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

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - **Action End date**: 30/04/2016 - **Year 4**: 1 July 2015 - 30 April 2016

Novel Integrated Gas Sensor Microsystem with Pre-Concentrator for Extremely High Sensitivity and Selectivity

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cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir

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

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Overview

- VOCs (Volatile Organic Compounds) – a challenge for IAQ
- The SENSIndoor project
- MOFs (Metal-Organic Frameworks) for pre-concentration
- Validation experiments
- Novel integrated microsystem with pre-concentrator
- Simulations
- First experimental results
- Summary and outlook

VOCs: key for Indoor Air Quality

LEHRSTUHL FÜR MESSTECHNIK

- Volatile Organic Compounds (VOCs) are highly relevant for IAQ
- Some are proven or suspected to be carcinogenic
- Resulting target concentrations are low ppb or even sub-ppb
  → High sensitivity required
- Benign VOCs (e.g. ethanol) can occur at much higher conc. (ppm)
  → High selectivity required
- Most relevant target VOCs according to European studies: formaldehyde, benzene, naphthalene

Target gas	Guideline values	
	µg/m³	ppb
Formaldehyde [1]	100	81.3
Benzene [2]	5	1.57
Naphthalene [1]	10	1.9

[1]: WHO guidelines for indoor air quality (2010)
[2]: Umweltbundesamt Infoblatt Benzol (12/2010)
Note: some national regulations target even lower concentration limits, e.g. France

Motivation

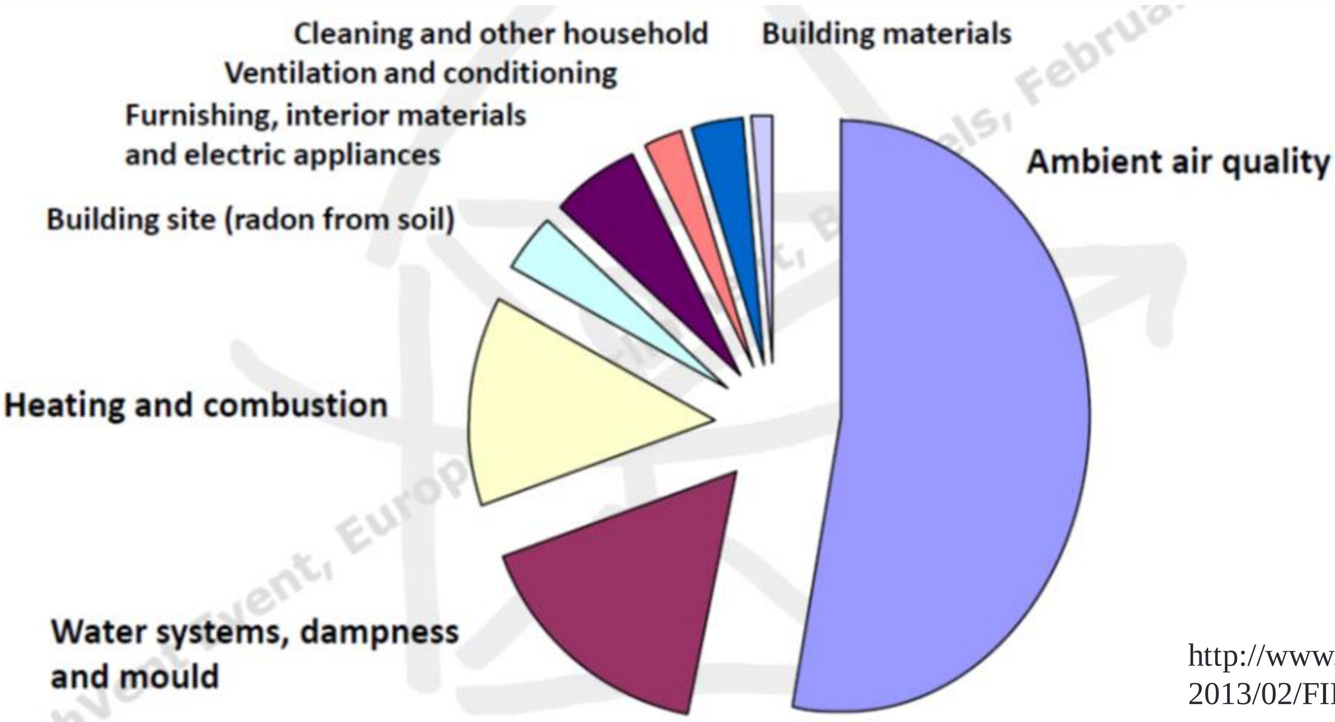
- People spend more than 80 % of their time indoors where fresh air exchange is increasingly limited to reduce energy consumption.
- Indoor air pollution contributes significantly to the global burden of disease.
- Continuous ventilation would greatly increase energy consumption for HVAC (heating, ventilation, air conditioning) systems.
- Low-cost sensor systems are required to provide ubiquitous Indoor Air Quality (IAQ) monitoring.

➢ **Core motivation for the SENSIndoor project**

Motivation

➢ **Core motivation for the SENSIndoor project**

2 Mio healthy life years are lost every year in the EU due to indoor exposure according to an analysis in the EU project EnVIE

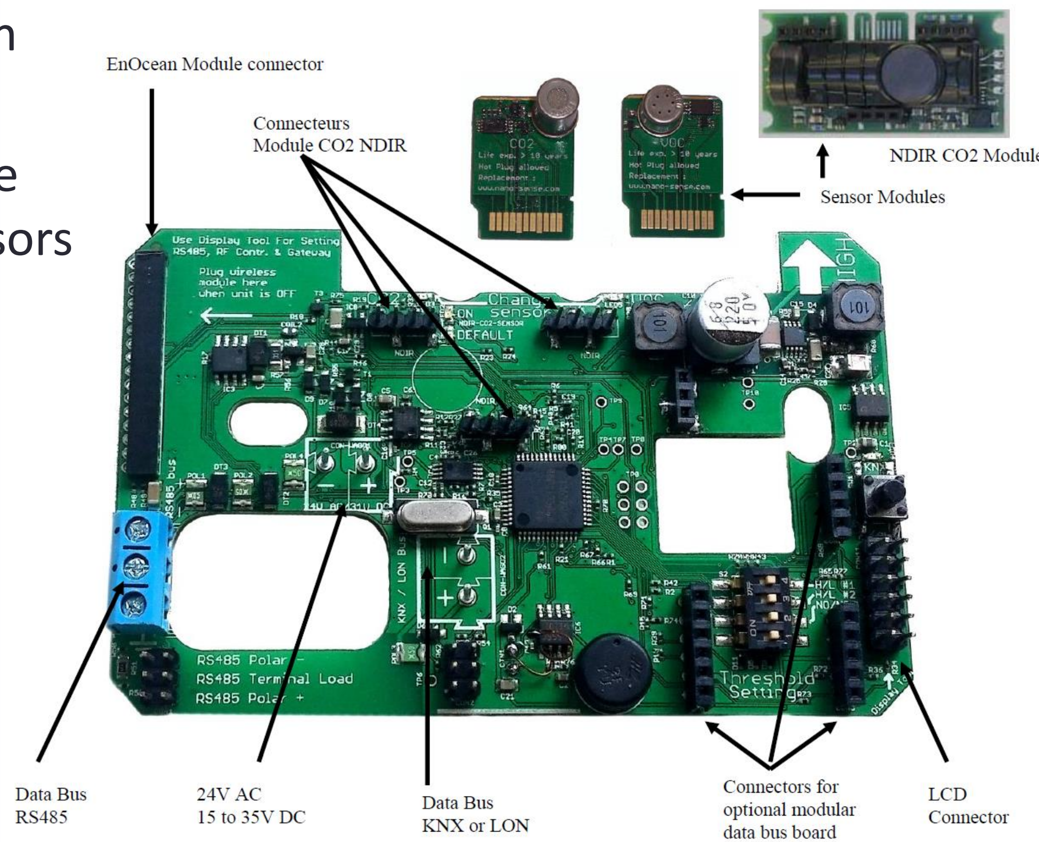


http://www.efanet.org/wp-content/uploads/2013/02/FINAL-Presentation-all.pdf

State-of-the-art

- Demand controlled ventilation today
  - mostly CO_2 monitoring, at best total VOC (TVOC)
  - CO_2 based on IR absorption or solid state electrolyte
  - TVOC based on metal oxide semiconductor (MOS) sensors

E4000 Air Quality Probe
(NanoSense SARL)

