European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

Final Meeting at PRAGUE (CZ), 5-7 October 2016

New Sensing Technologies for Air Quality Monitoring

Action Start date: 01/07/2012 - Action End date: 15/11/2016 - EXTENSION: 15/11/2016

Dosimeter-Type Sensor for sub-ppm NO_x Detection

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EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

COST is supported by the EU Framework Programme

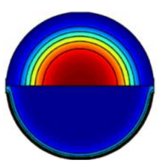
European Science Foundation — ESF provides the COST Office through a European Commission contract

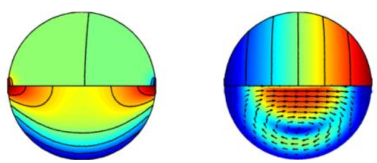
Scientific context and objectives in the Action

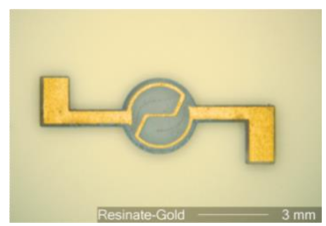
- **Background / Problem statement:**
  Development of novel gas sensing principles and new gas sensing materials for air quality monitoring (sub-ppm range) and automotive applications (ppm range)
- **Brief reminder of MoU objectives:**
  - Preparation of gas sensors in multi-layer technology and thick-film technology on alumina substrates and flexible substrates like steel
  - Characterization of gas sensing devices in synthetic exhaust gas test benches / engine test bench, e.g. NO_x, $O_{2,}$ HC, NH_3

Research Facilities available for the Partner

- **Powder and ceramic processing**
  - **preparation and development of novel functional materials**
- **Film technologies**
  - **thich and thin film technology/ Aerosol-Deposition-Method**
- **Ceramic Multilayer Technology**
  - **LTCC, HTCC**
- **Laser patterning**
  - **substrates, tapes, functional films**
- **Modelling and Simulation**
  - **with COMSOL-Multiphysics**







