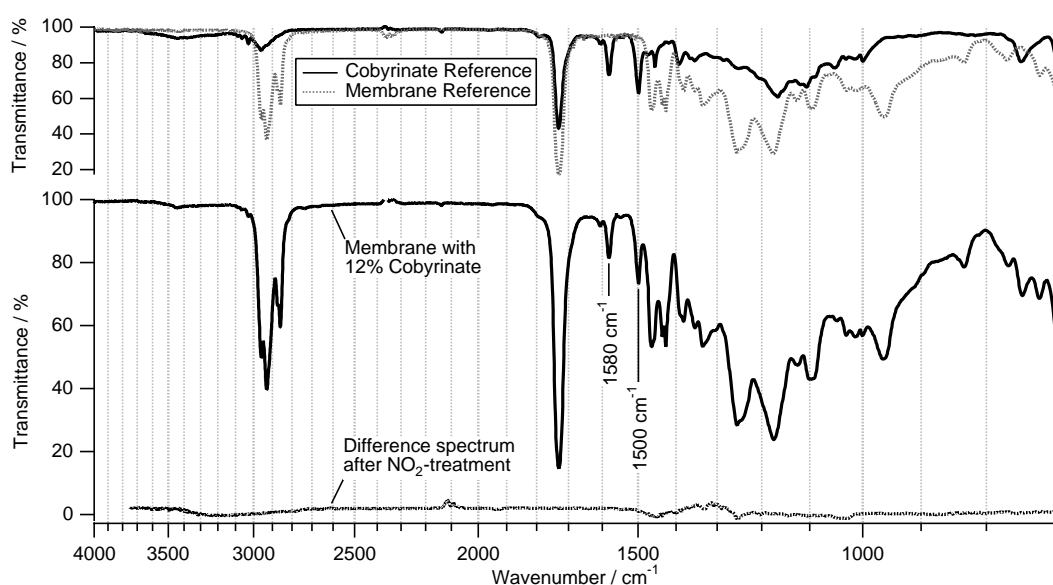


Figure 1. ATR FT-IR spectrum of a PVC/DOS-membrane containing the cobyrinate (middle). Below the difference spectrum of the membrane sample before and after treatment with NO₂. At the top, the reference spectra are shown.

Taking the signal-to-noise ratio into account, no significant spectral changes due to NO_2 uptake or binding could be found, although several measurements were carried out under different humidity conditions. Membranes containing 1 wt.-% of the chromoionophore ETH 5418 and of the cobyrinate did not result in spectral changes either. With these membranes only bands derived from the membrane matrix were visible.

The following conclusions were drawn: A quantity of cobyrinate (and chromoionophore) larger than 3 wt.-% might lead to a precipitation of the compounds within the membrane and then not be reactive. With lower concentrations, however, it is not possible with this method to monitor changes in the IR-spectra of these compounds. To observe absorption bands of NO_2 sorbed within the membrane, or derived products, higher NO_2 -concentrations would be necessary. In other studies the adsorption of NO_2 on surfaces and its reaction with adsorbed water was investigated using IR-spectroscopy. These suggest that concentrations of 0.6 torr (800 ppm) of NO_2 and more are necessary [2]. However, the working range of the optode is below 100 ppm. At higher concentrations a decomposition of membrane compounds would be expected due to a nitrosation.

Nevertheless, it might be possible with a more sophisticated method, such as "ATR FT-IR modulation spectroscopy", to detect very small changes in the IR-spectrum. Modulation spectroscopy enables selective scanning of those absorption bands that are the result of molecules (or parts of molecules) involved in a stimulation process [3]. A stimulus, such as a repeated change in the applied NO_2 -concentration, results in a periodic excitation of the investigated system and, therefore, a periodic change in the spectral range assigned to the compounds involved in the process. This technique enables "quasi-real-time" difference spectroscopy to suppress system instabilities. A further improvement in this respect can be achieved by introducing a single-beam sample reference (SBSR) technique [1].

5.2. Simulation of the NO_2 -Sensitive Membrane in Solution

In order to study the reaction of the aquacyanocobyrinate and of ETH 5480 with NO_2 , experiments in solution rather than in a polymer membrane were performed. A thin glass capillary containing a porous frit

at the end was produced. It was possible to place it into a quartz cuvette of a UV/VIS-spectrophotometer while avoiding an interference with the light beam. Thus, a liquid sample could be treated with gaseous NO_2 while simultaneously monitoring its UV/VIS-spectrum. Experiments using different solvents were conducted. The solvent most similar to the membrane matrix was the plasticizer of the membrane, DOS. Another solvent, which was suitable owing to its low vapour pressure, was DMSO. In addition, methanol was used as a solvent. However, the evaporation of the solvent due to purging with NO_2 was evident and a subsequent increase in the concentrations of the compounds dissolved had to be taken into account. The glass capillary was connected with the tubing of the gas measurement station to allow a controlled purging of the solution, with 2 ppm NO_2 as the maximum concentration.

Solutions containing either the cobyrinate or the chromoionophore, or both, were investigated. But no changes in the UV/VIS-spectra due to purging with NO_2 were observed. Although small bubbles were obtained, the partial pressure of NO_2 at the interface between an air bubble and the solvent phase might not have been high enough to have solvation of NO_2 . For further experiments in solutions, the usage of a gas liquid reactor has to be considered, such as that used in a similar study with NO_2 [4].

5.3. Stability of the Membrane

Based on forced lifetime experiments involving NO_2 -sensitive membranes, it was concluded that efforts had to be concentrated on improving the stability of the membranes in order to meet the requirements for use in fire detectors. The goal of these developments was to reach a shelf life of three years.

Sensor membranes were stored under clean air in the dark at elevated temperatures, as described in chapter 2. A decrease in sensitivity of the membranes was already observed after a couple of days. This loss in sensitivity increased with time and temperature. It was considered that the decomposition of a single membrane compound might affect the stability of the membrane. The stabilities of the single membrane compounds were investigated with thermogravimetric methods. No decrease in mass was

observed at temperatures up to of 200 °C with any compounds during a heating time of, in total, 50 minutes.

It was therefore, concluded that an unknown interaction between the different membrane compounds gave raise to the decrease in sensitivity of the membrane. As shown in chapter 2, the exchange of the two membrane compounds: polymer and plasticizer, did affect the stability and sensitivity of the membrane. Two possible explanations were found for the decrease in sensitivity. Either the matrix does itself react with the sensitive compounds (cobyrinate, chromoionophore), or it can facilitate any reaction where one of the sensitive compounds is degraded.

It was found that the chromoionophore of membranes that showed a loss in sensitivity could still be protonated with acids, reaching the maximum degree in protonation. Additionally, in the case of ETH 7058, the total absorbance was still the same as shortly after membrane preparation. This suggested that the cobyrinate was affected by an undesired interaction rather than the chromoionophore.

Two PVC/DOS-membranes containing two derivatives of aquacyanocobyrinate were prepared. One compound was the more lipophilic aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrinate perchlorate and the other was the aquacyanocobalt(III)-heptamethylcobyrinate perchlorate. The membranes were stored in the dark at ambient air and their UV/VIS-spectra were monitored for several months (Figure 2).

The spectra of both derivatives changed with time. A small decrease in absorbance was already observed after 3 days. As can be seen in Figure 2, not only a decrease in intensity could be ascribed to a precipitation of the compound within the membrane, but also an isosbestic point could be observed at 312 nm. At higher wavelengths the intensities were decreasing, whereas below 312 nm an increase in absorbance was observed. Thereby the whole spectrum showed a blue-shift. If the spectral changes consisted only of these changes in intensity, a decomposition of the compound could be assumed. But the shift to higher wavelengths goes against this. The binding of nitrite and other anions also leads to a blue-shift of the spectrum, but without a decrease in intensity. The existence of an isosbestic point shows that only one reaction takes place, changing the aquacyanocobalt(III)-cobyrinate to an unknown compound.

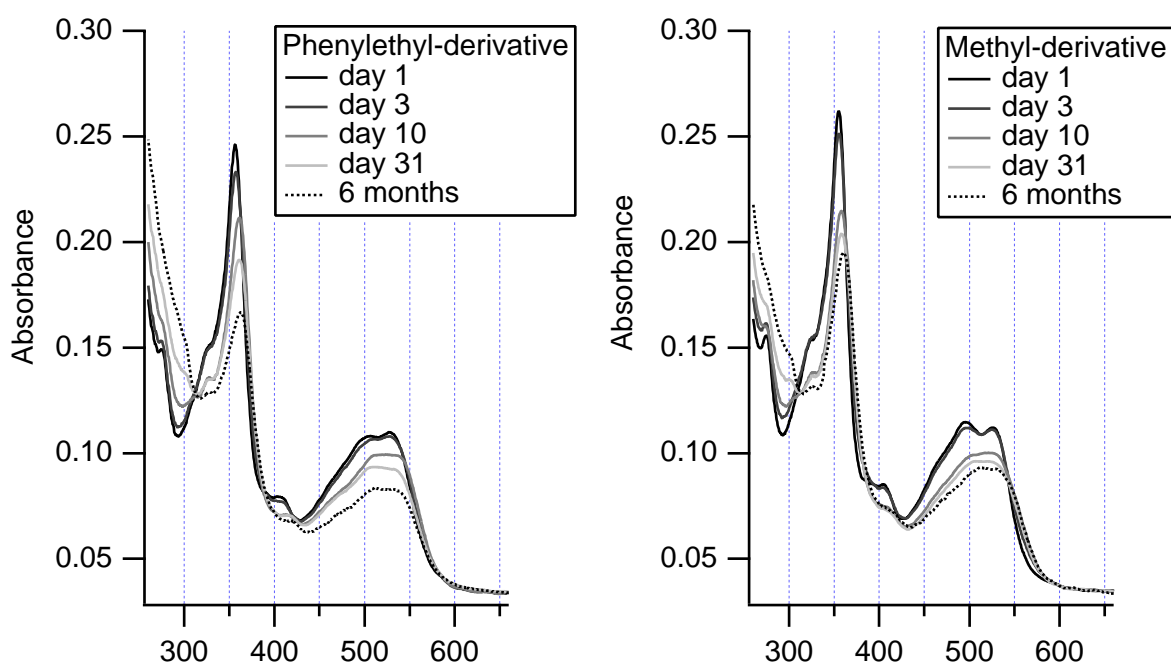


Figure 2. Spectra of aquacyanocobalt(III)-hepta(2-phenylethyl)cobyrinate perchlorate (left) and aquacyanocobalt(III)-heptamethylcobyrinate perchlorate (right) within a PVC/DOS-membrane for a time period of 6 months. The spectra are shaded from black (1. day) to grey (1 month), illustrating their time dependence.

Oxygenation of corrinoid cobalt(III) complexes leads to a cleavage of the corrin macrocycle and to a formation of dioxosecocorrins [5, 6]. During the reaction, the absorbance between 500 and 600 nm decreases with a simultaneous increase in the region between 400 and 500 nm. Therefore a reaction with atmospheric oxygen can probably be excluded.

The compound formed cannot be identified on the basis of these measurements. However, a coordination of the perchlorate to the metal centre might be considered.

5.4. Calculation of the UV/VIS-spectrum

When the UV/VIS-spectra of membranes containing only the aquacyanocobyrinate were examined, no changes due to exposure to NO_2 could be observed. Simultaneously, it was found that a reaction of NO_2 with the aquacyanocobyrinate did occur in such a membrane, although to a

lesser extent compared with a membrane containing the chromoionophore in addition. One conclusion derived from the experiments was that NO_2 does not coordinate to the cobalt(III) metal centre of the cobyrinate. In the case of a ligand exchange of H_2O with the strong electron acceptor NO_2 , a change in the UV/VIS-spectrum would have been expected.

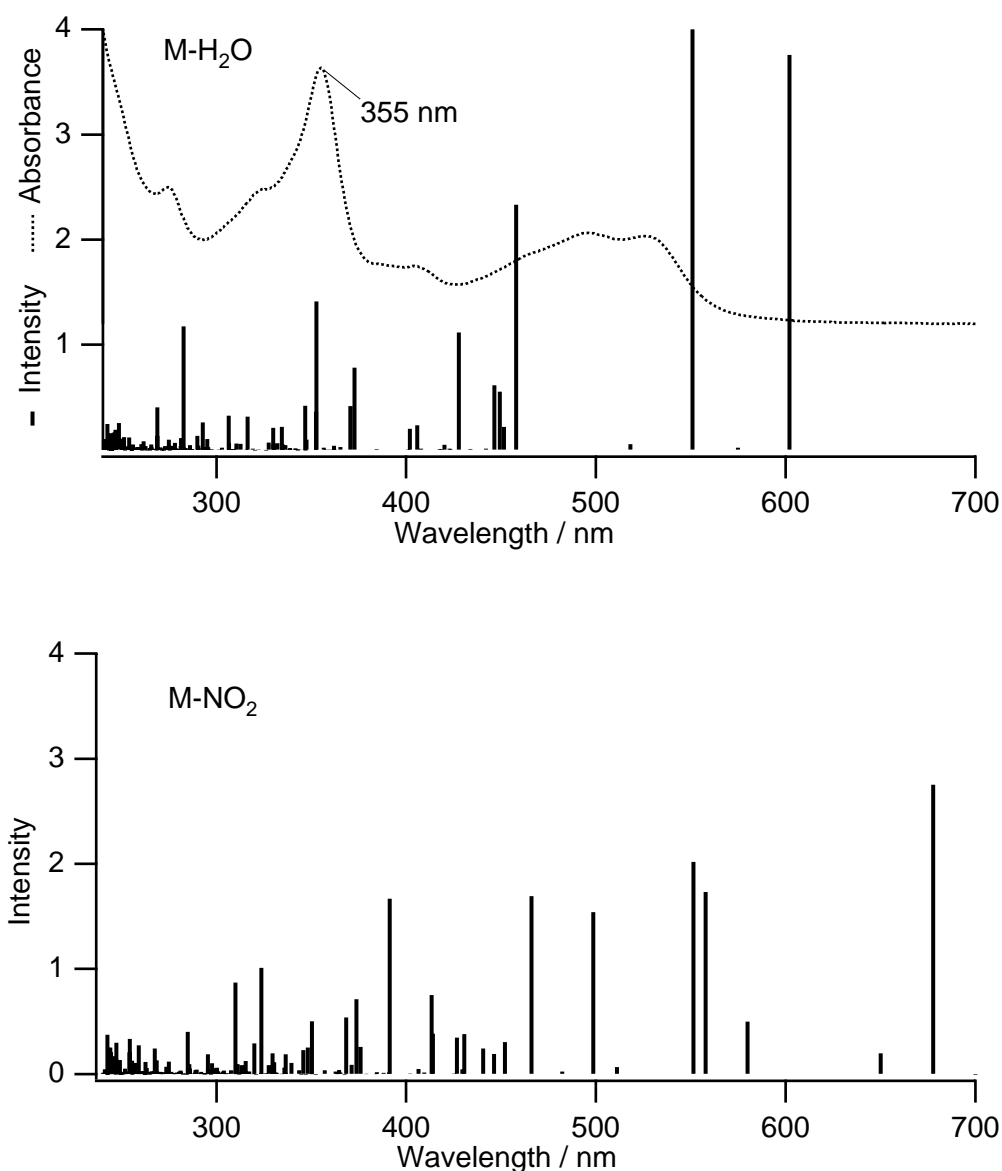


Figure 3. Calculated transitions in the UV/VIS-region of aqua- (top) and the nitro- (bottom) -cyanoheptamethylcobyrinate. The experimental absorption spectrum is also shown (top).