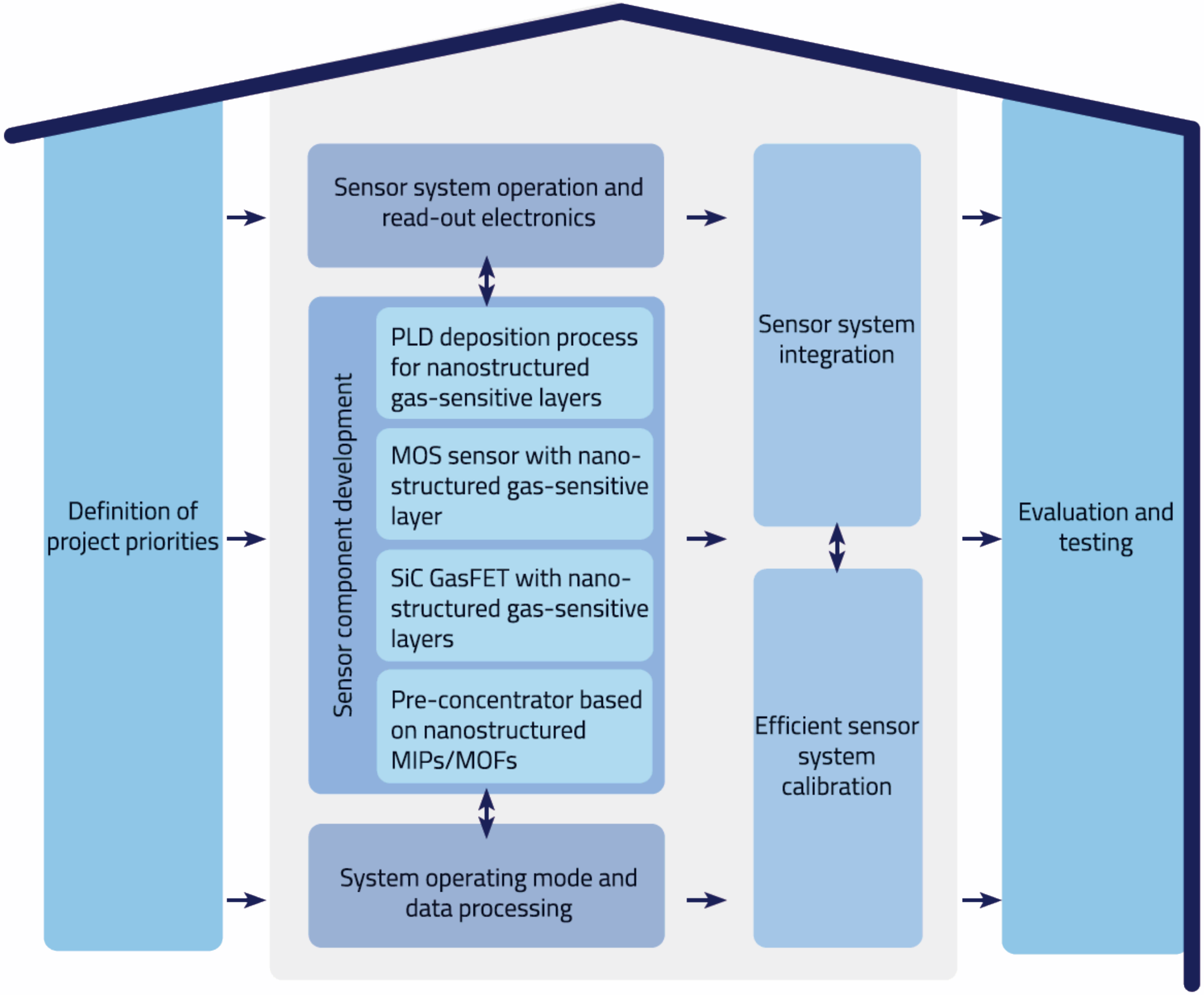


SENSIndoor overview

EU Project SENSIndoor:

Nanotechnology-based intelligent multi-**SEN**sor **S**ystem with selective pre-concentration for **Indoor** air quality control

www.sensindoor.eu

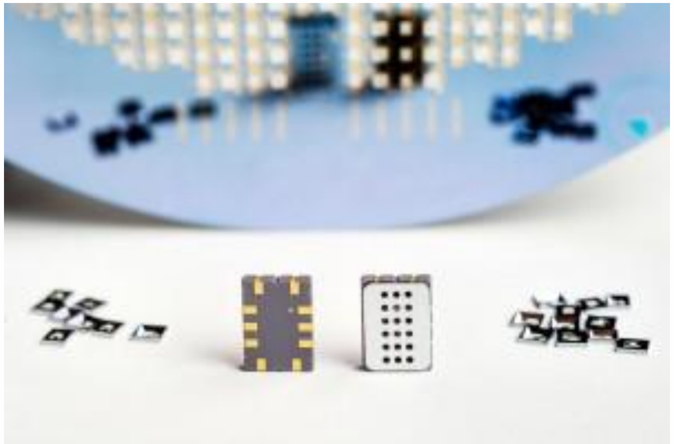


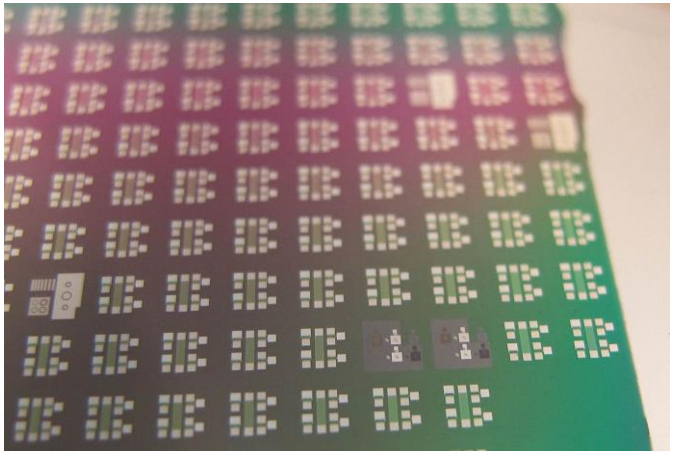
SENSIndoor origins

- **VOC-IDS** (MNT-ERA.net collaborative project)
  Volatile Organic Compound Indoor Discrimination Sensor
  - Partners: USAAR-LMT, IDMEC-FEUP - Instituto de Engenheria Mecânica, University Porto (P), UST Umweltsensortechnik GmbH (D), 3S GmbH (D), NanoSense SARL (F), Weinzierl Engineering GmbH (D), CIAT - Compagnie Industrielle d'Application thermique S.A. (F), ALDES Aéraulique S.A. (F)
- COST action TD1105 **EuNetAir**
  European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability
  - Partners: U Linköping (A Lloyd Spetz: vice chair of action), U Oulu, USAAR, 3S GmbH, SenSiC AB, SGX Sensortech S.A.
  - Several topics identified to be addressed in call **NMP.2013.1.2-1 Nanotechnology-based sensors for environmental monitoring**

SENSIndoor technologies 1

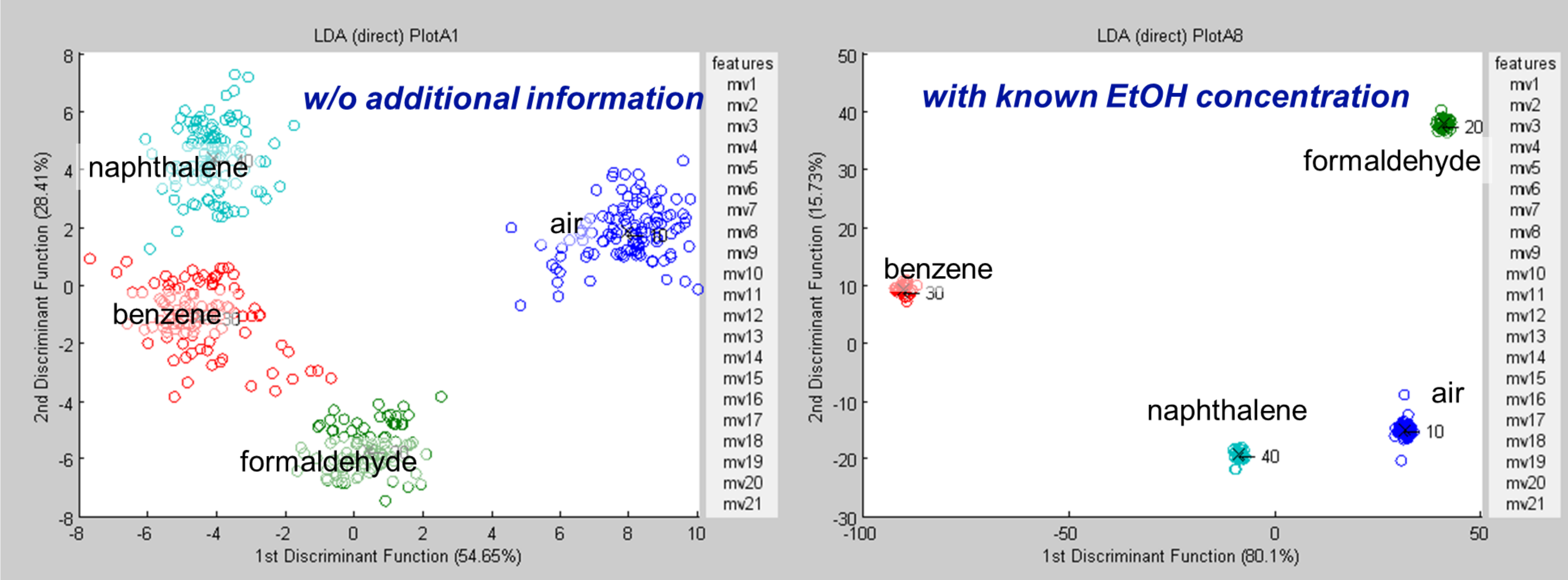
- Sensor technologies
  - **MOS – Metal oxide semiconductor** (*SGX Sensortech, USAAR-LMT*)
    - well known for high sensitivity and robustness @ low-cost
    - MEMS technology for mass production and low power consumption
  - **GasFET – Gas-sensitive Field Effect Transistors** (*LiU, SenSiC*)
    - complementary technology (polarity ⇔ reaction)
    - SiC technology for chemical robustness and high operating temperatures





