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COST Action TD1105

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Innovations and Challenges for Air Quality Control Sensors

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A New Approach for On-site Calibration and Calibrated Quantification of VOCs with Low-Cost Sensors

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VOCs: key for Indoor Air Quality

- 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

> Research projects focused on IAQ

VOC-IDS: Volatile Organic Compound Indoor Discrimination Sensor

- Transnational project funded within MNT-ERA.net
- Selective VOC detection, primarily formaldehyde, benzene
- Novel ceramic nanomaterial metal-oxide semiconductor gas sensors
- Intelligent signal processing based on temperature cycling
- Networked systems connected to KNX bus

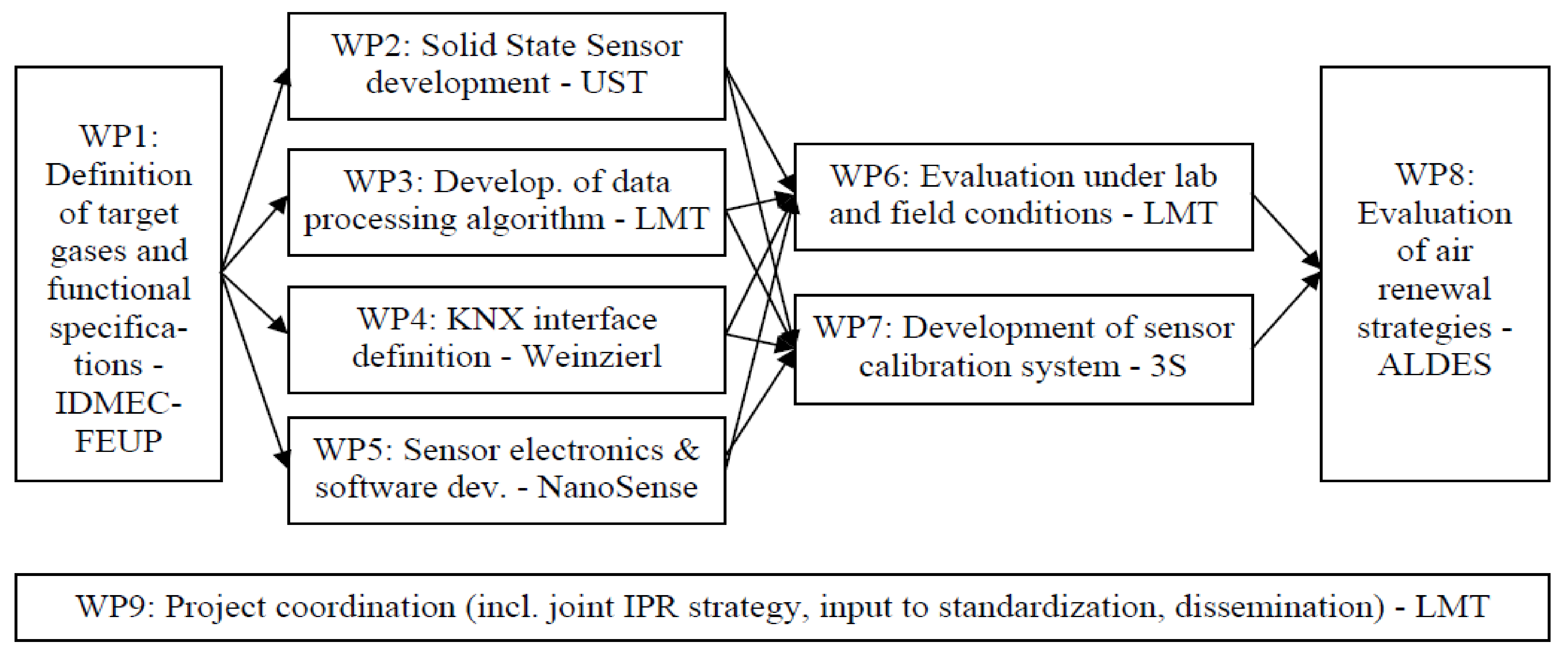
SENSIndoor: Nanotechnology based intelligent multi-SENsor System with selective pre-concentration for Indoor air quality control

- EU-FP7 project NMP.2013.1.2-1:
  Nanotechnology-based sensors for environmental monitoring
- Microtechnology based approach for MOS and SiC-GasFET sensors
- Pre-concentration to boost sensitivity and selectivity
- Integrated multi-sensor approach
- Application specific priorities and field tests