The UV/VIS-spectra was calculated to obtain additional informations. *Ab initio* calculations based on density functional theory (DFT) using the

software package, DMol3 [7], were performed at Robert Bosch GmbH. To reduce the calculation time, the methylester-derivative was introduced into the model and the perchlorate counterion was omitted, whereas the total charge of +1 was conserved. A single geometry optimization took, however, 8 days. The total energy of the aquacyanocobyrinate obtained with this model was -76'125 kJ/mol; replacing H₂O with NO₂ resulted in -76'415 kJ/mol. The QM calculations gave a gas-phase spectrum, so it can hardly be compared with the spectra obtained in solution or within a membrane. The strongest absorption band in the experimentally obtained spectrum of aquacyanocobyrinate was a sharp band at 355 nm. In the calculated spectrum, a moderate intensity was obtained at this wavelength (Figure 3, upper part). In the region from 420 - 560 nm, the calculations referred to two strong transitions, whereas experimentally two large absorption bands which overlap were observed. Transitions higher than 600 nm might be observed in the gas-phase spectrum but could not be traced when the compound was dissolved.

When the calculated spectra were compared, there was a significant difference between the spectra of aquacyanocobalt(III)-cobyrinate with H₂O as the axial ligand and with NO₂. The calculations above support the assumption that a binding of nitrogen dioxide to the cobyrinate would lead to a spectral change in the UV/VIS-spectrum.

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6

Iron Phthalocyanine Derivatives as NO₂-Sensitive Compounds in Polymeric Optode Membranes

6.1. Introduction

The final aim of the project was to develop an optical NO₂-sensor for application in fire detectors. The most difficult requirement is to ensure that the NO₂-sensitive membrane is stable. Such a sensor must have a lifetime of at least three years. But the membrane based on aquacyanocobalt(III)-cobyrrinate had already lost its sensitivity within less than one year. The critical parameter was found to be the stability of the cobyrinate within the polymeric membrane. Although different polymers and plasticizers were investigated, it was not possible to overcome this stability problem. With the chromoionophores used in the project, improvements were made concerning resistance to nitrosation and bleaching. However, the stability of the cobyrinate within the polymeric membrane remained the bottle neck.

Since it is uncertain whether the stability problems can be solved within a reasonable time, attempts were made to see if there was not another scheme to measure NO₂ optically. In the course of the development of the NO₂-selective membrane based on the aquacyanocobyrrinate, the idea emerged of exploring a sensing principle where an introduced metal complex changes its absorbance/ transmission spectrum in the visible range upon binding of NO₂. Unfortunately, only a few investigations into the interactions of NO₂ with metal atoms have been reported [1].

In order to allow transmission measurement in the visible spectrum, an adequate conjugated π -system similar to that of the corrin macrocycle would be needed. Typical classes of these kinds of compounds are metalloporphyrins and -phthalocyanines. The latter were preferred due to their absorbance at generally longer wavelengths.

6.1.1 Application of Phthalocyanines in Chemical Sensors

The exploitation of free and metal phthalocyanines (Pc and MPc), as well as porphyrins, as chemically interactive material in chemical sensors has become the subject of an enormous research effort [2, 3]. Solid state films of phthalocyanines are generally sensitive to strong electron-acceptor gases, such as oxygen, halogens, nitrogen dioxide and hydrogen chloride, and show a moderate response to donors, such as water, ammonia and hydrogen sulphide. Compounds which are neither strong electron acceptors nor donors, like hydrogen, carbon monoxide, carbon dioxide or methane on the other hand, show a negligible response [2]. Thus the sensing principle of these films can be compared with that of semiconducting metal oxide layers, which exhibit a similar lack of selectivity. They are also similar in that most of the pc-films need an operating temperature above room temperature. This is in many cases necessary for the layer to recover after exposure.

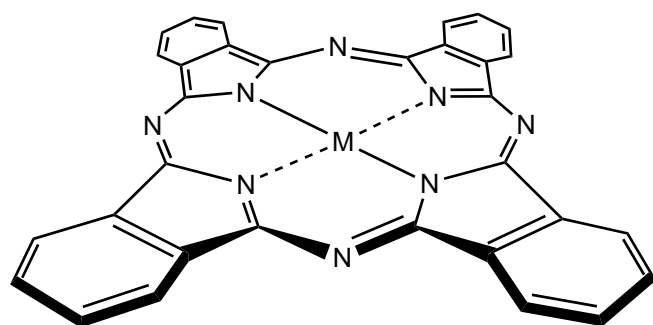


Figure 1. Chemical structure of a metal phthalocyanine.

Thin films of phthalocyanines or porphyrins can be produced by a variety of techniques, such as vacuum sublimation, plasma-activated evaporation, solvent evaporation from a fine suspension, spin-coating and Langmuir-Blodgett (LB) deposition [4-8]. One common way to detect gases with

such films is by measuring the change in electric conductivity induced by the adsorption of gas molecules on the surface of the organic semiconductors making use of chemiresistors. The change in conductivity is caused by the change in charge-carrier concentration due to the donor-acceptor states arising from the gas adsorption. Another way of detecting gases is the measurement of the mass enhancement or general changes in surface structure and viscoelastic properties due to the gas sorption using quartz microbalances (QMB) and surface acoustic wave devices (SAW) [3, 9, 10].

Crystals and solid state films of metallophthalocyanines form various types of aggregates. The process of production determines what kind of polymorphic structure is obtained [2]. For example, in LB films a one-dimensional linear stacking of the phthalocyanine molecules is observed, forming dimers, trimers, etc. [11]. For phthalocyanines containing a metal centre which bends out of the macrocycle, two molecules can stack in three different ways, but only concave-concave and convex-convex interactions occur frequently [12]. The molecular structure of the macrocycle is hardly influenced by interactions with its neighbours. These intermolecular interactions affect the electronic states and define which part of the molecule is planar and which bends out [12]. Therefore, films obtained from an identical phthalocyanine compound can show marked differences in their sensitivity. The fact that it is possible to obtain different sensitive layers with the same compound has simplified the development of such multi-layer sensors as electronic noses [2].

An increase in diversity was obtained by introducing peripherally substituted phthalocyanines [4, 6, 11, 13, 14]. Such modifications affect the electronic states as well as the aggregation of molecules.

6.1.2 NO₂-Sensors Based on Phthalocyanine Films

As described above, phthalocyanine films are suitably sensitive to detect NO₂. In the last decade, the development of NO₂-sensors has focused mainly on CuPc and PbPc [9, 15-21]. Other phthalocyanines used were: polyfluoro aluminium phthalocyanine [22], Ti(Pc)₂ [23], metal-free octahexyl-substituted [24] and 18-crown-6 substituted phthalocyanine

[11]. Sublimed films or Langmuir-Blodgett films of FePc were also considered for NO₂-sensing [19, 21].

Optical sensors for NO₂ were evaluated based on surface plasmon resonance (SPR) using metal-free Pc [25, 26]. A sensor based on evanescent wave excited fluorescence was made using metal-free self-assembled phthalocyanine monolayers [27]. Optical absorption was used in a study of LB film based on a CuPc derivative [18].

6.1.3 Phthalocyanines in Polymeric Layers

Pure phthalocyanine or porphyrin films have an amorphous or polycrystalline character. In the studies described here, MPcs incorporated into polymer layers were investigated since it was expected that the versatility of single molecules would be more pronounced than in aggregated films. It was assumed that with dissolved MPcs a more selective system could be achieved, which might be even more sensitive. It was expected that the UV/VIS-spectrum would show sharp absorption bands, similar to those when Pcs are dissolved and unlike those with aggregated Pcs. An interaction of NO₂ with single molecules of metallophthalocyanines might have significant influence on the absorbance of these MPcs.

Incorporating phthalocyanines into polymers for optical sensing had not yet been investigated. The easiest procedure to incorporate a Pc into a polymer-based optical sensor membrane is to dissolve both components in a common solvent and to spread them on an optical waveguide. It was expected that it would be difficult to maintain the metallophthalocyanine dissolved within a polymer matrix because of the metallic character. Unlike these metal complexes, it was possible to dissolve metal-free porphyrin within a polymer. The resulting polymeric layer was found to be sensitive to benzene, unlike films based on pure porphyrin [28].

The first attempts to combine metal phthalocyanines with polymers involved polymerizing these compounds [29], frequently using plasma polymerization. NO₂-sensitive films based on CuPc and ZnPc were obtained with this procedure [30, 31]. The combinations of polymers and phthalocyanines were used as chemiresistor films, where conducting polymers like polypyrrole were doped with NiPc or CuPc [32], [33].

6.2. Optical Properties of Phthalocyanines

VIS-spectra of phthalocyanines exhibit an intense band in the red region, the so-called Q band, which corresponds to the lowest energetic π - π^* ligand transition. A study showed that the highest energy occupied orbitals are macrocycle-ligand-like and not metal-3d-like orbitals [34]. Therefore the origin of the Q band must be a transition from the a_{1u} to the e_g^* orbital of the phthalocyanine ring (see Figure 2). The second lowest energetic transition, the so-called B band, lies already in the UV and has its origin in an overlap of several absorption bands. In contrast, for porphyrin complexes a clear band, the so-called Soret band, can be identified. Metallophthalocyanines show further charge-transfer (CT) bands, usually assigned to either metal-to-ligand (MLCT) or ligand-to-metal charge transfer (LMCT). Because CT transitions involve molecular orbitals (MOs) of the π ring, extensive mixing can occur so that the π - π^* set of transitions is blended into the CT set.

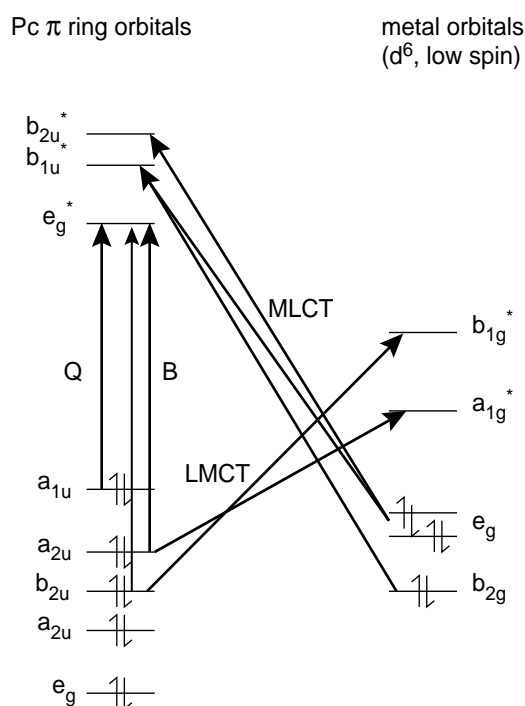


Figure 2. Origin of absorption in the region of the first two π - π^* transitions and possible directions for charge transfer transitions between the central metal and the Pc ring.

In Figure 2 a diagram is constructed which shows the possible transitions allowed by symmetry for a low spin d⁶ metal complex like iron(II)-phthalocyanine (FePc) [35]. Because transitions for MLCT end on the b_{1u}^{*} and b_{2u}^{*} orbitals, it can be expected that these bands will lie above the Q band in energy, whereas for LMCT the energies of the transitions can straddle the Q band. The Q band can be influenced by both the metal centre and the axial ligands. It is known that in metallophthalocyanines there is a π back-donation of electrons from the metal d orbitals to the macrocycle ligand π^{*} orbitals [36]. The π-π^{*} transition energy, and therefore the Q band, is strongly influenced by this π back-donation [37]. The introduction of axial ligands modifies the π back-donation to the macrocycle, and therefore the π-π^{*} transition energy is affected [38]. In the case of iron phthalocyanine with derivatives of pyridine as the axial ligands, it was found that the wavelength of the Q band is raised with increasing donor strength. With electron-withdrawing substituents at the pyridine, however, the band moves toward shorter wavelengths with increasing acceptor power. This observation will be important when

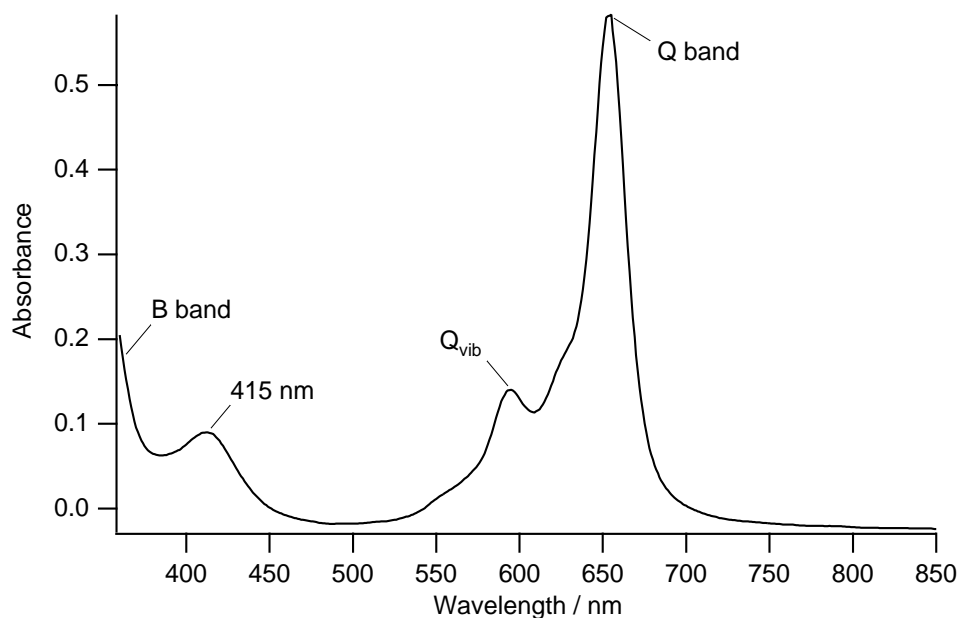


Figure 3. UV/VIS-spectrum of iron phthalocyanine dissolved in pyridine as the coordinating solvent.

discussing the different ligands used in this study. In the presence of strongly coordinating solvents or ligands like pyridine, λ_{max} for the Q

band is observed in the range of 650 - 670 nm with Q_{vib} components on the blue edge (Figure 3) [35]. A typical spectrum of a monomeric, low spin $L_2\text{Fe(II)Pc}$, with $L = \text{pyridine}$ as a strong coordinating solvent, is shown in Figure 3. In a study investigating the coordination of pyridine derivatives to FePc in non-coordinating solvents, the authors attributed the absorption band around 650 nm to the 2:1 complex and a shoulder which appeared around 690 nm to the 1:1 complex [38]. This observation will help to explain later some observed optical changes in the compounds used in this work.