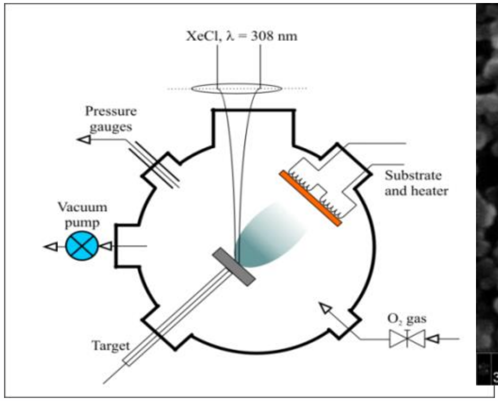
SENSIndoor technologies 2

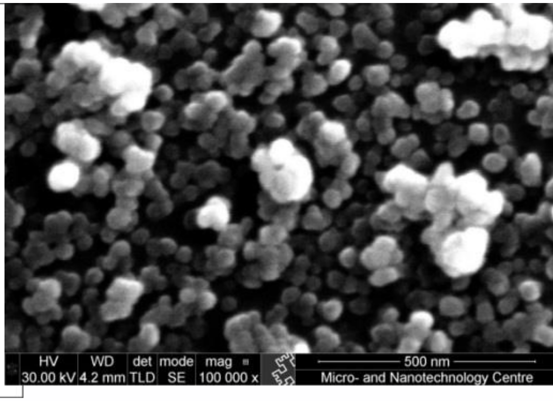
- Dynamic operation and intelligent signal processing
  - **Temperature Cycled Operation** (*USAAR-LMT, NanoSense, 3S*) to increase selectivity ("virtual multisensor") and stability



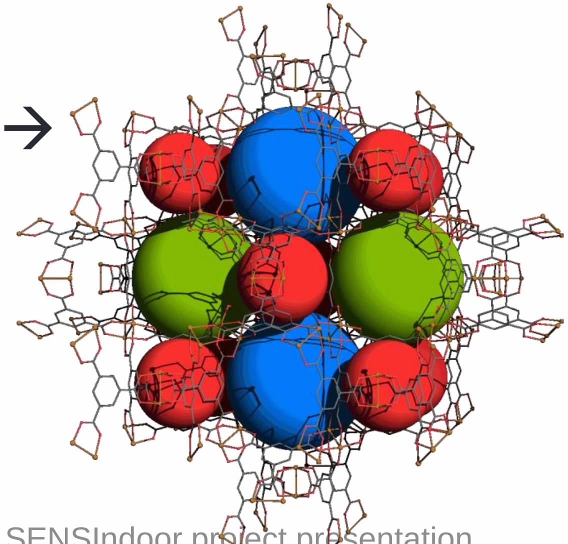
SENSIndoor technologies 3

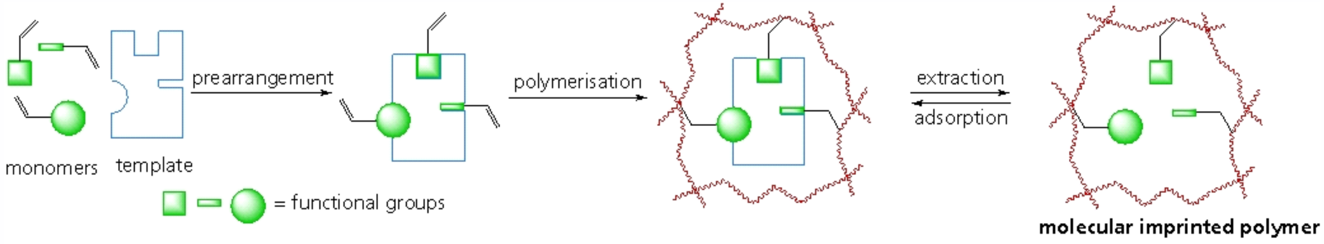
- Nanotechnology for improved sensor elements
  - **Pulsed Laser Deposition** (*U Oulu, Picodeon*) for novel, highly sensitive gas-sensitive layers suitable for wafer level mass production



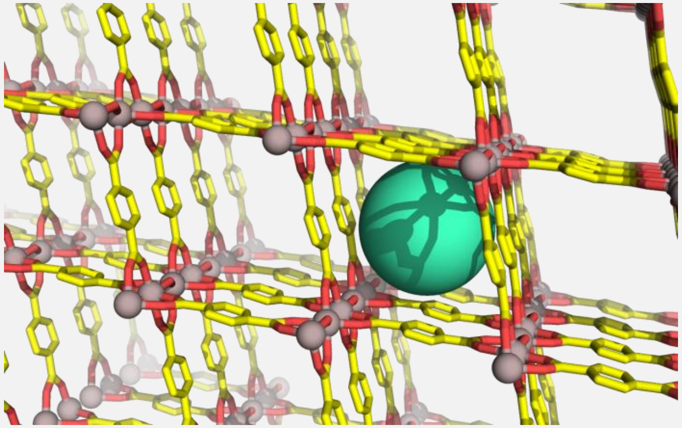


  - **Selective pre-concentration** (*FhG-ICT*) based on MOFs (metal-organic frameworks) → and MIPs ↓ (molecular imprinted polymers)

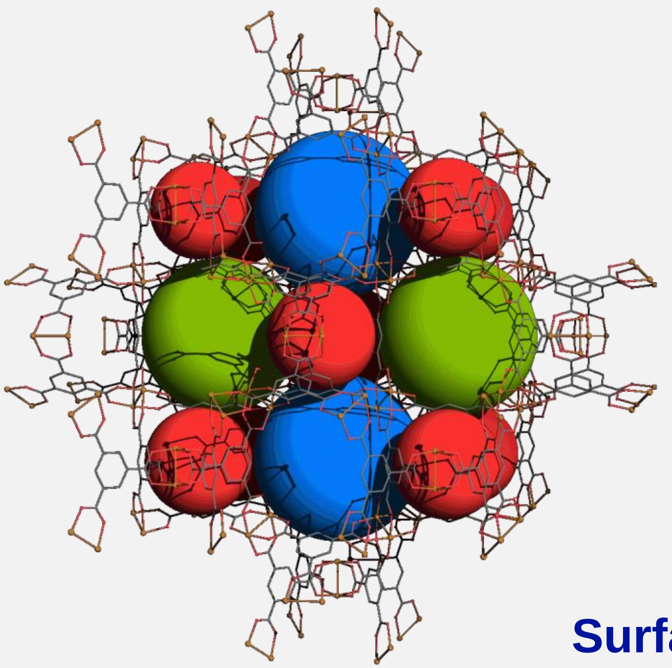




MOF candidates as PC material

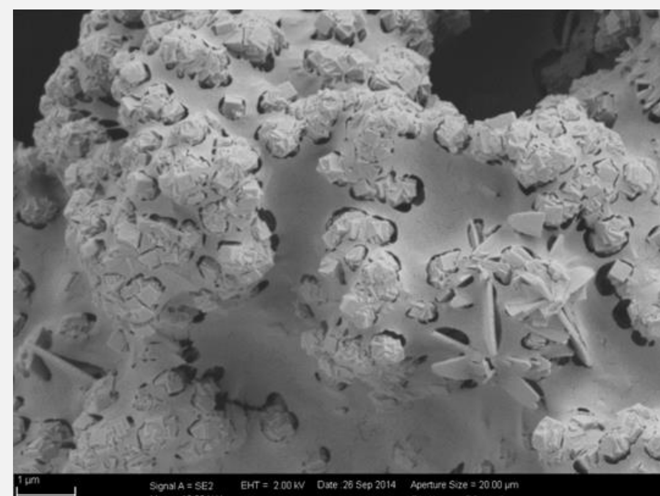


MIL-53
Aluminum 1,4-benzenedicarboxylate
$Al(OH)[O_2C\text{-}C_6H_4\text{-}CO_2]\cdot[HO_2C\text{-}C_6H_4\text{-}CO_2H]_{0.70}$