> Indoor Air Quality monitoring

MNT-ERA.net project VOC-IDS

- Volatile Organic Compound Indoor Discrimination Sensor
- Scenario specific detection of hazardous VOC
- Integration of sensor system into KNX building automation networks



WP1: Definition of target gases and functional specifications - IDMEC-FEUP

WP2: Solid State Sensor development - UST

WP3: Develop. of data processing algorithm - LMT

WP4: KNX interface definition - Weinzierl

WP5: Sensor electronics & software dev. - NanoSense

WP6: Evaluation under lab and field conditions - LMT

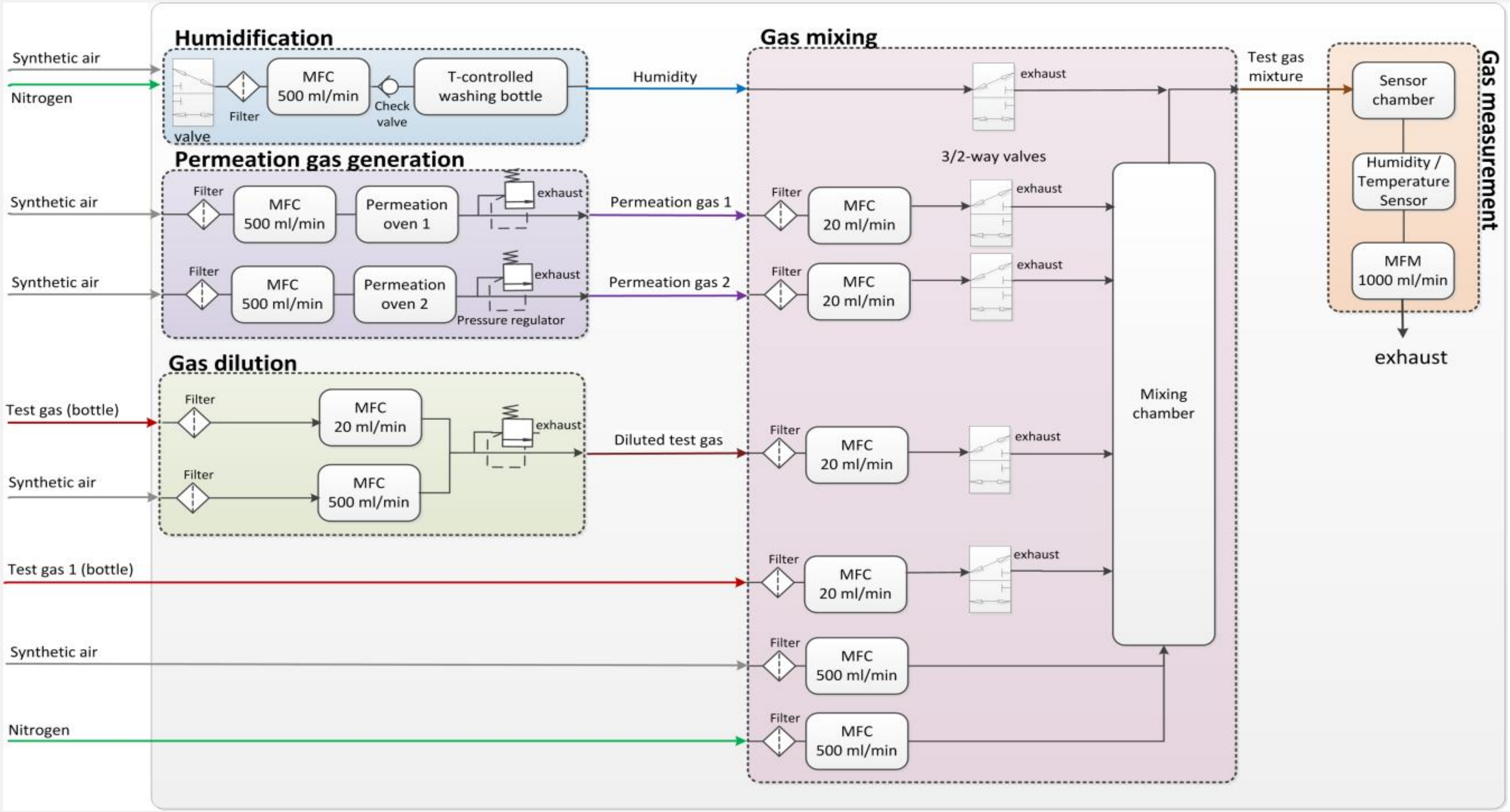
WP7: Development of sensor calibration system - 3S

