Colorimetric gas sensors for the detection of ammonia, nitrogen dioxide and carbon monoxide

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Laboratory for Gas Sensors
Prof. Dr. Jürgen Wöllenstein

• sensor based RFID labels
• micro machined gas sensor arrays
• gas sensitive materials
• micro optical gas sensors
• sensor systems
• gas measurement lab
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Thermoelektrische und integrierte Sensorsysteme TES
Gruppe: Integrierte Sensorsysteme ISS
gas sensor systems
Motivation and Applications

- Selective gas sensors
- No need for clean room processing
- Small and simple set-up
- Ultra low power consumption
- Possibility for wireless readout (RFID)

- Fire detection
- Process monitoring
- Environmental monitoring

- State-of-the-art: Dräger Tubes
State of the art

Optical fiber, tungsten lamp and spectrometer

- Bromocresol purple (BCP) in silica
  - Bulky
  - Expensive

Reflected light form LEDs

- Methyl red on a silica plate
  - Integration on flexible substrates difficult
  - Lower sensitivity

Two LEDs

- p-nitrophenylnitrosamine (NPNA) in PVC
  - lower sensitivity
Sensor Principle

![Diagram of sensor principle showing a gas-sensitive layer, light source, waveguide, and detector leading to a color change upon exposure to gas.](image-url)
Measurement System

- LED
- Optical sensor chip in measurement chamber
- Photo diode
- Power supply
- Electronics
- Gas in- and outlet
Ammonia color dye

Example: Bromocresol purple, pH-indicator within a porous polymeric matrix
Color change due to a (reversible) reaction with ammonia

\[ \text{Bromocresol purple} + \text{NH}_3 \rightleftharpoons \text{Ammoniated Bromocresol purple} \]

\[ \text{pH} = 5.2 \quad \text{pH} = 6.8 \]
Spectroscopic Gas Measurements

- Measurement over all the spectrum indicates where the maximum light absorption occurs.
- Film thickness: 2-5 µm.
- Data acquisition: Elmer-Perkin λ900 spectrometer.
- Light in the visible range: 200 – 700 nm, steps of 3 nm.
- Gas cell connected to gas mixing system.
- Available NH₃ concentration: 5-1000 ppm.
Ammonia sensor

Colorimetric Film Efficiency

Beer-Lambert law: \( I_{out} = I_{in} \cdot 10^{-\alpha l c} \)

- \( I_{in} \): Incoming light intensity
- \( I_{out} \): Light intensity after passing through the film
- \( \alpha \): absorption coefficient
- \( l \): path length
- \( c \): concentration of the absorbing material

<table>
<thead>
<tr>
<th>Abs coef. w ((\alpha)) [(\mu\text{m}^{-1})]</th>
<th>BPB</th>
<th>BCG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl butyral)</td>
<td>2.55</td>
<td>0.50</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>1.41</td>
<td>0.24</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.72</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Best results obtained with BPB
Ammonia sensor

Selectivity

- Film: BPB in Poly(vinyl butyral) and tributyl phosphate
- Gas carrier: synthetic air, 50%RH

![Graph showing transmission vs. wavelength for different gases in 50%RH air.]

- 50%RH air
- 30% O₂ in 50%RH air
- 200 ppm Ethylene in 50%RH air
- 10500 ppm H₂ in 50%RH air
- 30 ppm NO₂ in 50%RH air
- 200 ppm CO in 50%RH air
- 100 ppm NH₃ in 50%RH air
Film-Coated Waveguide

- Films on microscope slide cut with an angle of 45°
- Electronic circuit with feedback loop for keeping the light intensity constant

[Diagram of a film-coated waveguide and an electronic circuit with feedback loop]
Ammonia measurements with coated waveguide and LED

Gas carrier: synthetic air, 50% RH, 1000 sccm/min

BPB in PMMA was selected due to a good tradeoff between sensitivity and response/recovery time