Research Facilities available for the Partner

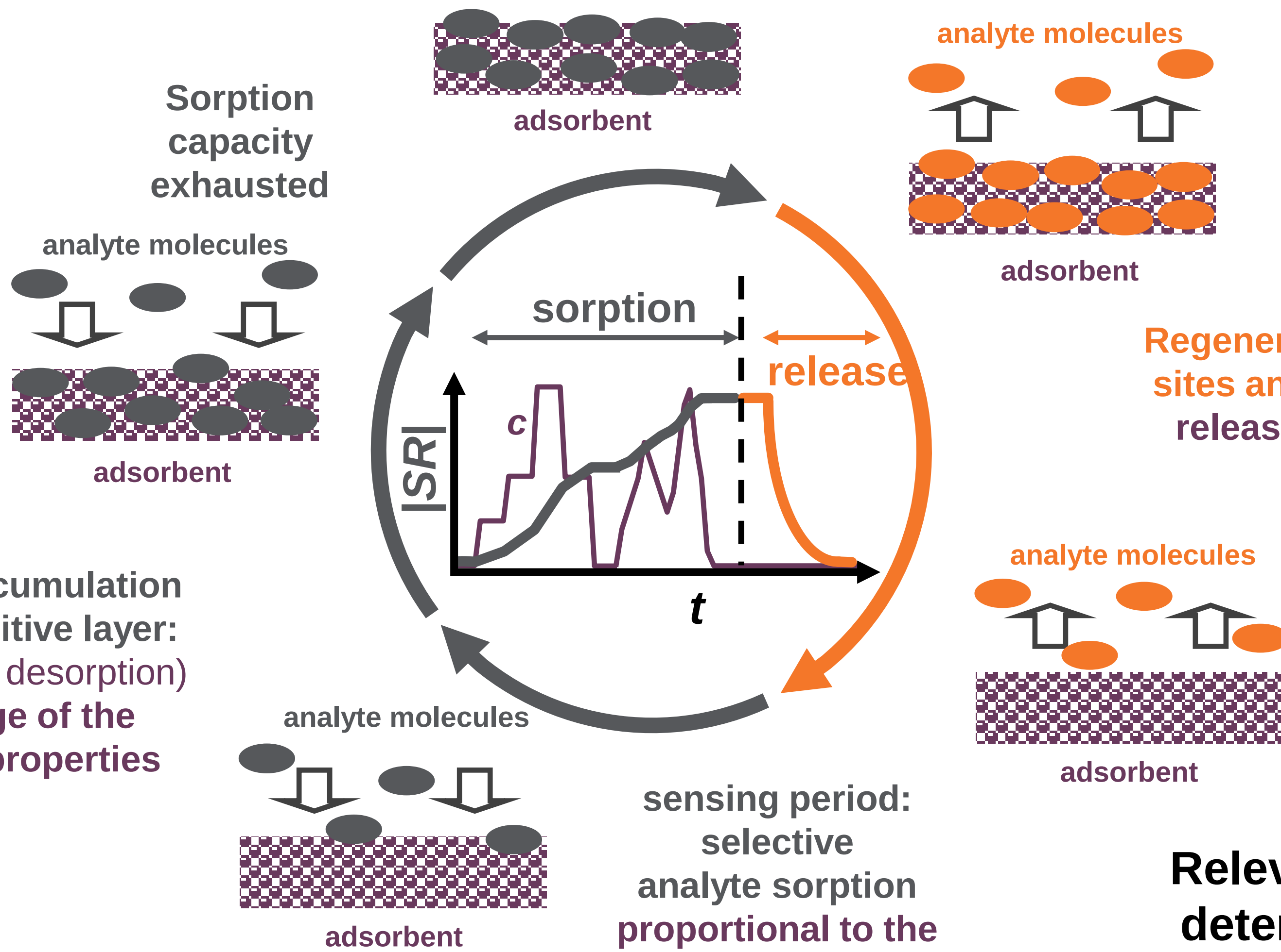
- **Material Characterization**
  - REM / EDX
- **Electrical Material Characterization**
  - impedance spectroscopy, high frequency technology
- **Electrochemical Methods**
  - Potentiostat
- **Gas Test Benches and Analytics**
  - sensor or catalyst with synthetic gas test benches
  - Gas analysis (FTIRs, CLD, NDIR, FID …)
- **Engine Dynamometer**
  - real exhaust gas

Dosimeter-type sensor

Working Principle of a Gas Dosimeter

Sorption capacity exhausted

Regeneration of sorption sites and sensor signal: release of the analyte



Analyte accumulation in the sensitive layer:
(sorption >> desorption)
→ change of the physical properties

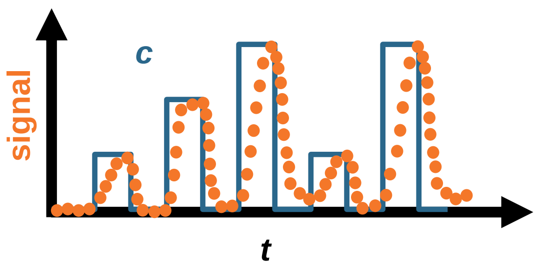
sensing period: selective analyte sorption proportional to the analyte concentration

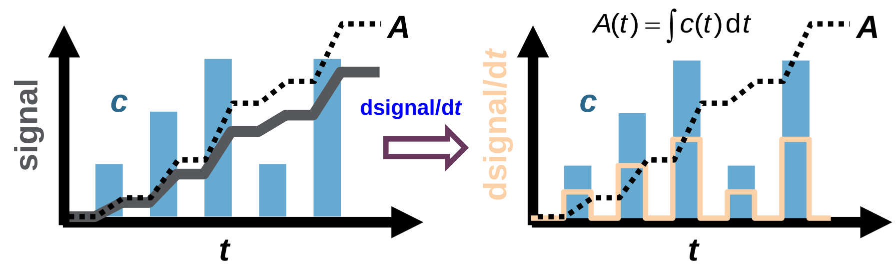
Relevance of determining *amount/dose* and *mean concentration*