WP8: Evaluation of air renewal strategies - ALDES

WP9: Project coordination (incl. joint IPR strategy, input to standardization, dissemination) - LMT

> Calibration

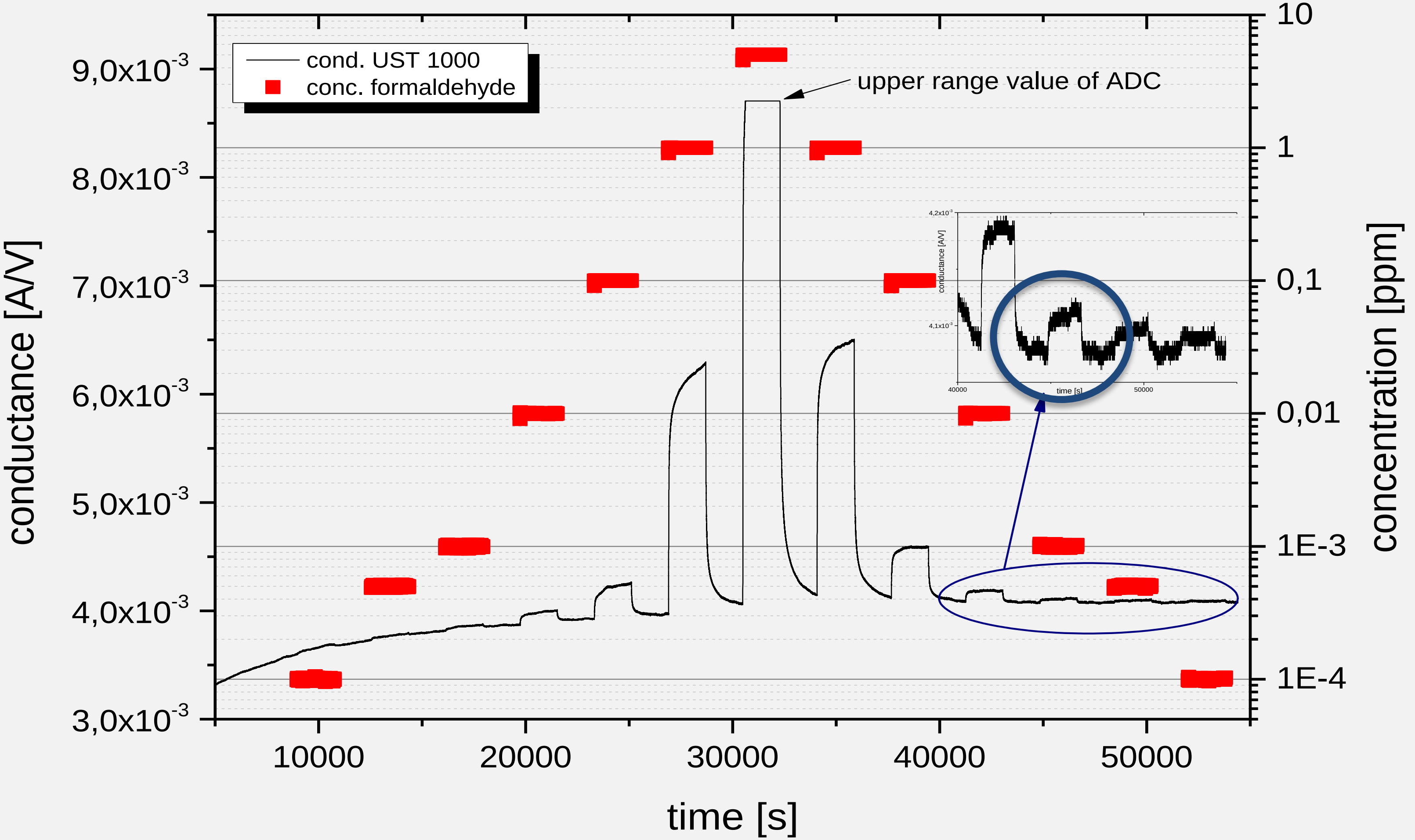
First step: novel gas mixing system for VOC testing/calibration @ (sub) ppb-level