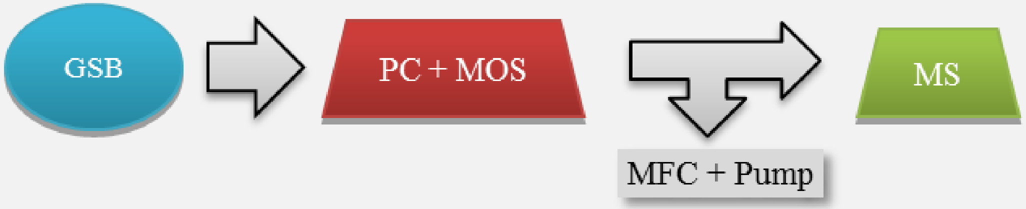


HKUST-1
Copper benzene-1,3,5-tricarboxylate

Surface area > 1000 m²/g



Verification of PC functionality

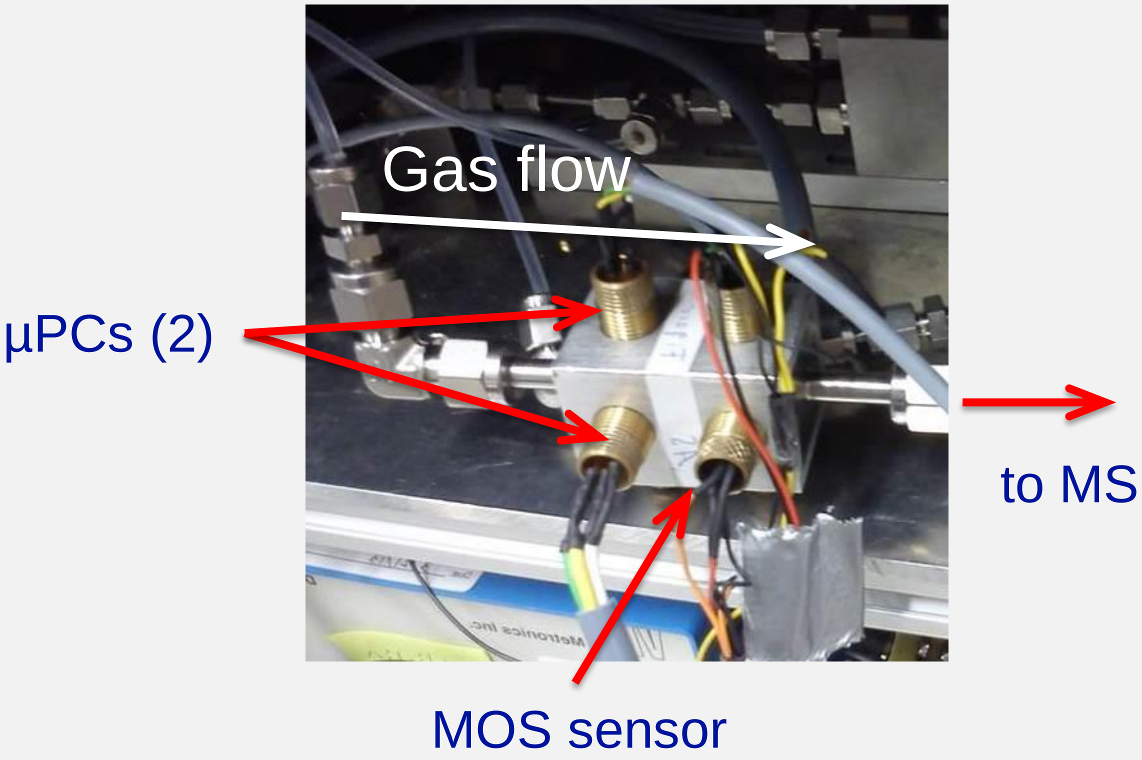


Are selected MOF materials suitable for PC devices?

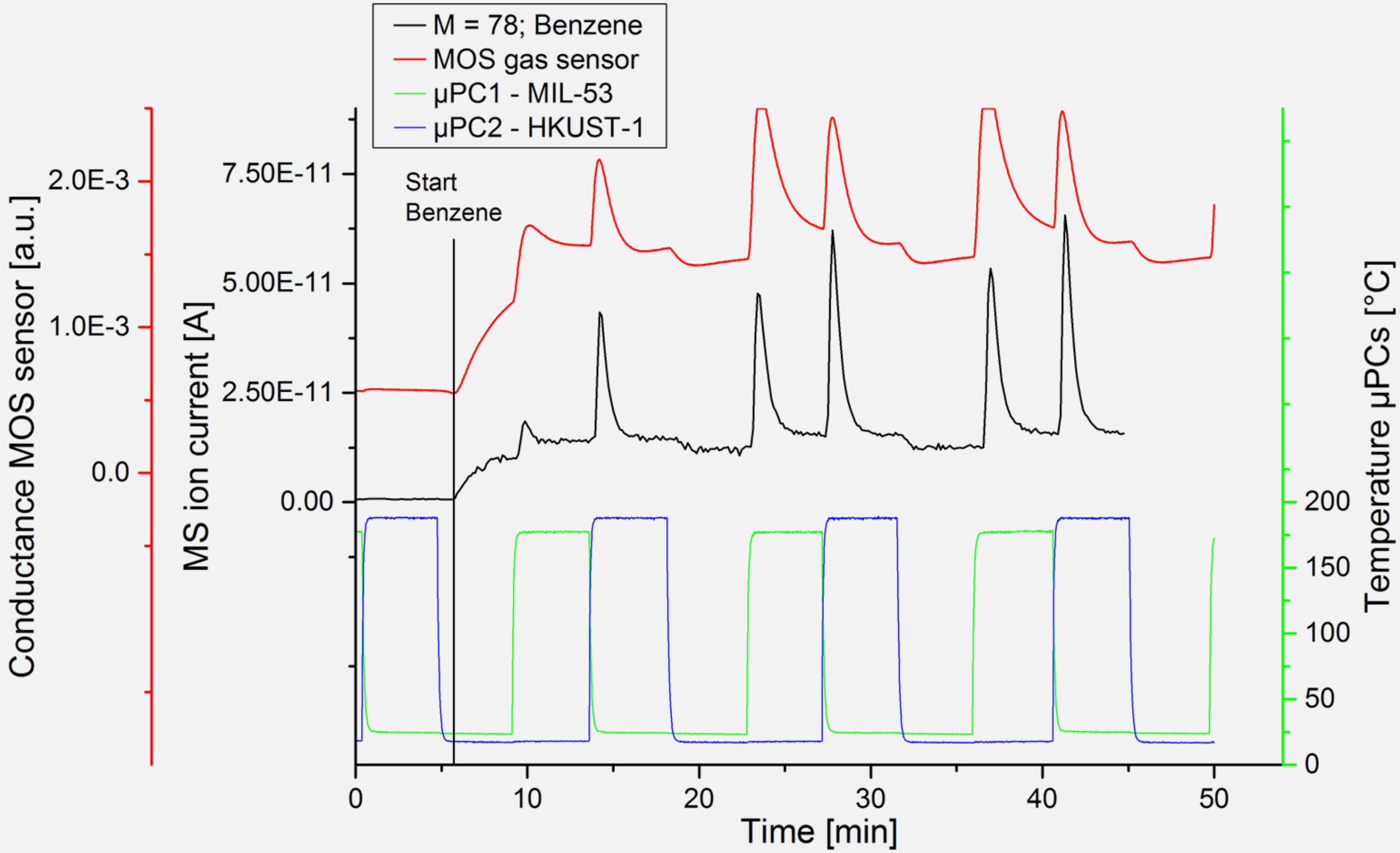
Here: tests with benzene

Verification with

- mass spectrometer (MS)
- commercial MOS sensor (UST5330)