I. Marr et al., *Journal of Sensors and Sensor Systems* 3, 29-46 (2014)

Dosimeter-type sensor

What are the differences between
Gas Sensor and *Gas Dosimeter*





- detection of a *concentration*
- sensor signal is caused by formation of a chemical *equilibrium* (reversible)
- determination of an analyte *amount* by *integration* of the sensor signal
- *fast response/relaxation times* required for reliable determination of concentrations and mean values
- *uncertainties* at low analyte levels due to
  - zero drift
  - slow equilibrium
  - non-linear measurement range

- detection of an *amount/dose*
- signal change due to *irreversible sorption*
- *chemical storage* enables detection of *lowest doses*
- real-time evaluation the sensor signal → *fast*
- Determination of the current *concentration* via *time-dependent derivative* of the sensor signal
- Re-definition of zero level after regeneration *avoids long-term drift*
- *measurement range* and *sensitivity adjustable* by temperature and layer thickness

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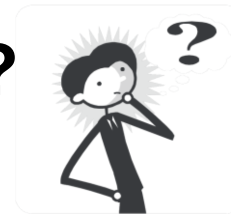
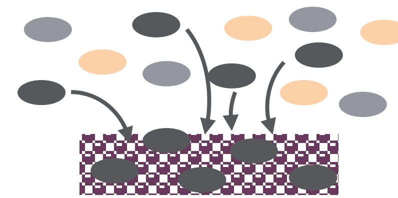
I. Marr et al., *Journal of Sensors and Sensor Systems* 3, 29-46 (2014)

Dosimeter-type sensor

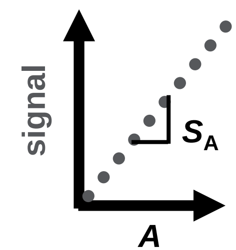
What are Essential Material Properties?





- ***Selective* sorption** under sorption conditions
- ***Strong bonds between analyte molecules and sorbent***

  → no desorption in the absence of the analyte



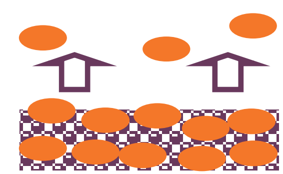
$A(t) = \int c(t)\,dt$

- ***Measurable physical property*** being proportional to the analyte loading level

  → linearity of the characteristic line (sorption rate $\propto$ analyte concentration)

- Sorption rate has to be ***independent*** of the loading level
- ***Actively initiated regeneration*** of sensor signal and material

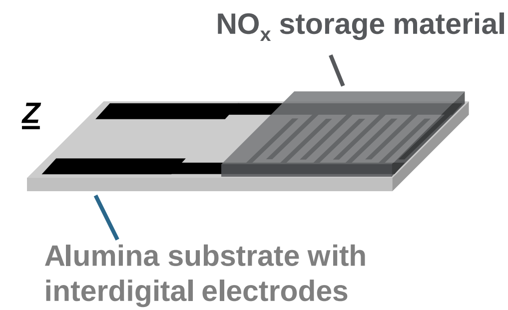
  → thermally initiated analyte release in defined periods



Dosimeter-type sensor

NO_x storage material

Mn/K/La-Al_2O_3



Mn: oxidation of NO to NO_2

$$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$$

K: storage of NO_2 as nitrate or nitrite

- *nitrate* route:
  NO_2 and adsorbed oxygen O^{2-} form nitrate NO_3^-
- *nitrite* route:
  NO_2 stored directly as nitrite NO_2^- and in the next step oxidation to nitrate NO_3^-

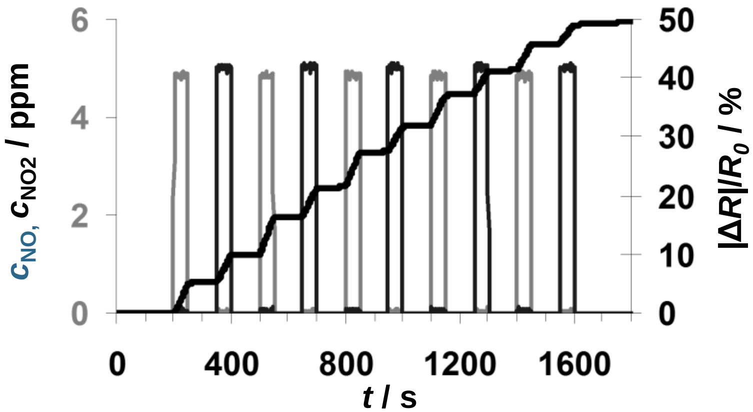
$$K_2O + 4NO_2(g) + O_2 \leftrightarrow 4KNO_3$$