With increasing σ donor strength of the axial ligand, a band around 415 nm becomes more prominent. Dale assigned this band to a MLCT [39], while Ouédraogo et al. analysing the influence of a wide range of nitrogen bases on the absorption spectrum, assigned this band to axial ligand-to-Pc CT [38]. This transfer should either occur by direct overlap between the equatorial macrocycle π orbitals and those of the axial ligands or through intermediate iron orbitals. These authors were able to establish a correlation between the band at 415 nm ($\lambda_{L-\text{Pc}}$) and the axial ligands. Additionally, they found a correlation between the two wavelengths, $\lambda_{L-\text{Pc}}$ and $\lambda_{\pi-\pi^*}$, which depended on the axial nitrogen ligands.

In the case of coordinating pyridine derivatives with electron-withdrawing substituents, an additional band between 440 - 530 nm was observed and attributed to an iron-to-axial-ligand CT [38]. This band was not detected for FePc(py)_2 or FePc with other donor ligands.

The spectra of dimeric complexes in solution show a strong absorption band near 620 nm. This results from exciton coupling between the π systems of the two Pc-rings, which leads to a blue-shifted Q band [35]. This information will be important in explaining some of the spectra obtained in this work.

The Q band region was shown to be very sensitive to metal oxidation too. The spectra of low-spin six-coordinated $(L)_2\text{Fe(III)Pc}$'s show an absorption maximum (λ_{max}) in the 670 - 690 nm region [35]. This shift to higher wavelengths due to oxidation will be relevant when discussing lipophilic FePc derivatives which are sensitive to atmospheric oxygen.

The optical properties of dissolved metallophthalocyanines have been the subject of many studies. The reactivity of iron porphyrin and phthalocyanine with axial nitrogen-ligands has been investigated to see if they could be good models for protein-active sites of hemoproteins [40]. In solution, the interaction of dissolved FePc with nitrogen dioxide has not been studied so far.

On the other hand, the interaction of solid phthalocyanine films with gaseous NO₂ has been investigated, although mainly from the point of view of changes in conductivity. There appear to be no reports about the influence of NO₂ on the UV/VIS spectrum of FePc due to chemical interactions. Spectroscopic analyses of sublimed copper and metal-free phthalocyanine films exposed to NO₂ were carried out in 1983 [41, 42]. Honeybourne et al. reported that the strong absorption at 700 and 625 nm decline in intensity with the appearance of a new absorption band at 560 nm, indicating the formation of the phthalocyanine radical cation. Subsequent heating to 150 °C partially reversed these spectroscopic changes. 10 years later Rousseau et al. recorded the EPR spectra of NO₂ adducts of Co, Ni and Cu tetra-*tert*-butyl phthalocyanines in solution [43]. They found that Cu and Co species gave no EPR signal, indicating the formation of a diamagnetic adduct. This observation was in agreement with their extended Hückel (EH) calculations of an electron transfer of an unpaired electron from the metal centre to NO₂, resulting in a covalently bonded species. In other words, they proposed that NO₂ bounded to the metal centre, which differs from Honeybourne et al.'s analysis. Furthermore, by examining the change in orbital occupancy with EH, they could explain why a certain electronic transition does not occur with the NO₂ adducts. They suggested that the missing transition was the reason for the observed decrease in intensity of the Q absorption band. After performing ZINDO calculations, they suggested that the NO₂-binding occurs via a linkage to the nitrogen atom rather than to the oxygen atom.

It will be shown that in all NO₂-sensitive membranes developed in this study the coordination of NO₂ led to a decrease in the absorbance of the Q band, rather than to a change in the wavelength.

6.3. The Development of the NO₂-Sensitive Membrane

Iron(II)-phthalocyanine (FePc) and its derivatives have been seen as potential target compounds for new optical NO₂-sensitive membranes. As explained in section 6.2, axial N-donor ligands are necessary to dissolve FePc and to obtain the monomer species of this metal complex. The Q band of FePc is sensitive to the ligand exchange of the axial coordinated ligands. In the following it is assumed that NO₂ can bind to the metal centre and does affect the Q band absorption.

6.3.1 *The First Experiments*

Iron phthalocyanine is one of the most insoluble of all the metallophthalocyanine compounds. It is a black powder which dissolved only to a small degree in THF (tetrahydrofuran), a solvent which was used for the preparation of a PVC/DOS membrane. The membrane obtained showed only a small absorbance in the red spectral region for a few hours before the Pc precipitated. However, a change in absorbance was observed on exposure to NO₂ followed by a recovery of the spectrum which was several times faster than that found for the membranes based on aquacyanocobyrinate. This observation encouraged further investigations.

6.3.2 *Deriving a Strategy*

Most phthalocyanines dissolve in solvents which coordinate as axial ligands simultaneously, and only a few in non-coordinating solvents. For FePc it was found that axial ligation is necessary to facilitate solubility. According to the literature, nitrogen ligands like pyridine, imidazole and piperidine strongly coordinate to some metals and allow some of these metal complexes to be dissolved. In order to investigate such an octahedral complex (L₂FePc) as an NO₂-sensitive compound, at least one axial ligand has to be exchanged with NO₂ during exposure to the analyte. Therefore the binding of the axial N-donor ligand must not be too strong. Considering the reversibility, the affinity and the rate constant must be adequate to allow the reverse ligand exchange. Additionally, evaporation and precipitation of the N-donor ligand from and within the membrane when it is not bound to the metal centre has to be avoided. The proposed

reaction for the exchange of one axial ligand with nitrogen dioxide is shown in Figure 4: The sensing mechanism is based on the ligand

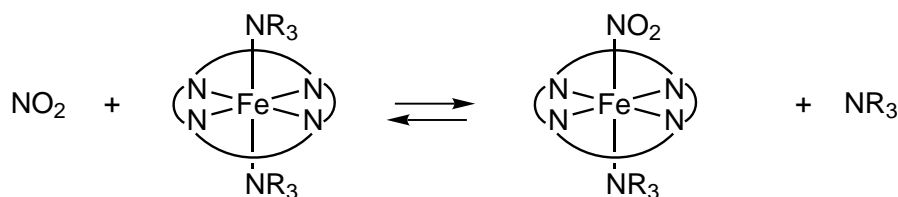


Figure 4. Proposed ligand exchange reaction of (NR₃)₂FePc with NO₂.

exchange of an electron donor (NR₃) with an π -electron acceptor (NO₂). This is assumed to be possible due to the low oxidation state of Fe(II) and its ability to undergo a π -backdonation. Many Fe(II)-complexes with π -acceptor ligands, such as CO, are well known. It is widely accepted that the π -acceptor ability of NO is higher than that of CO [44]. An even stronger effect is expected for NO₂, and the electron transferred to the gas molecule would probably be delocalized over the planar NO₂ structure.

The equilibrium is influenced not only by the strength of the bond of the N-donor ligand to the metal centre, but also by the quantity of this compound, which need not necessarily be proportional to the stoichiometric ratio. It is therefore advantageous to use it in excess, especially where the N-donor compound is the solvent of FePc. In order to facilitate the ligand exchange with NO₂, solvents which exhibit weaker affinity to the metal centre should be preferred. Under these conditions, the reverse reaction would be driven by the amount of the N-donor ligand when the NO₂-concentration is decreased. Having an excess of solvent would help to maintain FePc in solution and avoid aggregation when NO₂ is released. Such a compound must, however, be well compatible with the membrane matrix, not react with the polymer and not precipitate or evaporate. Hence, the target compound can be described as a *plasticizer-like* molecule, which is also able to coordinate to the iron centre.

A second strategy is to use polymers which themselves contain nitrogen donor atoms. The N-containing group should preferably be in the terminal position of a side chain in order not to hinder sterically the diffusion of NO₂ to the metal centre. This approach would avoid the problem of evaporation of an N-donor ligand.

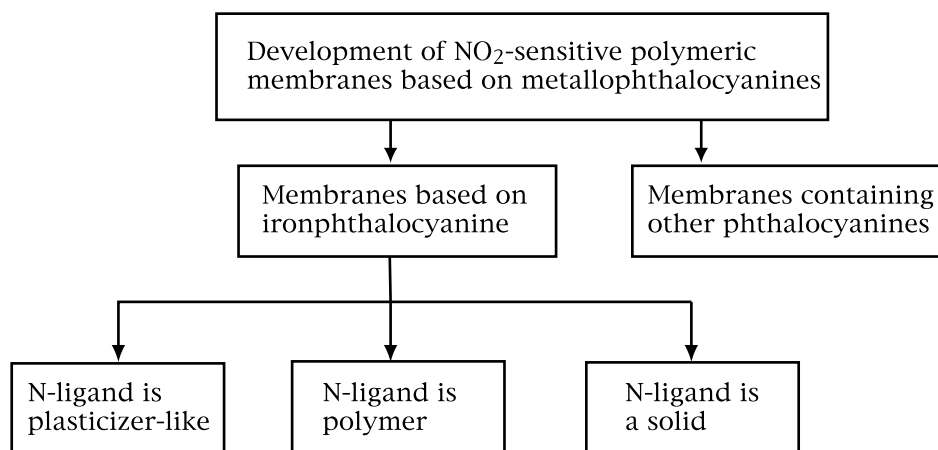


Figure 5. The development of a new optical NO₂-sensitive polymeric membrane.

A third possibility is using nitrogen-containing compounds which are neither polymers nor plasticizer-like, but solids under standard conditions.

Although in this study the focus has been on iron phthalocyanine and its derivatives as NO₂-sensitive compounds, other metallophthalocyanines have also been investigated for NO₂-sensitivity in polymeric membranes.

6.4. Membranes Based on Iron(II)-Phthalocyanine with Axial N-Donor Ligands

6.4.1 Solvents for Membrane Preparation

THF and, to a lesser extent, cyclopentanone are widely used for membrane preparations. FePc was found to be not soluble in THF, and producing a bluish or olive-coloured suspension. Thus the coordination of molecules containing oxygen as the only heteroatom are not favoured. Unfortunately, plasticizers are mostly ester derivatives and no plasticizers containing amine or imine groups could be found. Therefore, they cannot support the solubility of FePc within the membrane matrix. However, in CPOE and oNPOE, which both contain a nitrile group, FePc showed at least a tendency to dissolve.

Diethylamine (DEA) was found to be a suitable solvent for membrane preparation with FePc. 2 mg of FePc can be easily dissolved in 1 ml DEA. In addition, DEA has a high vapour pressure which is important for

membrane preparations. However, the solvent does not solubilize polymers. Therefore, in some other examples below, a combination of two solvents was considered.

6.4.2 Membranes with Plasticizer-Like N-Donor Ligands

As already mentioned, no plasticizers with a suitable amine or imine group which would coordinate to the metal centre of FePc were found. Nevertheless the solubility of the most common ones was examined. Iron phthalocyanine is completely insoluble in DOS, DBS, TOP, TOTM. In plasticizers containing a nitrile-group (CPDDE, CPOE, oNPOE), FePc shows a slight tendency to dissolve. This is, however, not pronounced enough to prepare optical membranes. Thus it was necessary to screen other compounds which both coordinate to the metal centre and show properties as similar to plasticizers as possible.

For the first attempt, solvents incorporating an amine as the functional group were chosen. The rest of the amine molecule should not be involved in any chemical reaction with the membrane compounds. In addition to being well compatible with the membrane matrix, the amine must maintain a very low vapour pressure to avoid evaporation from the membrane. It must also be liquid at the operating temperature of the sensor, and not precipitate within the membrane. Several compounds were chosen to cover the range of primary and secondary aliphatic and aromatic amines. Thus the influence of the ligand donor strength on the response behaviour could be investigated.

None of these amines was found to be able to completely replace the plasticizer in a PVC-membrane. Therefore PVC-membranes were made with a plasticizer but with a reduced amount to compensate for the decreasing viscosity due to the incorporation of the amine. Several different proportions of FePc, amine, PVC and plasticizer were used and their effects on the optical and physical properties of the membrane and on reversibility were investigated. A suitable composition was found to be: 0.3 mg FePc, 35 mg N-donor ligand, 50 mg PVC and 60 mg plasticizer dissolved in 0.6 ml THF. Membranes were obtained with spin-coating.

As an example, the UV/VIS-spectrum of a membrane based on FePc and dibenzylamine (DBA) before and after exposure to NO₂ is shown in

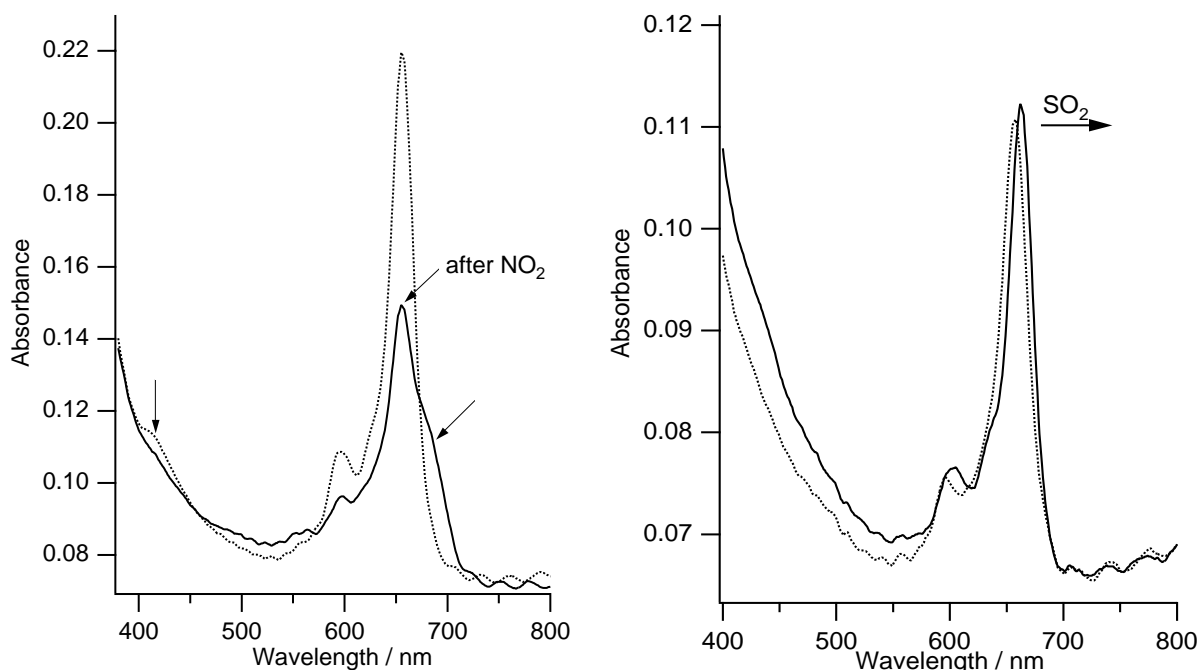


Figure 6. Spectra of the membrane based on $(\text{DBA})_2\text{FePc}$ in PVC/DOS at the initial state (dotted lines) and after exposure to NO_2 and SO_2 (solid lines).

