Novel optical NO\textsubscript{2}-selective sensor based on phthalocyaninato-iron(II) incorporated into a nanostructured matrix

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Abstract

A novel highly sensitive optical NO\textsubscript{2}-selective sensor was developed using phthalocyaninato-iron(II) as a selective complexing agent. In order to solubilize the iron II+ phthalocyanine and to obtain the monomer species, a N-donor ligand was used as a solvent. The membrane solution was deposited onto a novel aluminum oxide/hydroxide nanoporous material by a spin-coating technique. The chemical reaction principle and the preparation of this new sensor are presented in detail. The effect of the type and concentration of the N-donor ligand, and the influence of the iron phthalocyanine concentration were investigated as well as the effect of the composition and the morphological characteristics of the nanostructured material. In addition, the influence of some relevant external parameters such as flow-rate and interfering compounds were investigated. The results show that the sensor responds to NO\textsubscript{2} concentrations in the gas phase between 5 × 10\textsuperscript{-3} ppm and >0.5 ppm with a linear concentration range between 2 × 10\textsuperscript{-2} and 0.4 ppm, the detection limit being at 20 ppb. The dynamic range it is not influenced by the flow-rate, by humidity, NO, CO, CO\textsubscript{2} and SO\textsubscript{2}, and the NO\textsubscript{2}-selective optical sensor shows good stability to ambient in view of a long lifetime as a gas and fire alarm detector. Generally 1 ppm NO\textsubscript{2} gas corresponds to 2.0 mg m\textsuperscript{-3} and 44.5 × 10\textsuperscript{-6} mol m\textsuperscript{-3}.

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1. Introduction

In the last 100 years, industrial expansion has led to environmental damage caused by pollution. Nitrogen oxides (NO\textsubscript{x}) are among the most toxic gaseous pollutants\textsuperscript{[1]}. Nitrogen monoxide is oxidized in the atmosphere to nitrogen dioxide (NO\textsubscript{2}), one of the major components of outdoor air pollution, which directly affects human health. It reacts on soot particles to form HNO\textsubscript{2} which is known to contribute to global environmental problems such as photochemical smog, ozone formation, acid rain and corrosion of metal\textsuperscript{[2]}. In addition, it was found that the NO\textsubscript{2} concentration rises immediately in case of fire independent of the materials which are burning\textsuperscript{[3,4]}. Therefore, NO\textsubscript{2} in the gas phase is an early indicator of heat developed in case of fire and is much more effective than fire many alarm detectors on the market. Simultaneously false alarms will be reduced since smoke and ammonia can be distinguished from NO\textsubscript{2} of which the concentration rises immediately with increase of heat. Additionally, we found that energy consumption of optical sensors is much lower than that of electrochemical metal oxide sensors\textsuperscript{[4]}. Thus, novel gas detection instruments are increasingly attractive to control nitrogen oxide levels, especially at low ppb concentrations. Chemical sensors, especially optical sensors, are an elegant alternative to traditional analytical instruments and semiconductor sensors.

The Swiss Clean Air Act sets 15 ppb as the limit of average yearly exposure and 40 ppb as the maximum for an exposure over 24 h and the European Union (Council Directive 1999/30/EC) sets 19.5 ppb as the annual limit and 97.6 ppb as the hourly limit value both for the protection of human health (ppb, 2.05 × 10\textsuperscript{-6} g m\textsuperscript{-3}). For local monitoring, sensing devices that are smaller, cheaper and more sensitive than the analytical instrument currently used for atmospheric...
measurements are required. Most well-known are semiconductor metal oxide sensors made of ZnO, SnO\(_2\) and WO\(_3\) [5] which react with a change in the conductivity. The specificity is connected to the gas-specific catalytic temperature. The sensors are highly energy consuming, sensitive to humidity and, therefore, not attractive as gas and fire alarm detectors.