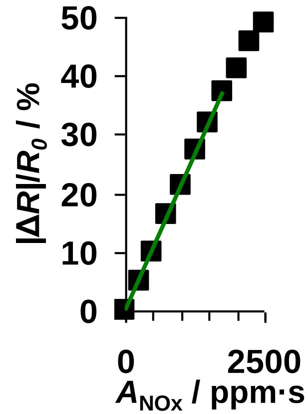
La-Al_2O_3: catalyst support – high specific surface area

Toops et al.: NO_x adsorption on Pt/K/Al_2O_3, *Catalysis Today*, 114 (2006) 112-124

Dosimeter-type sensor

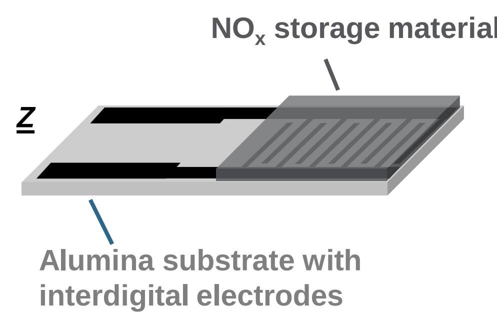
NO_x Dosimetry with NO_x storage material





NO_x dosimetry at 380°C in lean gas:

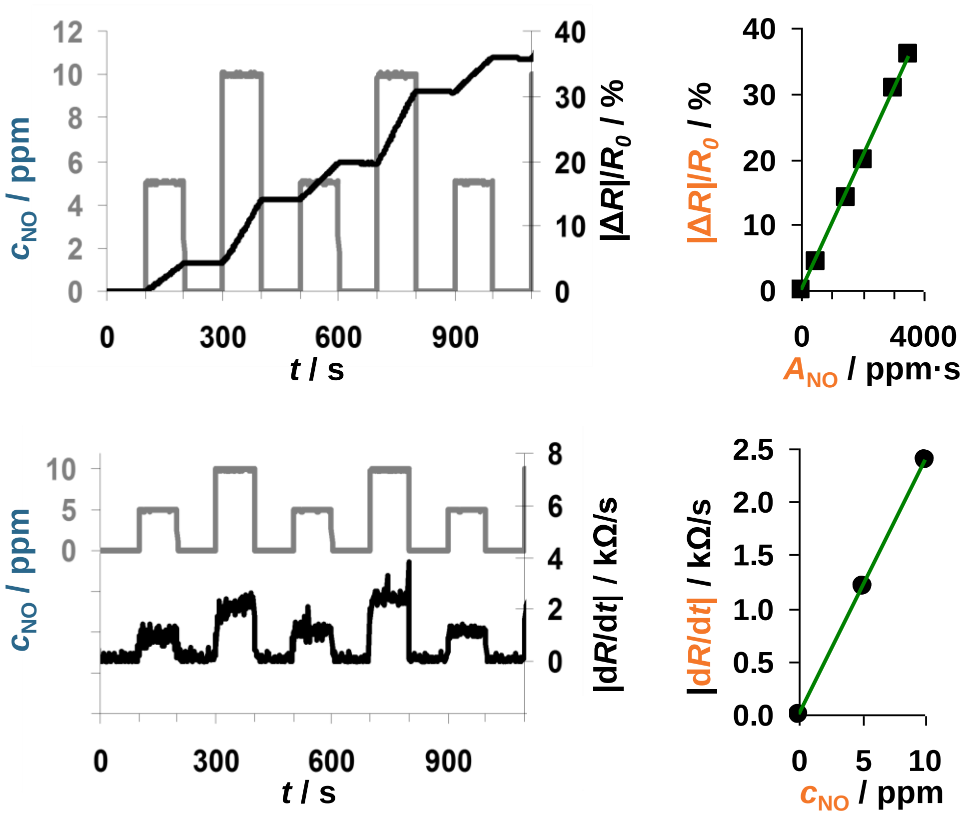
- Sensor signal $|\Delta R|/R_0$ increases in NO and NO_2
- Irreversibility: strong bonding of NO_x to the storage sites
- Comparable sensitivity to NO and NO_2 due to oxidizing components
- Linear characteristic line up to $|\Delta R|/R_0 \approx 40$ %
- Regenerable by heating to 650 °C in air