Figure 6. NO_2 causes the Q band at 659 nm to decrease, whereas a shoulder at 690 nm appears, indicating that only one DBA is coordinated to the metal centre (see 6.2.). Simultaneously with the decrease in the Q band, the small band at 415 nm vanishes. As mentioned in 6.2., Ouédraogo has reported a correlation between these two bands and shown that they depend on the axial coordinated ligand. The a decrease in intensity observed, rather than a change in wavelength, is ascribed to the same effect as reported by Rousseau et al. (see 6.2.). The spectral changes shown in Figure 6 indicate that a ligand-exchange reaction occurs and not the formation of a phthalocyanine radical cation.

An important goal for the application of NO_2 -sensitive membranes in fire detectors is to avoid cross-sensitivity to SO_2 . Additionally, the stability of the layer must not be affected by SO_2 -concentrations of up to 25 ppm. As shown in Figure 6 (on the right), exposure to SO_2 leads to a shift of around 5 nm to higher wavelengths. This change in the spectrum would not be really noticed by the optical detection system of a sensor based on a red light emitting diode (LED) as the light source. Because a standard LED

exhibits a bandwidth of around 15 nm at I₅₀ with a λ_{max} at 660 nm, the implemented photodiode would not respond to a change in light intensity. Concerning the stability, the membrane showed reproducible sensitivity to NO₂ after exposure to SO₂. Simultaneously λ_{max} recovered at 659 nm after exposure to NO₂.

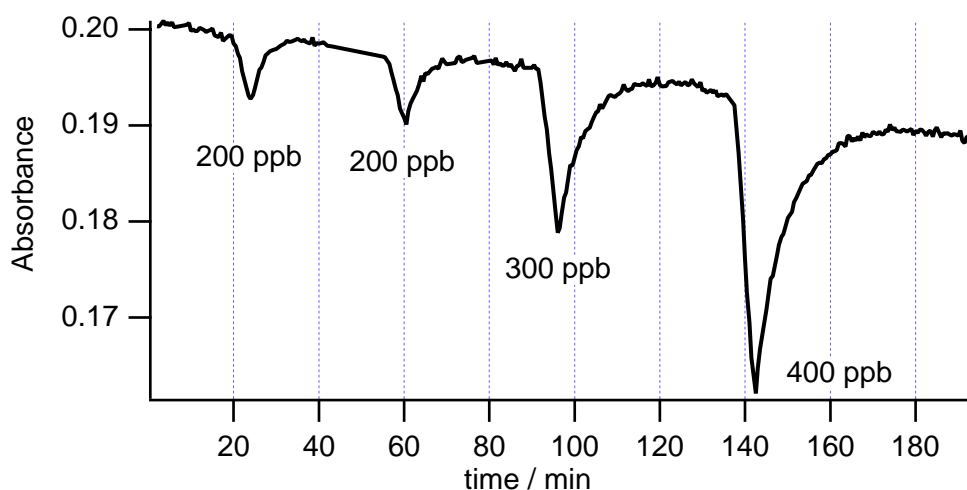


Figure 7. Changes in absorbance of (DBA)₂FePc at 659 nm due to exposure to different concentrations of NO₂ for 300 s.

The decrease in absorbance at the wavelength of the Q band correlates with the increasing concentration of NO₂ (see Figure 7). Unfortunately, the membrane showed a small baseline drift, which was probably due to the precipitation of FePc within the membrane. The aggregates are not optically active, so that a decrease in absorbance is observed. This effect was even more enhanced where dioctylamine was the solvent.

Several highly NO₂-sensitive membranes were obtained using plasticizer-like N-donor ligands. The results are summarized in Figure 8. The influence of the amines on the viscosity of the cocktail varied, so that layers with different thicknesses were obtained. In order to compare their response behaviours, the relative changes in absorbance are given, i.e. the change in absorbance divided by the initial absorbance, which was also the maximum absorbance. For comparison, membranes based on aquacyanocobyrinate give a relative absorbance, $\Delta A/A_0$, of 3% with ETH 7058 as the chromoionophore and 1% with ETH 5418 as the chromoionophore.

Amine:	Comments about the membrane:	λ_{\max}	$\Delta A/A_0$
Dibenzylamine (DBA)	sensitive, mostly reversible	659	11%
Decylamine (DA)	sensitive, partly reversible, membrane is little milky	658	10%
p-Decylaniline (pDA)	sensitive, completely reversible	664	2%
Dioctylamine (DOA)	sensitive, not reversible, strong drift	655	1%
Bis-(2-ethylhexyl)-amine	coordinates badly to FePc, probably sterically hindered	-	-

Figure 8. Amines examined as ligands for FePc. PVC/DOS-membranes based on these compounds were exposed to 300 ppb NO₂ for 300 s at 50% RH. As the response, the relative change in absorbance ($\Delta A/A_0$) is given as a mean value of three measurements.

Standard Measurement Procedure

With the membranes obtained in this study, the parameters sensitivity to NO₂, reversibility, cross-sensitivity to humidity and drift were measured with a standard procedure, as described in the following section. In Figure 9, the graphical representation of the results of a typical measurement cycle is shown. In the lower part of the figure, the parameters adjusted and monitored during the experiment are displayed (from the bottom): the total flow of the gas stream (ml min⁻¹), its relative humidity (RH%) and the adjusted NO₂-concentration in ppm. The upper part of the figure shows the response of the membrane in terms of the absorbance at a fixed wavelength. The wavelength corresponds to λ_{\max} (Q band) observed for each membrane throughout for all measurements presented in this study.

The baseline monitored using membranes based on (NR₃)₂FePc was not affected by changes in humidity, unlike membranes based on the cobyrinate derivative. Even the response to NO₂ remained nearly constant in the range of 0 - 100% of relative humidity (RH%) (Figure 9). However, for the more basic compounds DA and DBA, the changes in absorbance were slightly higher under humid than under dry conditions. The changes in absorbance (ΔA) at 100% RH were 11% with decylamine (DA) and 5%

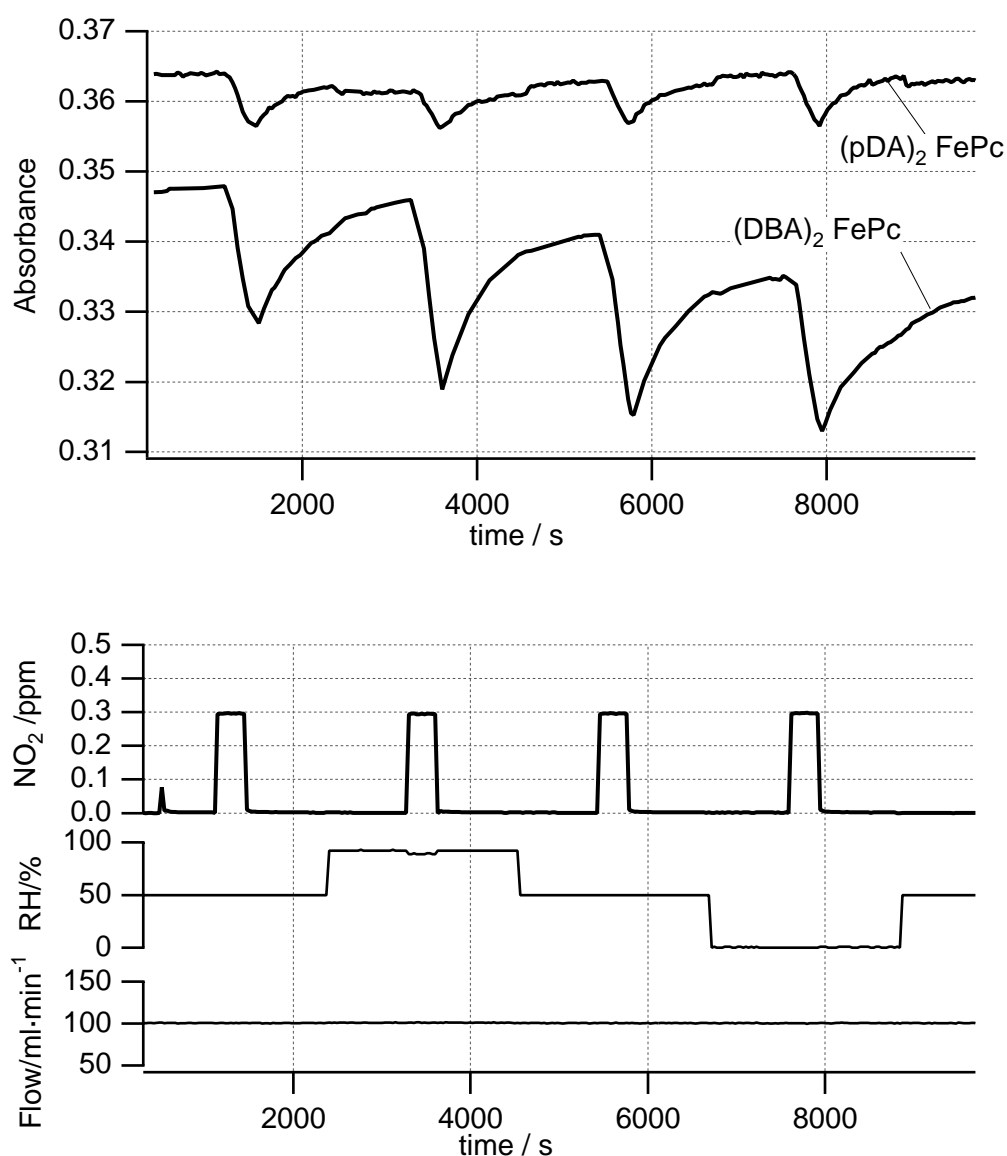


Figure 9. Membrane response of $(\text{DBA})_2\text{FePc}$ and $(\text{pDA})_2\text{FePc}$ to 300 ppb NO_2 for 300 s under different conditions of relative humidity.

with DBA, and were higher than the signal observed at 0% RH. This effect can be explained by the already known side reaction of NO_2 with membrane water, leading to a formation of small amounts of nitric and nitrous acid. Depending on their basicity, the amines become protonated and do not coordinate to the metal centre. Thus the protonation of amines has the same effect on the absorbance spectrum as a ligand exchange of the amine by NO_2 . This effect was not observed when the much less basic aniline was used as a solvent (p-decylaniline, pDA). As a matter of fact, the side reaction of NO_2 with membrane water cannot just vanish in such a

membrane. The acids are generally formed and thus the amount of $\text{NO}_2(\text{Mem})$ is reduced at humid conditions. The consequence of the amount of analyte within the membrane being lower under humid conditions is that the protonation of the aniline is masked. Indeed, at 100% RH the change in absorbance was around 40% lower than under dry conditions, which demonstrates this effect (Figure 9).

Membranes with only 14 wt.-% of amine (instead of 24 wt.-%) were found not to be reversible for any of the amines investigated here. With membranes containing 24 wt.-% of amine, the reversibility depended on the type of ligand, primarily on the affinity of the amine to the metal centre. Thus the best reversibility was observed with p-decylaniline, which provided the assay with the smallest sensitivity. On the other hand, membranes with decylamine and dibenzylamine showed a high sensitivity but were not completely reversible. In the case of membranes prepared with DA, a strong drift was also observed, which showed that other effects have to be accounted for. With all these membranes it was generally found that precipitation of phthalocyanine occurred. It was assumed that precipitation affected the reversibility during all the experimental cycles. After 3 weeks, all membranes became colourless. The membrane based on DBA even showed crystals.

6.4.3 Membranes Based on Polymers Containing Nitrogen Atoms

In this section, the screening process was focused on polymers containing nitrogen atoms which coordinated to FePc and which seemed to be promising for membrane preparation. Two different procedures were defined for preparing membranes where FePc coordinates to the N-atom of a polymeric chain. One possibility was to use two solvents, one, such as DEA, for FePc combined with another which could dissolve the polymer. Both liquids should obtain a high enough vapour pressure to obtain membranes after evaporation of the solvent within a reasonable time. Thus chemicals which are the only organic solvents for particular polymers but which have a low vapour pressure, such as xylene, are not suitable. Acids are not suitable because they would protonate the phthalocyanine.

Membrane preparations:

77 mg EG80A (a thermoplastic aliphatic polyurethane) were dissolved in 0.6 ml THF and 0.7 mg FePc were dissolved in 0.6 ml DEA. Afterwards 0.3 ml of each solution were mixed, and a cocktail deep green in colour was obtained. After casting, both solvents evaporated immediately leaving the solvent polymeric layer.

For poly(ethylenimine) and poly(N-methylvinylamine), a simpler procedure was found. The polymer was dissolved in a suitable solvent until saturation of the solution was observed. Solid FePc was added, leading to a suspension. Applying ultrasound in an ultrasonic bath or continuous shaking led to a coordination of FePc to the polymer and the amount of aggregated phthalocyanine decreased. By the end, the cocktail showed a green colour.

Poly(ethylenimine) could be dissolved in THF using an ultrasonic bath. Adding FePc resulted in a deep green colour, indicating the successful coordination of the imine group to the metal centre. Gas bubbles, however, meant that a reaction between the solvent and the polymer took place. A second solvent, CHCl₃, was found, but unfortunately it also reacted with the polymer.

Poly(N-methylvinylamine) was found to be partly soluble in CHCl₃ and EtOH. Adding FePc in such a suspension resulted a deep green solution in which all the compounds were dissolved. Note that FePc itself is insoluble in CHCl₃ and EtOH.

Poly(4-aminostyrene) was a very promising candidate because of its amine group at the end of the side chain. But no suitable solvent was found, even though THF, DEA, acetonitrile, CHCl₃, acetone, hexane, ethanol, ethylacetate, DMSO, DMF and H₂O were tested.

Membranes with and without plasticizers were prepared using spin-coating. DOS was used as a plasticizer with low polarity ($\epsilon_r = 3.9$) and CPOE as one with comparably high polarity ($\epsilon_r = 23.0$) (values of relative permittivity according to [45]).