Gas-selective chemical sensors allow to distinguish different gas species by their selective chemical interaction with an organic indicator compound such as organometallic complexes (OMCs). The chemical interaction between the specific gas molecule and the selective indicator compound are detected by a change in the optical absorption or emission spectrum. Organometallic complexes which react directly with the target gas are generally more attractive than recognition principles linked to chemosensors [3, 6] since the organometallic complex is generally more stable than the dye. Since, the solubility of a metal complex within the matrix might be a critical factor, it was proposed to immobilize OMCs to gas permeable support [7]. Chemical sensors based on specific interactions between a target gas and the metal complex are generally not sensitive to humidity. In addition, a broad range of OMCs are on the market which shows absorbance and emission spectra in the visible range. OMCs are well investigated especially in context with the detection of NO\(_2\). However, only a few investigations into the interactions of NO\(_2\) with metal atoms have been reported [8]. In account of transmission measurement in the visible spectrum, an adequate conjugated π-system similar to that of the porphyrin macrocycle is preferred [3, 6, 7]. Typical representatives of this class of compounds are phthalocyanines (Pc) [7, 9]. In view of the development of NO\(_2\)-sensors, investigations were mainly focused on CuPc and PtPc [10–18]. Other Pc used were compounds such as polyfluoro-porphyrinato-iridium(III) [19, TiPc] [20], metal-free octahexyl-substituted [21] and 18-crown-6 substituted phthalocyanine [22] and sublimated films or Langmuir–Blodgett films of phthalocyaninato-iron(II) (FePc) [15, 17]. Morishige et al. [23] demonstrated that in planar complexes of metal ions like metallophthalocyanines (MPC), it is possible for the core metal ion to bind a ligand molecule to one of its two available axial coordination sites forming a 1:1 complex. Specifically the d\(^6\) in 3d metal complexes such as Fe(II) and Fe(III) are active to NO\(_2\) due to unpaired electrons of the metal orbitals with π-symmetry which permit the interaction with the second unpaired electron in NO\(_2\). But, the main problem of FePc is that it is one of the most insoluble MPC compounds. For this reason, the interaction of dissolved FePc with NO\(_2\) has not been studied so far. In order to develop NO\(_2\)-sensors based on MP, the following gas-permeable supports were used: (1) pre-cleaned glass slides [14]; (2) gold-coated optical waveguides [24]; (3) thin-modified mesoporous silica [25]; (4) SnO\(_2\) [26]; (5) porous silicon [27]; etc. A variety of techniques such as vacuum sublimation, plasma-activated evaporation, solvent evaporation from a fine suspension, spin-coating, Langmuir–Blodgett and self-assembly deposition were used to produce these sensors. One very promising approach is to use porous material specified by a large specific surface areas [28]. Sensitivity enhancement by grain-size reduction is pronounced when the grain-size becomes smaller than the space-charge depth induced by surface chemisorbed gas species. In addition, sensitivity can be enhanced by designing a specific pore structure of the sensing layer and by metal doping of the sensing material. The possibility to control the porosity of nanostructured membrane films is of particular interest for gas sensor applications since the number of gas molecules, which interact with the surface, increases with the films surface area.

Nonporous metal oxides are characterized by a well-controlled nanoporous structure (pores are 10–50 nm in diameter). In addition to their characteristics of nano-sized crystallites or particles they show extremely high specific porosity and surface area. Since Lang et al. [29] made use of the metal oxide membranes to develop a catalytic gas sensor, more researchers investigated these materials to develop specific gas-sensitive membranes [30–37].

In this paper, a novel optical sensor based on phthalocyaninato-iron(II) which is dissolved in an organic solvent and deposited onto a nanostructured nonporous matrix (AlOOH) for determining NO\(_2\) in gas samples is presented. This sensor shows a stunning performance mainly relying on the controlled pore-size of the nanostructured sensing layer. The nonporous material and the procedure have the potential to be combined with all known chemical compounds which induce selectivity for a specific gas. The nanoporous structure permits the co-retention of more than one compound without aggregation. In addition, the insulation of reactive chemicals causes higher stability to ambient. The higher dispersion, the controlled capillarity and the excellent accessibility of selective complexing agents and indicators provide quick response time and lower aggregation probability of the organo metallic compound by insulation within the nanopores. Also, another aspect of the proposed optical sensor is the simple production method of the gas-selective nanostructured membrane.