N. Helwig et al.: Gas mixing apparatus for automated gas sensor characterization, Meas. Sci. Technol. 25 (2014) 055903

> Calibration

Novel gas mixing system: results of first sensor tests



N. Helwig et al.: Gas mixing apparatus for automated gas sensor characterization, Meas. Sci. Technol. 25 (2014) 055903

Sensor reaction to 1 ppb formaldehyde

Relevance? Legal limits in France for indoor air: Formaldehyde 25 ppb in 2015; Benzene 0.6 ppb in 2016

> Indoor Air Quality monitoring

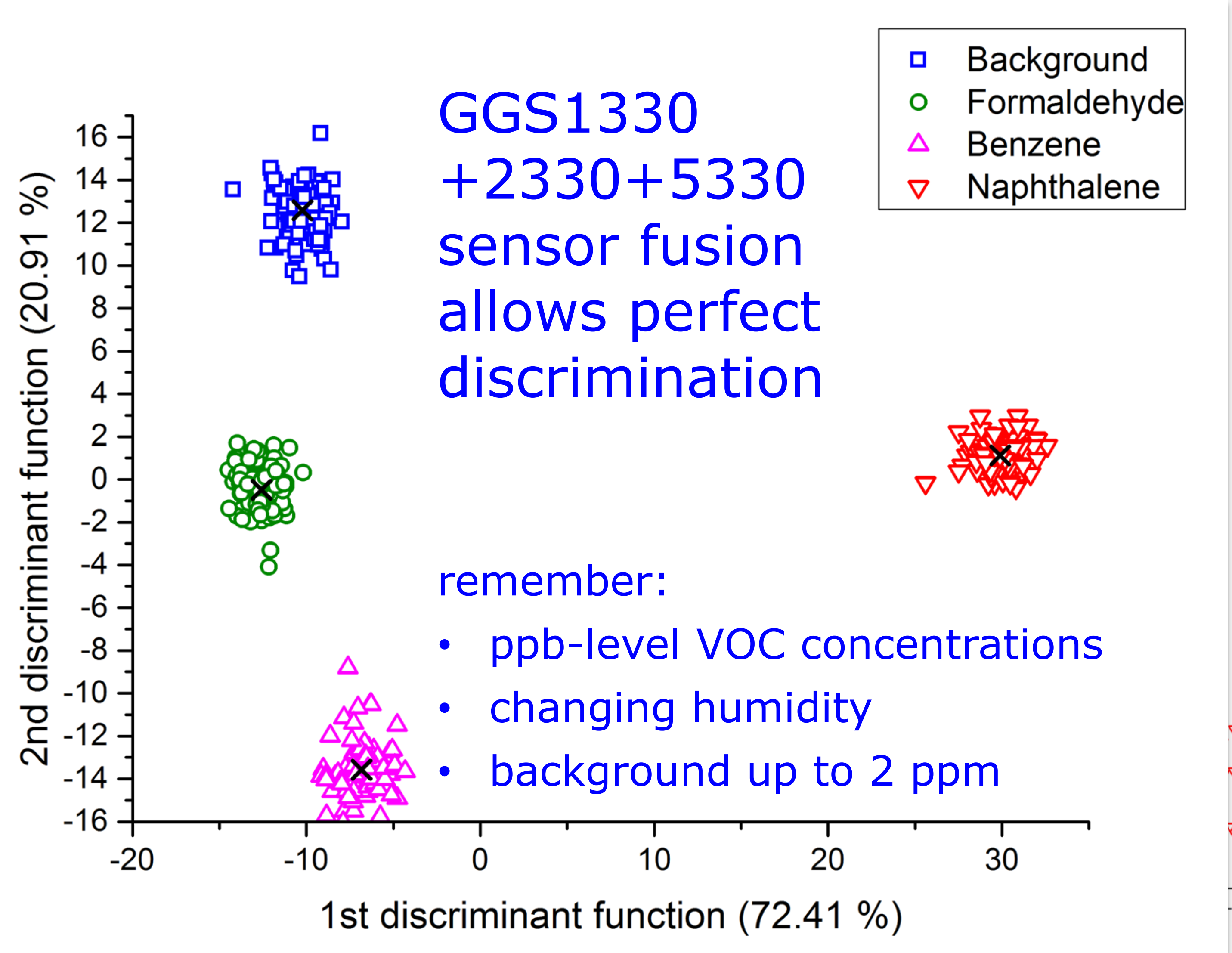
MNT-ERA.net project VOC-IDS

- Example for selective detection of VOCs in interfering background
- Classification of formaldehyde, benzene, naphthalene in the presence of ethanol

target gas	Concentration (ppb)	humidity	Interferents (EtOH ppm)
Air	NA	40%, 60%	none, 0.4, 2
Formaldehyde	10, 100	40%, 60%	none, 0.4, 2
Benzene	0.5, 4.7	40%, 60%	none, 0.4, 2
Naphthalene	2, 20	40%, 60%	none, 0.4, 2