An overview of the polymers used and a general comment about their characteristics is given in Figure 10. Although with some of the membranes a strong Q-band of the iron phthalocyanine was observed,

Polymer:	Comment:
EG80A	coordinates initially, membrane not stable
Poly(ethylenimine)	coordinates, membrane very liquid, not sensitive to NO ₂
Poly(4-aminostyrene)	not soluble
Poly(N-methylvinyl-amine)	coordinates, membrane hard not sensitive; plasticized membranes show a negligible sensitivity to NO ₂ but a strong sensitivity to changes in humidity
Poly(N-methylvinyl-amine) mixed with PVC	membrane is sensitive to NO ₂ , no cross-sensitivity to humidity, but colourless after 2 weeks

Figure 10. Polymers investigated as coordinating compounds for iron phthalocyanine to obtain NO₂-sensitive membranes.

none of them showed any sensitivity to NO₂. It is assumed that the polymeric network surrounds the phthalocyanine and renders it more difficult for NO₂ to approach the metal centre. Additionally these polymers are built of small monomer units and offer therefore many coordination sites for the metal, which are in competition with the analyte. An attempt was therefore made to reduce these effects by mixing such a polymer with PVC.

A solution of FePc/ poly(N-methylvinylamine) in CHCl₃ was mixed with a solution of PVC/ CPDDE (1:2) in THF and membranes were obtained with spin-coating. These membranes were found to be sensitive to NO₂ for concentrations as low as 50 ppb. Additionally no cross-sensitivity to humidity was found. Unfortunately, however, they became completely colourless after two weeks.

6.4.4 Membranes with Solid N-Donor Ligands

Octadecylamine (ODA) is solid and hardly soluble in THF. When adding FePc to such a suspension and after shaking, a deep green solution is obtained, indicating again the coordination of the amine to the iron phthalocyanine. When producing membranes with ODA, only

stoichiometric amounts relative to FePc could be used, because an excess would not be dissolved within the membrane. The membranes obtained were sensitive, but only partly reversible. It had, however, been expected that they would be not reversible at all because of the small amount of coordinating solvent, which encourages FePc to form aggregates. But the fact that such a membrane is at least partly reversible implies that a ligand exchange occurs and not, for example, a nitrosation of the amine, which would be irreversible. Because in such a membrane no additional amines are left, a response to NO₂ would be completely irreversible if it were due to a nitrosation. Since this reaction can, potentially, occur other N-donor ligands must be considered.

6.4.5 The Matrix

For all the membranes where the N-donor ligand was not a polymer, plasticized PVC was used. Further investigations were performed using c/t-polybutadiene (c/t-PBD) as the matrix. This polymer is a soft elastomere at room temperature ($T_g = -95\text{ }^\circ\text{C}$) and the membranes can be obtained without plasticizers. Sensitive membranes were produced with ODA and dioctylamine (DOA), but neither were reversible. With DA no sensitivity to NO₂ was found, and DBA led to the precipitation of FePc within the membrane. Thus the matrix does not only affect the ability of the metal complex to precipitate, but also the complex's sensitivity to NO₂.

6.5. Introducing a Lipophilic Iron Phthalocyanine

When using plasticizer-like N-donor ligands, the main problem was that an aggregation of the phthalocyanine occurred. Therefore lipophilic derivatives of iron phthalocyanine were considered to increase the solubility within the polymer matrix. Two kinds of derivatives with lipophilic side chains are described in the literature: substitution on the ring system with either an alkyl- or an alkoxy-group. First we investigated membrane preparations based on octasubstituted iron phthalocyanine μ -(oxo)bis(2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninatoiron(III)) (lip.FePc) which was synthesized by Shaik Zakeeruddin according to [46]. This compound exhibited significant differences in the molecular structure (see Figure 11) and in solubility compared to unsubstituted FePc. On the

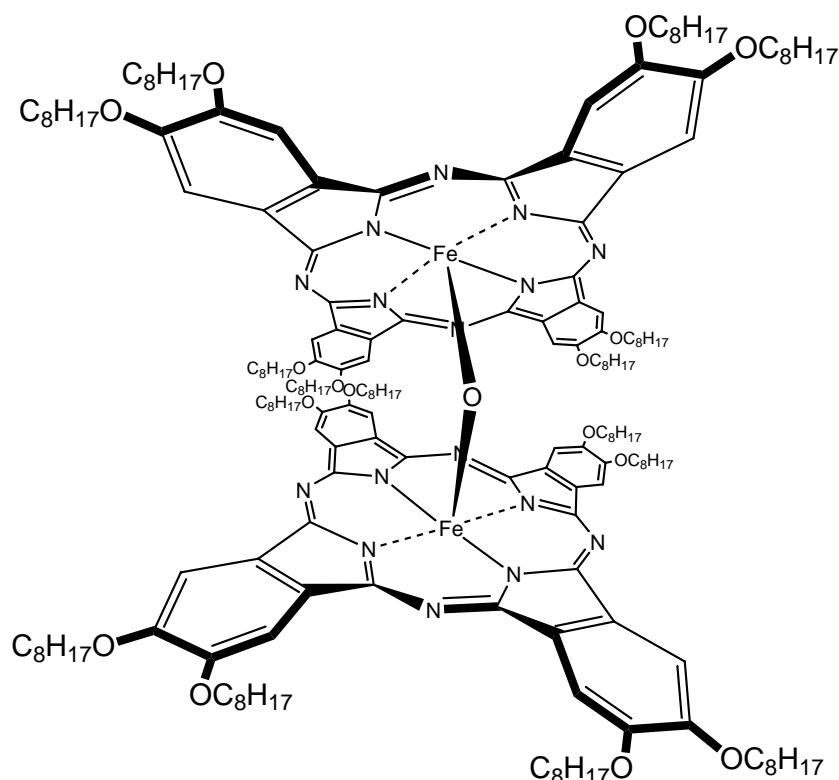


Figure 11. Chemical structure of μ -(oxo)bis(2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninatoiron(III))

one hand, it is highly soluble in all organic solvents but, on the other, the macrocycle exists as a μ -oxodimer where the oxidation state of Fe is (III) [47].

6.5.1 Membranes Based on Lip.FePc

In noncoordinating solvents like chlorobenzene, chloroform or THF, lip.FePc is dissolved as the dimer. In the visible spectrum the Q band is above 700 nm, whereas in the coordinating solvents it is clearly below 700 nm. In the strongly coordinating solvent pyridine, lip.FePc exhibits an identical electronic spectrum to that of the unsubstituted FePc, with $\lambda_{\text{max}} = 654$ nm indicating the formation of the monomer. The reduction of this Fe(III)Pc compound in pyridine was described in [47].

Preparations of membranes based on the same composition as that described for unsubstituted FePc (see 6.4.2) showed that the properties of lip.FePc are remarkably different (Figure 12). The membrane based on lip.FePc with DBA (Dibenzylamine) showed two bands in the visible

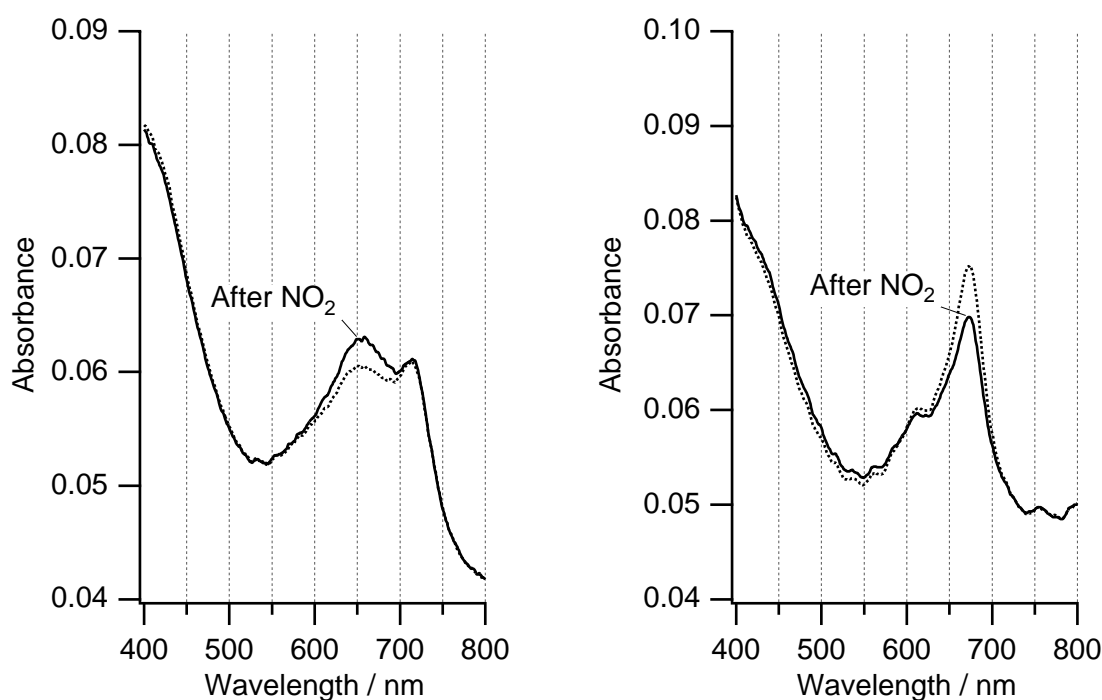


Figure 12. Spectral changes in membranes based on lip.FePc with DBA (left) and pDA (right) after exposure to 300 ppb NO₂ for 500 s.

spectrum indicating a mixture of two species. Surprisingly, the band at 658 nm increased on exposure to NO₂. The membrane based on lip.FePc with p-DA (p-Decylaniline) showed one band at 673 nm, but the reverse reaction was surprisingly slow. Additionally the membrane signal was drifting (Figure. 13). As a result of spin coating, both membranes were poorly coloured because of the high solubility of lip.FePc in THF. Dissolving lip.FePc in a simple PVC/BBPA membrane without any amines resulted in a membrane where λ_{max} was at 585 nm and did not show any sensitivity to NO₂ (BBPA, bis(1-butylpentyl)adiapate was the only plasticizer found, that lip.FePc would dissolve in).

6.5.2 Lip.FePc and the Interaction with Amines

Experiments in solution were carried out to get a better understanding of the conversion of the dimer to the monomer of lip.FePc and its interaction with N-coordinating ligands. In THF solutions of lip.FePc, the change from the μ -oxodimer to the monomer with coordination of amines could clearly be monitored with UV/VIS-spectroscopy. On adding p-DA, 100% yield of the monomer was obtained after 13 minutes (Figure 14). But with

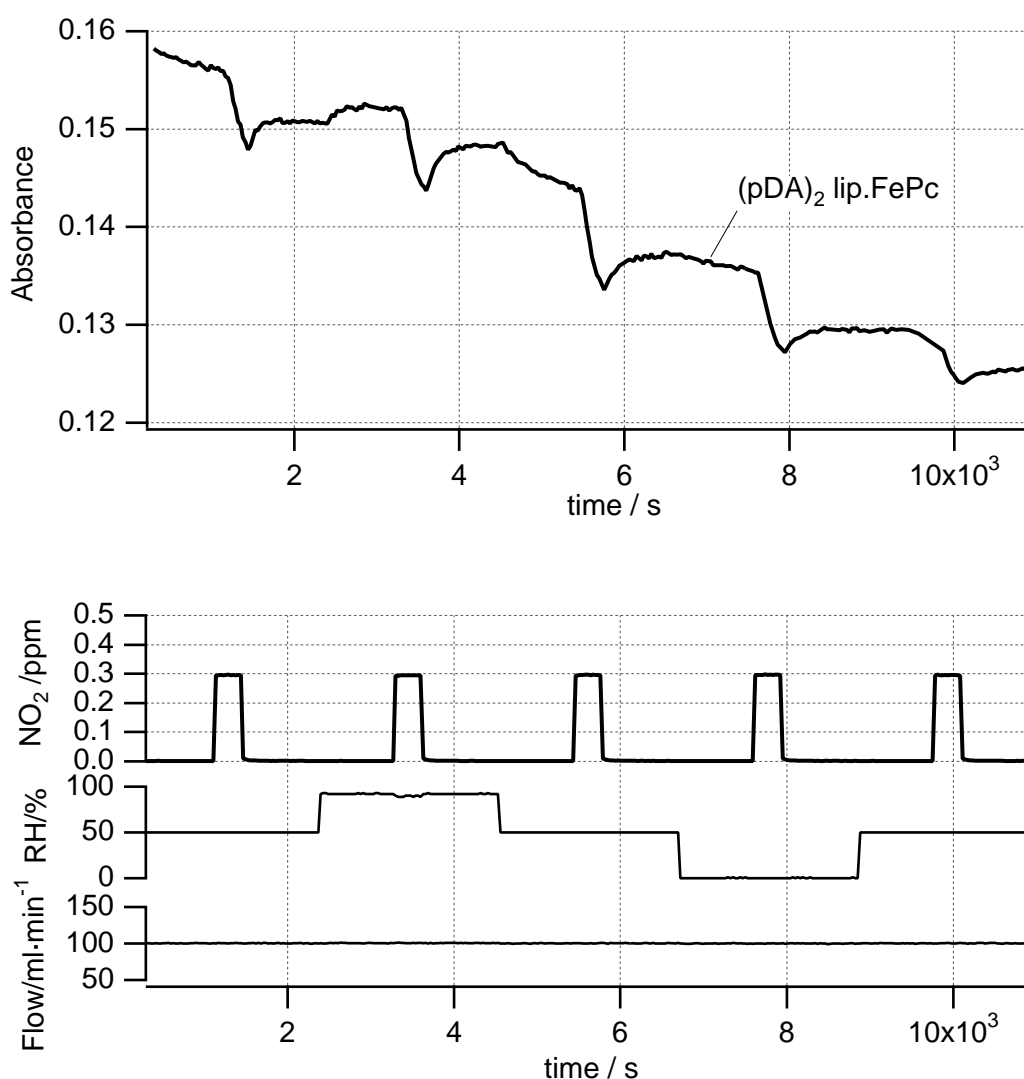


Figure 13. Membrane responses of $(pDA)_2 lip.FePc$ to 300 ppb NO_2 for 300 s under different conditions of relative humidity.

DBA, even after 18 minutes, still a part of lip.FePc remained as the dimer. Spectra obtained when lip.FePc is dissolved in pure p-DA or DBA showed that the solubility is not optimal in either case in comparison with spectra obtained when lip.FePc is dissolved in pyridine or when unsubstituted FePc is dissolved in these amines. The slow response time suggests that the interaction between the lipophilic ironphthalocyanine and these amines is too weak. Spectra of lip.FePc dissolved in other amines such as dioctylamine or dibenzylamine showed additional bands at shorter wave lengths (Figure 15). The absorption band around 620 nm indicates the dimerization of phthalocyanine in the amine solution, as this band is attributed to a coupling between the two π systems (see 6.2.).