2. Experimental

2.1. Chemicals and reagents

For the preparation of the selective-cocktail the following compounds were used: phthalocyaninato-iron(II), THF, decylamine (DA), dibenzylamine (DBA) (all puriss. from Fluka Chemie AG, Buchs., http://www.sigmaaldrich.com) and p-decylaniline (pDA) (puriss. from Aldrich, Switzerland, http://www.sigmaaldrich.com).

For the preparation of aluminum oxide/hydroxide membranes the following compounds were used: aluminum oxide/hydroxide (AlOOH) DISPERAL HP 14/2 (from Sasol GmbH, Hamburg, Germany, http://www.sasoltechdata.com), concentrated acetic acid 80% (from Aldrich Chemie,
Buchs, Switzerland), polyvinyl alcohol (PVA) 10% by weight and molecular weight 85,000–146,000 (from Aldrich Chemie, Buchs, Switzerland) and transparent polyester (PET) support 175 μm thickness (from Dupont de Nemours, http://www.dupont-imagineering.com) called P72.

The gas supply was provided from 30 L gas bottle at 200 bars with dry synthetic air quality 5.5 (Sauerstoffwerk Lenzburg AG, http://www.slgas.ch), 10 L gas bottles at 200 bars with NO2 (10 ppm in synthetic air from Carbagas, Switzerland, http://www.carbagas.ch), NO (10 ppm in nitrogen from Carbagas, Switzerland), CO2 (quality 4.8 from Messer Griesheim GmbH, Notruf, http://www.messer.de) and SO2 (200 ppm in nitrogen from Carbagas, Switzerland).

2.2. Preparation of nanostructured nanoporous membranes

Their preparation is exemplified for the case of AlOOH [38]. Fifty grams of the aluminum oxide/hydroxide were dispersed for 15 min in vigorous mechanical stirring at a temperature of 20°C in 948 g of doubly distilled water. Afterwards temperature was increased to 90°C and stirring was continued for 15 min at this temperature. The solid was filtered, washed three times with doubly distilled water and dried to 110°C. Eight grams of this solid were added to a mixture of 63 g of doubly distilled water and 0.96 g of concentrated acetic acid. The resulting dispersion was exposed for 3 min at 40°C to ultrasound. Afterwards, 8 g of a solution of polyvinyl alcohol were added and the resulting coating solution was again exposed to ultrasound for 3 min. Then, 100 cm2 of this coating solution were coated at a temperature of 40°C onto a transparent polyester support. The coated support was then dried 60 min at a temperature of 80°C.

Using similar procedures [39] nanoporous membranes with agglomerate particles of 10–60 nm diameters with controlled and reproducible porosity consisting of nanopores of 1–50 nm diameter and macropores of >50 nm diameter were obtained. The thickness of these membranes is between 1 and 100 μm under dry conditions and the pore volume can oscillate between 0.1 and at least 1.4 mL g−1.

2.3. Optical sensor preparation and characterization

The cocktails were prepared in sealable 4 mL flasks. 1.5 mg mL−1 of FePc and 12.5 mg mL−1 of DA were weighed into the flask on a AT 261 balance (Mettler-Toledo, Greifensee, Switzerland, http://www.mt.com) with ±0.1 mg precision and were then fill up with THF. Then, they were shaken on an IKA-Vibraxmas-VXR (IKA-Labortechnik, Staufen, Germany, http://www.ika.de) until all components were dissolved. The filling of AlOOH pores was made using a spin-coating technique: 0.1 mL of the cocktail was injected onto a rotating AlOOH support of a spinning device at 150 rpm. The membranes are transparent to visible light.