Classification target	interferent concentrat.	relative humidity	number of LDA steps for charac.	Estimated # of LDAs
generalized classification	0, 0.4, 2	40%, 60%	1	1
classification w known r.h.	0, 0.4, 2	known	1 (2)	(1+) 5*1
classification w known EtOH	known	40%, 60%	2	1+10(?)*1

> IAQ monitoring with MOS sensors



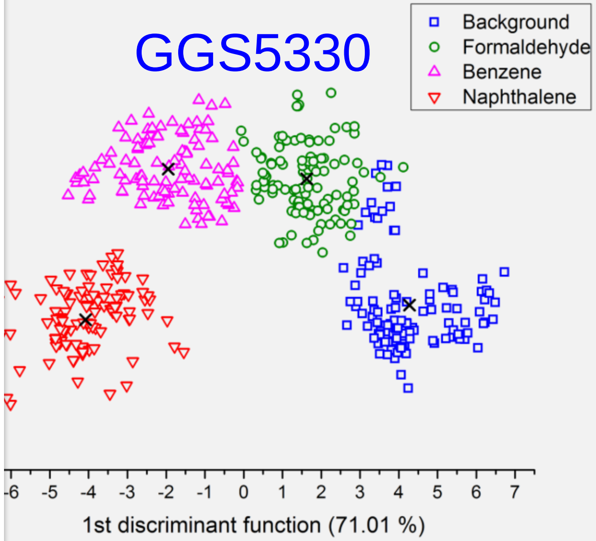
GGS1330 +2330+5330 sensor fusion allows perfect discrimination

remember:

- ppb-level VOC concentrations
- changing humidity
- background up to 2 ppm

mnt-era.net

GGS5330



> IAQ monitoring: field test systems

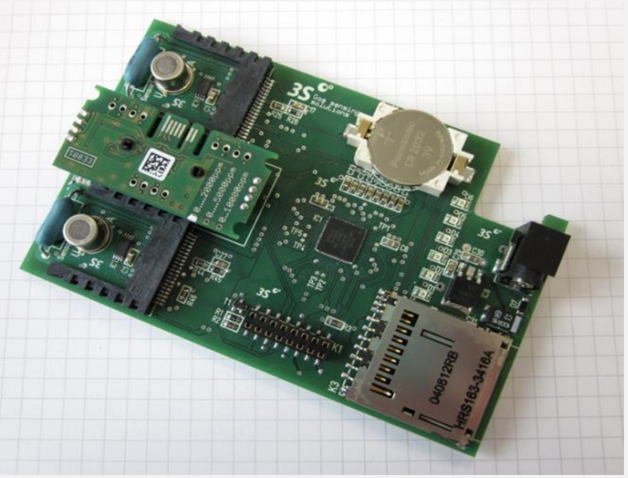
- Stand-alone field test systems by 3S GmbH (Saarbrücken, Germany)
- 2 MOS gas sensors (+ CO_2 + humidity) with independent temperature control
- Data storage on SD card

