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

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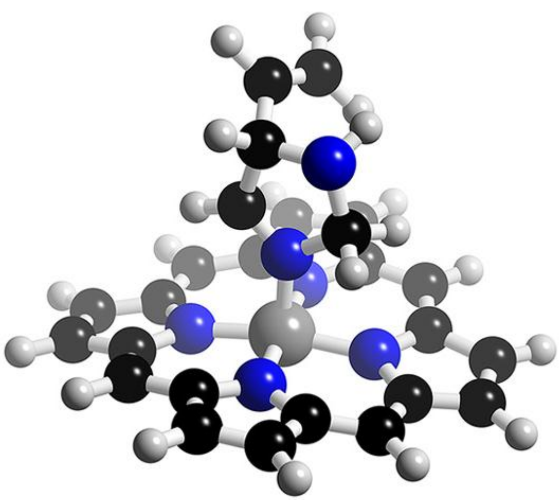


+ CO =

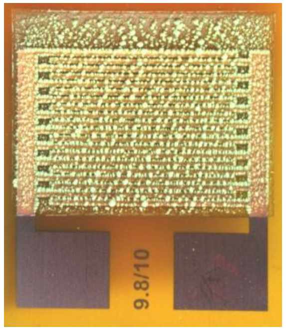
University of Freiburg
Department of Microsystem technology

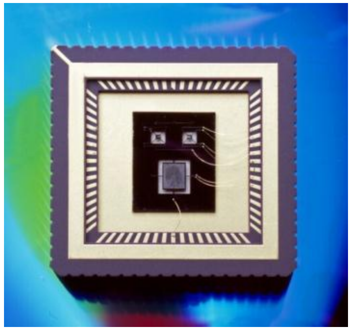
Laboratory for

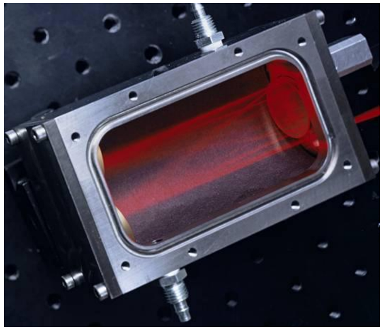
Gas Sensors

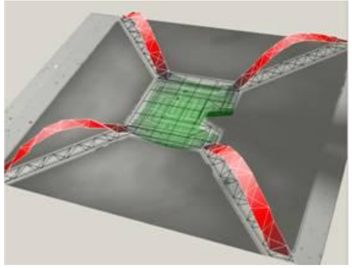
Prof. Dr. Jürgen Wöllenstein

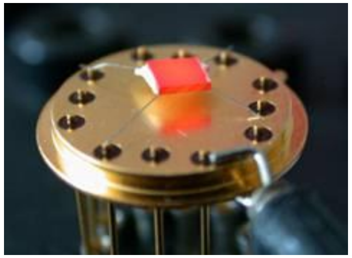
- sensor based RFID labels
- micro machined gas sensor arrays
- gas sensitive materials
- micro optical gas sensors
- sensor systems
- gas measurement lab

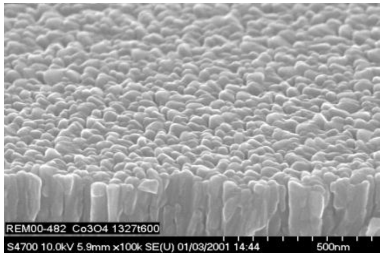












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Fraunhofer-Institut für Physikalische Messtechnik IPM

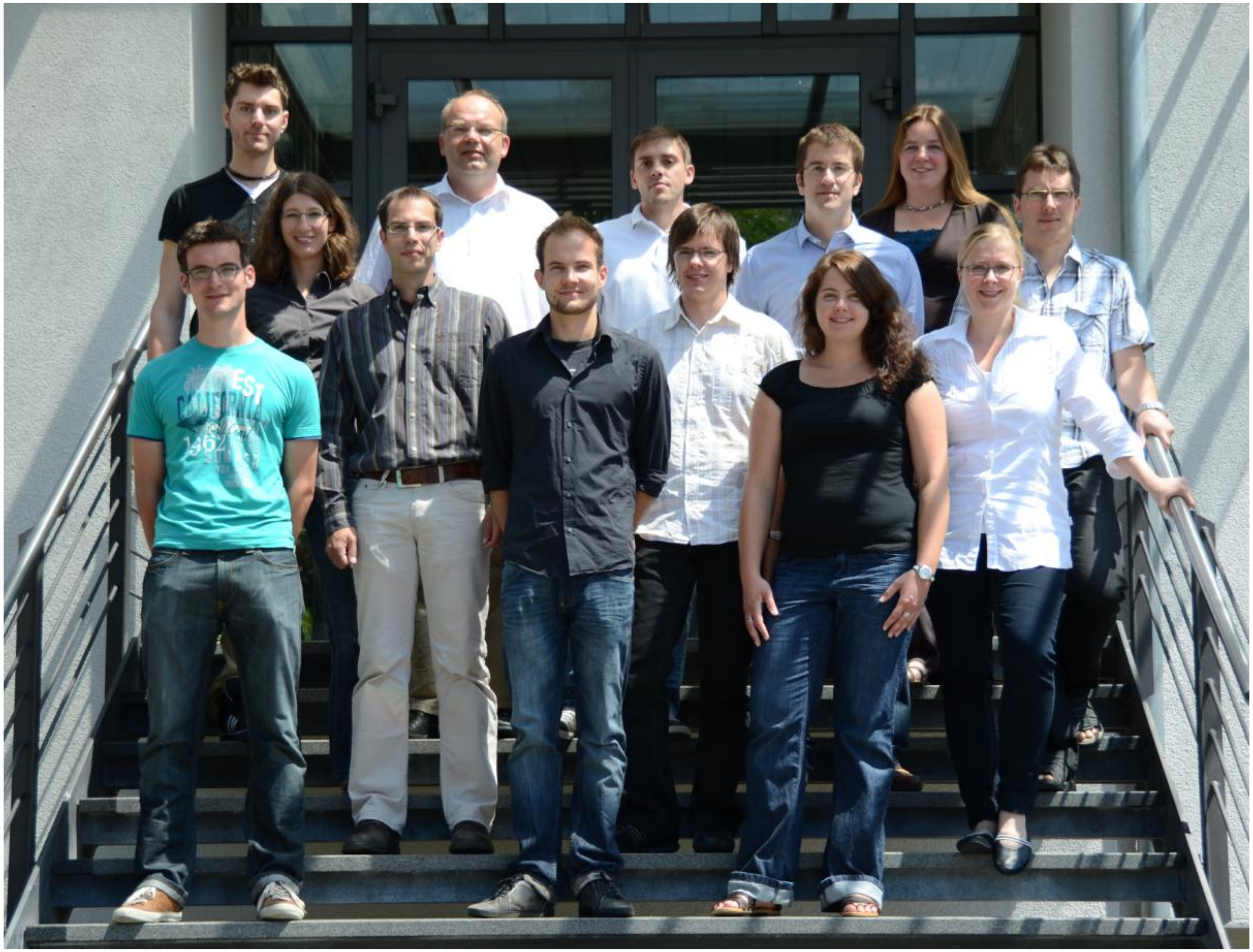
Heidenhofstrasse 8

79110 Freiburg

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)

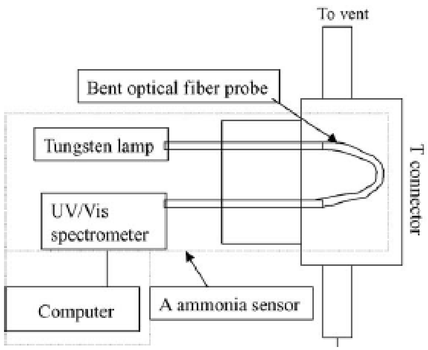
- Fire detection
- Process monitoring
- Environmental monitoring

- State-of-the-art: Dräger Tubes

Dräger

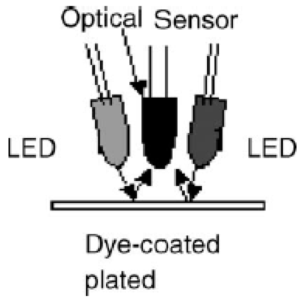
State of the art

Optical fiber, tungsten lamp and spectrometer



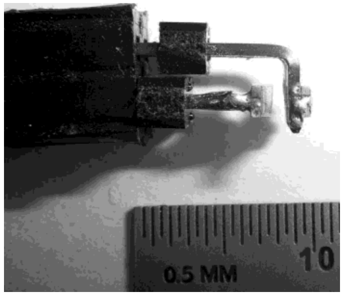
- Bromocresol purple (BCP) in silica
  - **S. Tao et al., Sens & Act, B115 (2006) 158-163.**
  - → Bulky
  - Expensive

Reflected light form LEDs



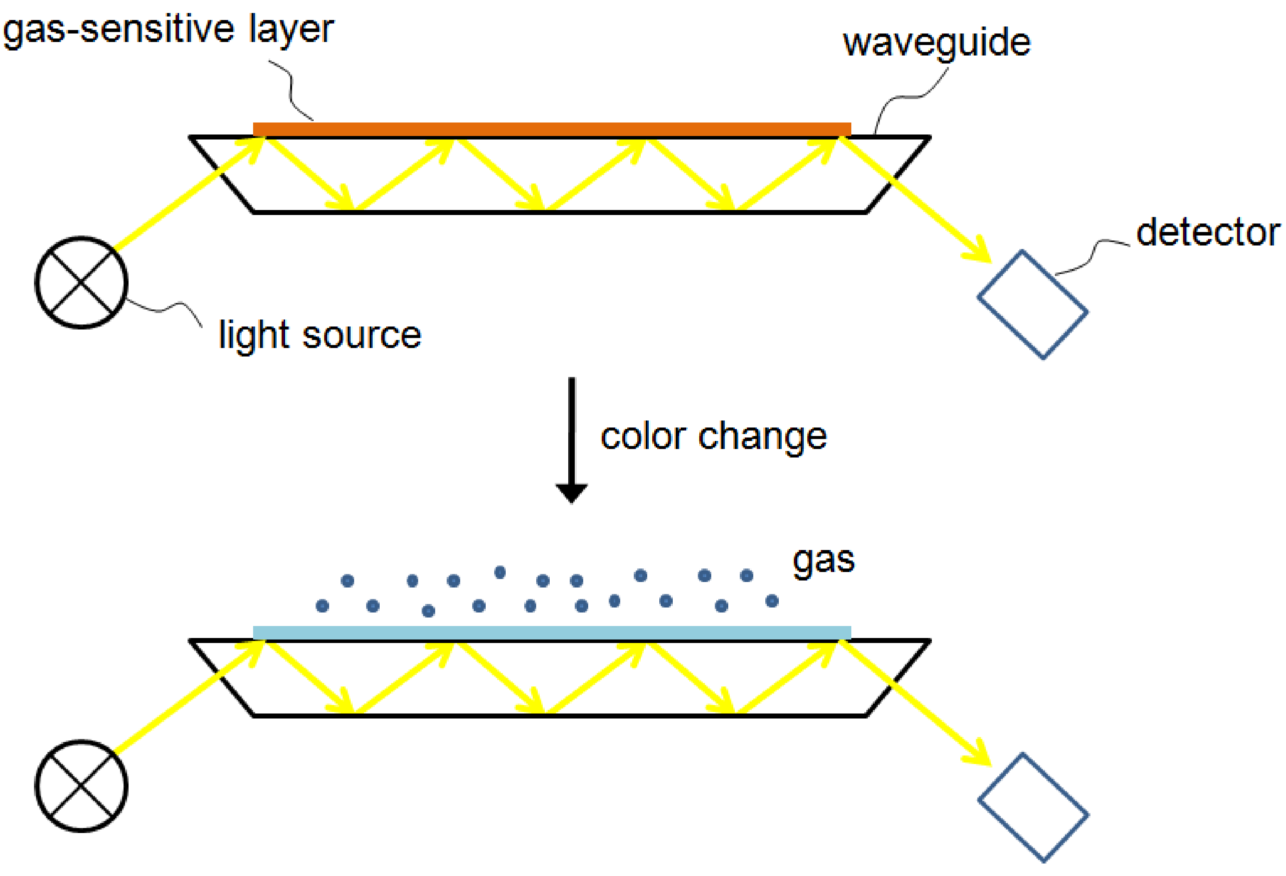
- Methyl red on a silica plate
  - **T. Nakamoto et al., Sens & Act, B116 (2006) 202-206.**
  - Integration on flexible substrates difficult
  - Lower sensitivity