The optical sensors were characterized measuring the called sensor response which was taken to be the absolute value of the difference between absorbance at 659 nm in presence of NO2 (200 ppb of NO2 and 50% of relative humidity into a synthetic air carrier stream at 200 mL min−1 during 300 s; A1) and background signal (absorbance at 659 nm in absence of NO2; synthetic air carrier stream at 200 mL min−1 with 50% of relative humidity; A0). All the measurements were carried out in triplicate to evaluate the error and all the experimental results have been expressed as the average of three replicas ± error (s/√n) where s is the standard deviation, t is the Student’s t and n is the number of replicas.

3. Results and discussion

3.1. Solubilization and optical properties of FePc

Pure phthalocyanine films show generally an amorphous or polycrystalline character. Due to the metallic character of metallophthalocyanines and due to its association to dimers bridged by axial ligands such as oxygen, it was expected that it would be difficult to maintain the compound in solution in a polymer film. Nevertheless, the higher accessibility


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of the metal organic compound to axial ligands and to ligand-exchange rendered it attractive to dissolve FePc in a polymer film. In addition, changes in the electromagnetic spectrum in solutions can easily be monitored if the polymer is cast onto a waveguide. Several attempts to incorporate phthalocyanines into a polymer film were made (see Section 1). From the known features of metallophthalocyanines and earlier studies in sensor technology, it was concluded that a stable solution of the complex can only be achieved by axial ligands which support the solubilization of the metal complex within a polymer and, in parallel, admit the ligand exchange by an analyte gas. Reagents which were investigated in view of its potential to coordinate as axial ligands reversibly were dibenzylamine, decylamine, 4-decylaniline, dioctylamine (DOA) and bis-(2-ethylhexyl)amine (BEHA). The solubilization effect of these solvents was investigated by monitoring the electromagnetic spectrum in the visible range. In another attempt, phthalocyanine was addition- ally octa substituted by an octyloxy-group in order to increase the solubility within the organic environment [7].

The electromagnetic spectrum of FePc in solution shows an intensive absorption band in the red region, the so-called Q band, which corresponds to the lowest energetic transition (see Fig. 1).

A study by Berkowitz [40] showed that the highest energy occupied orbitals are macrocycle-ligand-like and not metal-3d-like orbitals. In addition, it is known that in metallophthalocyanines there is a π-back donation of electron from the metal d-orbitals to the macrocycle ligand π* orbitals [41]. The π–π* transition energy and, therefore the Q band, is strongly influence by this π-back donation. The introduction of axial ligands modifies this π-back donation to the macrocycle and therefore the π–π* transition energy is affected by axial ligands [42]. In the case of FePc dissolved in pyridine and its derivatives, pyridine acts as an axial ligand. However, it was found that the spectrum of the Q band shows a bathochromic shift with increasing donor strength of the substituents. With electron-withdrawing substituents at the pyridine, λπ–π* for the Q band is observed in the range of 650–670 nm [43], the absorption band around 650 nm is attributed to the 2:1 complex [42] and a band around 560 nm indicates the formation of the phthalocyanine radical cation [44] (see Fig. 1).

Fig. 1 also shows that NO2 induces the Q band at 659 nm to decrease in intensity, whereas a shoulder at 690 nm indicates that only one ligand is coordinated to the metal centre. The spectral changes shown in Fig. 1 indicates that a ligand-exchange reaction occurs and not the formation of a phthalocyanine radical cation.

Fig. 2 shows the proposed sensing mechanism for the recognition of NO2. It is based on the ligand exchange of an electron donor (NR3) with an π-electron acceptor (NO2) which results in a decrease in the absorbance of the Q band.