A. Groß et al., *Solid State Ionics* 225, 317-323 (2012);
A. Groß et al., *Sensors* 12, 2831-2850 (2012)

Dosimeter-type sensor

Dual Mode Functionality



NO dosimetry at varying NO concentrations (380°C):

- **Sensor signal $|\Delta R|/R_0$ increases irreversibly in 5 or 10 ppm NO**
- **Signal slope increases with c_{NO} → $|\Delta R|/R_0 \sim A_{NO}$**
- **Time derivative of the resistance → $|dR/dt| \sim c_{NO}$**

Gas dosimeter
=
direct amount detection
+
indirect concentration information

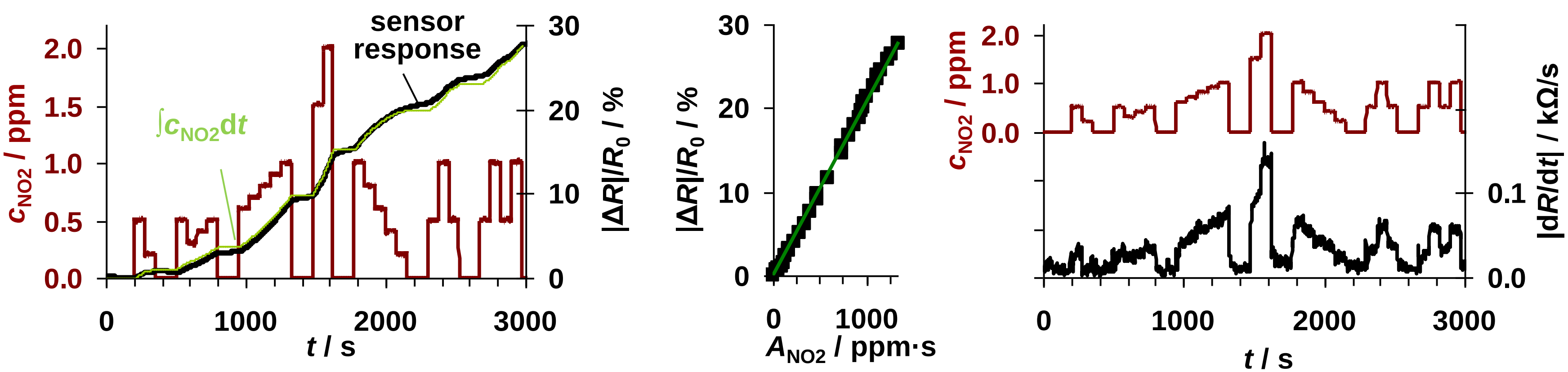
A. Groß et al., *Sensors* 12, 2831-2850 (2012)

Dosimeter-type sensor

Is Air Quality Monitoring Possible?

EU Directive 2008/50/EC on ambient air quality:

- **hourly mean value of *200 µg/m³* NO_2 ≙ 0.1 ppm NO_2**
- ***peak concentrations* may be *higher***