Verification of PC functionality

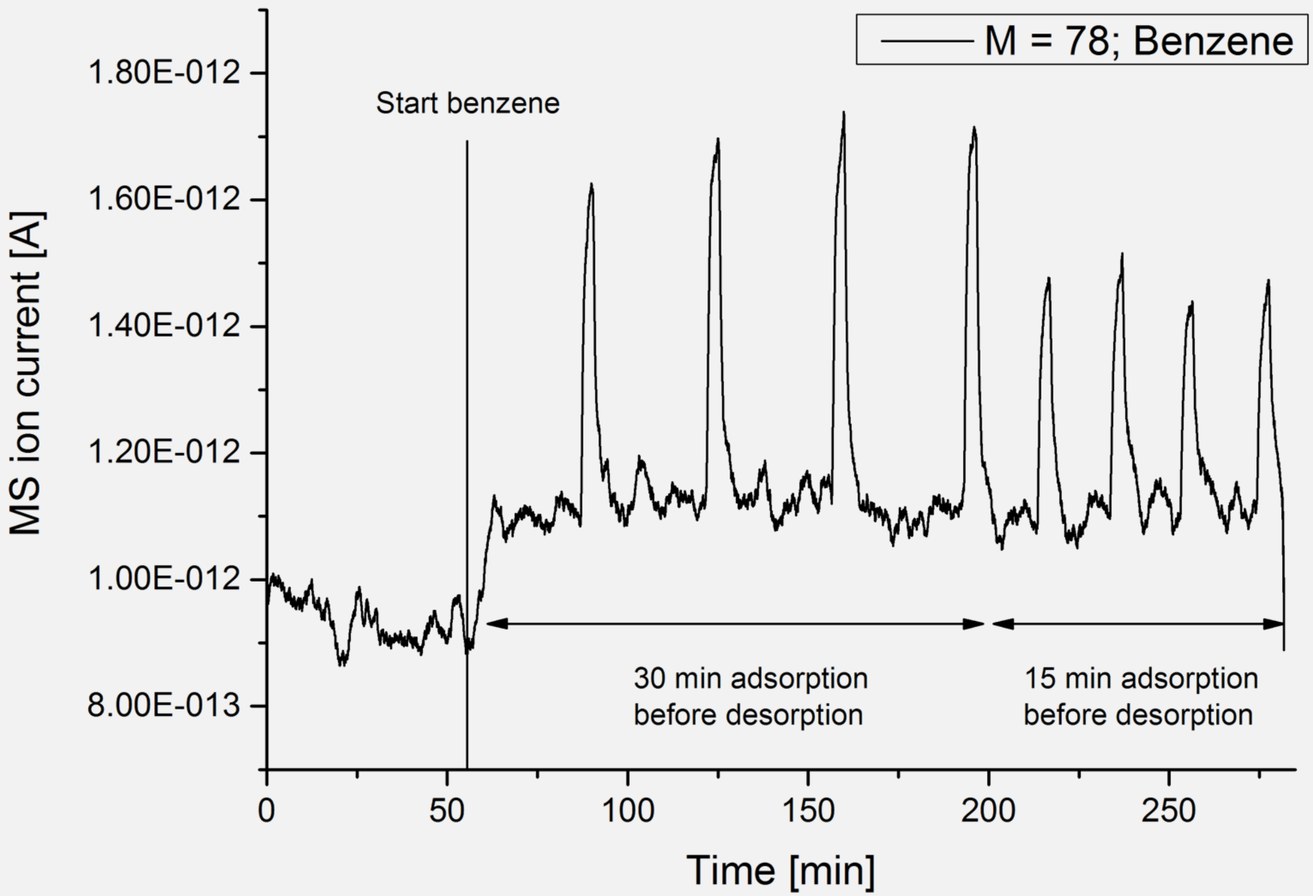


High benzene concentration: 30 ppm (according to mass spectrometer)

→ Clear signal peaks after heating of MOF coated pre-concentrators

→ Relative peak heights of MS and gas sensor different for both MOFs (water?)

Verification of PC functionality

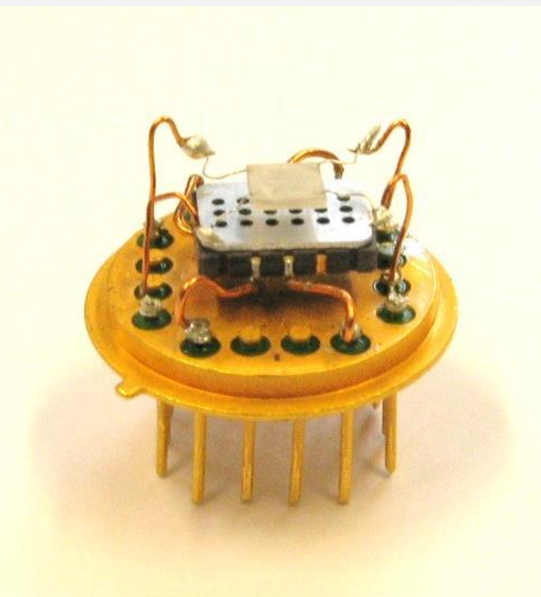


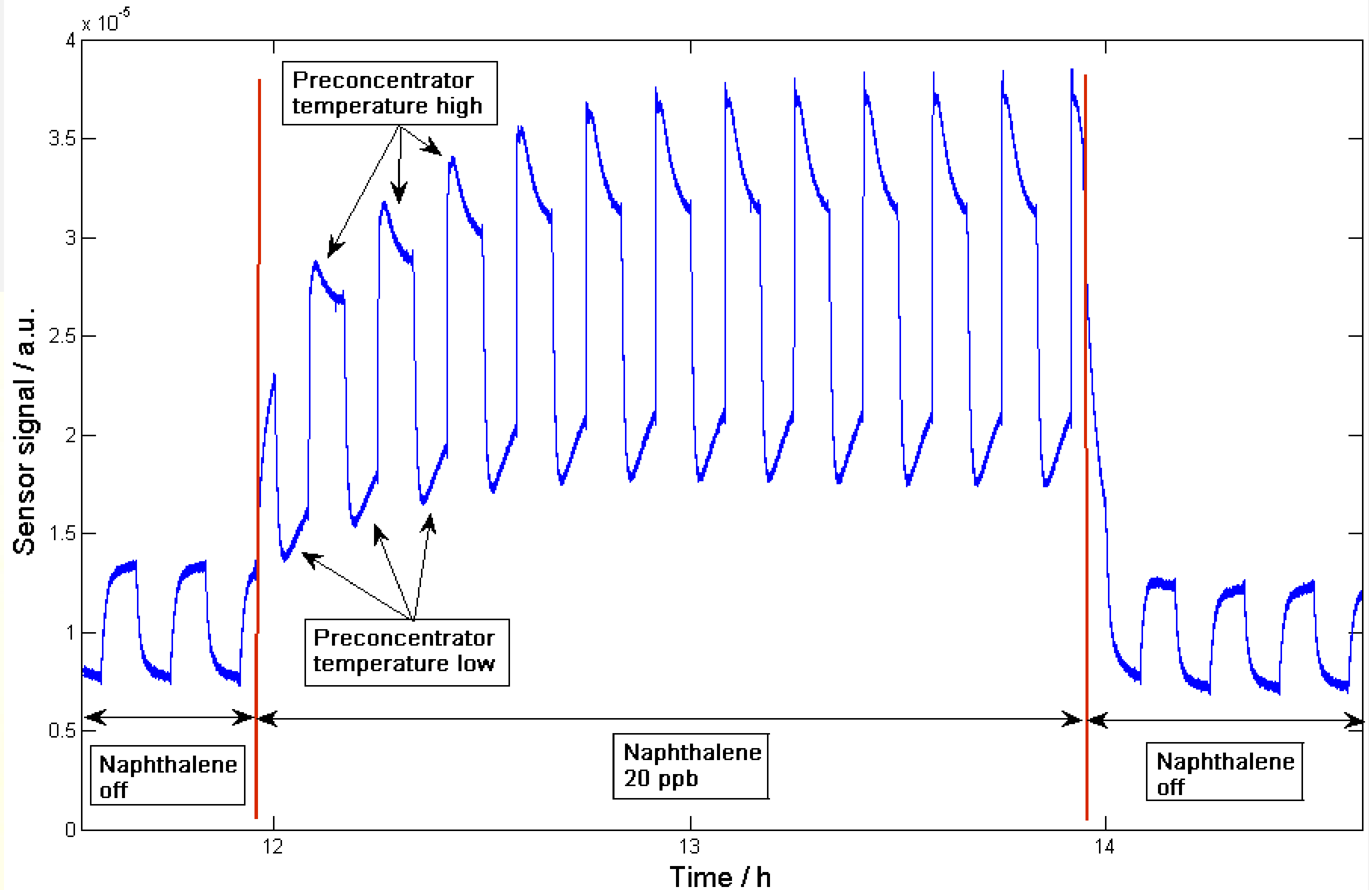
Tests with lower concentrations, here: 1 ppm

→ Influence of accumulation period on signal height during desorption

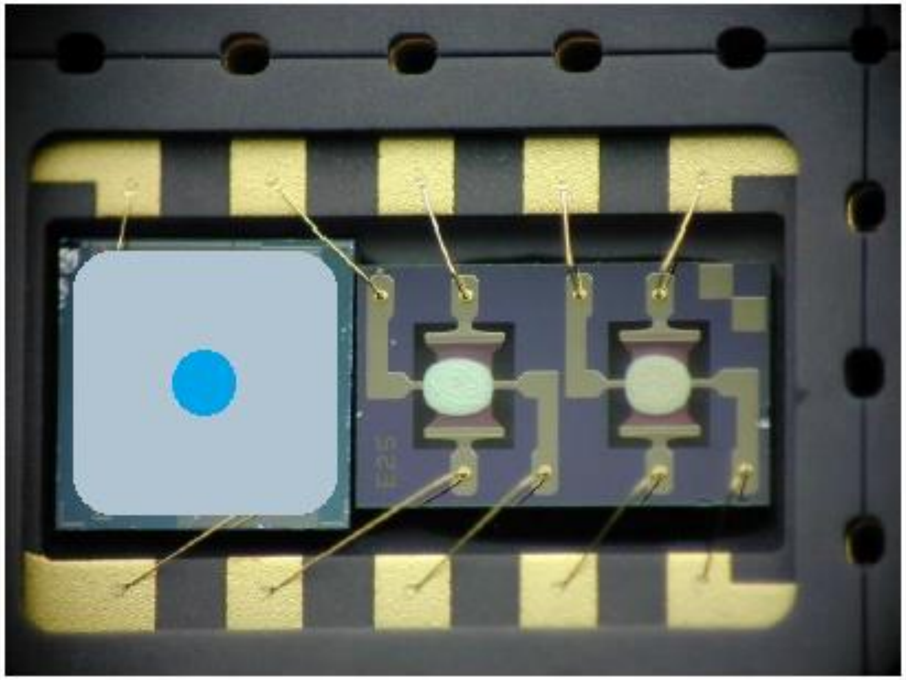
Micro pre-concentrator (µPC):
first proof-of-concept measurements (end 2014) with test gas naphthalene