3.2. Kind and concentration of N-donor ligand

As explained in Section 3.1, axial N-donor ligands are necessary to dissolve the FePc and to obtain the monomer species of this metal complex. 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 this case, one axial ligand has to be exchanged with NO2, therefore the binding of the axial N-donor ligand must not be too strong. So the selection of the N-donor ligand is an important parameter to keep in mind. But the equilibrium of the system is influenced not only by the strength of the bond of the N-donor ligand to the metal center, but also by the concentration of this compound, which needs not necessarily to be proportional to the stoichiometric ratio.

In the following section, the relationship between the type and concentration of the N-donor ligand and the sensitivity of the polymer film to NO2 was studied and the concentration of the solubilization agent was optimized.

Five different N-donor ligands were studied by Nezel [7]: dibenzylamine, decylamine, p-decylaniline, dioctylamine and bis-(2-ethylhexyl)amine were used as solubilizers for the metal complex. Table 1 shows the experimental results for an optical sensor membrane obtained with 0.1 mL cocktail made from 12 mg solubilizer mL−1 cocktail and 1.5 mg FePc mL−1 cocktail dissolved in THF. The solubilizer which provided the most sensitive (ΔΑ/Α0) and also reversible membrane reaction was DA. Therefore, DA was selected as a N-donor solvent to facilitate the solubility of FePc.

Optical sensor membranes were prepared with cocktails containing 1.5 mg mL−1 FePc whereas the concentration of DA was varied between 5 and 100 mg DA mL−1 cocktail and the absorbance change of the optical sensor membranes to
NO$_2$ was evaluated (see Fig. 3). An increase in the DA concentration produced an increase in the absorbance difference $A_0 - A_x$ at 659 nm where $A_0$ is the absorbance in the absence of NO$_2$ and $A_x$ is the absorbance on exposure to 200 ppb NO$_2$. The absorbance difference is raised up to 10 mg mL$^{-1}$, between 10 and 15 mg mL$^{-1}$ the $A_0 - A_x$ remains constant upon exposure to 200 ppb NO$_2$. At higher concentrations than 15 mg mL$^{-1}$, $A_0 - A_x$ starts to decrease. Concentrations of the N-donor ligand higher than 15 mg mL$^{-1}$ obviously limit the accessibility of NO$_2$ to the metal center and inhibit the exchange of one axial ligand to NO$_2$. Therefore, throughout this paper, a concentration of 12.5 mg DA mL$^{-1}$ cocktail was selected as optimum concentration of DA. Under this condition the molar ratio of DA relative to FePc is 30:1.

### Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>Comments</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\Delta A/A_0$ (%)</th>
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</thead>
<tbody>
<tr>
<td>DBA</td>
<td>Sensitive, not reversible</td>
<td>652</td>
<td>5</td>
</tr>
<tr>
<td>DA</td>
<td>Sensitive, mostly reversible</td>
<td>659</td>
<td>12</td>
</tr>
<tr>
<td>pDA</td>
<td>Not response with NO$_2$</td>
<td>654</td>
<td>2</td>
</tr>
<tr>
<td>DOA</td>
<td>Not reversible</td>
<td>655</td>
<td>1</td>
</tr>
<tr>
<td>BEHA</td>
<td>Coordinates badly to FePc, probably sterically hindered</td>
<td>–</td>
<td>–</td>
</tr>
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</table>

$\Delta A/A_0$ is the relative change in absorbance.

* These values are given as a mean of three replicas.

3.3. Concentration of FePc

The effect of the concentration of FePc in 100 µL THF applied to the AlOOH substrate was evaluated in order to obtain the most favorable conditions to prepare the NO$_2$-selective optical sensor and to study the mechanism and distribution of the chemicals within the substrate. Fig. 4 shows the results.