Presented NO_x dosimeter is suitable for Air Quality Monitoring

cost
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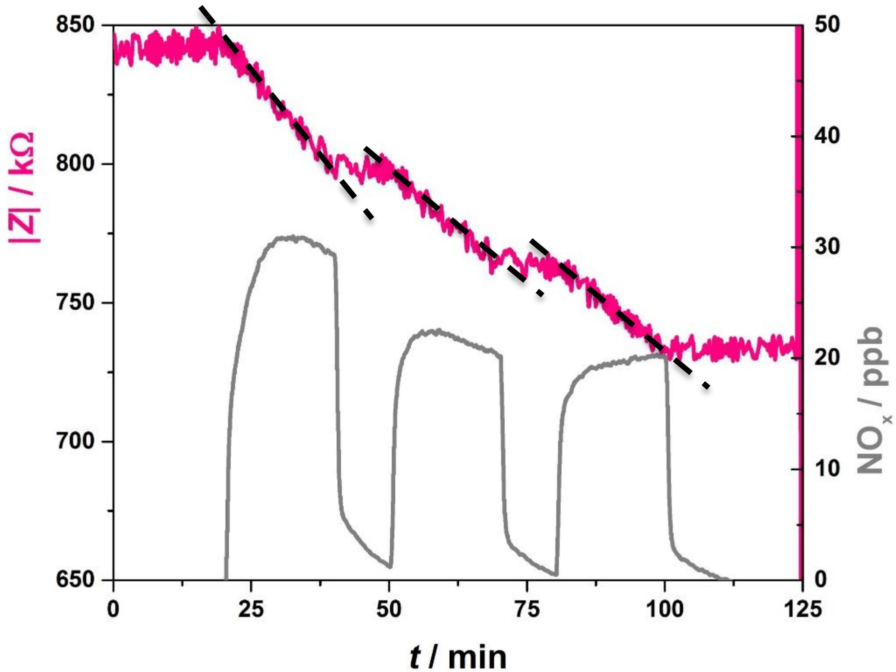
A. Groß et al., *Sensors* 12, 2831-2850 (2012)

Dosimeter-type sensor

Sub-ppm NO_x detection



NO_x dosimetry at 350°C in 20% O_2, 2% H_2O, N_2:

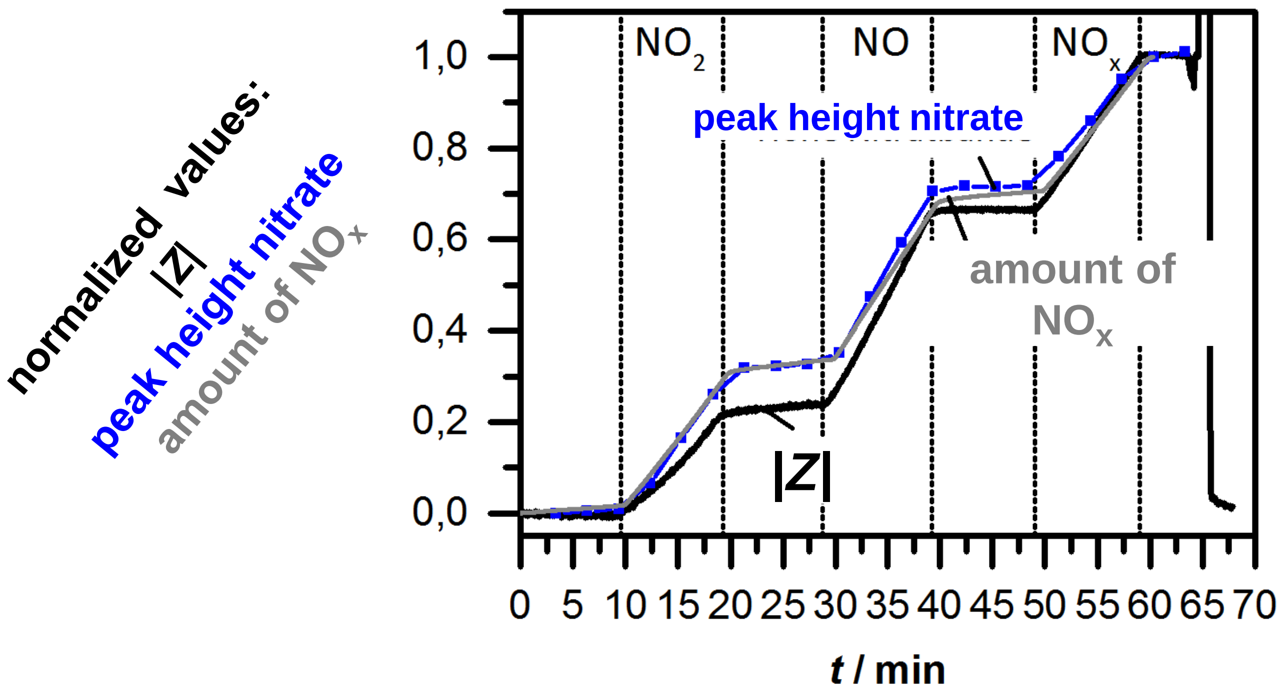
- detection of 20 ppb NO_x is possible (each step 20 min): total NO_x amount: around 84000 ppb·s
- slope of $|Z|$ depends on NO_x concentration
- $|Z|$ stays constant during NO_x pauses: no desorption
- sensor response $|\Delta Z|/Z_0$ linear with amount of NO_x
- Max. loading of these sensor (@ $|\Delta Z|/Z_0$ = 40%): around 500 s with 750 ppb NO_x (A_{NOx} = 375000 ppb·s)