Two LEDs



- p-nitrophenylnitrosamine (NPNA) in PVC
  - **R.L. Shepherd et al., IEEE Sensors Journal, 6 (2006) 861-866.**
  - → lower sensitivity

Sensor Principle



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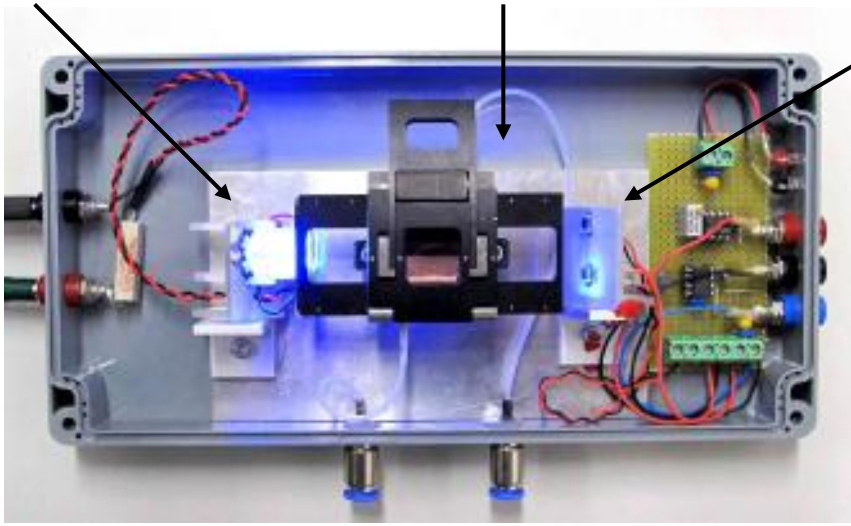
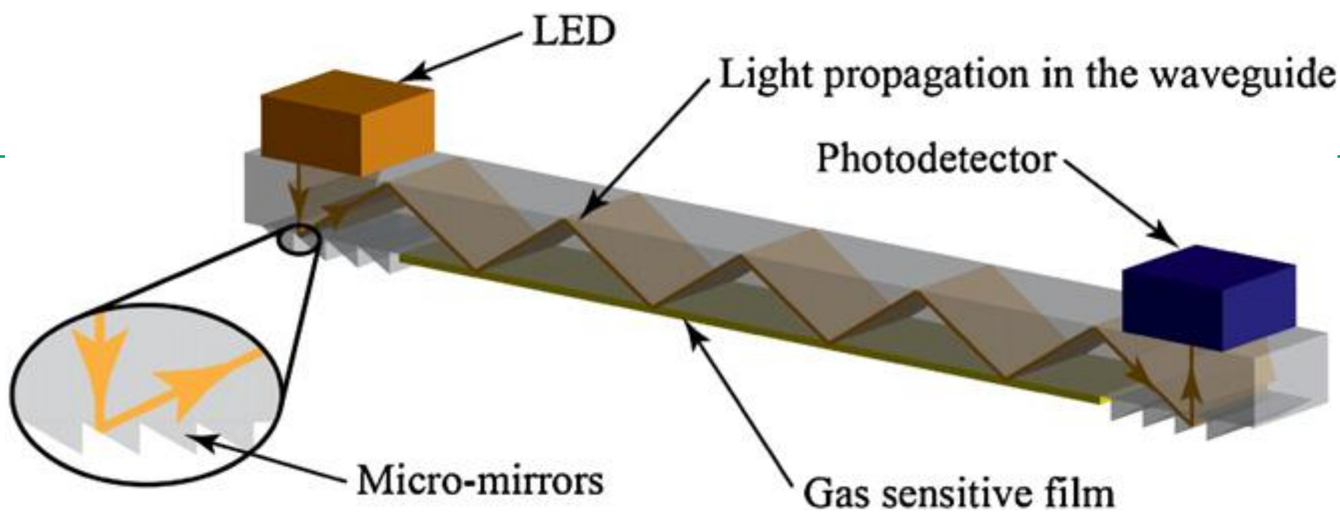
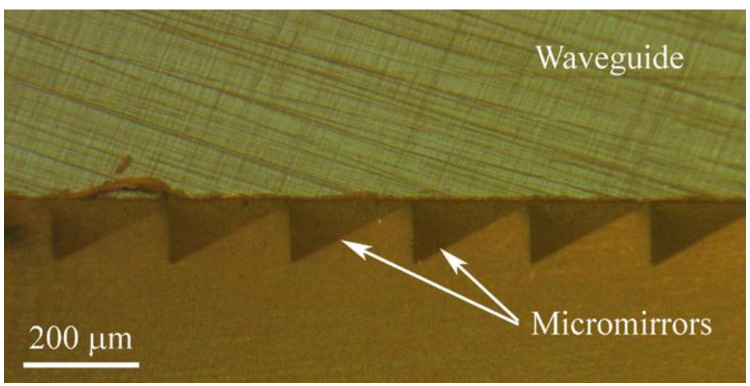
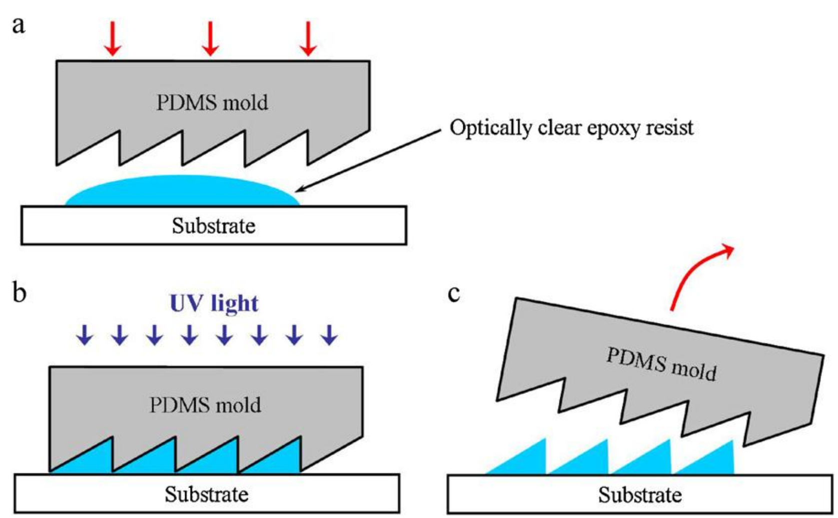
Measurement System

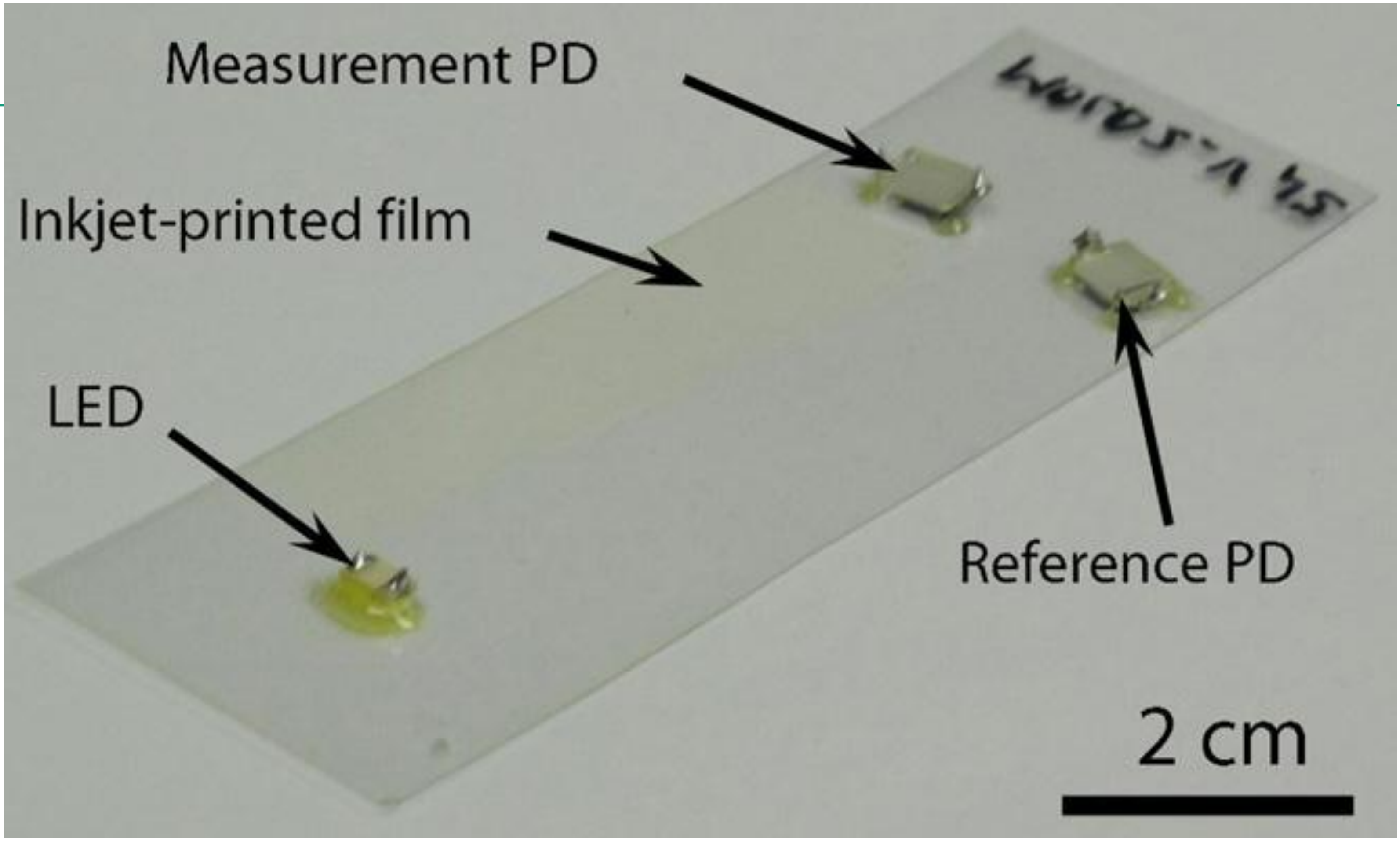








J. Courbat et al. / Sensors and Actuators B 160 (2011) 910– 915



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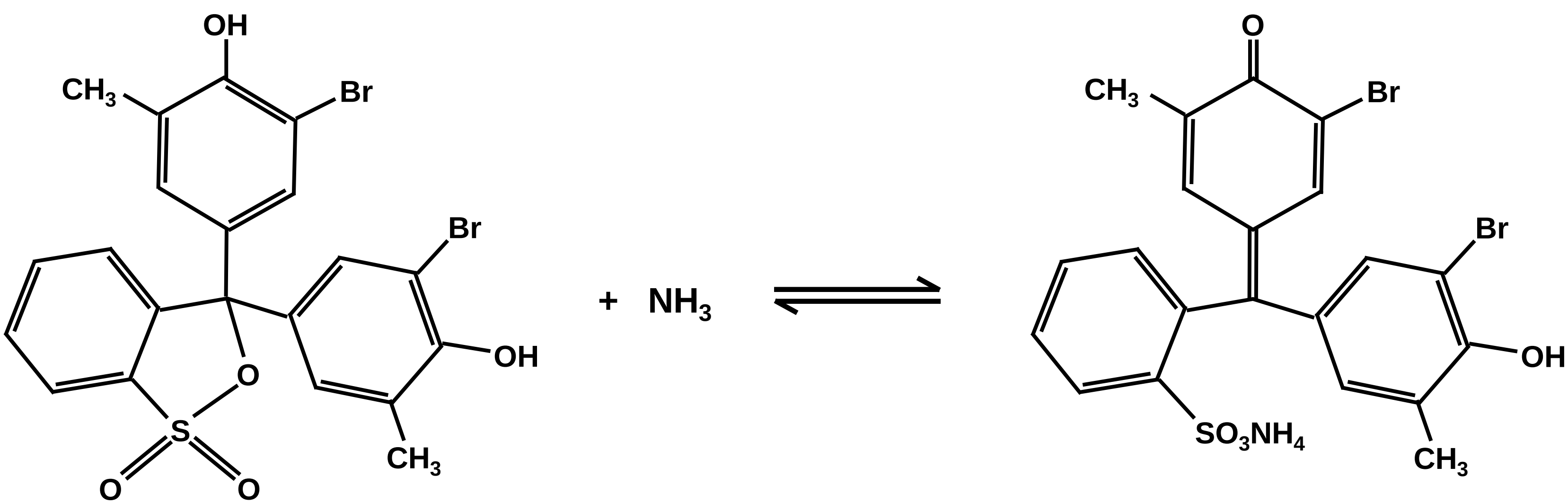
Ammonia color dye