Market: Smoke detectors

Optical smoke detectors

Common fire detectors are based on the scattered light principle

Partikel detection

False alarms (moisture, dust, particulate matter,…)
<table>
<thead>
<tr>
<th>No fire</th>
<th>CO2</th>
<th>H2O</th>
<th>CO</th>
<th>H2</th>
<th>NO2</th>
<th>NO</th>
<th>HC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 500 ppm</td>
<td>25%</td>
<td>1-3 ppm</td>
<td>0.1 – 1 ppm</td>
<td>10 ppb</td>
<td>10 ppb</td>
<td>1 ppm</td>
</tr>
<tr>
<td>TF 1</td>
<td>4000 ppm</td>
<td>40%</td>
<td>30 ppm</td>
<td>20 ppm</td>
<td>1 ppm</td>
<td>200 ppb/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>750 ppm/min</td>
<td>1,5%</td>
<td>6 ppm/min</td>
<td>3 ppm/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>700 ppm</td>
<td>28%</td>
<td>30 ppm</td>
<td>120 ppb</td>
<td>70 ppb</td>
<td>20 ppb</td>
<td>5 ppm/min</td>
</tr>
<tr>
<td></td>
<td>25 ppm/min</td>
<td>0.4%</td>
<td>6 ppm/min</td>
<td>100 ppb/min</td>
<td>10 ppb/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF 3</td>
<td>800 ppm</td>
<td>28%</td>
<td>100 ppm</td>
<td>25 ppm</td>
<td>40 ppb</td>
<td>100 ppb/min</td>
<td>30 – 40 ppm</td>
</tr>
<tr>
<td></td>
<td>40 ppm/min</td>
<td>0.4%</td>
<td>15 ppm/min</td>
<td>20 ppm/min</td>
<td>6 ppm/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TF 4</td>
<td>1800 ppm</td>
<td>30%</td>
<td>12 ppm</td>
<td>3 ppm</td>
<td>3 ppm</td>
<td>10 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td></td>
<td>520 ppm/min</td>
<td>2.5%</td>
<td>4 ppm/min</td>
<td>1 ppm/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2000 ppm</td>
<td>30%</td>
<td>15 ppm</td>
<td>5 ppm</td>
<td>1 ppm</td>
<td>2 – 3 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>750 ppm/min</td>
<td>1.5%</td>
<td>5 ppm/min</td>
<td>0.5 ppm/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7000 ppm</td>
<td>5 ppm</td>
<td></td>
<td></td>
<td>2 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 ppm/min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Standard test fires and according gas types and concentrations.
TF = open wood fire, TF2 = smoldering wood, TF3 = smoldering wick (cotton), TF4 = Polyurethane (foam), TF 5 = n-heptane, TF6 = ethanol fire.

Quelle: Siemens
Gas sensor based fire detectors

Objective of developments:

- CO / NO$_2$ sensor
- Production cost: 1 Euro
- Ultra low power consumption
- Less than 1 W
- Lifetime: five years
- No cross sensitivities
- Small package

- Market 10 billion Euro
- Big player: Honeywell, Siemens

=> one possible solution: Colour dyes
Metalloporphyrins for NO$_2$ detection

- Most common natural pigments
- Famous example: hemoglobin (1 kg in human circulatory system)
- Chemical structure: 4 pyrrole rings, connected by methines
- Component of many proteins
- Use in sensors based on fluorescence-quenching
- Examples:

  **Zinc-porphyrin:**
  
  5,10,15,20-tetraphenylporphyrin-zinc (ZnTPP)

  **Iron-porphyrin:**
  
  5,10,15,20-tetraphenyl-21H,23H-porphyrin iron(III) chloride (FeTPP)
ZnTPP: Chemical Reaction Principle

Two-step mechanism causes changes in infrared and visible range

"\[
\text{ZnTPP:} \quad \begin{array}{c}
\text{Zn} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\xrightarrow{\text{NO}_2}
\begin{array}{c}
\text{Zn} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\cdot [\text{NO}_2]^- \\
\xrightarrow{\text{NO}_2}
\begin{array}{c}
\text{Zn} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\cdot [\text{NO}_2]^- \]
"
Zinc-porphyrin (ZnTPP)

Preparation of sensor film:

<table>
<thead>
<tr>
<th>Function</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>ZnTPP</td>
</tr>
<tr>
<td>Polymer</td>
<td>PVC</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Hexamoll™DINCH</td>
</tr>
<tr>
<td>Solvent</td>
<td>Tetrahydrofuran</td>
</tr>
</tbody>
</table>

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ZnTPP: Reaction to 5 ppm NO₂
Analysis in UV/VIS-Spectrometer

Change of transmission:

Absorption @ 450 nm:
ZnTPP: Waveguide-based Measurements

- Reaction to 5 ppm NO₂
- Color change from pink to yellow
- Reversible but very long relaxation time (several days)
ZnTPP: Cross Sensitivity

- Ammonia (100 ppm)
- Ethanol (50 ppm)
- Carbon dioxide (2000 ppm)
- Carbon monoxide (200 ppm)
Iron-porphyrin (FeTPP)

Preparation of sensor film:

<table>
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<tr>
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<tr>
<td>Dye</td>
<td>FeTPP-Cl</td>
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<td>Polymer</td>
<td>PVC</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Hexamoll™ DINCH</td>
</tr>
<tr>
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<td>Tetrahydrofuran</td>
</tr>
</tbody>
</table>
Fe-TPP: Reaction to NO$_2$

- Change of transmission

- No observable cross-sensitivity to ethanol, carbon monoxide, carbon dioxide, ammonia
Colour dyes for CO-detection
First try: molybdenum blue / palladium

