DOI 10.5162/sensor2015/E5.1

Chemosensitive gas detection

Carolin Pannek[1], Katrin Schmitt[1], Jürgen Wöllenstein[1,2]
[1]Fraunhofer Institute for Physical Measurement Techniques, Heidenhofstr. 8, 79110 Freiburg
carolin.pannek@ipm.fraunhofer.de
[2]Albert Ludwigs University Freiburg, IMTEK, Georges-Koehler-Allee 102,
79110 Freiburg im Breisgau

Abstract:

The chemosensitive gas detection is one opportunity of low-cost and selective gas sensing. Absorption changes of the dye, due to the gas reaction can be detected in different ways, depending on the application and requirements. We give an overview of the state of the art of gasochromic sensing and of the different measurement principles. Following this, we describe our investigation on gasochromic materials for the detection of CO, NO_2 and NH_3.

Key words: absorption measurement, gasochromic color dyes, selective gas detection

Introduction

Gas sensors based on chromosensitive dyes are a promising alternative to nowadays commercially available low-cost gas sensors. The measuring effect relies on changes in the absorption of the dye during exposure to a specific gas. Ideally this chemical reaction is selective to only one gas and completely reversible.

The investigation of color dyes for sensing has a very long history. The most prominent representatives are surly pH indicator stripes, which are used for the determination of the pH value of liquids. Next to pH stripes there are other commercially available chemosensitive sensors. Gas sensitive color dyes, further called gasochromic dyes, are chemically known since many years.

Often sensors do not need a high accuracy, but a compact setup, long-term stability, low energy consumption and low fabrication costs. Chemosensitive sensors, in combination with a suitable measurement technique, enable such a development for manifold applications, like fire detectors, environmental monitoring, control of perishable goods, biomedicine etc.

In this presentation we will give an overview of the gasochromic detection of CO, NO_2 and NH_3, concerning different color dyes, measurement principles and their advantages and disadvantages.

State of the Art gasochromic sensing

One gasochromic reaction of CO was already described by Martinek in 1928 [1]. He detected CO in air and blood using iodine pentoxide, which changes its color from white to brown. The detection limit was determined to be 10 ppm. Unfortunately this reaction is irreversible, so itis not suitable for the application in many fields. Other frequently used color dyes are palladium compounds like palladium chloride or palladium ammonia molybdate [2]. In 1984 Herskovitz patented a CO sensor basing on ammonium molybdate. Shuler and Schraunzer patented another CO sensor in 1977 [3]. This patent focuses on the reversibility of the reaction. Other CO sensitive dyes are metal-complexes like porphyrines. The most famous CO sensitive porphyrine is the “color dye” of our blood – hemoglobin. Another complex, with reported high selectivity features, is an iron pincer complex. As solid state, the color changes from yellow to red, in solution from yellow to blue. The reverse reaction takes 5 minutes at 100°C, which is far too long for many sensing applications [4] In our work we investigated another complex family, which was first described by Esteban in 2010 [5]. It is a binuclear rhodium complex, which can bind up to two CO molecules in axial position. The reaction principle was already described in [6].

As for CO detection, there are a lot of different gasochromic materials to detect NO_2. The first published and mostly cited gasochromic proof of NO_2 was described by Saltzman et al. in 1954 [7]. Due to their chemical nature, many metal complexes are also suitable. The working

group around Spichiger-Keller published investigations on NO_2 sensitive membranes. They consist of a Co(III)-cobyrinate and chrome ionophore. In contact with NO_2, the chrome ionophore gets protonated to a Nile blue derivate. This leads to a reversible color change from blue to yellow. The Co(III)-cobyrinate catalyzes the reaction resulting in decreasing reaction constancy [8, 9]. This sensing mechanism was pushed to develop a low-power gas sensor for fire gas detection. Therefore the membranes were deposited on photo detectors and arranged as an array of always four detectors surrounding a red LED. The measurement range was described between 25 and 800 ppb NO_2. Yet the dye could not be used due to the low chemical stability of the dye above 50°C. Next to this there are a couple of further complexes with chromosensitive behavior described in [10 - 13]. The gasochromic reactions of chinonimine color dyes to NO_2 were described by Alexy in 2006 [14]. He detected the color change of N,N'-diphenyl-1,4-phenylendiamine, o-dianisidin, N,N'-diphenylbenzidine and N,N,N',N'-tetramethyle-p-phenylene diamine (TMPD) in transmission. Long term stabilities of about 1 year were stated. The detection limit is below 0.1 ppm. We investigated TMPD, which is also known as Wursters blue [15].