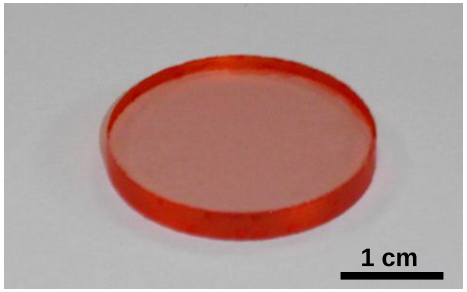
Example: Bromocresol purple, pH-indicator within a porous polymeric matrix
Color change due to a (reversible) reaction with ammonia

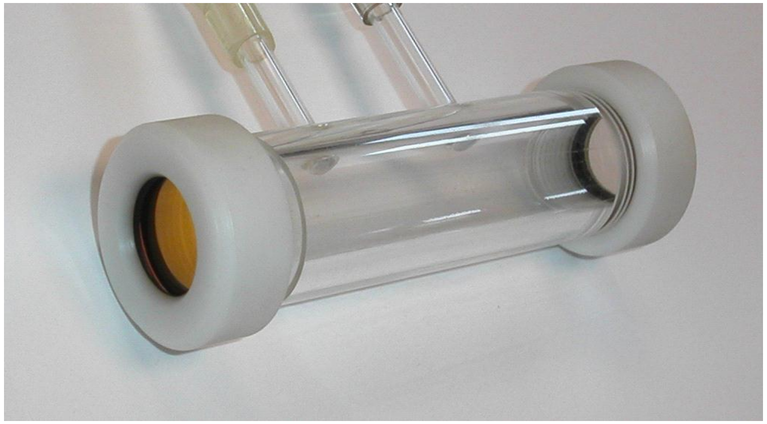


pH = 5.2 pH = 6.8

Spectroscopic Gas Measurements

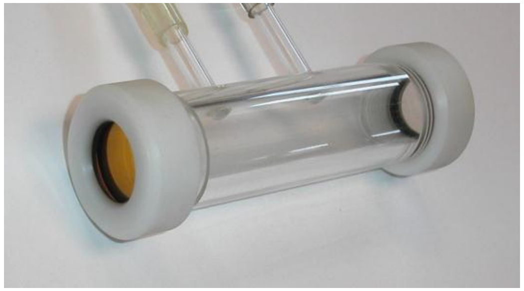
- Measurement over all the spectrum indicates where the maximum light absorption occurs.
- Film thickness: 2-5 µm.
- Data acquisition: Elmer-Perkin λ900 spectrometer.
- Light in the visible range: 200 – 700 nm, steps of 3 nm.
- Gas cell connected to gas mixing system.
- Available NH_3 concentration: 5-1000 ppm.





Colorimetric Film Efficiency

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



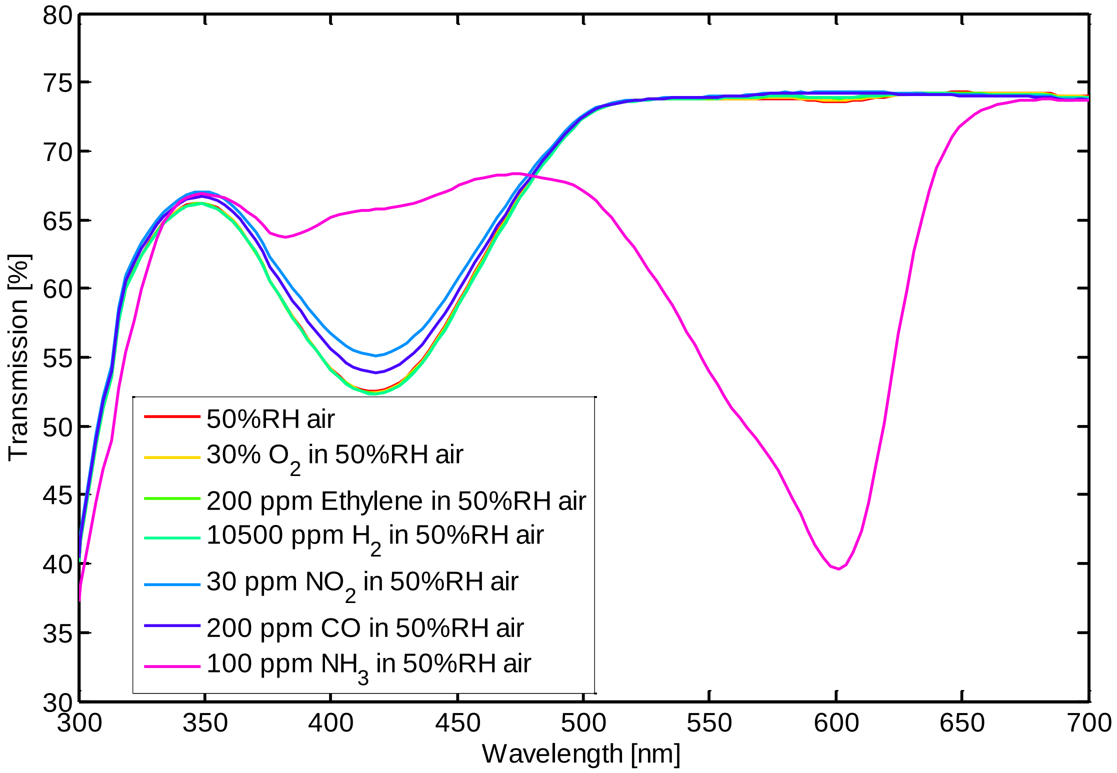
I_{in}: Incoming light intensity
I_{out}: Light intensity after passing through the film
α: absorption coefficient
l: path length
c: concentration of the absorbing material

Abs coef. w (α) [µm^{-1}]	BPB	BCG
Poly(vinyl butyral)	2.55	0.50
Ethyl cellulose	1.41	0.24
PMMA	0.72	0.10

Best results obtained with BPB

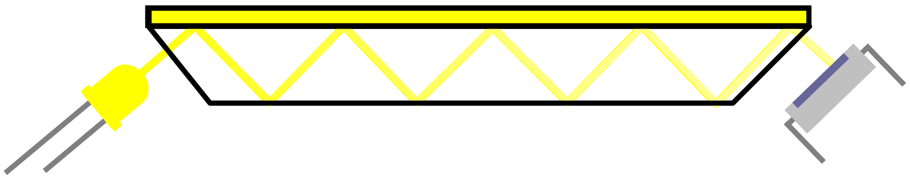
Selectivity

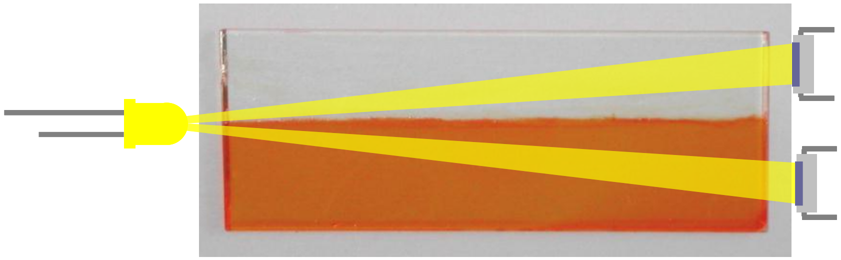
- Film: BPB in Poly(vinyl butyral) and tributyl phosphate
- Gas carrier: synthetic air, 50%RH

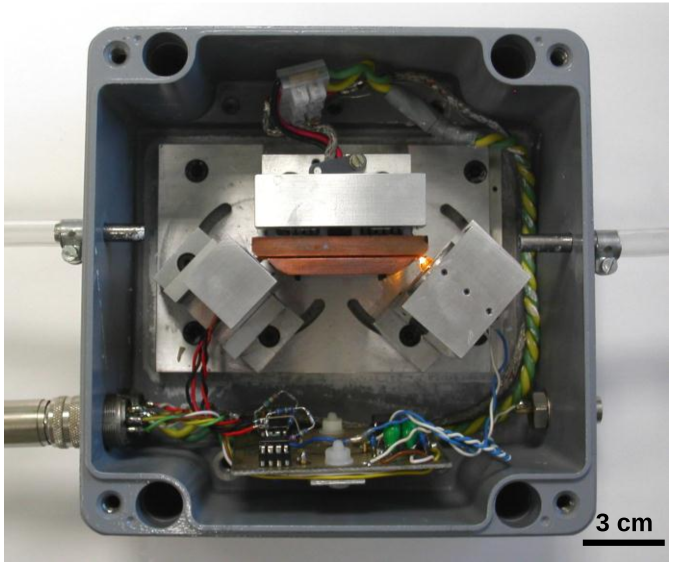


Film-Coated Waveguide

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



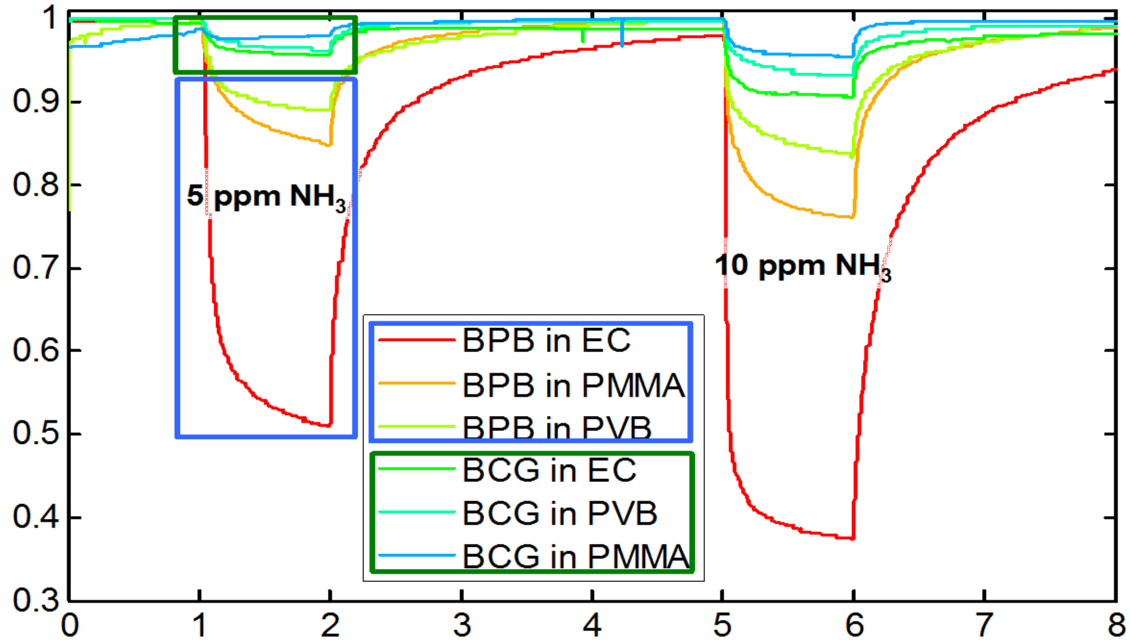




Ammonia measurements with coated waveguide and LED

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



J. Courbat, D. Briand, J. Damon-Lacoste, J. Wöllenstein, N.F. de Rooij "Evaluation of pH Indicator-Based Colorimetric Films for Ammonia Detection Using Optical Waveguides", Sensors and Actuators B Chemical, 2009