New trend
Rhodium complexes for CO-detection

- reversible
- High sensitive to CO
- Very low cross sensitivities (H₂O, O₂, N₂, NO₂, SO₂)
Synthesis

- Cotton et al.: "Structural and Electrochemical Characterization of the Novel Ortho-Metalated Dirhodium(II) Compounds \( Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2 \cdot 2L \) In: Organometallics 1985, 4, 8-13

- reactants
  - Triphenylphosphine
  - Rhodiumacetate
  - glacial acetic acid
  - reflux condenser
  - Inert gas
  - Evaporation of solvent
Synthesis

cis-\([\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{O}_2\text{CCH}_3)_2](\text{HO}_2\text{CCH}_3)_2]\)
Color change

1·(CH₃CO₂H)₂ ⇌ CH₃CO₂H·Rh·Rh·HO₂CCH₃ + CO

1·(CO, CH₃CO₂H) ⇌ CO·Rh·Rh·CO·P·O·O

1·(CO)₂
Color change due to CO exposure

UV/VIS transmission spectra of $1 \cdot (\text{CH}_3\text{CO}_2\text{H})_2$ before and after exposure to 100 ppm CO. The color of the sample changes from violet to yellow.
Waveguide based CO-measurement

$\lambda = 470 \text{ nm}$

Transmission / %

Zeit / min

Konzentration CO / ppm

Transmission

Konzentration CO
In order to increase the sensitivity and stability, we have synthesized the new complex 2 by substitution of the acetate ligands with trifluoroacetate.

Fig. 1. Synthesis of the Rh complex 2 and its reaction with CO. Complex 2 features weakly bound trifluoroacetate ligands. The latter are replaced by CO.

C. Courbat et al, Procedia Engineering 25 (2011) 1329 – 1332
Spectrophotometric measurement of complex 2 in solution when exposed to air and to CO (1 atm).

C. Courbat et al, Procedia Engineering 25 (2011) 1329 – 1332
Gas response of the colorimetric film when exposed to CO. The gas carrier was synthetic air with a flow of 500 sccm and humidity background of 30%. (b) Colorimetric sensor exposed to different test fires: Smoldering cotton, n-heptane, and smoldering wood. The sensor showed a completely reversibility and a suitable response time for the application. As reference, the CO concentration was monitored with a Binos® 100 from Rosemount Analytical.
Test fire at SBT facilities

- Fire lab
- 6 different standard test fire
- Sensor system on top of the room
- Reference sensors (CO, CO₂, NO, NO₂, temperature)
Results: 5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride

- In PVC → NO₂ Sensor
- Test fire 6 ethanol fire
- Gas concentrations after 10 min:
  - CO: 4.68 ppm; CO₂: 8110 ppm;
  - NO: 1785 ppb; NO₂: 695 ppb
- T90 after fresh air inlet: 24 min
Results Rh-complex (Esteban et al)

- Rh/EC-Chip → CO - Sensor
- Test fire 2 smouldering wood
- Gas concentration after 10 min: CO: 86 ppm
- T90 after fresh air inlet: 4.7 min

Graph showing CO concentration over time:
- X-axis: Zeit / min
- Y-axis: CO / ppm
- Graph shows two peaks with labels: Heizplatte an, Lüftung an
Application Integration on RFID-platform

- Development of an RFID platform
- Credit card size
- Working at 13.56 MHz standard
- ISO 15693
- Direct integration of the read-out electronics
RFID-Tag with optical ammonia / CO sensor

Melexis 13.56 MHz RFID-Transponder
µController
battery
Photodiodes
Sensorchip
LED
RFID-Tag

Very first measurements

- Ammonia measurement
- 500 ppb, 1 ppm and 5 ppm NH₃ in air.

→ Detection limit in the lower ppb range!
Application:
RFID – CO sensor system ---- Field tests

- Spitzenclusterprojekt Microtec Südwest Sens-RFID, Goal: Energy self-sufficient CO-sensor for iron making
- Thermoelectric power converter, Colourimetric CO-Sensor, Wireless communication
- Field tests: Thyssen Krupp Steel Duisburg
- Measurement at torpedo ladle with liquid pig iron (600 Tons)
Field tests ---- Impressions
Field tests ---- Measuring results

- 24 h measurement at Torpedo ladle
- Thermoelectric generator supplies enough energy
- Filling in blast furnace
Conclusions

- Color dyes for NO$_2$, CO and NH$_3$ detection
- Integration as waveguide-based system
- Detection in the low ppm-range
- Extremely low cross-sensitivities
Further Research

- Analysis of different polymers as a matrix
- Synthesis of chromogenic substances
- Long term stability
- Response time
- Improvement of deposition process
  - Dip coating
  - Spin coating
  - Inkjet printing
- Polymer waveguide
- Miniaturisation of sensor system
Thanks to the gas sensors group at IPM and EPFL

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