The chemosensitive proof of NH_3 is certainly one of the first.. Already in 1976 David et al. reported on the gasochromic detection of gaseous ammonia. They coated quartz cylinders with ninhydrin and polyvinylpyrrolidone. By this they reached detection limits in the lower ppb range. Unfortunately this reaction is irreversible and not suitable for gas sensors. Guiliani et al. coated capillaries with pH-sensitive oxacine perchlorate and used them as optical waveguides. This detection is reversible for ammonia concentrations between 60 and 1000 ppm. Often the pH-indicator dye bromophenol blue is used [16, 17]. Due to its high sensitivity to NH_3 and easy handling, we used this dye throughout the experiments described in this paper. A detailed overview on the state-of-the-art on pH-based ammonia sensors is given in [18].

Measurement principles

The most famous gasochromic sensors are Dräger gas tubes [19]. These are glass tubes, packed with a specific gasochromic material, see fig. 1. They are used by fire departments to determine the composition of a fire. The endings of the glass tubes are broken and the gas is pumped through the tube. In case of a matching between gas and gasochromic material the packed material changes its color. The gas concentration can be directly read on the imprinted scale. The main advantage of such sensors is the selective behavior of the gasochromic material. The main disadvantage is the need of manual handling and readout.

Figure 1. *Picture of Dräger gas tubes before (left) and after (right) exposure to the target gas. The gas concentration can be directly read on the imprinted scale [19].*

In laboratory environment, gasochromic materials can be investigated in transmission by UV/VIS-measurements. The sample is exposed to the target gas directly inside a measurement chamber, and changes in the transmission spectra can be recorded simultaneously. A sketch of this laboratory set-up is shown in fig. 2. This measuring principle is very fast, but requires expensive equipment and is thus not useful for gas detection outside of laboratories. We performed UV/VIS-spectra analyses for extensive characterization.

To obtain flexible measurement conditions, it is important to move from laboratory and manual measuring principles to an autonomous sensor set-up.

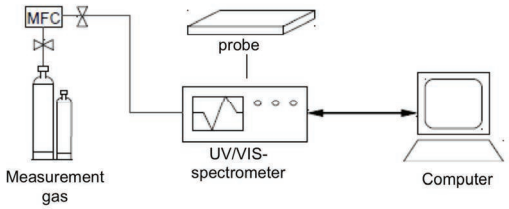

Figure 2. *Laboratory set-up for UV/VIS-based material analyses.*

One opportunity is to measure absorption changes in the reflected light of the chemosensitive probe. Fig. 3 shows the set-up. The sample is illuminated by a light source which can simply be an LED, and the reflected light can be measured by a photo detector [20]. In this case the sample has to be prepared as a planar solid. In combination with NH_3 sensitive dyes this principle was described by [21]. The

color of the LED depends on the spectral range of the color change of the dye.

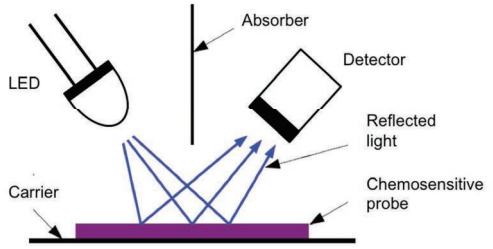

Figure 3. *Measurement set-up to detect gas dependent color changes of a dye by the reflected light of a LED.*