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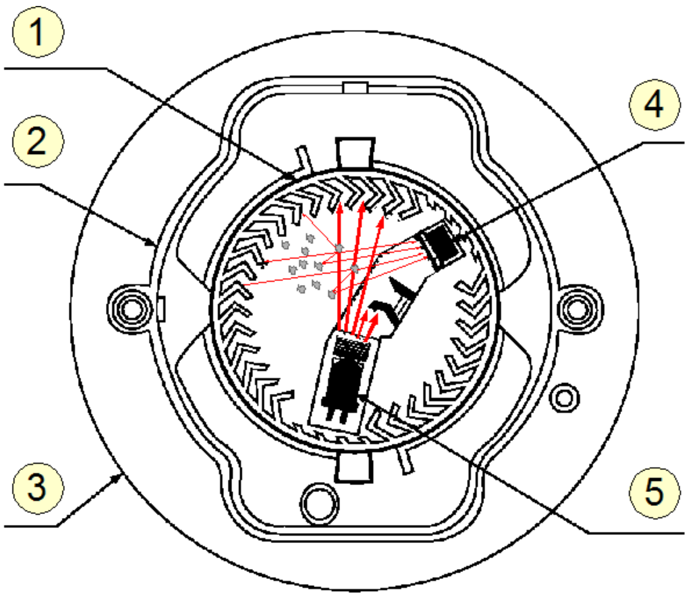
Market: Smoke detectors

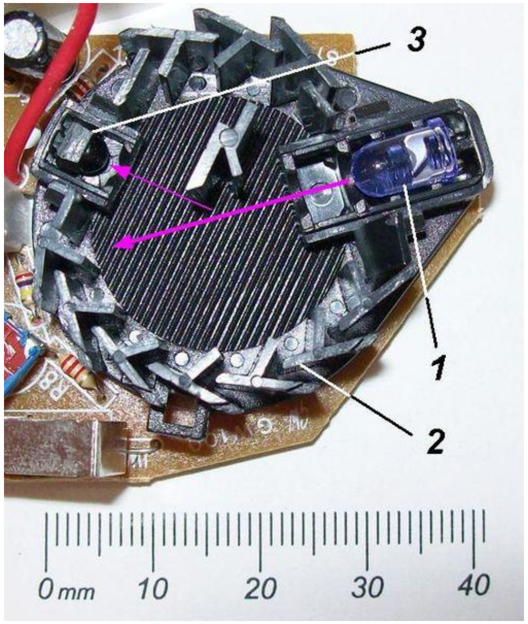
Optical smoke detectors

Common fire detectors are based on the scattered light principle

Partikel detection

False alarms (moisture, dust, particulate matter,….)





Fire detectors, test fires

	CO_2	H_2O	CO	H_2	NO_2	NO	HC
No fire	< 500 ppm	25%	1-3 ppm	0,1 – 1 ppm	10 ppb	10 ppb	1 ppm
TF 1	4000 ppm 750 ppm/min	40 % 1,5%/ min	30 ppm 6 ppm/min	20 ppm 3 ppm/min	1 ppm 200 ppb/min		
TF 2	700 ppm 25 ppm/min	28% 0,4%/min	30 ppm 6 ppm/min	120 ppb 100 ppb/min	70 ppb 10 ppb/min	20 ppm 5 ppm/min	
TF 3	800 ppm 40 ppm/min	28% 0,4%/min	100 ppm 15 ppm/min	25 ppm 20 ppm/min	40 ppb 10 ppb/min	100 ppb 20 ppb/min	30 – 40 ppm 6 ppm/min
TF 4	1800 ppm 520 ppm/min	30% 2,5%/min	12 ppm 4 ppm/min	3 ppm 1 ppm/min	3 ppm 1 ppm/min	10 ppm 5 ppm/min	< 5 ppm
TF 5	2000 ppm 750 ppm/min	30% 1,5 %/min	15 ppm 5 ppm/min	5 ppm 1 ppm/min	1 ppm 0,5 ppm/min	2 – 3 ppm 0,7 ppm/min	< 5 ppm
TF 6	7000 ppm 1000 ppm/min		5 ppm		2 ppm	2 ppm	

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

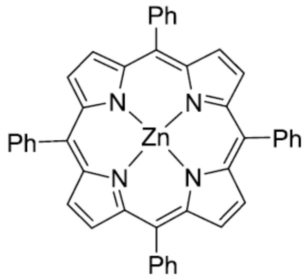
- Market 10 billion Euro
- Big player: Honeywell, Siemens

- => one possible solution: Colour dyes

Metalloporphyrins for NO_2 detection

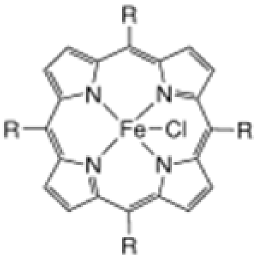
- Most common natural pigments
- Famous example: hemoglobin (1 kg in human circulatory system)
- Chemical structure: 4 pyrrole rings, connected by methines
- Component of many proteins
- Use in sensors based on fluorescence-quenching
- Examples:

<u>Zinc-porphyrin:</u>



5,10,15,20-tetraphenylporphyrin-zinc (ZnTPP)

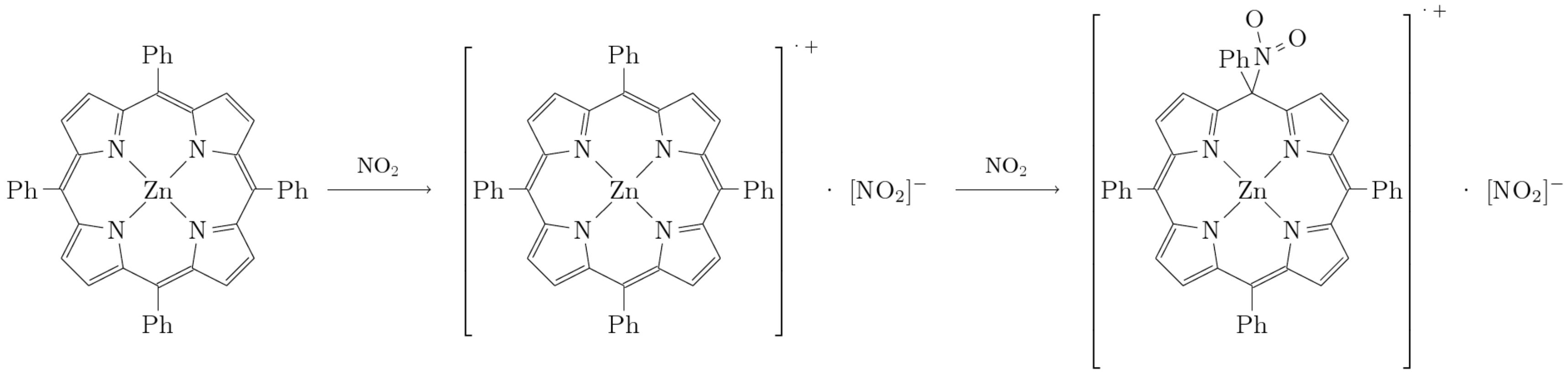
<u>Iron-porphyrin:</u>



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



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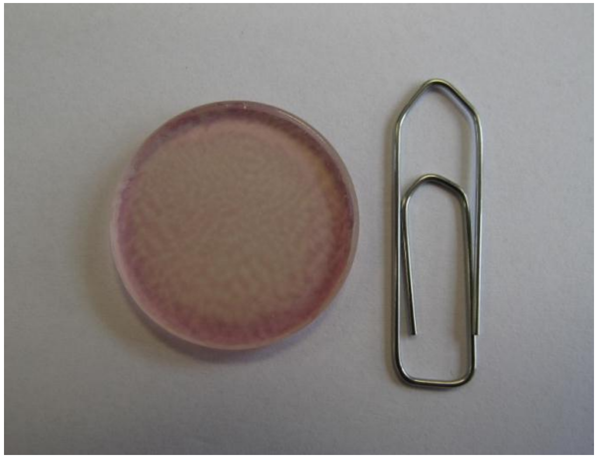
Zinc-porphyrin (ZnTPP)

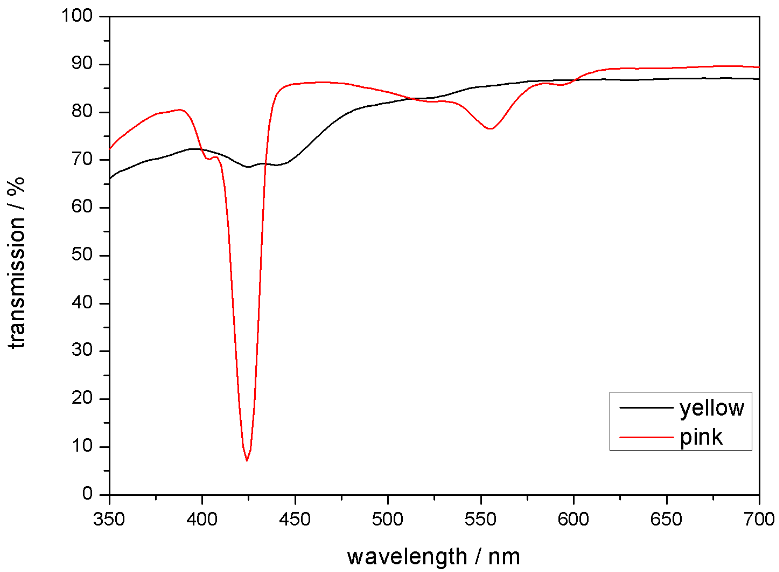
Preparation of sensor film:

Function	Material
Dye	ZnTPP
Polymer	PVC
Plasticizer	Hexamoll™DINCH
Solvent	Tetrahydrofuran

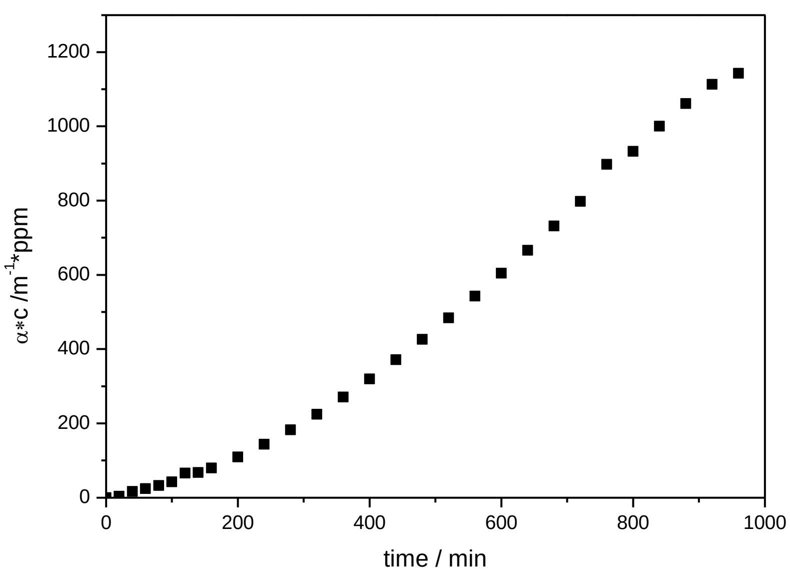


ZnTPP: Reaction to 5 ppm NO_2
Analysis in UV/VIS-Spectrometer

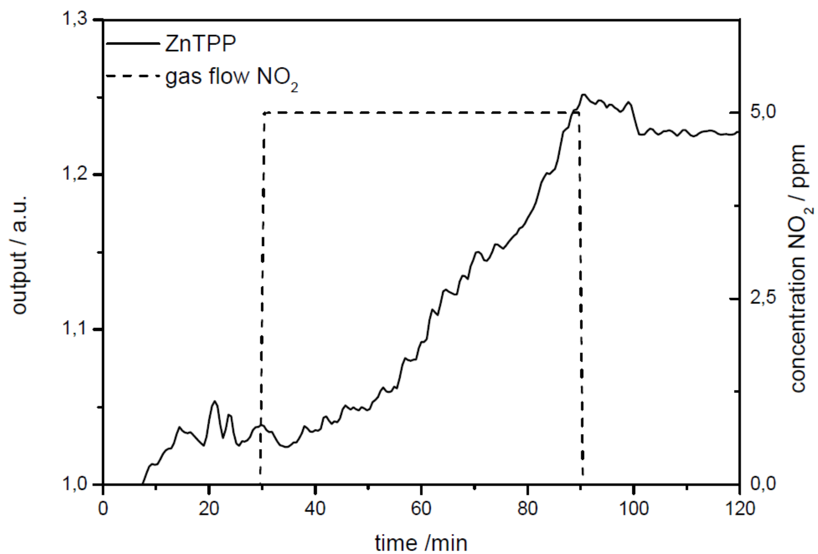
Change of transmission:

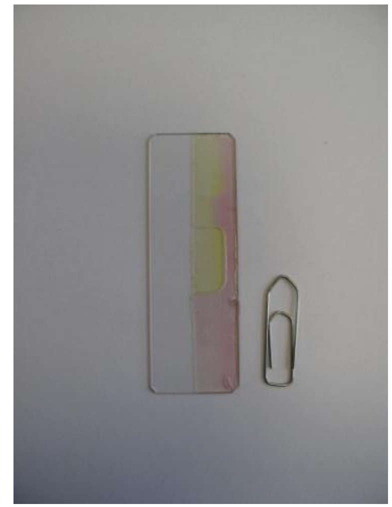


Absorption @ 450 nm:



ZnTPP: Waveguide-based Measurements





- Reaction to 5 ppm NO_2
- Color change from pink to yellow
- Reversible but very long relaxation time (several days)

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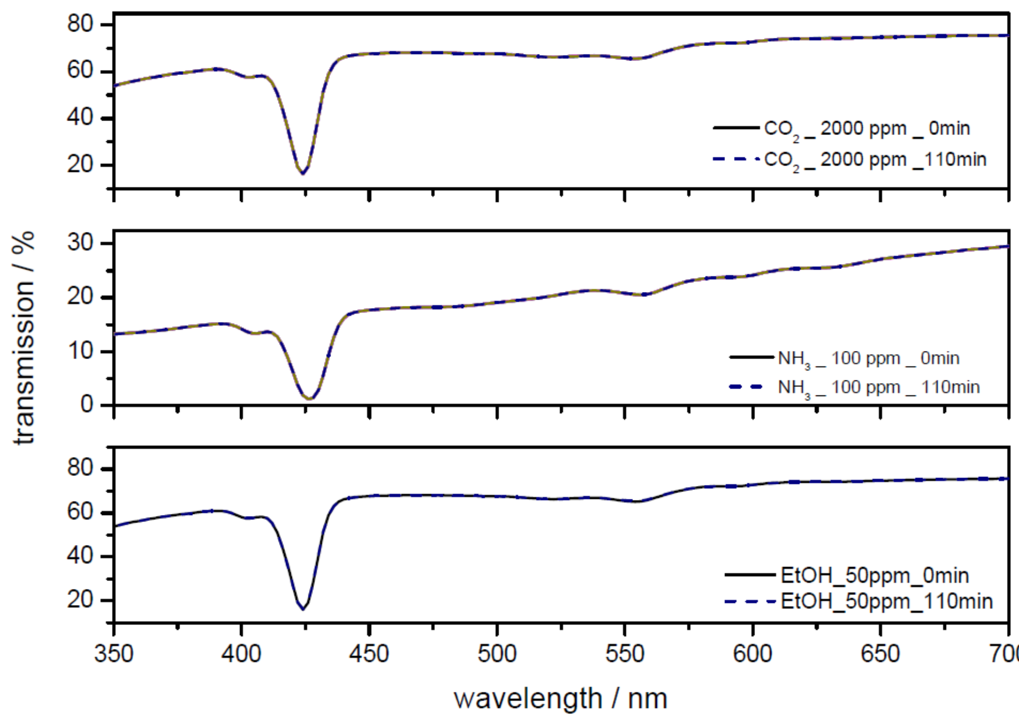
ZnTPP: Cross Sensitivity

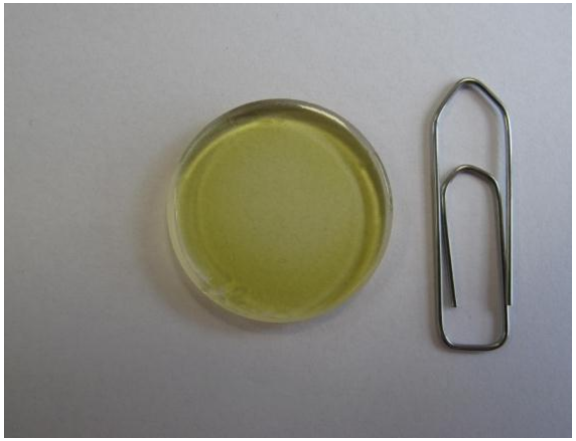
- Ammonia (100 ppm)
- Ethanol (50 ppm)
- Carbon dioxide (2000 ppm)
- *Carbon monoxide (200 ppm)*



Iron-porphyrin (FeTPP)

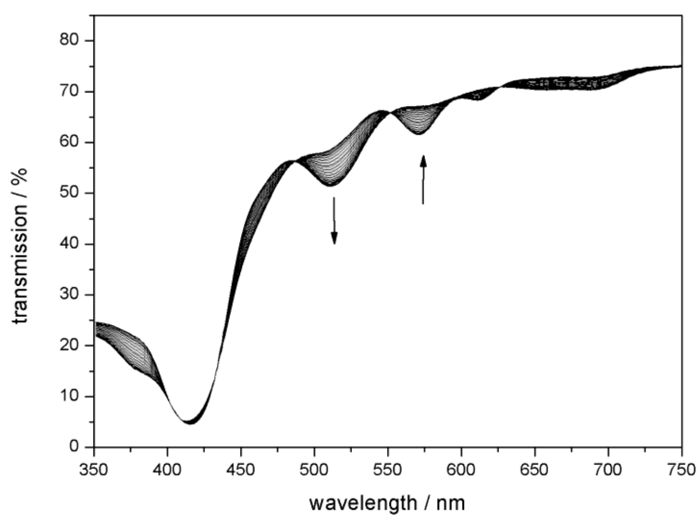
Preparation of sensor film:

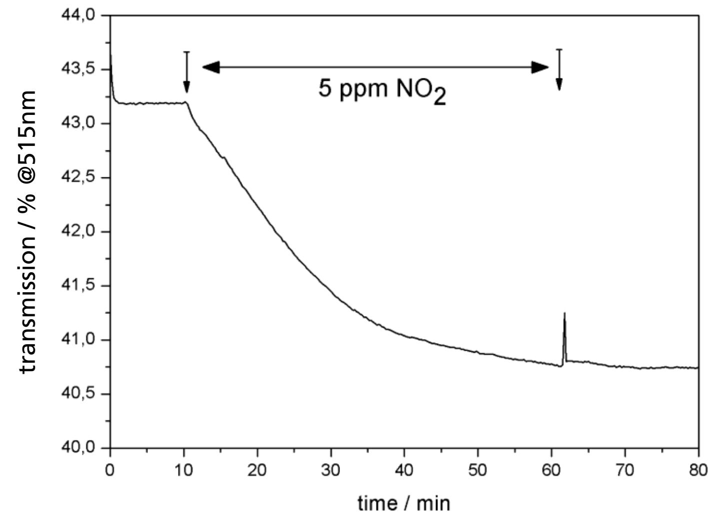
Function	**Material**
Dye	FeTPPCl
Polymer	PVC
Plasticizer	Hexamoll™DINCH
Solvent	Tetrahydrofuran



Fe-TPP: Reaction to NO_2

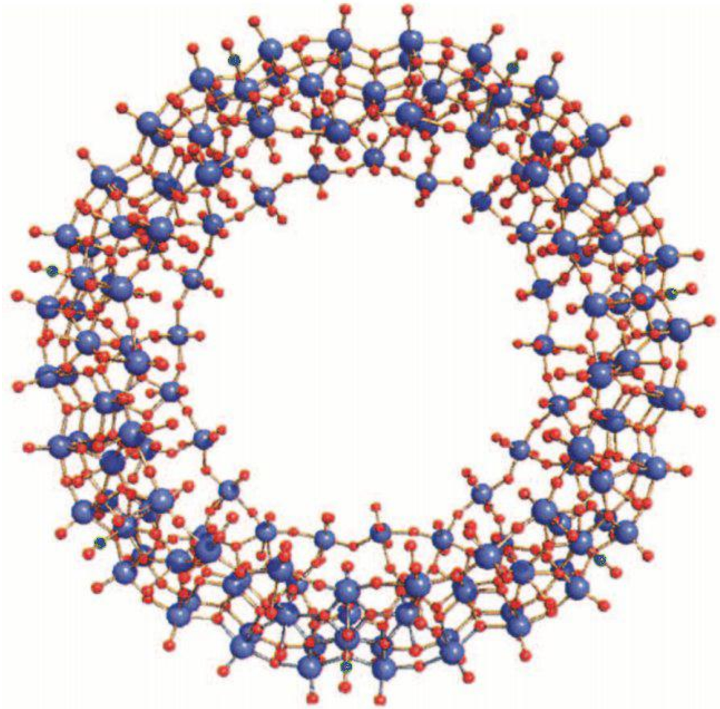
- Change of transmission



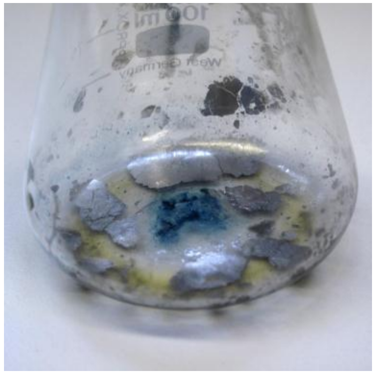


- No observable cross-sensitivity to ethanol, carbon monoxide, carbon dioxide, ammonia

Colour dyes for CO-detection
First try: molybdenum blue / palladium



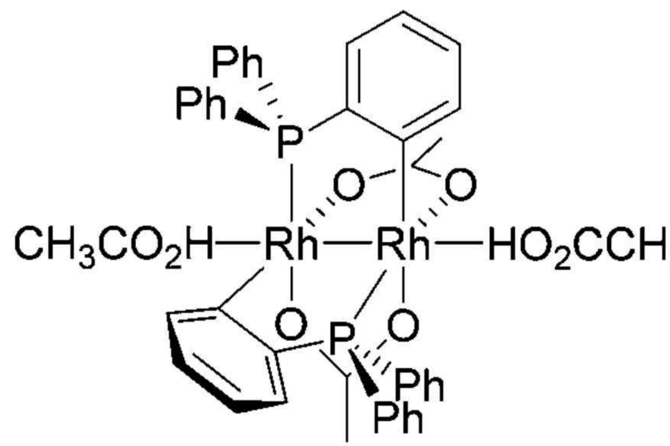
Bielefelder Rad



Tianbo Liu, Ekkehard Diemann, Achim Müller: Hydrophilic Inorganic Macro-Ions in Solution: Unprecedented Self-Assembly Emerging from Historical "Blue Waters". In: Journal of Chemical Education, Volume 84 Nr. 3, March 2007.