➢ **Conclusions:**

  ➢ better sensitivity and selectivity required

  ➢ **on-site calibration required**

Setup for system calibration



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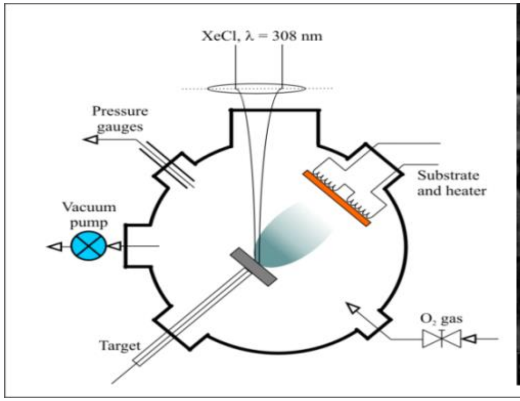
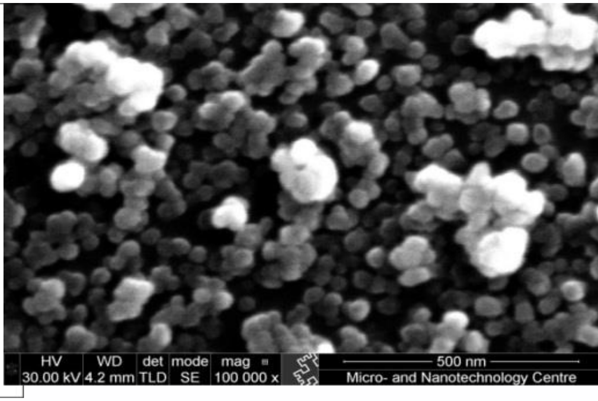
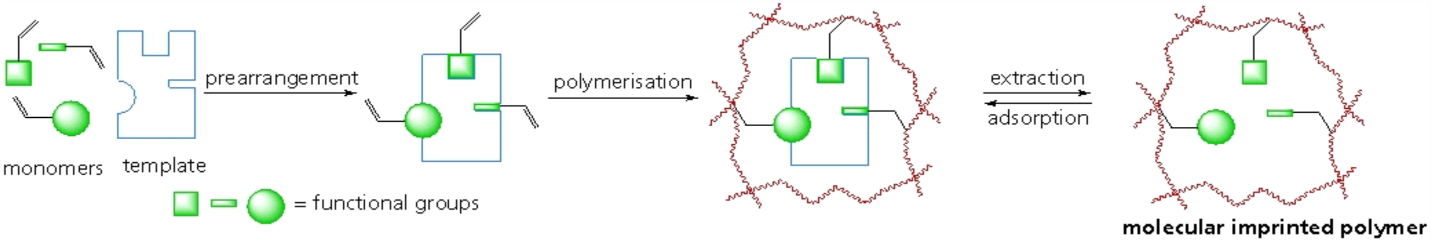
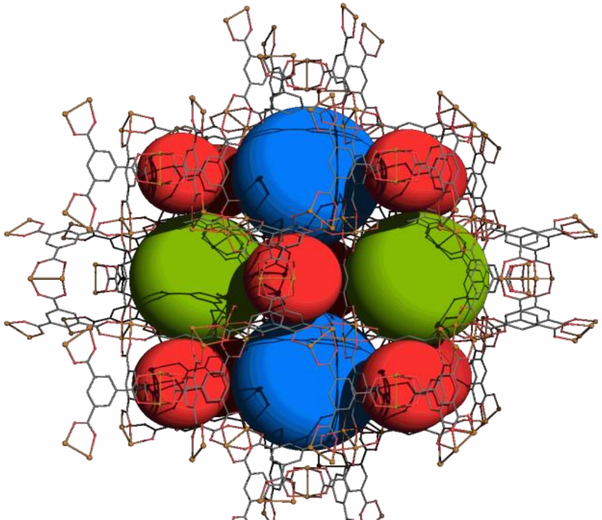
SENSIndoor technologies

- 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)









Approach for calibration/quantification

***Calibration idea**: based on two-phase equilibrium*

***Quantification idea**: make use of rate constants measured in temperature cycled operation*

Approach

(1) Realization of mobile calibration standards, based on a two-phase equilibrium

- General approach studied with simulations
- Reproducible preparation of various concentrations
- Comparison of calibration standards with analytical reference measurements (GC-MS)

(2) Improved quantification using MOX sensors: model-based approach using rate constants after temperature step changes (limited to µsensors, low thermal time constants)