In both cases, the detectable signal is often very small, although the color change is clearly visible. In case of UV/VIS-measurements, the sample will be measured only once - regarding the law of Lambert-Beer, it is obvious that the thickness of the probe is crucial. By measuring the reflected light as in fig. 3, only changes at the surface of the dye are detected. Changes inside the sample are not captured. One way to improve the sensitivity of the sensor system is to apply waveguide based measurements. Here, the color dye is deposited onto an optical waveguide. The light of an LED is coupled into one end of the waveguide and passes through it under the conditions of total internal reflection (TIR). The color change of the sensitive dye can be detected by absorption changes inside the layer and by changes in the evanescent field. After coupling out, the light is focused on a photo detector. Changes in the dye induce direct changes in the intensity of the light. Compared to measurements in transmission, the waveguide principle has much lower detection limits, caused by the longer optical path. As in the case with reflection-based measurements, the LED should cover the spectral range of the color change. This measurement principle has already been described in [16, 20]. To be independent from environmental influences, a reference channel is embedded additionally.

A continuative approach to improve waveguide-based measurements is the use of on optical fibre as waveguiding substrate. In this case the specific surface increases due to a complete coverage of the fibre. Our results on the fibre-based detection of ammonia were already shown in [22]. Fig. 4 demonstrates the reaction of planar waveguide-based sensor set-ups .

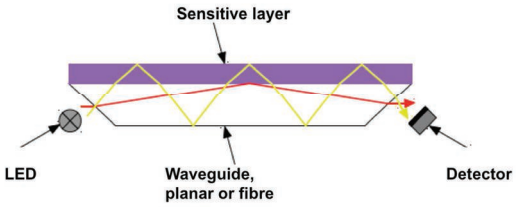

Figure 4. *Sketch of the gasochromic sensor, consisting of a planar optical waveguide, covered with the chemochromic film. The light of an LED is coupled into one end of the waveguide and travels trough it under TIR before it is focused onto a photo detector. The gas reaction leads to changes in the detector signal. Red light beam: Light, which induces an evanescence field inside the sensitive layer; Yellow light beam: multi transmitted light through the sensitive layer. The sum of both effects yields in the sensor signal.*

Investigated color dyes

Within our work we investigated several color dyes for different gases with suitable incorporation matrices.
For all transmission-based measurements we embedded the color dye, which is usually a powder, in a polymer matrix. This matrix has to fulfill the following requirements: high porosity for diffusion of the target gases, inert to environmental influences like humidity, temperature and radiation, inert to the colorimetric material and ideally the same solvent as the dye. Possible polymers are poly vinyl chloride (PVC), polydimethylsiloxan (PDMS), ethyl cellulose (EC) and/or poly methylmethacrylate (PMMA). Each dye/polymer combination is unique and has to be determined individually. The liquid sensitive matrix can be deposited onto the waveguide by dip- or spin coating.

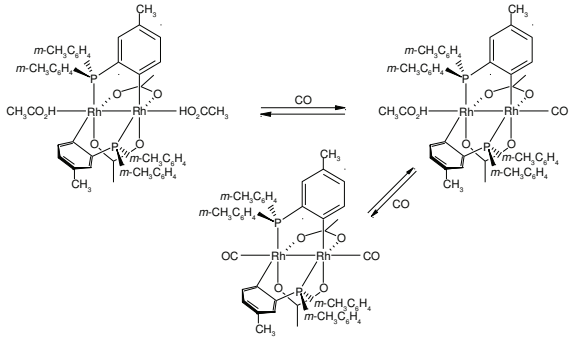

Fig. 5. *Reaction of the rhodium complex to CO. This reaction induces a color change from violet to yellow [23].*

As gasochromic material for CO detection we used a binuclear rhodium complex embedded in a porous EC matrix. The complex has been characterized in [23] and been synthesized as described in [24]. Figure 5 shows the reaction of the rhodium complex to CO.
For NO_2 detection we investigated N,N,N',N'-tetramethyl-phenylene-diamine (TMPD). The TMPD, also called *Wurster's blue*, is a chinonime dye, which was embedded into a polyvinyl chloride (PVC) matrix. Fig. 4 shows the reaction of TMPD (left) to NO_2. The centered molecules are two different forms of the radical cation, which is blue. A second oxidation step reacts to the colorless di-cation (right). The equilibrium lies on the side of the blue cation.