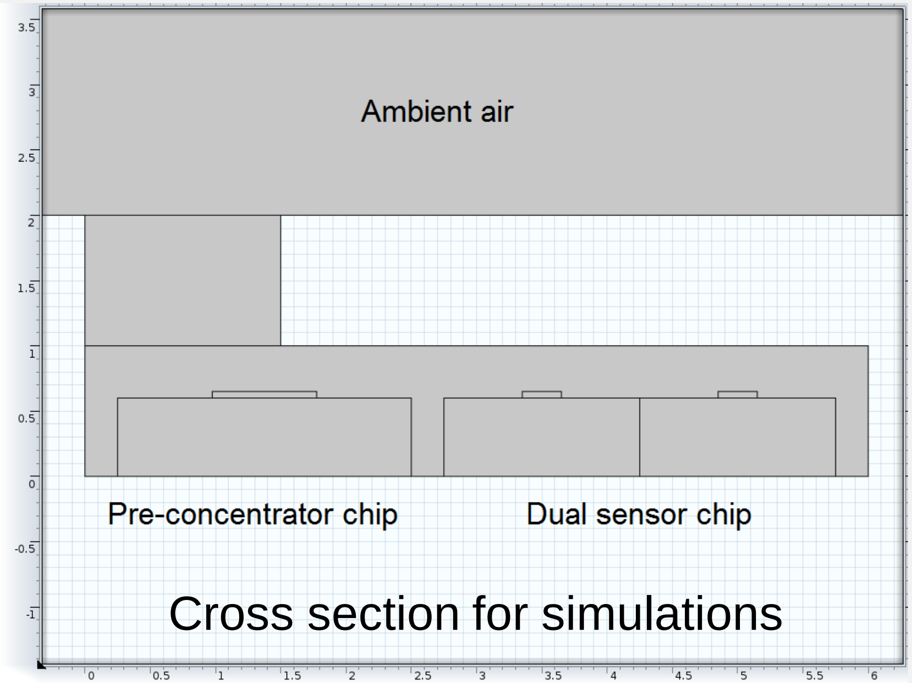
- µPC unheated: signal low, then increases
- µPC @ high temp: signal high, then decreases
- thermal crosstalk





Integrated gas sensor microsystem





SMD ceramic package
(5x7 mm² footprint)

Lid with gas access
not shown

Left:
µPC chip

MOF material
Ø ≈ 300 µm

Right:
Dual gas sensor chip
(SGX Sensortech)
1x WO_3 undoped
1x WO_3 doped

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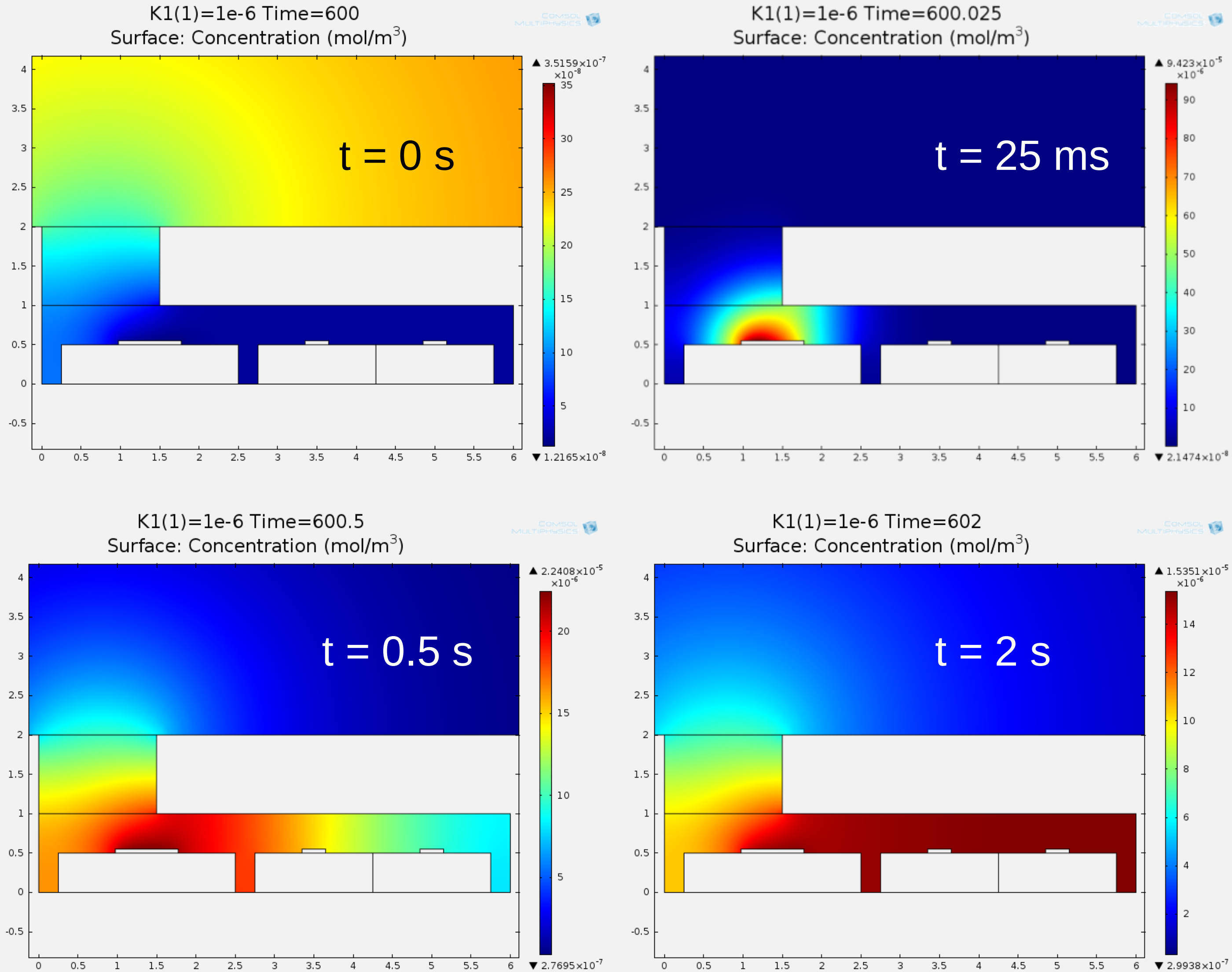


Background gas concentration: $4*10^{-7}$ mol/m³ (approx. 10 ppb)