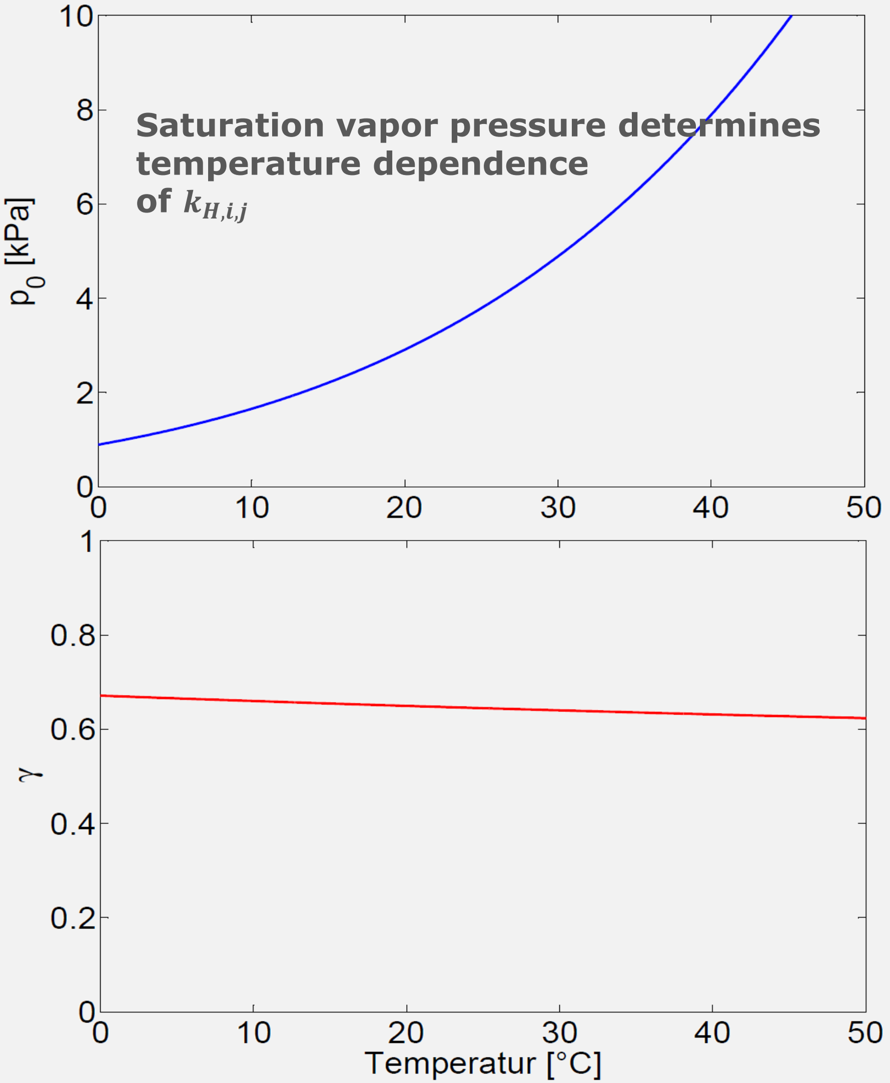
(3) Field tests (limited so far)

Realization of mobile calibration standards

- **Basics**
  - Gas phase concentration in a **two phase** system in thermodynamic equilibrium is determined by **vapor pressure** p_0
  - Vapor pressure of an ideal (liquid) mixture is proportional to the fraction x_i of substance i:

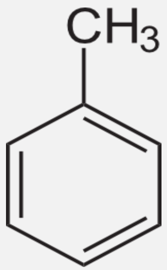
    Henry´s law $\boldsymbol{p_i = k_{H,i,j} \cdot x_i}$
  - Henry constant is specific for each combination of substances (modelling of the **activity** $\boldsymbol{a = \gamma \cdot x = \frac{p_i}{p_0}}$ can be based on UNIFAC model)
    („***uni****versal quasichemical* ***f****unctional group* ***a****ctivity* ***c****oefficients*")

[PA01]

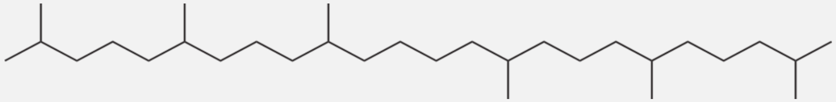


Saturation vapor pressure determines temperature dependence of $k_{H,i,j}$

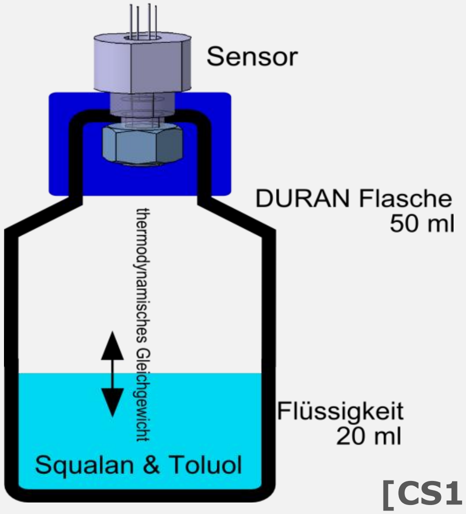
Realization of mobile calibration standards