In Fig. 4a, the y-axis corresponds to the sensitivity of the sensor given by the absorbance difference ($A_0 - A_x$) whereas $A_0$ is the absorbance of the membrane before NO$_2$ exposure and $A_x$ is the absorbance of the membrane on exposure to 200 ppb NO$_2$ in air (50% RH). The graph shows that an increase in the FePc concentration provides an increase in $A_0 - A_x$ up to 1.5 mg mL$^{-1}$ THF. Higher FePc concentrations produce, first, a plateau and, at higher concentrations, a decrease in $A_0 - A_x$. In Fig. 4b, the y-axis represents the absolute absorbance $A_0$ of the optical sensor membrane without any previous exposure to NO$_2$. $A_0$ increases steeply (slope 0.48 mL mg$^{-1}$) up to a concentration of 1.5 mg FePc mL$^{-1}$ THF (see Fig. 4b). In this concentration range, the increase in absorbance goes along with an increase in sensitivity. Nevertheless, a further increase in the amount of metal complex added to the nanoporous substrate does not provide a proportional increase in the $A_0 - A_x$. This phenomenon shows that the organometallic complex is subjected to two different environments which obviously influence its absorption coefficient whereas the electromagnetic spectrum is not modified. This phenomena was supposed to be due to the two different types of pores (nanopores and macropores) in the nanostructured AlOOH membrane (see Fig. 5). The metal oxide membranes are formed from agglomerated particles of metallic oxide where the nanopores are located inside while the macropores appear between agglomerated particles. So, the membrane solution begins to fill up the nanopores due to the dominant capillary forces ([FePc] < 1.5 mg mL$^{-1}$); subsequently when the nanopores are filled ([FePc] = 1.5 mg mL$^{-1}$), the macropores start to fill up. For this reason, Fig. 4b shows two different slopes at concentrations below and above 1.5 mg mL$^{-1}$, indicating different molar absorption coefficients. In a second step, the volatile solvent THF evaporates and the FePc
solubilized by DA adsorbs to the wall of the nanopores. When the nanoporous structure is exposed to NO₂, NO₂ diffuses immediately into the nanopores due to capillary forces. At a concentration level of NO₂ as low as 200 ppb, primarily the FePc adsorbed within the nanopores is involved in the reaction. Nevertheless, the fraction of FePc adsorbed to macropores increases the total absorbance of the transparent optical sensor membrane. At higher NO₂ concentrations, there is no longer a direct relationship between the NO₂ concentration and the absorbance change.

### 3.4. Effect of nanoporous membrane characteristics

To evaluate the effect of the nanoporosity of membranes in order to develop a NO₂-selective optical sensor, five different membranes were prepared and investigated. Table 2 shows the nomenclature and the composition of every membrane tested. In this section, the effect of the kind of oxide, the sign of the charge, the total pore volume (TPV; obtained by multiplying the pore volume and the coating weight), the pore diameter (PD) and the PV A concentration of the nanoporous membrane have been analyzed to obtain the best conditions for developing a NO₂-selective sensor.

As Table 2 shows, the kind of oxide (AlOOH and SiO₂) does not affect the sensor response since the sensitivity (A₀ − Aₓ at 659 nm) of the positively charged substrate-membranes AP171/14 to SP88/31 to 200 ppb NO₂ (50% RH) is nearly identical. Also, the total pore volume and pore diameter do not also affect the sensitivity. Therefore, substrate AP200/19 (TPV = 20.0 mL m⁻²/PD = 19.2 nm) shows a similar response as substrate SP88/31 (TPV = 8.8 mL m⁻²/PD = 31.8 nm). In conclusion, more important than PD and TPV, seems the charge sign of the substrate which might be linked to the charge sign of the organometallic complex which is positive for FePc. Referred to Table 2, the positively charged substrate-membranes provide higher A₀ − Aₓ than the negatively charged ones but both positively and negatively charged substrates show the same absorption spectrum with similar A₀. It was shown in the last section that the metal complex dissolved in DA enters the nanopores quickly. The lower sensitivity with the same absorption spectra may primarily be explained by a rather strong interaction of the metal center (FeII⁺) with the negative charge in the cavity of SiO₂ nanopores which maintains the chemical structure of the complex (complex 1:2; (SiO₂)(DA)FePc with a very similar absorption spectra than (DA)₂FePc) and simultaneously inhibits the exchange of an axial ligand by NO₂.