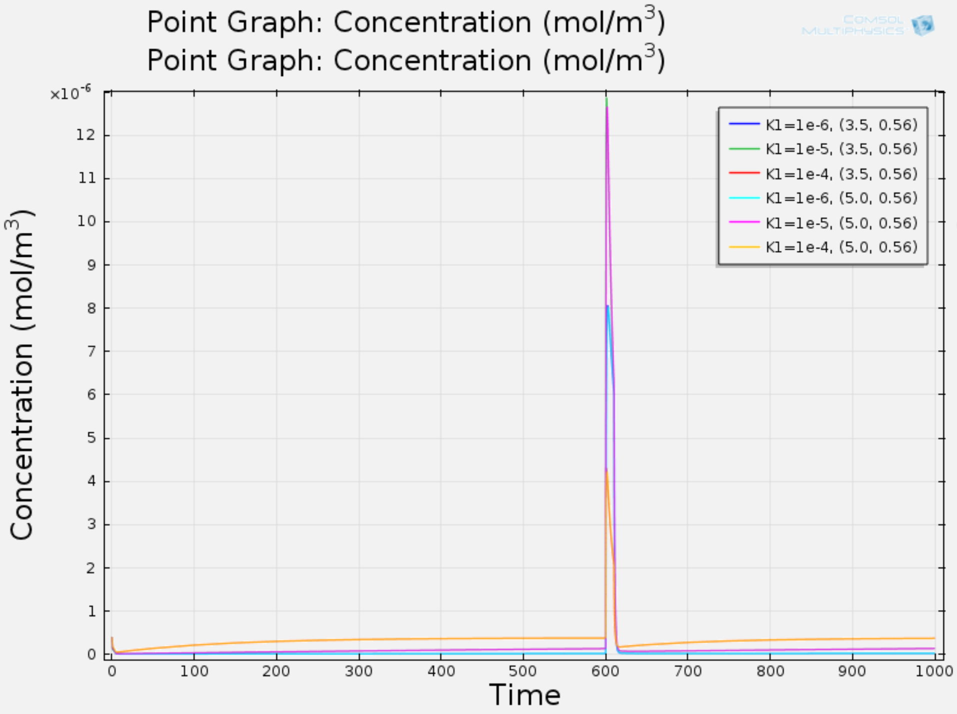
Accumulation period: 600 s

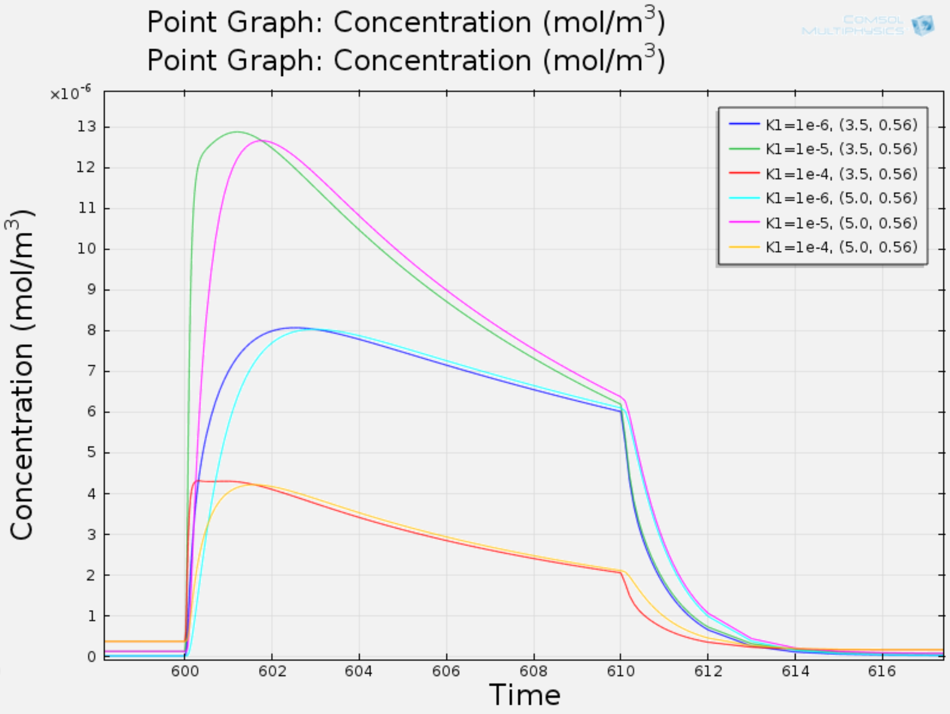
Desorption period: 10 s

Simulations show approx. 2 orders of magnitude higher concentration

Note: colors show relative scales in each image

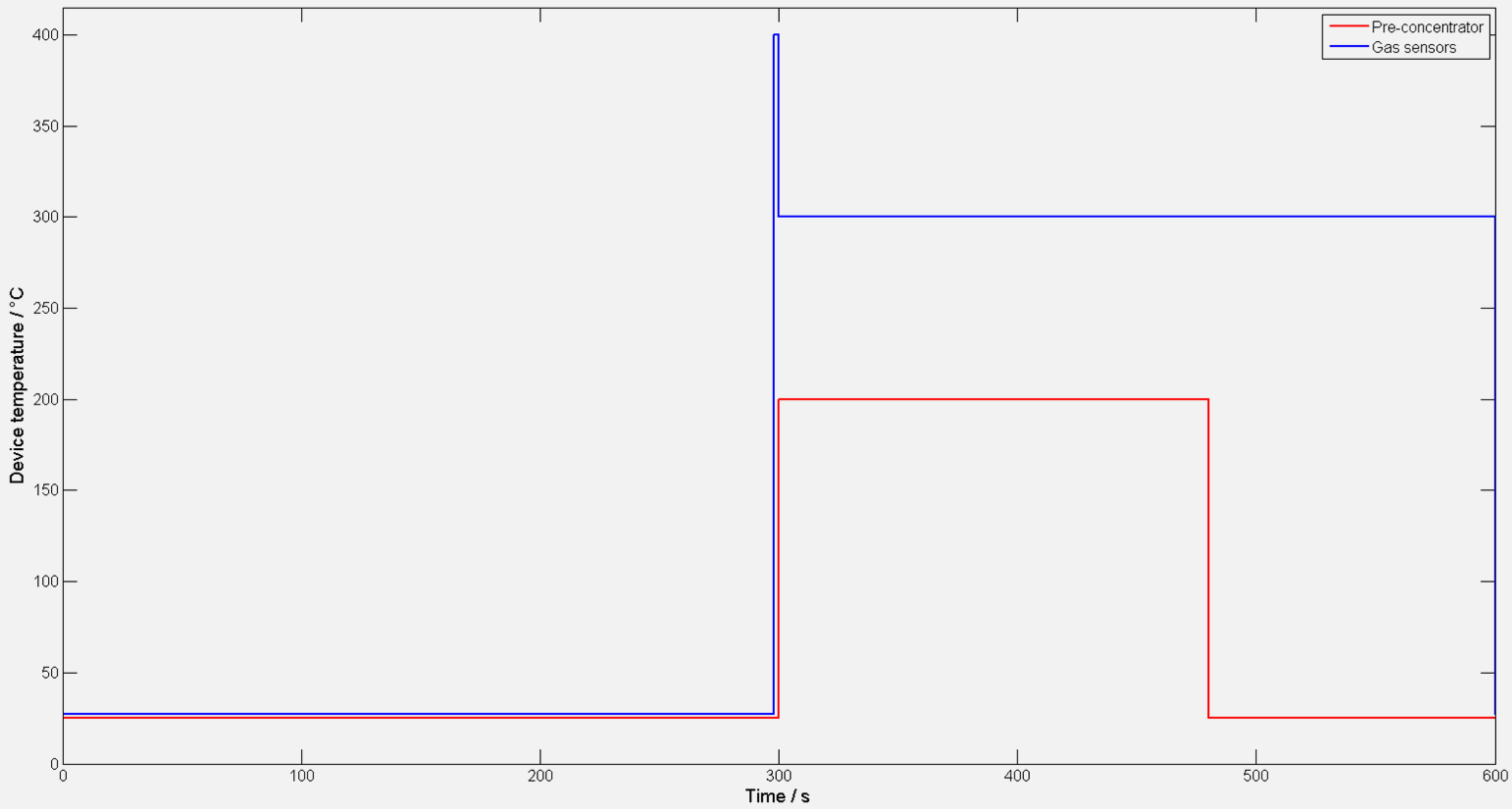
Simulations





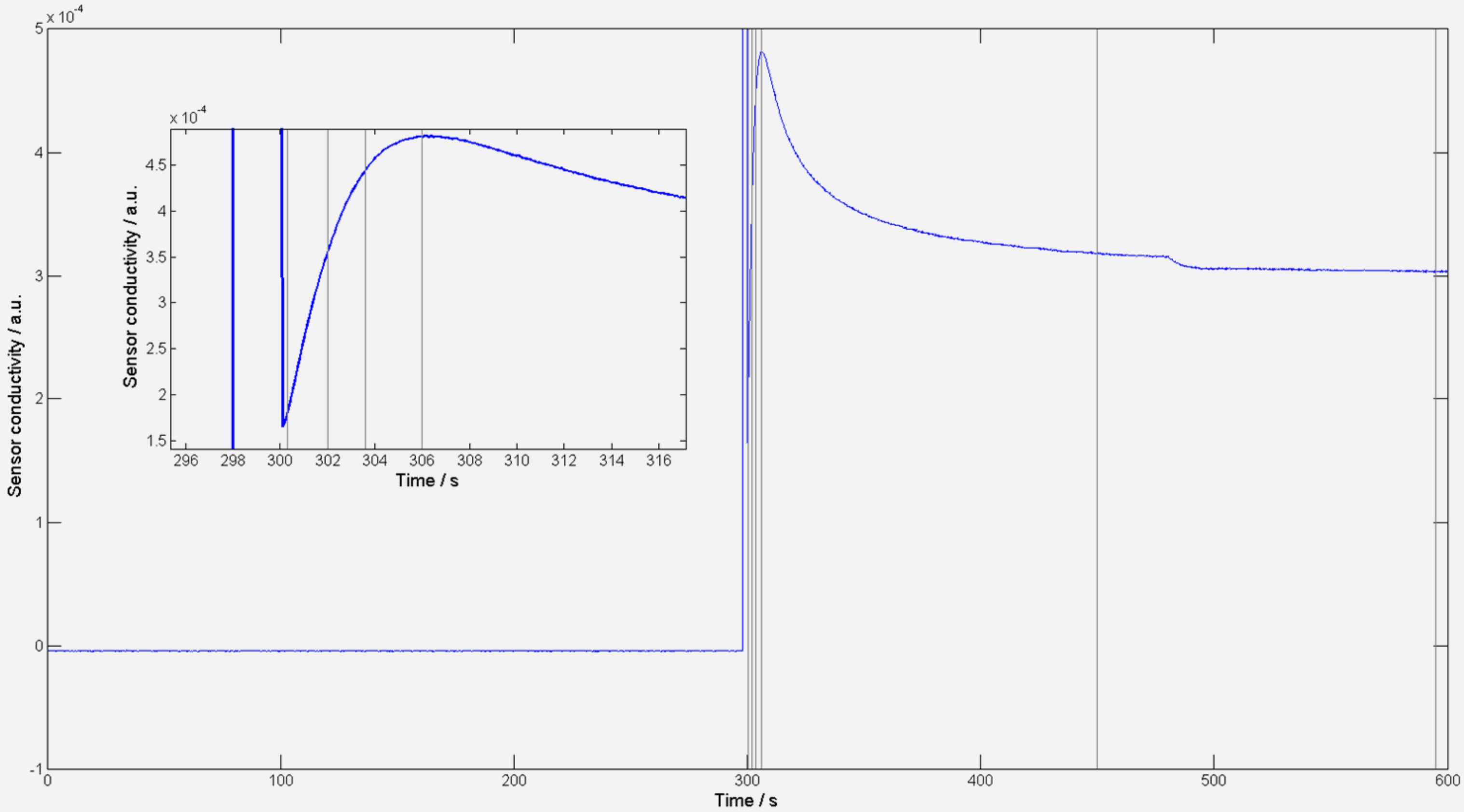
- Simulation parameters: accumulation period: 600 s, desorption period: 10 s
- Parameter variation: distribution coefficient MOF vs. air (10^{-6}, 10^{-5}, 10^{-4})
- Gas concentrations at both sensor sites – slight delay for second sensor
- Boost in gas concentration (peak): 32x / 20x / 11x
- Higher boost factor corresponds to shorter peaks (typ. few seconds)