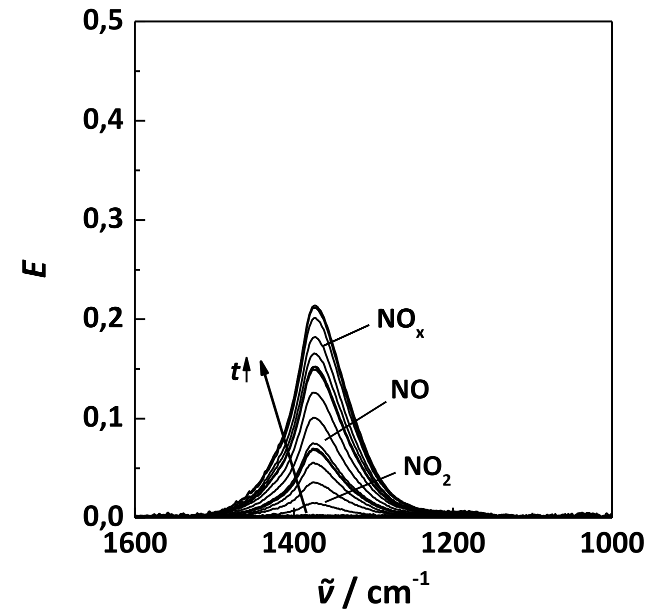
→ **Dosimeter-type sensor is suitable for reliable NO_x detection**

→ **Presented NO_x dosimeter is suitable for Air Quality Monitoring**

Dosimeter-type sensor

DRIFTS study of sensing mechanism





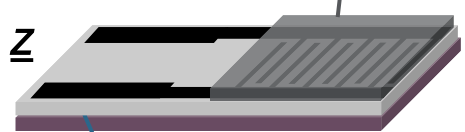
-> formation of nitrates on K sites is determined by DRIFTS and the nitrate formation is detected electrically

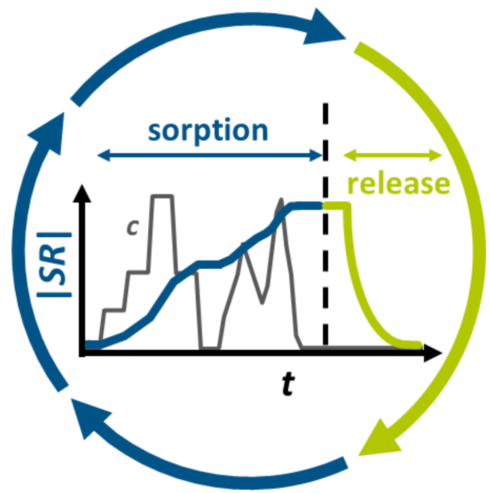
-> typical dosimeter-like behavior only with Mn/K/La-Al_2O_3

Dosimeter-type sensor

Conclusion

- NO_x dosimetry is suitable for sub-ppm detection
- Amount and concentration of NO_x can be measured by dual mode functionality
- Detection limits can be optimized by thickness of functional layer
- Comparison with established sensing devices (chemical & electrochemical sensors) showed promising results [R. Moos, I. Marr, Proceedings IMCS2016]





Thank you for your kind attention!