New trend
Rhodium complexes for CO-detection

- Esteban et.al.:
  „Sensitive and Selective Chromogenic Sensing of Carbon Monoxide by Using Binuclear Rhodium Complexes"
  In: Angew. Chem. 2010, 122, 5054 –5057
- reversible
- High sensitive to CO
- Very low cross sensitivities (H_2O, O_2, N_2, NO_2, SO_2)



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

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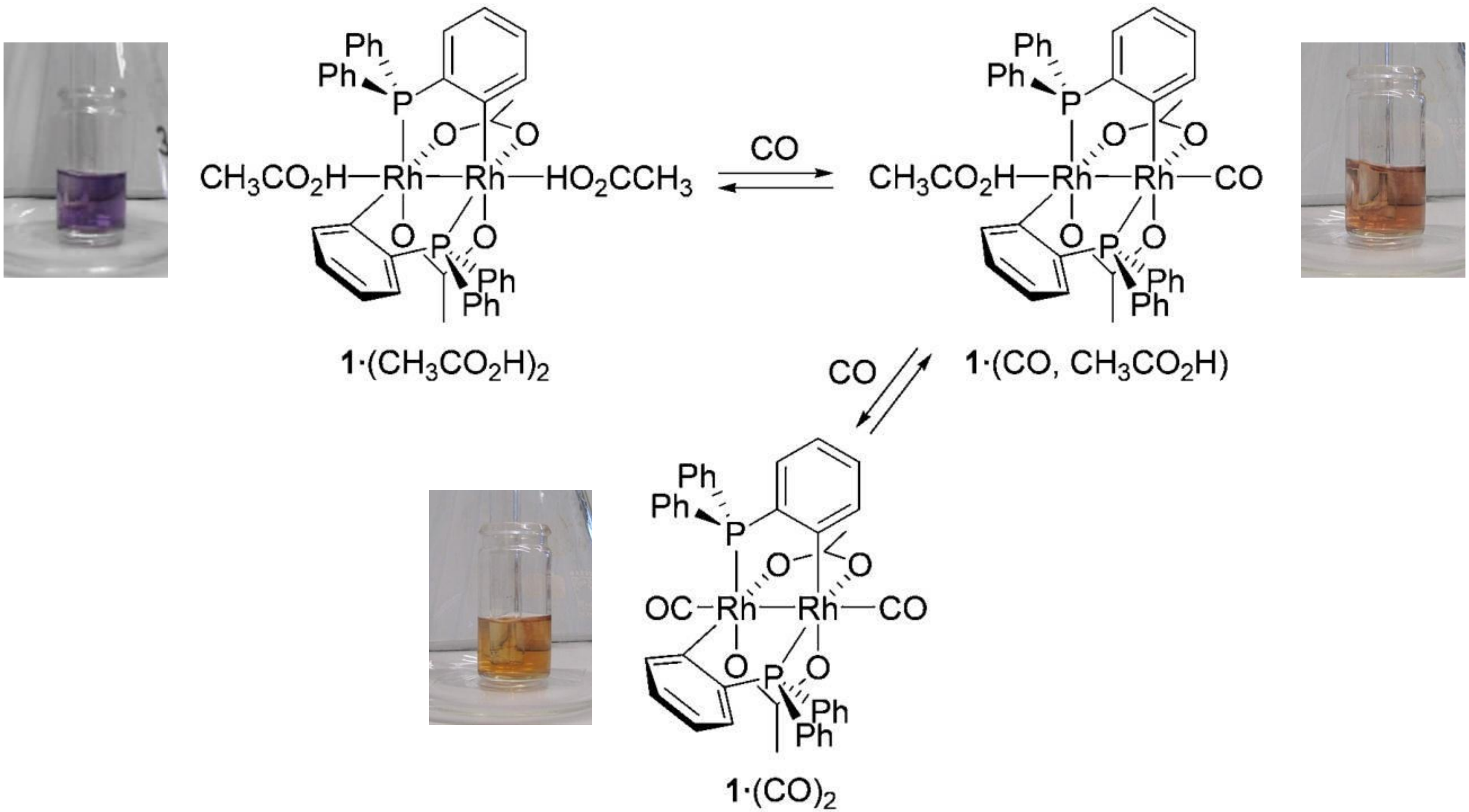
Synthesis

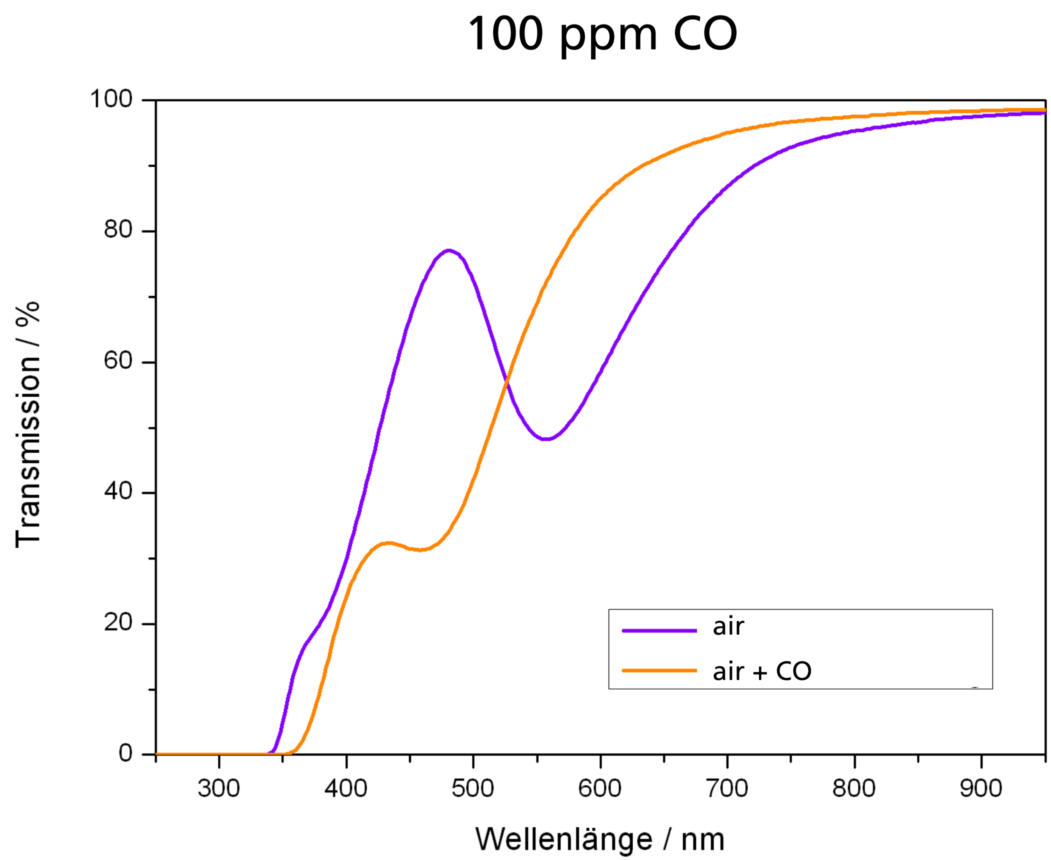
cis-[$Rh_2(C_6H_4PPh_2)_2(O_2CCH_3)_2](HO_2CCH_3)_2$

Color change

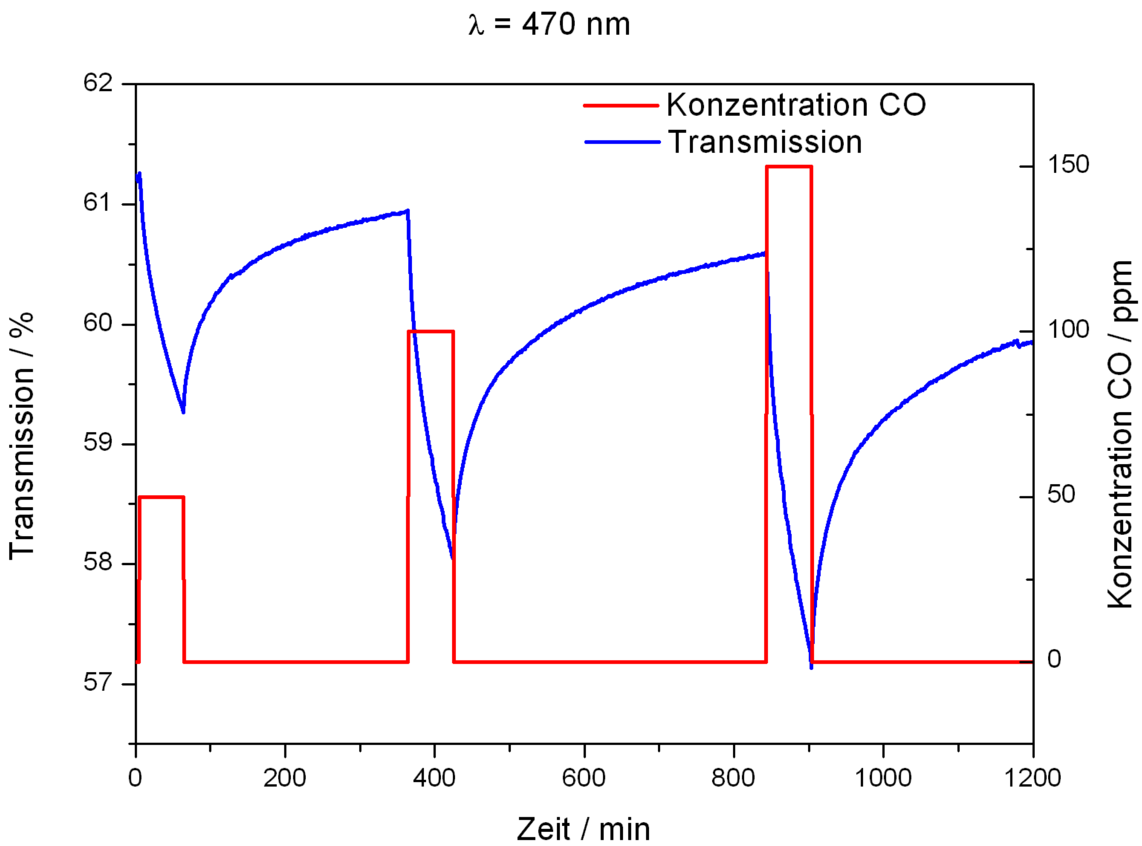


Color change due to CO exposure

UV/VIS transmission spectra of $1 \cdot (CH_3CO_2H)_2$ before and after exposure to 100 ppm CO. The color of the sample changes from violet to yellow.



Waveguide based CO-measurement



Modification
EPFL: Kay Severin

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

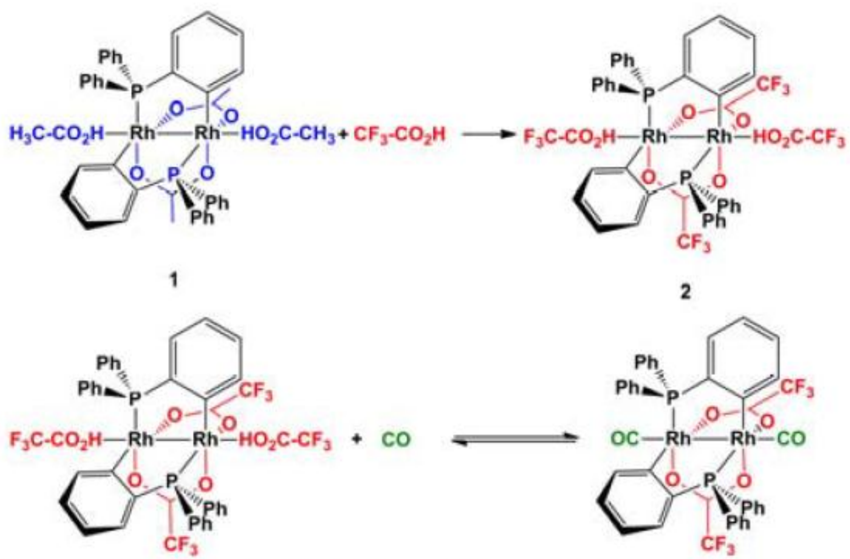
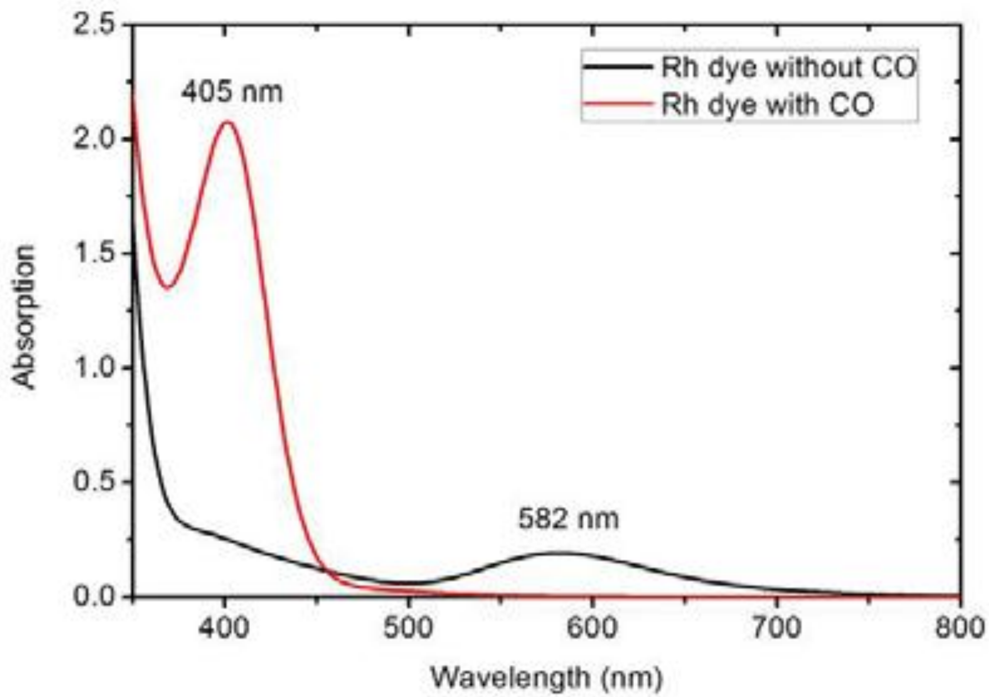


Fig. 1. Synthesis of the Rh complex **2** and its reaction with CO. Complex **2** features weakly bound trifluoroacetate ligands. The latter are replaced by CO.

