Gas-Selective Optical Sensors for Fire Detectors

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Sandmeyer Prize Winners 2001

Abstract: At the Center for Chemical Sensors (CCS) of ETH-Zürich, gas-sensitive membranes have been developed during the last three years. In co-operation with Pentapharm AG, Basel, and Bosch Telecom GmbH, Frankfurt, the research 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.

Keywords: Ammonia · Chemical sensor· Fire detector· Nitrogen dioxide · Optical gas sensor

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 are the solid state sensors based on metal oxides and includes sensors using various transducers [4].

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].

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 assessment of luminescence resonance energy transfer [12]. However this type of 'optode' still exhibited 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. In the case of a solvent polymeric NH₃-selective sensor layer, 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 pKₐ of the indicator together influence the dynamic range of the optode [17].

In order to investigate the sensing principles for neutral analytes, their nucleophilic addition to trifluoroacetanilide 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 hypochromic spectral shift in the visible range. Optical sensors, incorporating chromo-reactands 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 NO₂, which achieves its selectivity due to the reactivity of NO₂ with aquacyanocobalt-(II)-cobyrinate 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 NH₃-selective optode, was developed for detecting NH₃, 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 CO₂ and CO which are produced during combustion, have been tested. These sensors were provided by other research groups and are under consideration for implementation in fire detectors [25].

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 puts this figure into context. 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, CO₂, NO, NO₂ and H₂, 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, seem 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%.

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.

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 SO₂, CO and CO₂, NO and NO₂ 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 NO₂ (up to 2 ppm) than smoldering fires of wood [25].

Gas monitoring is also concerned with interfering gases such as SO₃ and NH₃. For SO₃ long-term contact at room temperature, which may induce such damage as corrosion, is crucial, whereas for NH₃ it is primarily cigarette smoke which can be detected as an interferent for smoke detectors.

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 absorbance changes in the region around 660 nm to be monitored 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.
shifts toward higher wavelengths 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 NO₂.

It is assumed that disproportionation of NO₂, 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 (Scheme: b). Absorbance is measured in transmission on the planar diode-sensor chip. The reaction rate of the sensor strongly depends on the amount of aquacyanocobyrinate 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 preferable as the water source. The reaction is not completely reversible. The high acidity of nitric acid and the consequent nitrate enrichment seem to be

![Fig. 1. Optical chip used for gas sensing at CCS, consisting of an LED as the light source and four photodiodes as detectors. The photodiodes serve at the same time as substrates for the gas-sensitive polymer layers.](image)

2.2. Influence of the Cobalt(III)-cobyrinate 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 NO₂⁻, 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 layer. One membrane component, however, was omitted due to stability problems.

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 (Scheme: a). The selectivity is introduced by complexation of NO₂⁻ 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

![Fig. 2. Structure of an aquacyanocobalt(II)-cobyrinate derivative as used for nitrite sensing, which was incorporated into the polymer layer](image)

a) Reaction with nitrite

\[
\text{NO}_2^- + \text{H}^+ + [\text{L-H}_2\text{O}]^+ + \text{C} + \text{H}_2\text{O} \rightarrow [\text{L-NO}_2] + \text{CH}^+ + \text{CH}_2\text{O}
\]

b) Reaction with nitrogen dioxide

\[
2 \text{NO}_2 + [\text{L-H}_2\text{O}]^+ + 2 \text{C} + \text{H}_2\text{O} \rightarrow \text{CH}^+ + \text{NO}_2^- + \text{CH}_2\text{O}
\]

Scheme. Reactions which occur in the membrane due to exposure a) to nitrite and b) hypothetically to NO₂.
the reason for this. However, the reaction mechanism with NO\textsubscript{2} has to be investigated further.

The sensor response is linear during the initial phase of the reaction and the slope strongly depends on the NO\textsubscript{2} concentration. Therefore it is possible to obtain a dynamic range of 25 - 800 ppb NO\textsubscript{2} within the very first seconds (Fig. 3 and 4). The NO\textsubscript{2}-sensitive membrane was found not to show any cross-sensitivity to either NO or CO.

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 permitted yearly average as determined in the Swiss Clean Air Act). The membrane had a thickness of 25 \(\mu\)m and the concentration of the chromoionophore was \(4.27 \times 10^{-3}\) M. 10\% of this amount was protonated after exposure to a gas stream of 15 ppb NO\textsubscript{2} for 4 h. This concentration of NO\textsubscript{2} corresponds to \(6.7 \times 10^{-10}\) M in air. Compared with \(4.27 \times 10^{-4}\) M of protonated chromoionophore as the reaction product or as the NO\textsubscript{2}-concentration, which was extracted into the membrane, it gives an enrichment factor of \(6.4 \times 10^5\) (Table). This extraordinarily high value reflects the further reaction of the absorbed NO\textsubscript{2} whereby additional extraction of NO\textsubscript{2} 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.

![Fig. 3. Response of the optical NO\textsubscript{2}-sensor in voltage [V] to 25 - 800 ppb NO\textsubscript{2} in air with 50\% relative humidity and a flow rate of 50 ml/min.](image)

![Fig. 4. Slope of the sensor response to different NO\textsubscript{2} concentrations within the first minute of contact.](image)

| NO\textsubscript{2} concentration outside: | 30 \(\mu\)g / m\(^3\) | 15 ppb |
|------------------------------------------|----------------|--------|
| Amount of NO\textsubscript{2} in a volume of 25 nl: | \(7.5 \times 10^{-6}\) ng | \(9 \times 10^6\) molecules |
| Extracted amount of NO\textsubscript{2}: | 0.48 ng | \(6 \times 10^{12}\) molecules |
| Sensitive compound within the membrane: | 125 ng | \(6 \times 10^{13}\) molecules |

Table. Calculated values for a membrane with a volume of 25 nl and a gas concentration of 15 ppb NO\textsubscript{2}.
2.4. Flow-through Systems and Cross-sensitivity to Humidity and SO₂

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 host molecules within the membrane.

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 aquacyanocobyrinate, 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 SO₂, compared to 0.5 and 1 ppm NO₂. With both membranes the observed protonation of the chromionophore caused by such high SO₂-concentrations was irreversible (12 ppb is the yearly average concentration permitted by the Swiss Clean Air Act).

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 1.5x1.5 mm. The diameter of one optically sensitive area is then 300 μm (Fig. 5). Long-term measurements were performed to test the reproducibility and reversibility of the sensor response (Fig. 6).

Several measurements were carried out to obtain approval for the application of the NO₂-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, part 5 and 7). For a gas sensor to be admitted to the market, an operational and shelf-life of at least two years at temperatures up to 60 °C have to be demonstrated. Considerable efforts were made to reach this 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 only 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.
Fig. 8. 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.

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.

4. Methods

4.1. Chemicals and Reagents

The NO₂-sensitive membrane (polymer layer) incorporates 0.5 to 10 weight% of a Co(m)Cobyrinate complex (aquacyanocobalt (III)-heptacyclophosphorane, 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

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 fulfills 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.

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 cyclohexane. 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].

4.3. Measurement Setup

A measurement setup to test gas sensors under various conditions was built at CCS. Dry synthetic air (quality 5.5, Sauерstoffwerk 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 to 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 analyze the sensor data. A data acquisition (DAQ) multifunction card (Lab-PC-1200 from National Instruments, Eningen) 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.

Received: July 19, 2001

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