Next to TMPD we also investigated a metallo-porphyrine zinc for NO2 sensing. The results are reported in [25].

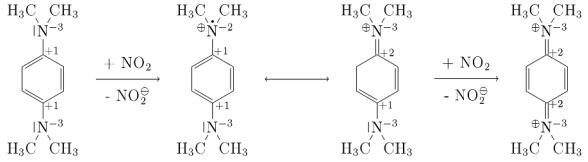

Fig. 6: *Reaction of TMPD (Wurster's blue) to NO_2. The TMPD (left) gets oxidized to a blue cation. Another oxidation steps generate the colorless di-cation (right). The equilibrium lies on the first oxidation step (middle).*

As mentioned above, bromophenol blue is a suitable color dye for NH_3 detection. The reaction principle is shown in fig. 7.

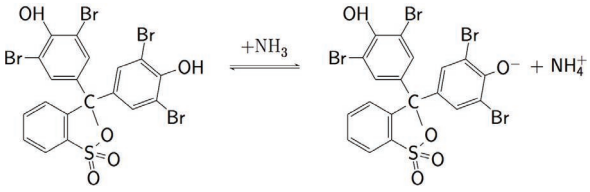

Fig. 7: *Reaction of bromophenol blue to gaseous ammonia. Due to the strong alkaline behavior of NH3, on proton of the hydroxyl group gets dissociated.*

Results

In the following we will give an overview of the results of our work and selected measurements will be shown.

Figure 8 shows the transmission changes of the rhodium complex to 50 ppm, 100 ppm and 150 ppm CO recorded with the UV/VIS-spectrometer Lambda 900, Perkin Elmer. This result demonstrates the sensitivity and reversibility of this gasochromic reaction. The time to equilibrium is several minutes. Yet the equilibrium depends on the target gas concentration and no dosimeter effect occurs.

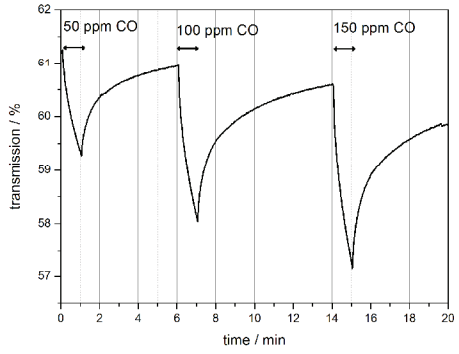

Fig. 8. *Transmission changes of the binuclear rhodium complex to 50 ppm, 100 ppm and 150 ppm CO in synthetic air, recorded with an UV/VIS-spectrometer.*

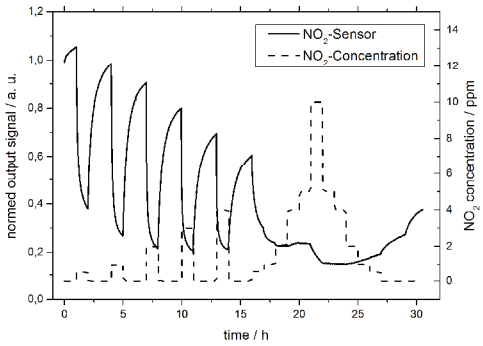

Fig. 9. *NO_2 dependent measurement of TMPD in PVC, realized with a planar optical waveguide set-up. The sensor was exposed to 0.5 ppm, 1 ppm, 2 ppm 3 ppm and 4 ppm NO_2, each for one hour.*

Figure 9 shows the absorption changes of TMPD to different concentrations of NO_2 between 500 ppb and 4 ppm as changes in the output signal of the photodiode. This measurement was performed using a planar waveguide set-up. Different concentrations of NO_2 can be detected. In contrast to the gasochromic reaction of the rhodium complex to CO, the reaction of TMPD has an irreversible part. Depending on the application, this dye might be not useful.
The gasochromic reaction of bromophenol blue (BPB) is shown in figure 10. The color dye was deposed to 10 ppm, 100 ppm and 1000 ppm NH_3. This measurement was performed using an optical fibre set-up, where the fibre was completely covered with the color dye. The sensor responds to all concentrations, with response times between four and ten minutes depending on the concentration. The detection limit of this sensor can be estimated to 5 ppm.