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).



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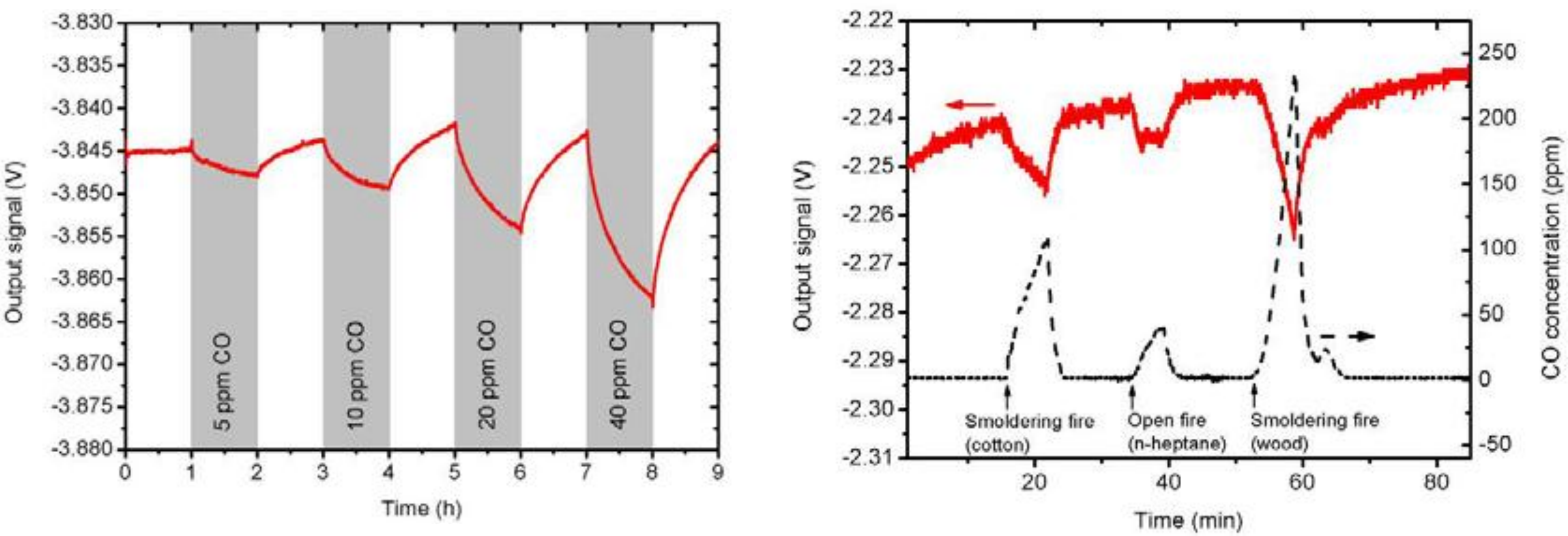
CO exposure and test fires



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*.

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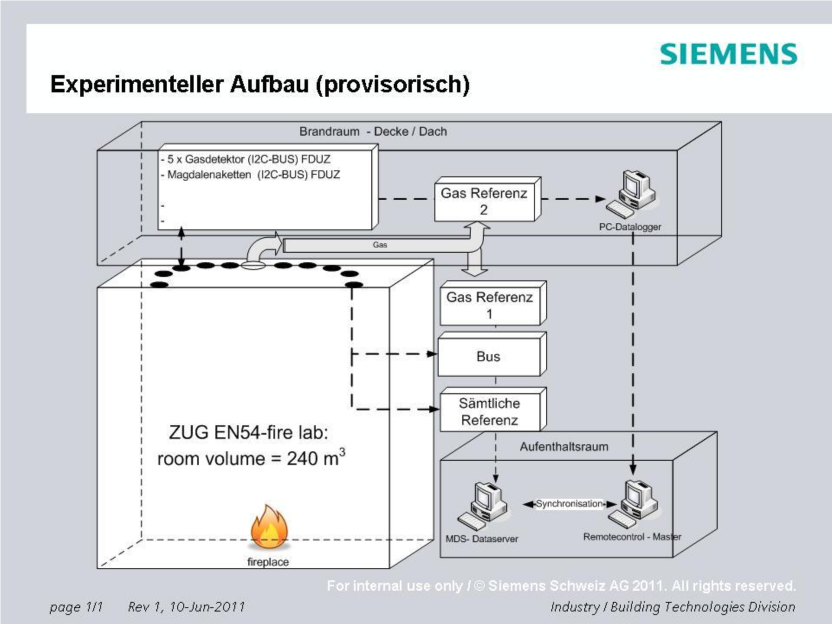
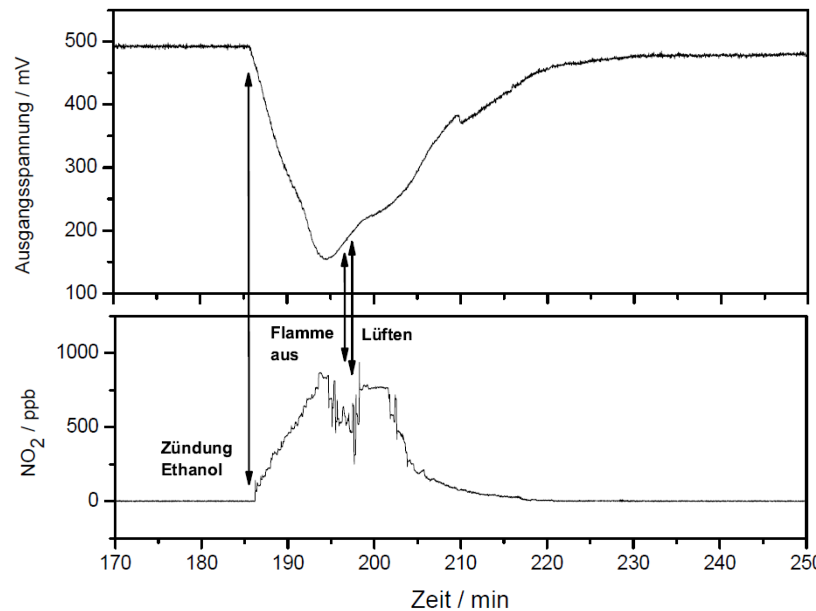
Test fire at SBT facilities

- Fire lab
- 6 different standard test fire
- Sensor system on top of the room
- Reference sensors (CO, CO_2, NO, NO_2, temperature)



Results: 5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride

- In PVC- → NO_2 Sensor
- Test fire 6 ethanol fire
- Gas concentrations after 10 min:
  CO: 4,68 ppm; CO_2: 8110 ppm;
  NO: 1785 ppb; NO_2: 695 ppb
- T90 after fresh air inlet: 24 min



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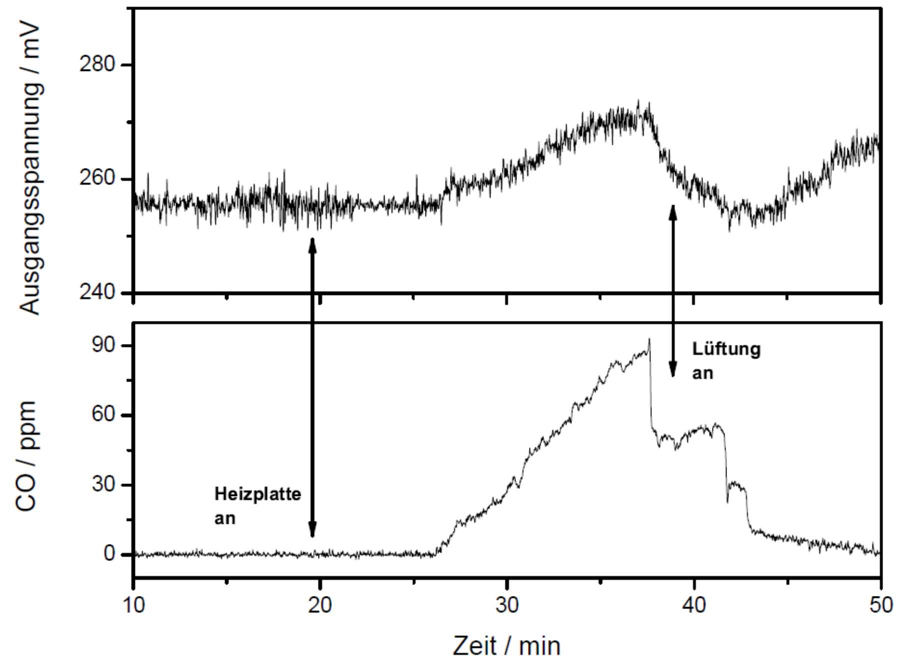
Results Rh-complex (Esteban et al)

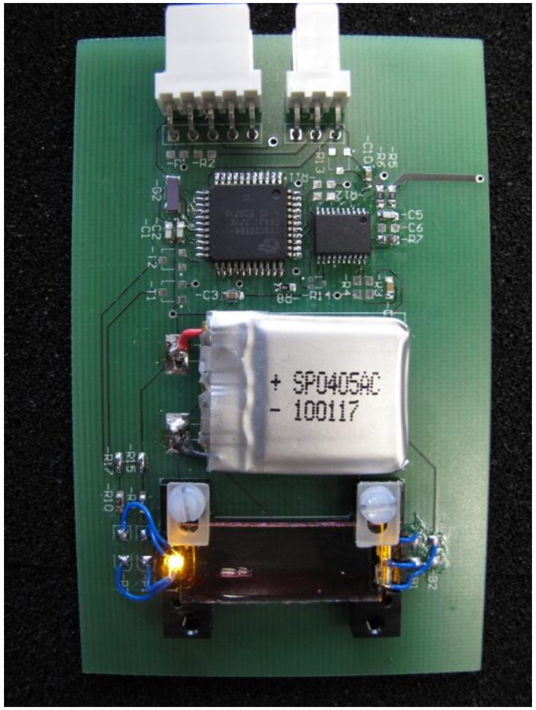
- Rh/EC-Chip → CO - Sensor
- Test fire 2 smouldering wood
- Gas concentration after 10 min:

  CO: 86 ppm
- T90 after fresh air inlet: 4,7 min



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

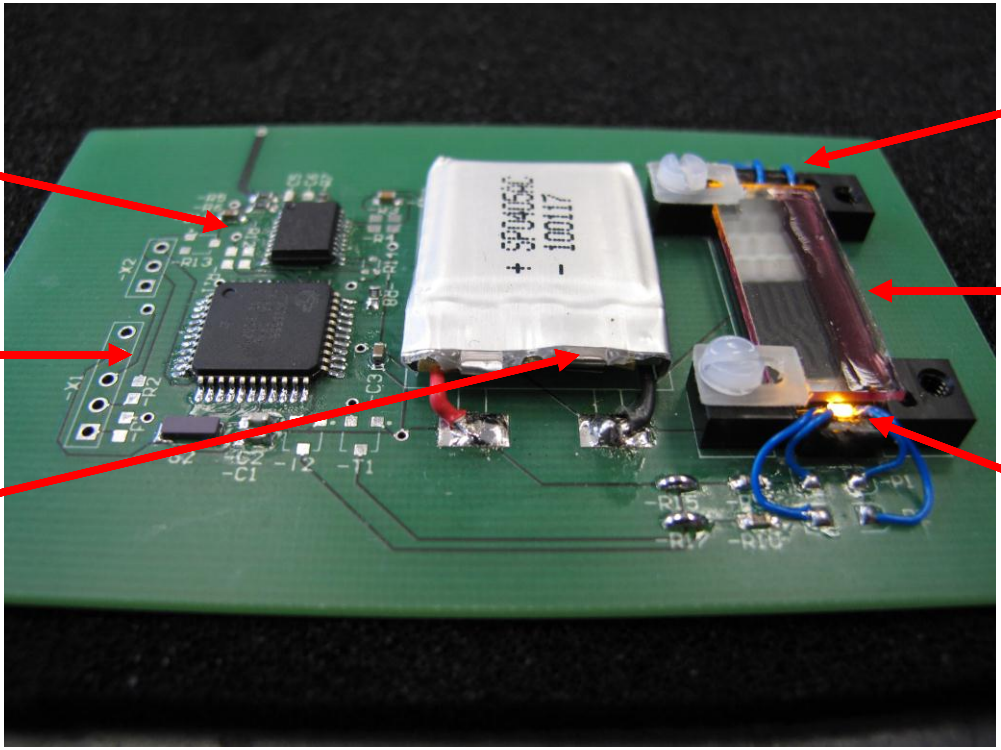


RFID-Tag with optical ammonia / CO sensor

Melexis 13,56 MHz RFID-Transponder

µController

battery



Photodiodes

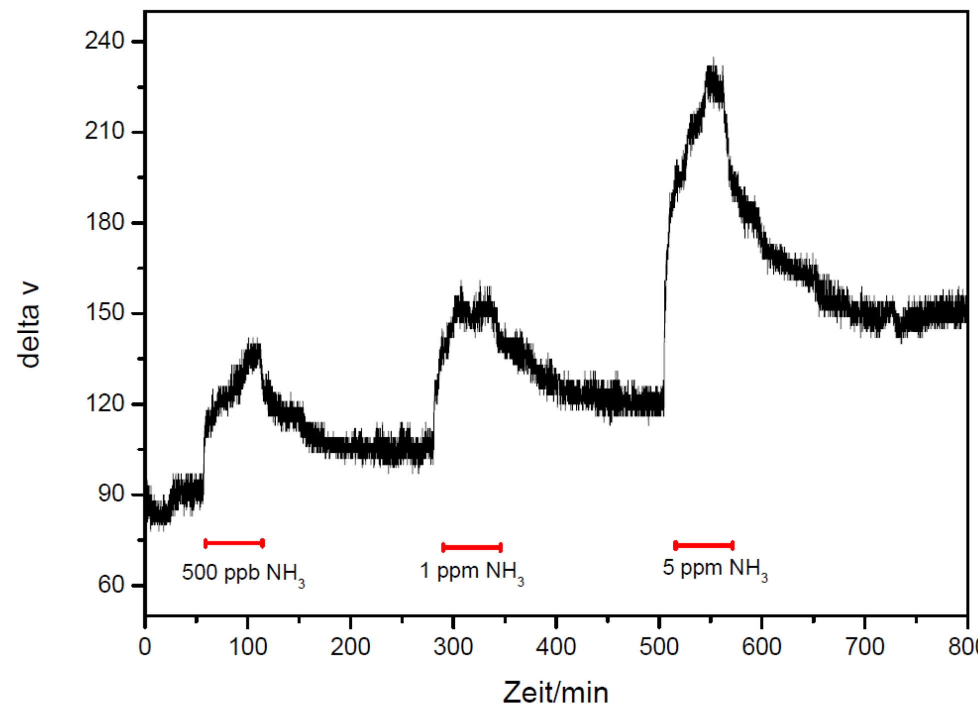
Sensorchip

LED

RFID-Tag
Very first measurements

- Ammonia measurement
- 500 ppb, 1 ppm and 5 ppm NH_3 in air.

  → Detection limit in the lower ppb range!



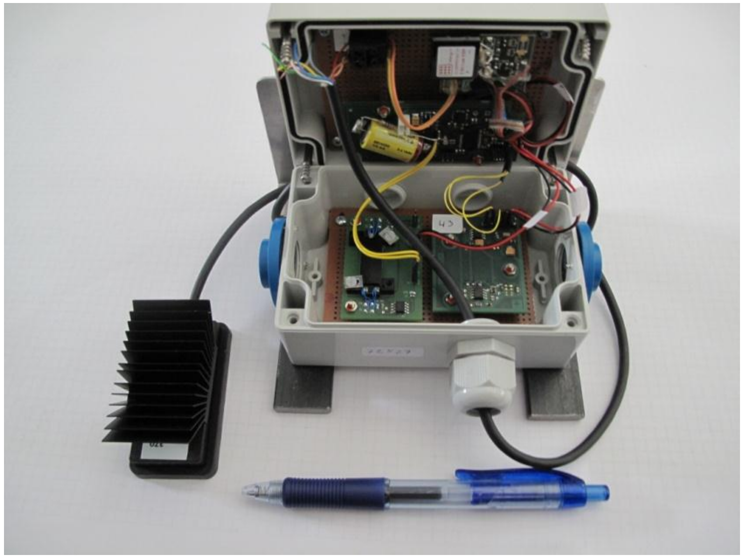
Application:
RFID – CO sensor system ---- Field tests

- Spitzenclusterprojekt Microtec Südwest

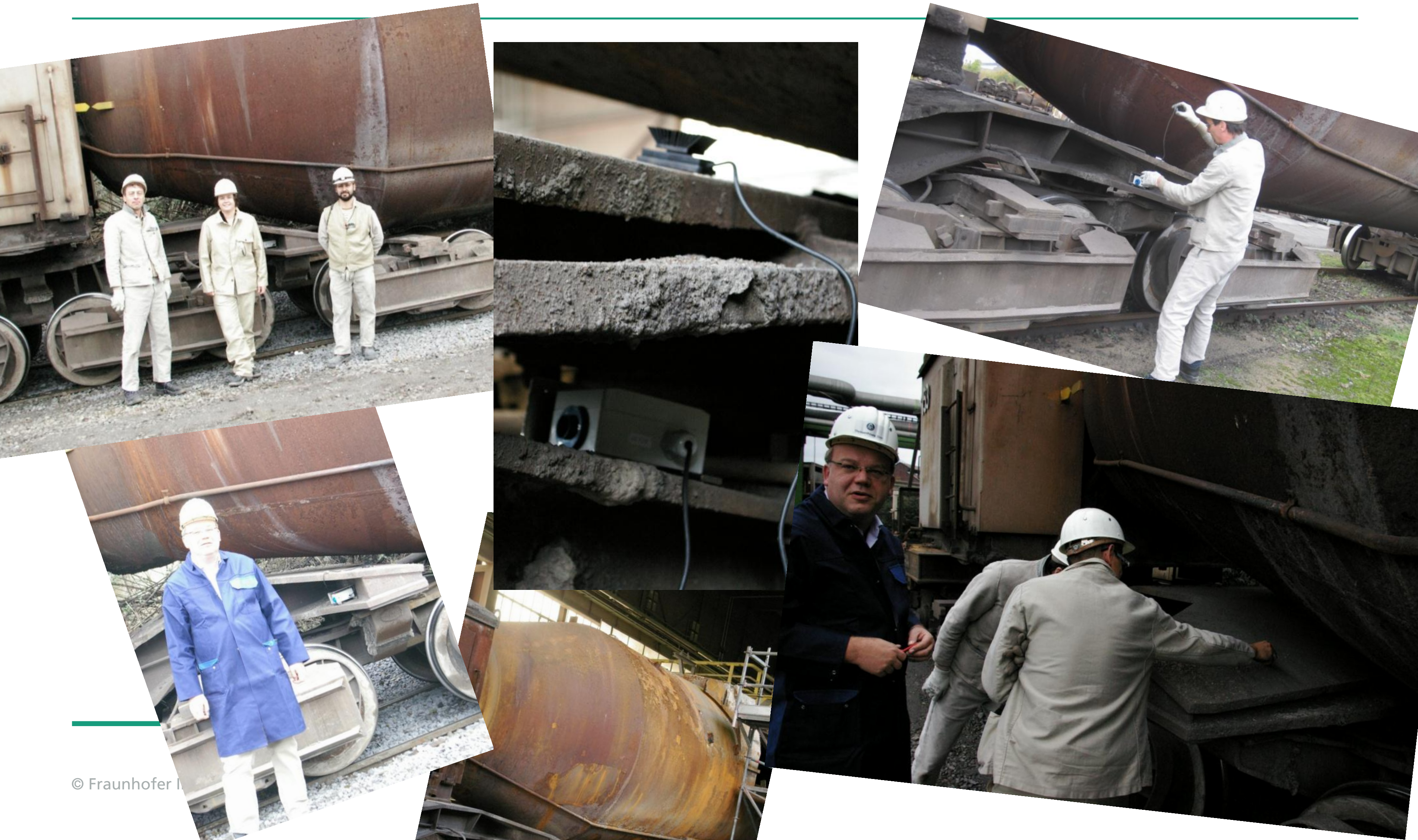
  Sens-RFID , Goal: Energy self-sufficient CO-sensor for iron making
- Thermoelectric power converter,

  Colourimetric CO-Sensor,

  Wireless comunication
- Field tests: Thyssen Krupp Steel Duisburg
- Measurement at torpedo ladle with liquid pig iron (600 Tons)

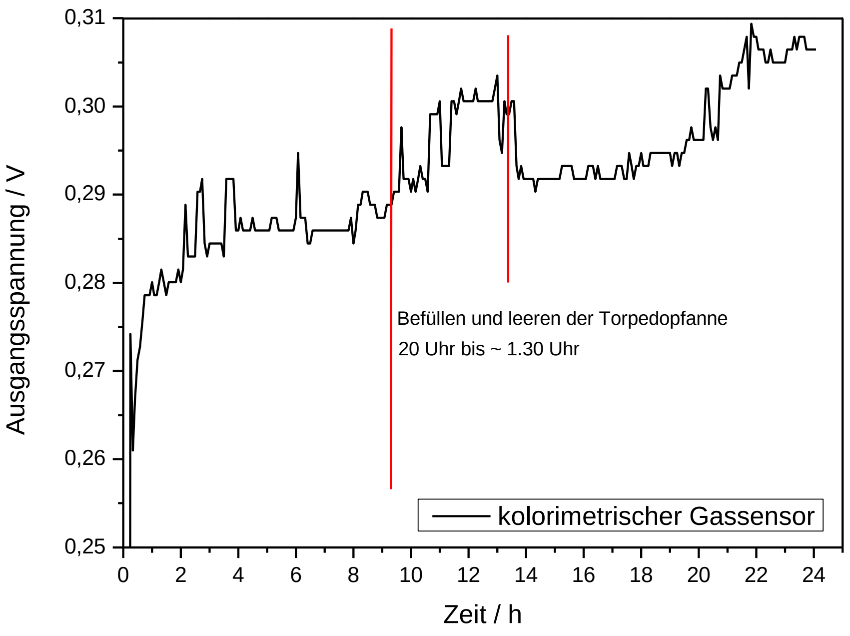


Field tests ---- Impressions



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

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Thank you for your attention!