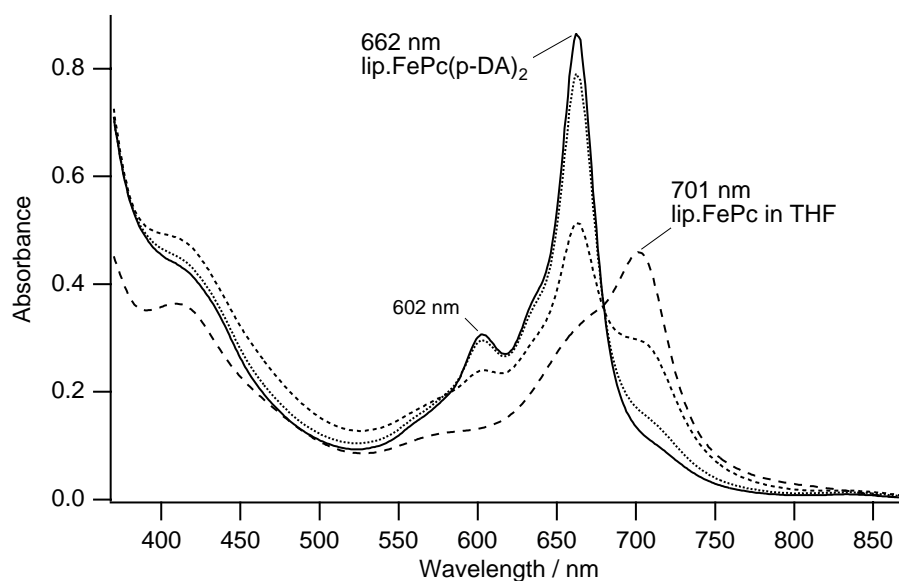


Figure 14. Spectrum of lip.FePc when changing from dimer to monomer with coordination of p-DA.

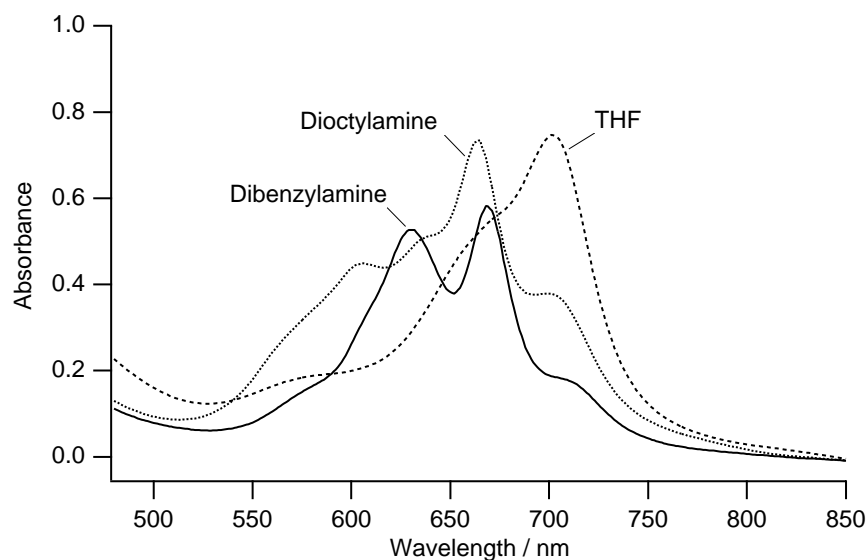


Figure 15. Spectra of Lip.FePc in different solvents showing several absorption bands. Bands above 700 nm indicate the μ -oxo-dimer, around 660 nm the monomer and below 630 nm the dimer and probably higher oligomers.

6.5.3 Lip.FePc and the Interaction with N-Polymers

In section 6.4.3 a second approach to producing NO₂-sensitive membranes is to use polymers as N-donor ligands for the iron phthalocyanine.

Membranes based on such polymers have been shown to exhibit strong interactions with the unsubstituted FePc, but they showed no sensitivity to NO₂. In the case of lip.FePc this interaction was either not as strong as in the case of FePc, showing a peak for the dimer too (poly(N-methylvinylamine)), or the spectrum had additional bands (poly(ethylenimine)). Poly(vinylchloride-*co*-1-methyl-4-vinylpiperazine (hydrogen ionophore polymer I, Fluka) mixed with PVC gave only a small band at 655 nm, which might be due to the interaction with the piperazine. There was a second, broad band around 580 nm similar to that in the PVC/BBPA-membrane.

It was not possible to disperse the dimer completely, except with poly(p-vinylpyridine). With this polymer, a strong Q band was observed, but the membranes showed only a very small sensitivity to NO₂. Even in combinations with other polymers and various plasticizers the strong binding of this N-donor to the metal centre could not be broken by NO₂. Thus the same insensitivity was observed as with unsubstituted FePc using polymers as N-donor ligands.

6.5.4 Lip.FePc with Pyridine Derivatives as Ligands

Since the use of amines did not result in a complete transformation of the dimer to the monomer, pyridine derivatives were introduced as axial ligands for lip. FePc (μ -(oxo)bis(2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninatoiron(III))). Commercially available pyridine derivatives were screened with regard to the criteria defined for plasticizer-like compounds and 4 derivatives were chosen (listed in Figure 16). All the derivatives evaluated led to a clearly distinct Q-band in the red region, showing that lip.FePc was present as the monomer. Moreover, all the membranes based on lip.FePc and one of the pyridine derivatives showed a moderate sensitivity to NO₂. After one month no precipitation could be observed, which indicated that the pyridines were more compatible with the matrix than the amines were. However, compared with the membranes based on FePc, these membranes were about four times less sensitive. This might be due to the influence of the octyloxy groups (σ -acceptor) at the periphery of the ring system, which means that there is less electronic density on the metal available for π -backdonation to

Ligand:	Comments about the membrane:	$\Delta A/A_0$ (n=3)
p-Decylaniline (pDA)	sensitive, partly reversible, strong drift	9%
p-Methoxypyridine (pMP)	sensitive, not reversible, spectrum vanishes	5%
p- <i>tert</i> -butylpyridine (ptBP)	sensitive, not reversible, drift	3%
p-Ethylpyridine (pEP)	sensitive, not reversible, drift	2%
p-(m-Phenylpropyl)-pyridine (pPPP)	sensitive, reversible	1%

Figure 16. Ligands tested for lip.FePc. Membranes based on these compounds were exposed to 300 ppb NO₂ for 300 s at 50% RH. For each the resulting relative change in absorbance ($\Delta A/A_0$) is given as a mean value of 3 measurements.

NO₂. It was therefore hoped that a higher sensitivity could be obtained with an alkyl-substituent (σ -donor).

Unfortunately, only the membrane with 4-(3-Phenylpropyl)pyridine showed a reversible response. The results obtained with membranes based on lip.FePc are summarized in Figure 16.

6.5.5 Comparison between *N*-Donor Ligands towards Lip.FePc

Ouédraogo et al., investigating the coordination of FePc with several substituted pyridine derivatives and with imidazole and piperidine, have reported a dependence of the wavelength of the Q band on the axial ligands. They observed that, when the donor strength of the ligand increases, the absorption wavelength shows a bathochromic shift, while when acceptor power increases, it moves toward shorter wavelengths. In this study an influence on the wavelength was also found on changing the ligands. In the following, the donor strength was estimated by semiempirical quantum mechanical calculations and the correlation with the observed wavelength was studied. It was assumed that, by simply

calculating the partial charge at the nitrogen-atom of the ligand, a reasonable value for the electron donor power of the molecule would be obtained. The calculations were performed using CS Chem3D Pro from CambridgeSoft Corporation. Gas-phase geometry optimizations were performed and the Mulliken charges (additional the method of Wang-Ford with AM1) at the nitrogen atoms were calculated. The semiempirical calculations were carried out using different models: MINDO/3 (Modified Intermediate Neglect of Diatomic Overlap revision 3), MNDO (Modified Neglect of Differential Overlap), AM1 (Austin Model 1) and PM3 (Parameterized Model revision 3) [48].

Only with MINDO/3 was a tendency observed which showed that, the higher the partial charge at the nitrogen, the higher the wavelength at which the Q-band of the corresponding metal complex occurs (Figure 17).

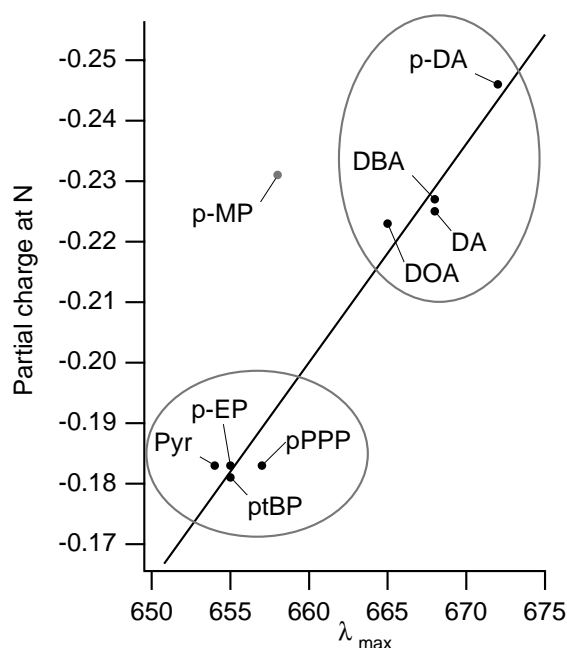


Figure 17. Calculated partial charges at N of different ligands depending on λ_{\max} found for lip.FePc dissolved in a solution of the ligand.

The results are clearly different for the pyridine derivatives and the amines, except in the case of p-methoxypyridine, where the obtained value was much higher than the others. For the strong donors, the amines, an increase in negative charge correlates well with an increase in the wavelength. For the pyridine derivatives no such correlation was found. This might be due

to the fact that the π -backdonation has a major influence on these aromatic ligands which is not taken into account in the model calculations. Both the observed wavelength and the calculations imply that the pyridine derivatives are weaker donors than the amines. But in the experiments with lip.FePc they turned out to be stronger coordinating ligands than the amines. Therefore, when going from amines to pyridines, it is reasonable to assign the increase in the strength of the ligand-metal bond to a π -backdonation from the metal centre to these aromatic ligands.

6.6. Investigations with an Alkyl-Substituted [(Fe(III)Pc)₂(μ O)]

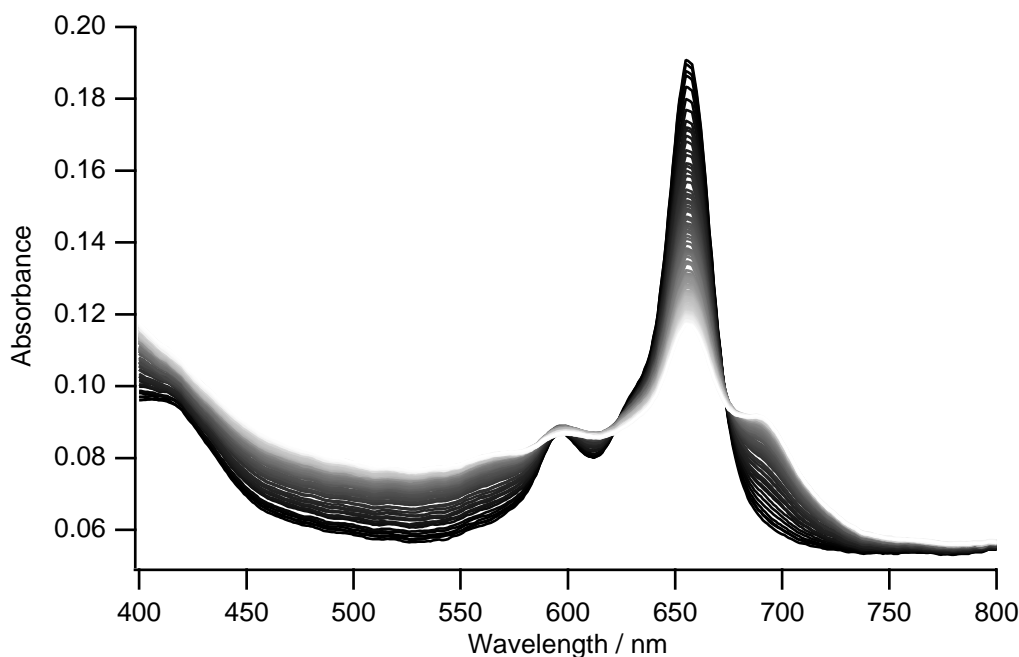


Figure 18. Spectral change in the membrane based on μ -(oxo)bis(2,9,16,23-tetra-*tert*-butyl phthalocyaninatoiron(III)) with coordinated *p*-ethylpyridine (pEP) on exposure to 2 ppm NO₂. The decrease is shown with spectra shaded from black to grey.

As mentioned in 6.5.4, it was assumed that an iron phthalocyanine derivative with alkyl-substituents at the Pc-ring would show a higher sensitivity to NO₂ than the investigated octyloxy-substituted derivative. The derivative iron 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (lip.FePc II) was therefore synthesized by S. Zakeeruddin according to

[47]. This alkylated derivative is a μ -oxodimer, again with iron in the oxidation state (III). Membranes were produced with the same four pyridine derivatives as were used for lip.FePc. Unlike with the octyloxy-substituted FePc, this derivative with σ -donor substituents was not washed away with THF during spin-coating and therefore a higher concentration of the compound could be dissolved within the membrane. All the membranes based on these pyridine derivatives showed again a strong Q band without additional absorption bands, indicating that the phthalocyanine is present only as the monomer. In Figure 18 an example