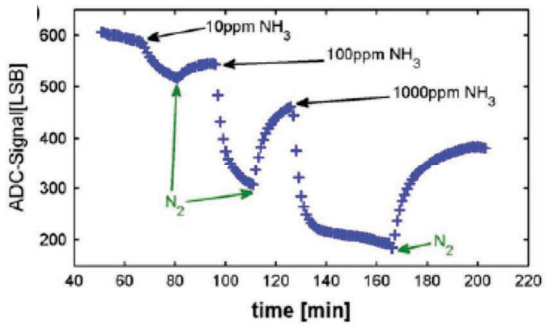

Fig. 10: *Sensor reaction of the fibre optical sensor upon exposure to 10 ppm, 100 ppm and 1000 ppm NH_3. The sensor response times were several minutes. The detection limit of this sensor can be estimated to 5 ppm [22].*

All gas dependent measurements were performed at ambient conditions in synthetic air with 40% r.H.

Conclusion

In this paper we give an overview of different gasochromic materials for the detection of CO, NO_2 and NH_3. Varying measurement principles and sensor set-ups are described. Their advantages and disadvantages are resumed in table 1. In table 2, the parameters of the color dyes are summarized regarding the color change, the wavelength of maximum color change, the measurement range, cross sensitivities and suitable polymer matrices.

Tab. 1: Summarized results of the different measurement set-ups, regarding the sensor reaction, sensitivity, costs and sample preparation.

	UV/VIS spectro-scopy	**Reflection based set-up**	**Wave-guide based set-up**
Kinetics	+	++	+
Sensitivity	0	0	++
Costs	-	+	+
Sample preparation	-	+	-

Tab. 2: Overview of gasochromic materials for CO, NO_2 and NH_3 detection [6, 16, 18].

	Parameters
Color dyes	CO: metal complex with transition metal ion, e.g. binuclear rhodium complexes (RhComp) NO_2: Chinonime color dyes like N,N,N',N' teramethyl-p-phenylenediamine (TMPD, wursters blue) or diphenylbenzidin (DBB) NH_3: pH-indicators like bromphenol blue (BPB), bromcresol green (BKG) or methy red (MR)
Color change	CO (RhComp): violet to yellow NO_2 (TMPD): brown to blue NH_3 (BPB): orange to blue
λ (max)	CO (RhComp): 480 nm NO_2 (TMPD): 460 nm NH_3 (BPB): 560-630 nm
Measurement range	CO: 10 – 1.000 ppm NO_2: 100 ppb – 10 ppm NH_3: 0,5 – 50 ppm
Cross sensitivities	CO: NO_2 > 10 ppm NO_2: no NH_3: no
Suitable polymer	CO: ethyl cellulose NO_2: poly vinyl chloride NH_3: ethyl cellulose

References

[1] M.J. Martinke, W.C. Marti, *Modified iodine-pentoxide method for determination of carbon monoxide in air and blood*, American Journal of Public Health, 1928

[2] R.L. Shepherd, *Low-Cost Surface Mount LED gas sensor*, Sensor Journal 2, 2005

[3] K.E. Shuler, G.N. Schraunzer, *Catalyst and method for oxidizing and reducing gases* , US 4,043,934, US Patent 1977

[4] D. Garagorri, et al. *Stereospecific and Reversible CO Binding at Iron Pincer Complexes*. Angewandte Chemie International Edition, 2008, 47. Jg., Nr. 47, 9142-9145

[5] Esteban, J.; Ros-Lis, J. V.; Martinez-Manez, R.; Marcos, M. D.; Moragues, M.; Soto, J., Sancenon, F. *Sensitive and Selective Chromogenic Sensing of Carbon Monoxide by Using Binuclear Rhodium Complexes*. *Angewandte Chemie International Edition, WILEY-VCH Verlag,* **2010***, 49*, 4934-4937.