### 3.5. Analytical performance for the FePc-DA-AlOOH optical sensors

The NO₂-selective sensor was calibrated between 0.05 and 0.4 ppm NO₂ (50% RH) at 659 nm. The standard linear calibration graph was drawn according to recommended procedures. The regression equation was

$$ A = 0.0018 + 0.216C $$

where C is the concentration of NO₂ in ppm and A is the sensor response (A₀ − Aₓ at 659 nm). The intercept corresponds to the uncertainty of the absorbance measurement. The correlation coefficient (r) was 0.999. All the features of the proposed sensing substrate are summarized in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Analytical parameters of proposed sensor</th>
<th>Estimated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear range (ppm)</td>
<td>0.02–0.40</td>
</tr>
<tr>
<td>Limit of detection (ppm)</td>
<td>0.02</td>
</tr>
<tr>
<td>Limit of quantification (ppm)</td>
<td>0.07</td>
</tr>
<tr>
<td>Precision (R.S.D.) (%)</td>
<td>0.05 ppm 19.0</td>
</tr>
<tr>
<td></td>
<td>0.10 ppm 3.1</td>
</tr>
<tr>
<td></td>
<td>0.20 ppm 0.3</td>
</tr>
<tr>
<td></td>
<td>0.30 ppm 2.9</td>
</tr>
<tr>
<td></td>
<td>0.40 ppm 1.1</td>
</tr>
</tbody>
</table>
The wide linear range, the small standard deviation and the correlation coefficient close to unity indicate a very good calibration linearity. The detection and quantification limits of the flow-rate on the sor which was used to determine 200 ppb of NO2 during 1 month at room temperature. No change in the absorbance of the background signal remained constant. In conclusion, the NO2-selective optical sensor is not affected by the humidity except between 0 and 25% RH where the absorbance increases simulating a false negative response.

CO2 does not cause any interference in the determination of NO2 in ambient air for up to 15 vol.% CO2. Also the false positive result induced by SO2 is considered to be neglectable. Concentrations of SO2 >25 ppm increase the signal and decrease the absorbance due to NO2 by 5%. And CO produces false positive results for concentration higher than 15 ppm CO. These results refer to a concentration of 200 ppb NO2 (50% RH). NO does not cause any interference up to a level of 1 ppm.

### 4. Conclusion

A new optical NO2 sensor was developed which is based on a nanostructured substrate of AIOOH and SO2 with controlled porosity and pore diameter. The substrate is doped with FePc dissolved in decylamine. This novel nanoporous AIOOH membrane shows characteristics which are very attractive for developing optical sensors especially compared to earlier developments: FePc shows an absorption maximum at 659 nm which is modified by axial ligands typically NO2 gas. No additional chromoionophores are necessary. Therefore, the optical sensor membrane based on FePc is more stable.

The solubility problems of FePc had been solved by using decylamine as a solvent. The transparent NO2-selective film reacts reversibly to the specific gas showing a detection limit at 20 ppb (μg m−3) and no relevant interference by humidity, NO, SO2 and CO2. These features allow the sensor to be used as fire alarm detectors and to monitor the admitted daily emission to NO2 to be surpassed. The nanostructured membrane provides increased photostability and stability of the compounds to ambient, higher dispersion and accessibility of the active chemicals and, therefore, quick response time, lower aggregation probability of the organo metallic compound by insulation within the nanopores.

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Ursula E. Spichiger-Keller has founded the “Center of Chemical Sensors and Chemical Information Technology (CCS)” at ETH Zürich in 1994. CCS is a non-profit organization which works without financial support by the university. Ursula Spichiger was awarded the title of a professor in 1996. She was awarded the price “Technologie-Standort Schweiz” and the “Sandmeier Award”. The later is donated by the Swiss Chemical Society for excellent collaboration with the industry, especially with Bosch GmbH, Germany, in the development of fire alarm sensors.