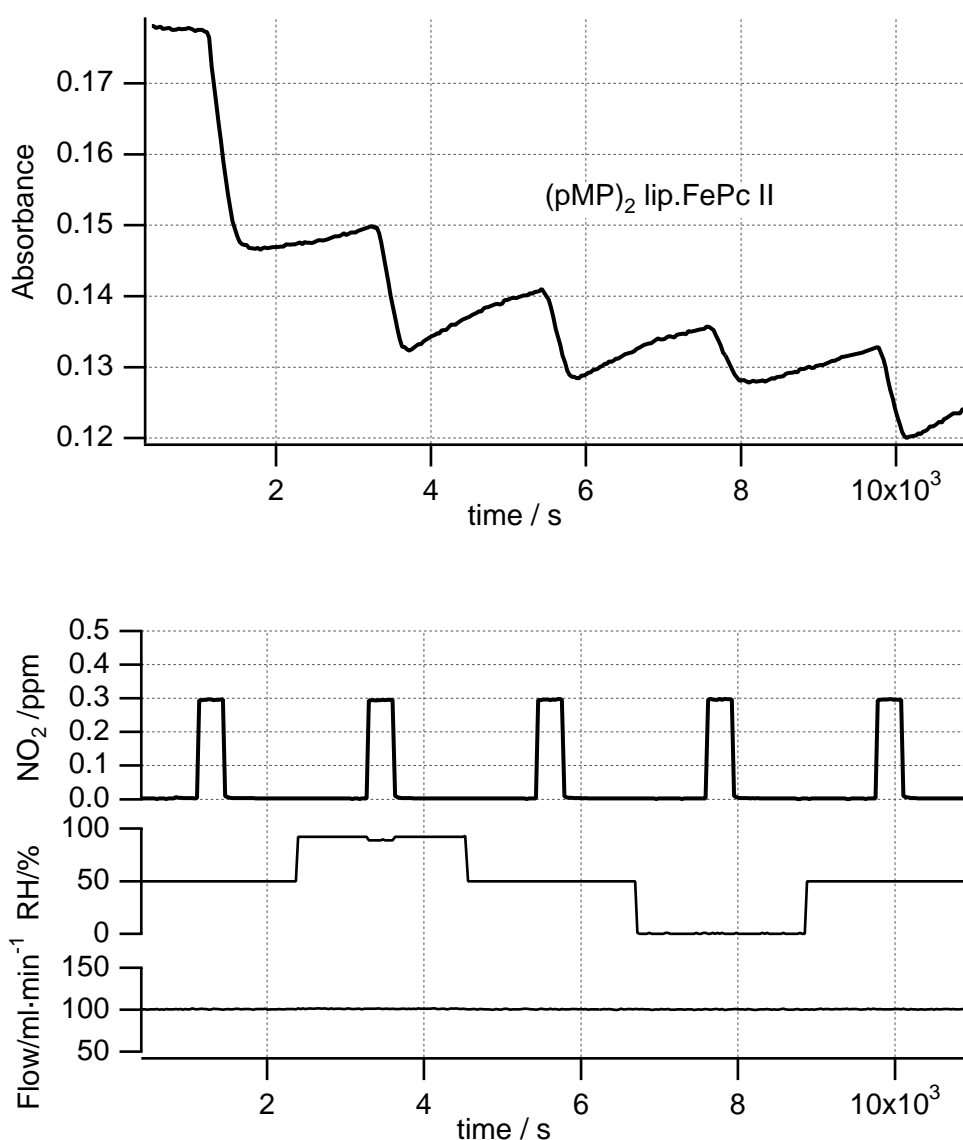


Figure 19. Membrane response of (pMP)₂lip.FePc II to 300 ppb NO₂ for 300 s under different conditions of relative humidity.

of a spectrum is given and the change due to exposure to NO₂ is shown. Measurements were performed with the resulting membranes according to the defined standard procedure. In Figure 19 the response of the membrane based on lip.FePc II with p-methoxy-pyridine is shown.

The cross-sensitivity to SO₂ of the membrane based on lip.FePc II/pMP was investigated. An exposure to 25 ppm SO₂ for more than a half hour did not change the UV/VIS-spectrum. After the treatment with SO₂ the membrane was still sensitive to NO₂.

6.6.1 N-Donor Ligands and Lip.FePcII

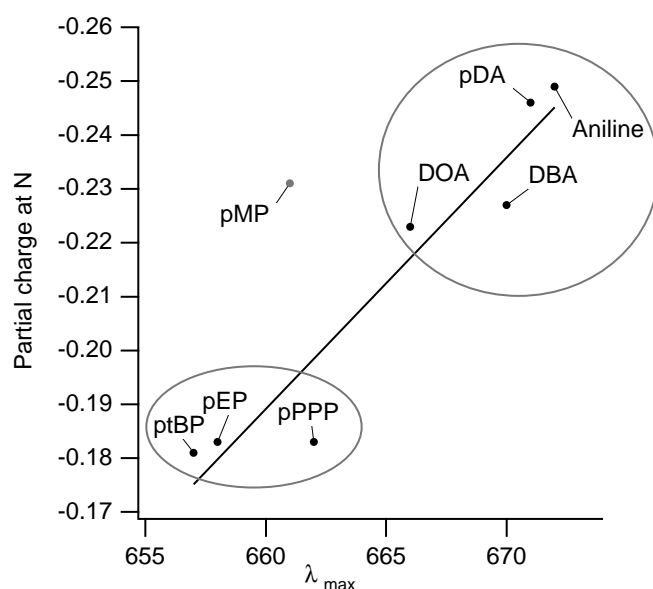


Figure 20. Calculated partial charges at N of different ligands depending on λ_{\max} found for lip.FePc II dissolved in a solution of the ligand.

The dependency of the Q band in the wavelength on the axial ligands differed for lip.FePc II and for lip.FePc. Whereas with the amines the absorption occurred at the same wavelength as for the octyloxy-substituted FePc, with the coordination of the pyridine derivatives, the Q band of the *tert*-butyl-substituted FePc was at higher wavelengths. This difference is due to the change in the σ -acceptor groups with σ -donor groups at the periphery of the ring system.

Despite this difference, with both lip.FePc II and lip.FePc there was a similar tendency for the calculated partial charges at N of the ligands and

the observed wavelength of the Q band of the corresponding metal complex (Figure 20).

6.7. Other Lipophilic Metallophthalocyanines

6.7.1 Membranes Based on Cobalt(II)-Phthalocyanine

Unlike FePc, cobalt(II)-phthalocyanine (CoPc) can be dissolved in THF to give a blue solution. Therefore CoPc should be soluble in any compound containing an ether. Indeed, it turned out that it is soluble in CPOE and oNPOE but not in DOS and similar plasticizers containing an ester group. With CoPc the membrane preparation was very simple but only small amounts of CoPc were obtained in the polymer matrix. 0.7 mg of this metallophthalocyanine were dissolved with 50 mg PVC and 100 mg CPOE or oNPOE in THF. Slightly blue membranes were obtained with spin-coating because CoPc was washed away with the THF. Unlike FePc, an increase in absorbance was observed due to NO₂. Unfortunately the sensitivity of these membranes was even lower than with FePc/pDA.

6.7.2 Membranes Based on Lipophilic Cu(II)Pc and Zn(II)Pc

Other peripherally substituted metallophthalocyanines which are commercially available were tested. With Ni(II)-2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine and Cu(II)-2,3,9,10,16,17,23,24-oktakis(octyl-oxy)-29H,31H-phthalocyanine, it was not possible to obtain membranes because they were not soluble. With Zn(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine and Cu(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine, however, strongly coloured PVC/DOS-membranes could be produced. With these two compounds membranes with and without DBA (dibenzylamine) were made, but no significant difference could be observed in the spectrum and in sensitivity due to the presence of DBA. The membranes showed an NO₂-sensitivity which was about 10 times lower than that with FePc/p-DA membranes or even less if compared with FePc/DBA membranes. With both membranes the absorbance decreased on exposure to NO₂. The membrane based on the substituted ZnPc showed a Q band at a wavelength of 678 nm (Figure 21, left). But this membrane

had the most pronounced cross-sensitivity to changes in humidity observed in this study. The membrane based on the *tert*-butyl-substituted CuPc showed a band at 672 nm and a second, more intensive one, at 620 nm (Figure 21, right). Unlike the reported investigations of a sublimed

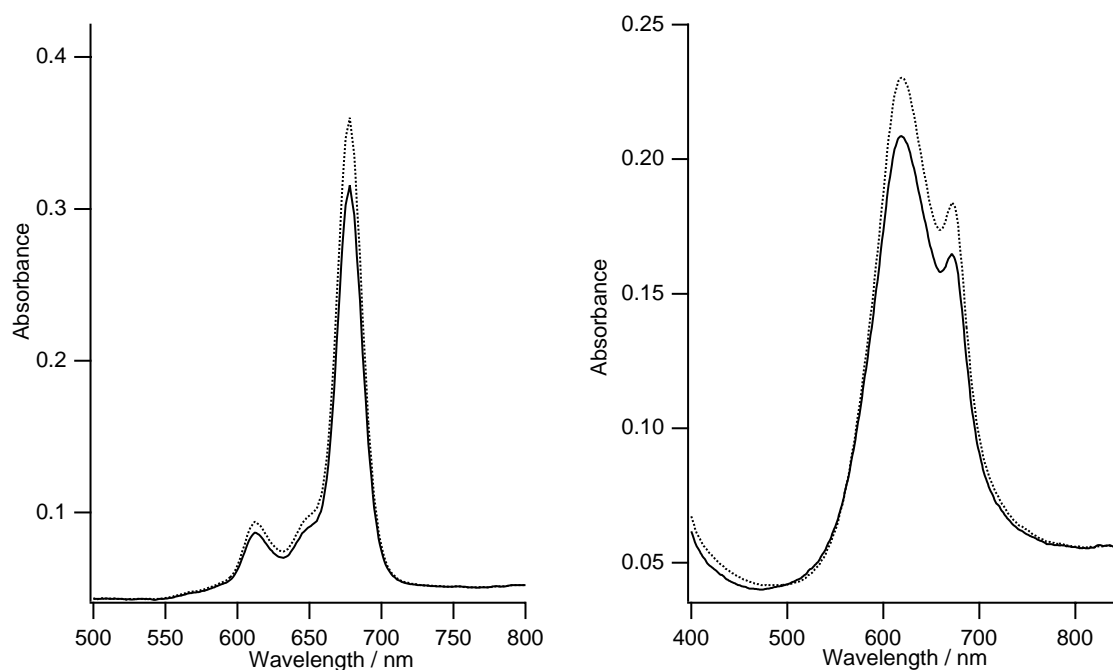


Figure 21. Spectral changes in membranes based on Zn(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (left) and Cu(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (right) on exposure to NO₂.

CuPc-film, no appearance of a new band was observed on exposure to NO₂.

With both, exposure to SO₂ led to an increase in absorbance. With the membrane based on Cu(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine, the affinity to SO₂ compared with that to NO₂ was investigated. The competitive influence of these two gases was monitored with UV/VIS spectroscopy, see Figure 22. Adding SO₂ to the carrier gas caused an increase in absorbance. When NO₂ was mixed into the gas stream, a slight decrease was observed. The reason for the decrease is the competition between these two molecules to coordinate to the metal centre. When the SO₂-concentration was set to zero, a decrease in absorbance was observed due to the binding of the NO₂. Finally, NO₂ was also switched off, leading to the reverse reaction, the coordination of the plasticizer DOS. When SO₂

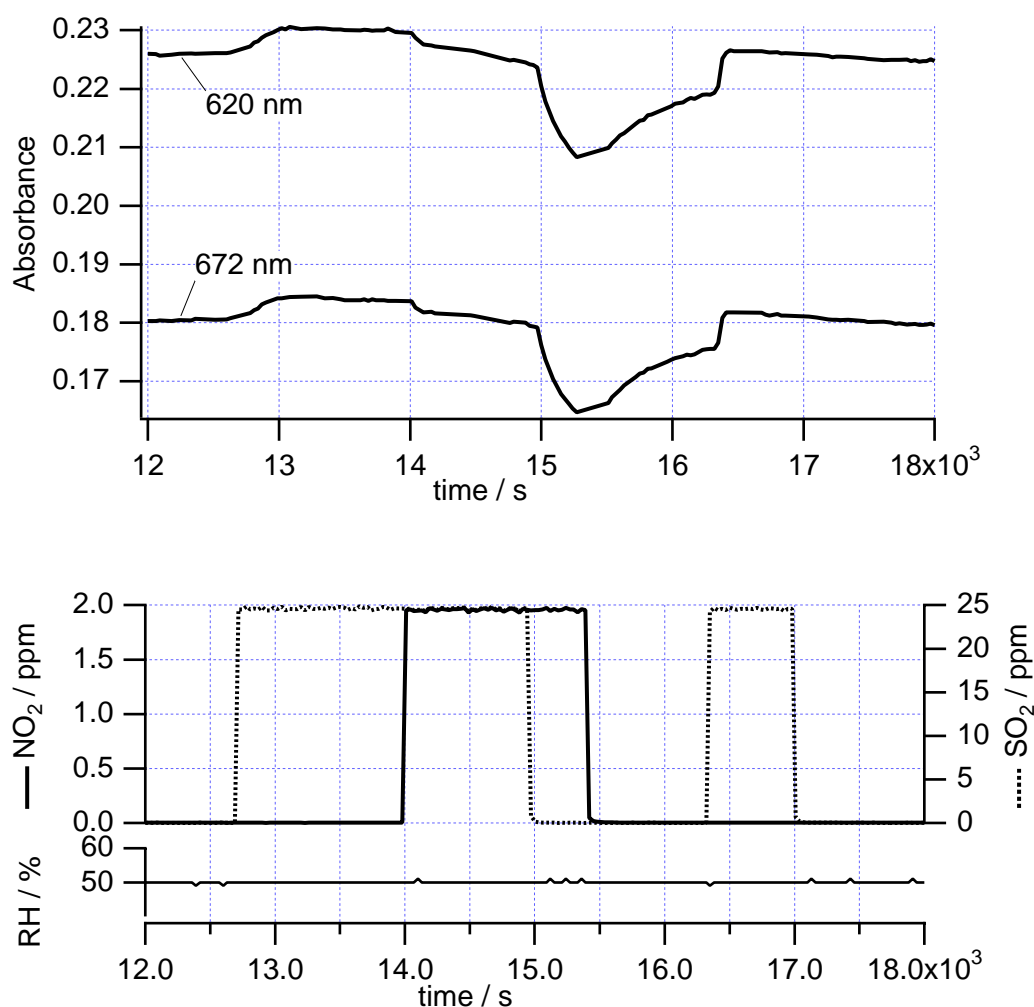


Figure 22. Competition between NO₂ and SO₂ on Cu(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine dissolved within a PVC/DOS membrane. Lower part: The dotted line shows the applied SO₂-concentration, the straight line the NO₂-concentration. Upper part: Changes in absorbance at the wavelengths of the two bands.

was again mixed into the gas stream, the increase in absorbance was enhanced due to the binding of SO₂.

6.8. Examination of CO-Sensitivity of Metallophthalocyanines

CO is known to adsorb on iron phthalocyanine monolayers [49]. Additionally, FePc has a structural similarity to the haem-group, and

haemoglobin is known for its affinity to CO. Therefore the sensitivity of lip.FePc to CO was investigated. No sensitivity was found for up to 200 ppm CO. The membranes based on Cu(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine and Zn(II)-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine also showed no sensitivity. The selectivity for NO₂ in this concentration range can be ascribed to the higher π -acceptor strength of NO₂ compared with CO, similar to that found for the layers of pure phthalocyanines [2]. Whether, at higher concentrations of CO, a binding to the MPc occurs, cannot be excluded with this experiment. But for sensor applications, CO is only relevant in the ppb and the lower ppm-range.

6.9. Conclusions

In this study various attempts were made to develop optical, NO₂-sensitive polymer membranes based on iron phthalocyanine and its lipophilic derivatives. The strategy of using amines or derivatives of pyridine as the coordinating solvent within a polymeric liquid membrane gave the best results. These are summarized below (Figure 23).