[6] C. Peter et al, *Low-cost roll-to-roll colorimetric gas sensor system for fire detection, Solid-State Sensors*, Actuators and Microsystems Transducers & Eurosensors XXVII (2013), 2632-2635, DOI: 10.1109/Transducers.2013.6627346

[7] B.E., Saltzman: *Colorimetric Microdetermination of nitrogen dioxide in atmosphere*. Anal. Chem., 26, 1954.

[8] A. Hensel, *Optoden für die Brandmeldetechnik,* Die Deutsche Staatsbibliothek, 2002

[9] Nezel, T., Spichiger-Keller U.E., Ludin C. und Hensel A.: *Gas-Selective Optical Sensors for Fire Detectors*. CHIMIA International Journal for Chemistry, 55, 2001

[10] Filippini, D., Alimelli A., Di Natale C., Paolesse R., D'Amico A. und Lundström I.: *Chemical Sensing with Familiar Devices*. Angewandte Chemie Internationale Edition, 45, 2006

[11] Kurtikyan, T.S., Stepanyan T.G. und Gasparaya G.A.: *Interaction of nitrogen dioxide with sublimed ms of meso-tetraphenylporphyrinzinc*, Russian Chemical Bulletin, 47, 1998.

[12] Nakano, N.: *Development of a monitoring tape for nitrogen dioxide in air*. Analytica Chimica Acta, 321, 1996

[13] Wayland, B.B. und Olsen L.W.: *Spectroscopic Studies an Bonding Model for Nitric Oxide Complexes of Iron Porphyrins*. Journal of the American Chemical Society, 96, 1974

[14] Alexy, M., Hanko M., Rentmeister S. und Heinze J.: *Disposable optochemical sensor chip for nitrogen dioxide detection based on oxidation of N,N'- diphenyl-1,4-phenylenediamine*. Sensors and Actuators B, 114, 2006

[15] Nickel, U.: *Reaktionen mit Wursterschen Kationen*. Chemie in unserer Zeit, 12, 1978

[16] Courbat J, Briand D, Damon-Lacoste J, Wöllenstein J, de Rooij NF, *Evaluation of pH indicator-based colorimetric films for ammonia detection using optical waveguides,* Sensors and Actuators B 143 (2009), 62-70

[17] Courbat J, Briand D, Wöllenstein J, de Rooij NF, *Colorimetric gas sensors based on optical waveguides made on plastic foil*, Procedia Chemistry 1 (2009): 576-579

[18] J. Courbat, *Gas sensors on plastic foil with reduced power consumption for wireless applications*, Dissertation, EPFL, 2010

[19] Dräger AG. online, 04.2014. http://www.draeger.de/sites/assets/Publishing Images/Segments/Industrie/Dokumente/sensorhandbuch br 9046570 de.pdf.

[20] C. Pannek, *Mikrosystem zur Brandgasdetektion nach dem Farbumschlagprinzip*, Dissertation Universität Freiburg, 2015

[21] T. Nakamoto, M. Yosihioka, Y. Tanaka, K. Kobayashi, T. Moriizumi, S. Ueyama, and W. Yerazunis, "*Colorimetric method for odor discrimination using dye-coated plate and multiled sensor*," Sensors and Actuators B: Chemical, vol. 116, pp. 202 – 206, 2006.

[22] K. Schmitt, J. Rist, C. Peter, J. Wöllenstein, *Low-cost fiber-optic waveguide sensor for the colorimetric detection of ammonia*, Microsystems Technology 2012, V 18, 843-848

[23] Moragues, M. et al.: *Sensitive and Selective Chromogenic Sensing of Carbon Monoxide via Reversible Axial CO Coordination in Binuclear Rhodium Complexes*. J. Am Chem. Soc., 113, 2011

[24] Esteban, J. et al.: *Sensitive and Selective Chromogenic Sensing of Carbon Monoxide by Using Binuclear Rhodium Complexes*. Angew. Chem. Supporting Informations, 49, 2010.

[25] C. Peter, K. Schmitt, M. Apitz, J. Wöllenstein, *Metallo-porphyrin zinc as gas sensitive material for colorimetric gas sensors on planar optical waveguides*, Microsystems Technology 2012, V 18, 925-930