First experiments: test protocol



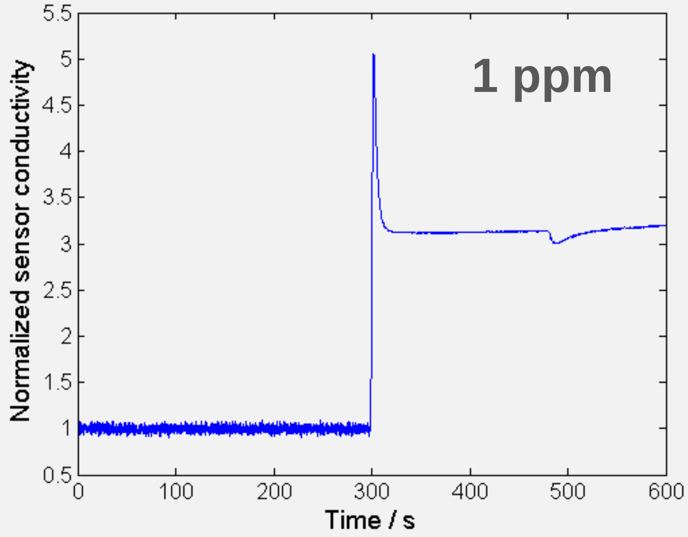
- 300 s accumulation, both sensors and PC off to prevent thermal crosstalk
- @ 298 s: sensors heated to 400°C for 2 s → surface “cleaning”
- @ 300 s: pre-concentrator device heated to 200°C for 180 s → desorption

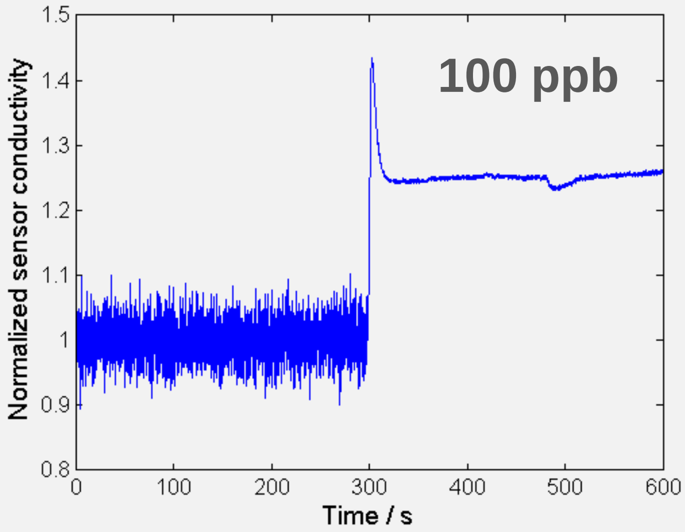
First results for benzene

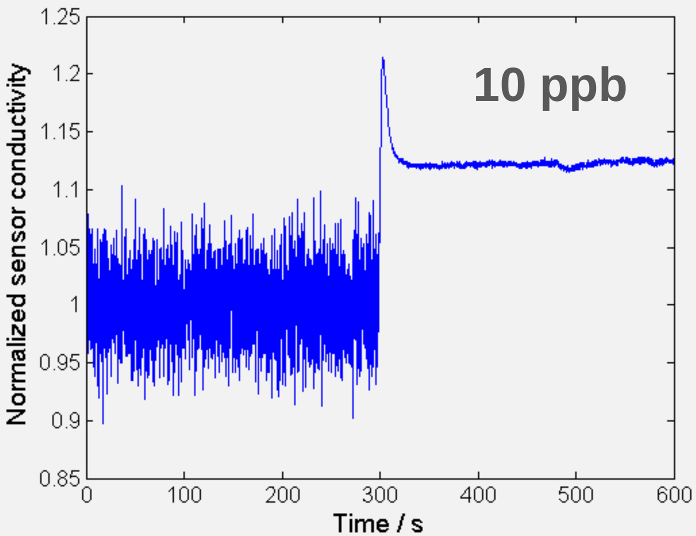


- Peak @ 298 – 300 s caused by high temperature (not evaluated)
- Sensor response at t > 300 s caused by temperature (sensor/housing) **and gas**
- Several points selected and plotted as quasi-static sensor signals

First results for benzene





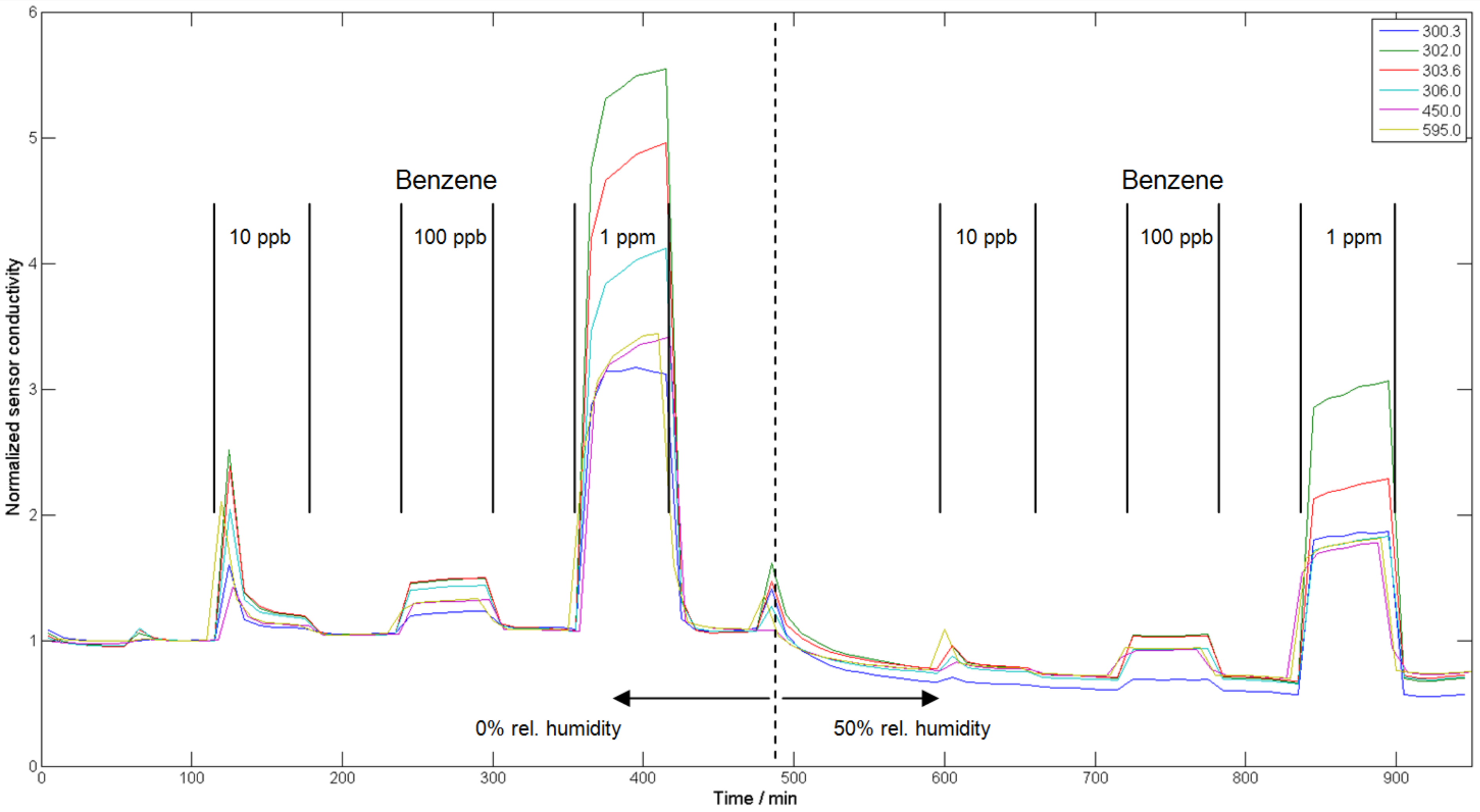


G/G_0 (cycle with gas / cycle in air)

Signal @ 10 ppb during pre-concentrator desorption nearly as high as for 100 ppb without pre-concentrator

→ **boost in sensitivity**

First results for benzene



Maximum sensitivity in cycle changes with concentration → additional information

Summary and outlook

- Novel integrated low-cost microsystem with pre-concentration
- Boost in sensitivity was demonstrated, but lower than expected
- Problems of first integrated prototypes:
  - µPC heater area was not used efficiently (optimum: 8* larger)
  - Poor adhesion of MOF materials on micro hotplate
  - Interfering signal in mounted systems (caused by glue?)
- Outlook
  - New MOF deposition methods to be tested (screen printing?)
  - Improved adhesion
  - Optimized dynamic **system** operation (PC T ramp, sensor T cycle,…)
  - Boost in selectivity needs to be verified

SENSIndoor consortium
2^{nd} progress meeting, Pfinztal, Jan. 2015

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SEVENTH FRAMEWORK PROGRAMME