Membrane:	NO ₂ /ppm:	ΔA_1 :	ΔA_2 :	ΔA_3 :	ΔA_{mean} / A_0 :	Rever- sibility:
FePc/DBA	0.3	0.019	0.025	0.024	11%	yes*
FePc/DA	0.3	0.039	0.041	0.039	10%	partly*
FePc/pDA	0.3	0.007	0.006	0.006	2%	yes
Lip.FePc/pDA	0.3	0.008	0.010	0.003	~9%	partially*
Lip.FePc/pPPP	0.3	0.001	0.002	0.002	1%	yes
Lip.FePc/ptBP	0.3	0.001	0.003	0.006	~3%	no*
Lip.FePc/pEP	0.3	0.001	0.002	0.002	2%	no*
Lip.FePc/pMP	0.3	0.005	0.006	0.005	5%	no**
Lip.FePcII/pPPP	0.3	0	0	0	0%	-
Lip.FePcII/ptBP	0.3	0	0	0.001	1%	-
Lip.FePcII/pEP	0.3	0.005	0.005	0.006	4%	yes
Lip.FePcII/pMP	0.3	0.029	0.012	0.013	~10%	yes
Lip.ZnPc	1.0	0.005	0.013	0.018	~24%	partially*
Lip.CuPc	1.0	0.007	0.008	0.009	7%	yes
Pefa10105/ETH5418	0.3	0.004	0.002	0.002	1%	yes
Pefa10105/TIFOE	0.3	0.021	0.012	0.007	~3%	yes

Figure 23. Overview of the NO₂-sensitive membranes investigated. ΔA_n : Change in absorbance due to the n-th exposure to NO₂ at 50% RH; ΔA_{mean} is the mean value of ΔA_1 to ΔA_3 ; A_0 is the initial absorbance.

* : drift (due to precipitation)

** : strong drift (due to precipitation)

ΔA : Change in absorbance

A : total absorbance of the compound

DBA: Dibenzylamine

pPPP: p-(m-Phenylpropyl)pyridine

DA: Decylamine

ptBP: p-*tert*-butylpyridine

pDA: p-Decylaniline

pEP: p-Ethylpyridine

DOA: Dioctylamine

pMP: p-Methoxypyridine

Figure 24. Compounds used as axial coordinating ligands for iron phthalocyanine and its lipophilic derivatives.

Lip.FePc: μ -(oxo)bis(2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninatoiron(III))

Lip.FePcII: μ -(oxo)bis(2,9,16,23-tetra-*tert*-butylphthalocyaninatoiron(III))

All measurements were performed under identical conditions according to the standard procedure described in section 6.4.2. The membranes were exposed repeatedly to nitrogen dioxide for 300 seconds. In the Table the changes in absorbance obtained at a relative humidity of 50% are listed.

Generally, the pyridine derivatives were more compatible with the membrane material than were the amines, e.g. the membranes had a longer life time. Additionally, for the lipophilic iron phthalocyanines, the pyridines were able to produce a complete transformation of the dimer to the monomer. It was found that, only with membranes where the lipophilic FePc is dissolved as the monomer, can NO₂ be measured optically. But compared to unsubstituted FePc, the membrane response was generally slower.

The cross-sensitivity of all membranes based on iron phthalocyanine and its derivatives to humidity is considerably less than that of membranes based on aquacyanocobalt(III)-cobyrate (see chapter 4). Additionally, SO₂ was found not to affect the stability of the sensor membranes and, in the case of the lipophilic FePc, did not show a cross-sensitivity.

Compared with other dissolved metallophthalocyanines investigated in this study, the FePc-derivatives were more sensitive to NO₂. But membranes based on the lipophilic CuPc had a longer shelf life.

Unlike films of pure phthalocyanines, those membranes described here which are based on dissolved FePc-derivatives exhibit a high sensitivity and selectivity to NO₂. They showed no cross-sensitivity to NO, CO or, as discussed in section 6.4.2 and 6.6., to SO₂.

With the incorporation of axial coordinated FePc-derivatives in polymer membranes to allow optical measurement of NO₂, a new sensing principle for nitrogen dioxide was introduced. Further investigations will have to be carried out to find out how to solve the main problem confronted so far, namely the precipitation and aggregation of the phthalocyanine within the membrane matrix.

6.10. Chemicals and Reagents

The compounds used in this study were purchased from the following sources and used as received:

From Fluka: aniline (puriss. p.a.), bis-(2-ethylhexyl)amine (purum), decylamine (puriss.), dibenzylamine (puriss.), didecylamine (puriss.), diethylamine (puriss. p.a.), dioctylamine (purum), 4-ethyl-pyridine (purum), octadecylamine (puriss.), tridecylamine (purum).

BBPA: bis(1-butylpentyl)adiapate, CPDDE: 2-(dodecyloxy)benzonitrile, CPOE: 2-(octyloxy)benzonitrile, DOS: bis(2-ethylhexyl)sebacate, DBS: dibutylsebacate, oNPOE: 2-(nitrophenyl)octylether, TOP: tris(2-ethylhexyl)phosphate, TOTM: tris(2-ethylhexyl)trimellitate

From Aldrich: 4-*tert*-Butylpyridine (99%), 4-decylaniline (97%), 4-(3-phenylpropyl)-pyridine (97%), poly(ethylenimine) (linear), poly(ethylenimine) (high molecular weight), poly(4-vinylpyridine) (M_w ca. 160'000).

From Polysciences Inc.: poly(4-aminostyrene), poly(N-methyl vinylamine).

From Thermedics Inc.: The polyurethane Tecoflex EG80A (synthesized from methylene bis(cyclohexyl)diisocyanate, poly(tetramethylene ether glycol) and 1,4-butanediol).

6.11. References

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7

Outlook

The two polymer membranes, described in this thesis offer a new way of measuring nitrogen dioxide. With both membranes, based either on derivatives of aquacyanocobalt(III)-cobyrrinate or of iron phthalocyanine, concentrations of NO₂ in the ppb-range can be measured with a high selectivity. Additionally, with these membranes optical low-priced micro sensors can be constructed which have a very low power consumption. These features mean that the introduced sensing principle is more suitable for application in fire detectors than other NO₂-sensors developed to date. With both types of membranes it is possible to fulfill the requirement to detect an increase in NO₂-concentration to 200 ppb within 200 seconds. Membranes based on iron phthalocyanine derivatives showed less cross-sensitivity to SO₂ and humidity but with the current state of research they have a shorter shelf life than membranes based on the cobyrrinate derivative.

Both kinds of membrane have the disadvantage that the sensitivity of their sensitive compounds diminishes over time. An interesting alternative might be, instead using the cobyrrinate perchlorate and a phenoxazine derivative, to form a salt of the aquacyanocobyrrinate and an erythrosin derivative like ETH 7058, and to use this compound as both the sensitive species and the optical transducer. Additionally, that such a system might result in a faster response, the perchlorate-ion is omitted. This might have a positive effect on the stability of the membrane and its cross-sensitivity to humidity.

In the case of the membranes based on iron phthalocyanine and its derivatives with plasticizer-like N-donor ligands, the instability is attributed to a precipitation of membrane compounds with time. In the case of amines as ligands, a reaction with the membrane matrix can also occur. The loss in intensity of the Q band, and generally the loss in colour, derive from the aggregation of the metallophthalocyanine molecules. It is assumed that this process arises because the amines and pyridine derivatives are insufficiently compatible with the polymer matrix. Membranes where the coordinating ligand is the polymer still exhibit the typical green colour even after already one year.

It is proposed that both strategies should be taken further to produce Plasticizer-like N-ligands and polymers containing N-atoms. In the second case block-polymers could be used to reduce the coordination sites within a chain and facilitate the coordination of NO_2 . In both cases a combinatorial approach would probably be best to improve these membranes. It should be noted that derivatives of pyridine and aromatic amines gave the best results with the substituted iron phthalocyanines.

The precipitation of the phthalocyanine could be reduced with a covalent linkage between the macrocycle and the polymer. But there will be still phthalocyanine molecules within the matrix which come close enough and π -stacking can occur.

Substitution at the macrocycle with sterically pretentious groups would antagonise an aggregation of the phthalocyanines and improve the solubility. One step further would be to consider phthalocyanines with peripherally substituted, bridged alkyl chains lying above the metal centre. Enough space has to be left inside the macromolecule to allow the exchange of the axial ligand with NO_2 .

Or, it would probably be desirable to enclose single phthalocyanine molecules in caves of zeolites to prevent them aggregating. This could be done by synthesising the phthalocyanines directly in the zeolite framework.

Schematic of the Measurement Station for Gas Sensors

First of all, a measurement station was built which allowed the investigations of gas-sensitive polymer membranes. A schematic of the gas handling system is given in Figure 1. Copper, stainless steel and Teflon tubing has been used up to the flow-through cell. NO_2 is known to stick on steel and therefore Teflon was used in the last part. The carrier gas was obtained from 50 l / 200 bar gas bottles with nitrogen or synthetic air (Sauerstoffwerk Lenzburg), both quality 5.5. Mass flow controllers (MFC) of type 1179 were used (MKS Instruments Deutschland GmbH): Analog MFCs (0 - 200 ml/min) for the carrier gas and digital MFCs (0 - 10 ml/min) for the gas mixed with analyte or interfering gas (Carbagas, Rümlang). The analog MFCs were driven via a data acquisition (DAQ) multifunction card (Lab-PC-1200, National Instruments, Ettlingen) and the digital MFCs via a RS-485 interface.

The spectrophotometer Specol 1100 (Analytic Jena) was controlled via an additional RS-485 interface of the IBM PC 330 computer. The controlling of the MFCs and the data acquisition was performed with a self-written program coded in LabVIEW (National Instruments, Ettlingen). The program enabled stand-by and fully automatic measurements specified by a protocol, in connection with the spectrophotometer or the optical chip. The code for the communication with the digital MFCs and the Specol 1100 was written by Thomas Roth. The functionality of the measurement system is described in detail in Chapter 3.4.3.

Gas Measurement Station - Setup A (Detail)

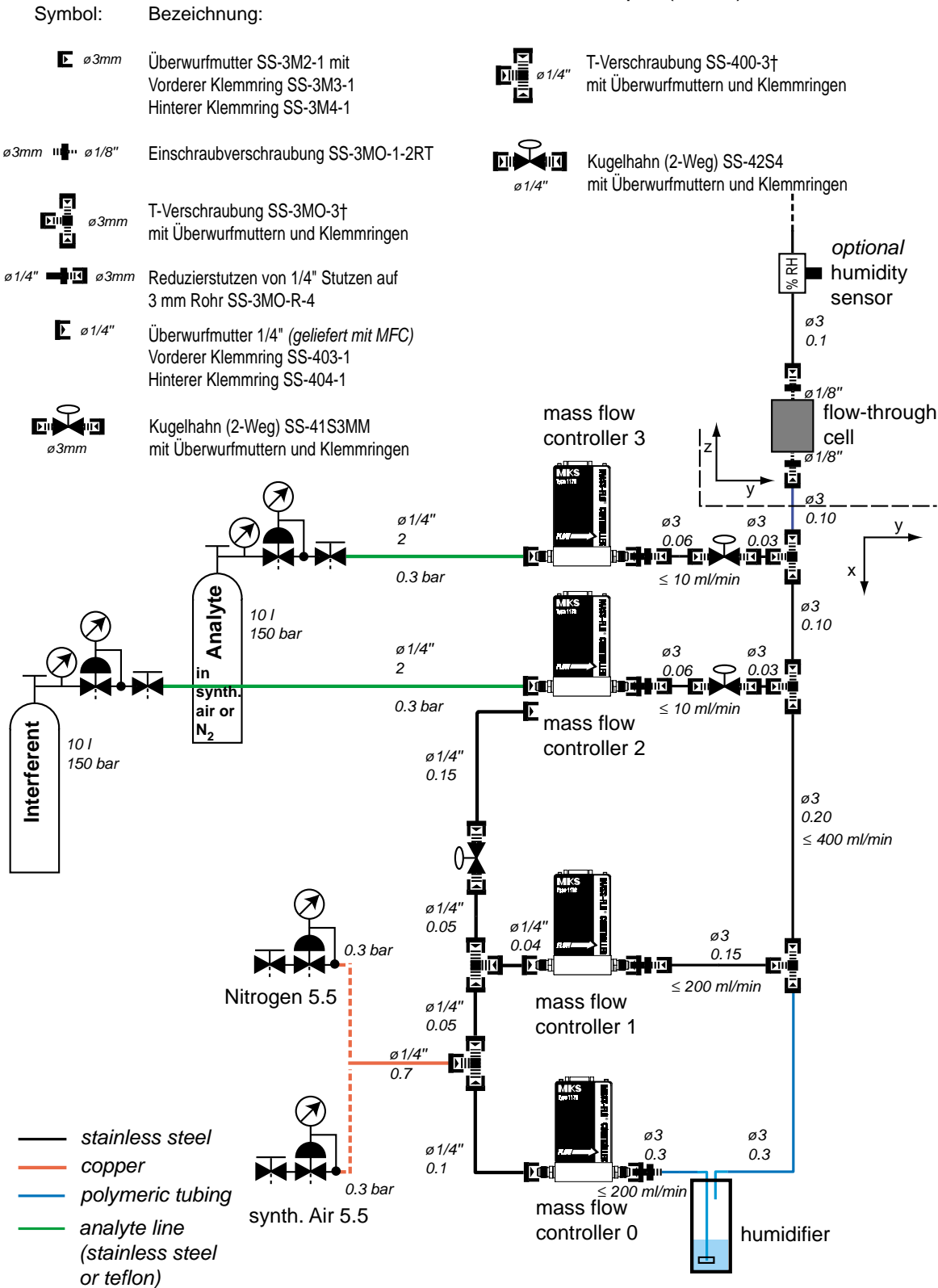


Figure 1. Schematic of the gas handling system.

Curriculum vitae

- 1968 Born on February 19, in Olomouc (Czech Republic)
- 1975-1982 Elementary school and Sekundarschule Bichelsee/Balterswil (TG)
- 1982 - 1988 High school at the Gymnasium Bühl in Zürich
- 1989 - 1992 Study of physics at the University of Zürich
- 1992 - 1997 Completed chemistry studies (emphasis on computational chemistry and industrial chemistry) at the Swiss Federal Institute of Technology (ETH) Zürich
- 1997 Developing new reactive hot melt adhesives in the laboratory of Dr. Th. Abend, Laboratory of Industrial Chemistry, ETH Zürich
- 1997 Diploma thesis *Investigations on the selective reduction of nitro groups in azo compounds* in Prof. P. Rys's group, Laboratory of Industrial Chemistry, ETH Zürich
- 1998-2002 Ph.D. thesis in the group of Prof. Dr. Ursula Spichiger, Centre for Chemical Sensors, Technopark, ETH Zürich
- Research cooperation with Bosch Telecom GmbH (München, Stuttgart), Pentapharm (Basel), Research group of Prof. H. Baltes (Zürich)
- Teaching responsibilities at the University of Applied Science in Wädenswil, and supervision of students during their semester and diploma thesis