- **Substances**
  - Toluene C_7H_8 → model VOC
    - Non-polar liquid, vapor pressure 2.91 kPa (20 °C) [AO14]
    - Used as reference for total VOC values in gas chromatography [MS13]
    - Simple handling



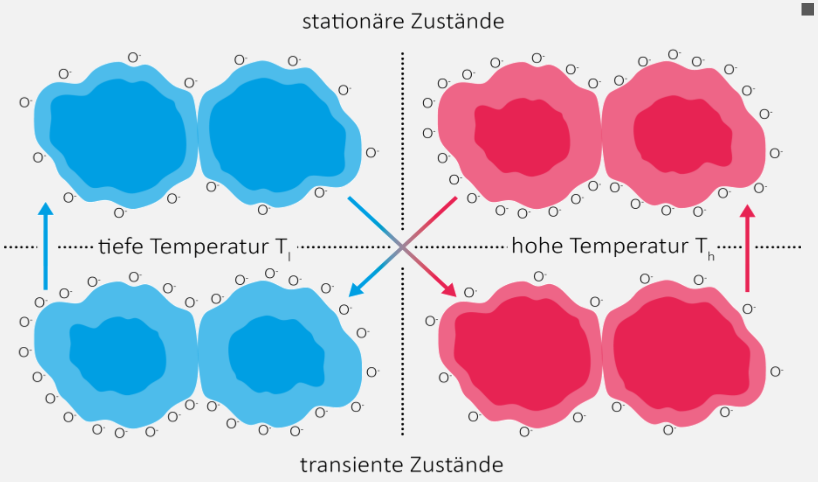
  - Squalane $C_{30}H_{62}$
    - Long-chained alkane, very low vapor pressure 0.02 µPa [VP94,SA14]
    - Non-polar liquid, no health concerns



[CS15a]

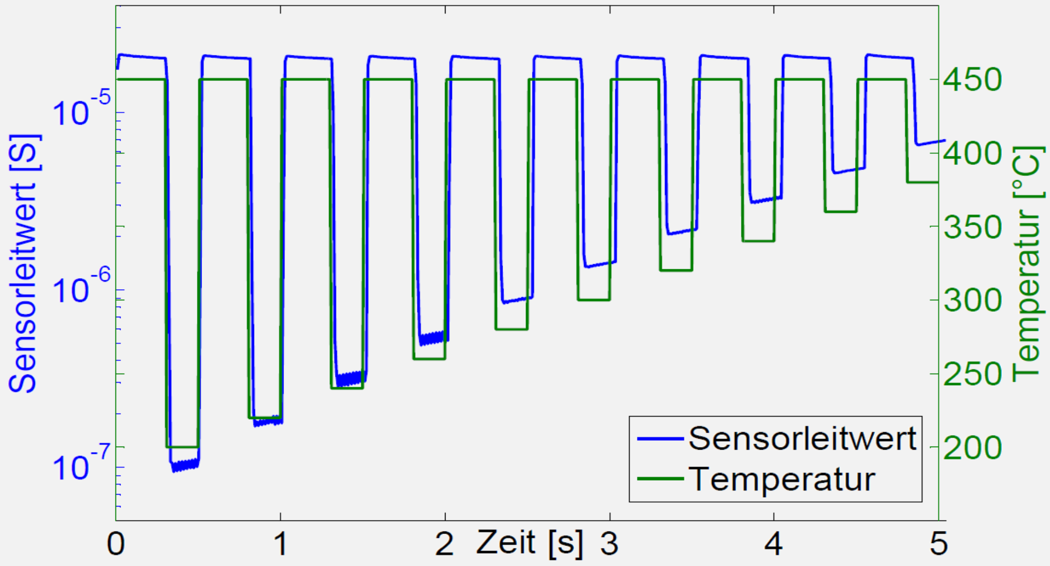
- **Simple test set-up**
  - Standard lab bottles (Duran Protect), volume 50 ml
  - Sensor mounted in regular PP screw cap
  - Measurement duration: min. 30 minutes
  - Magnetic stirrer for faster equilibration

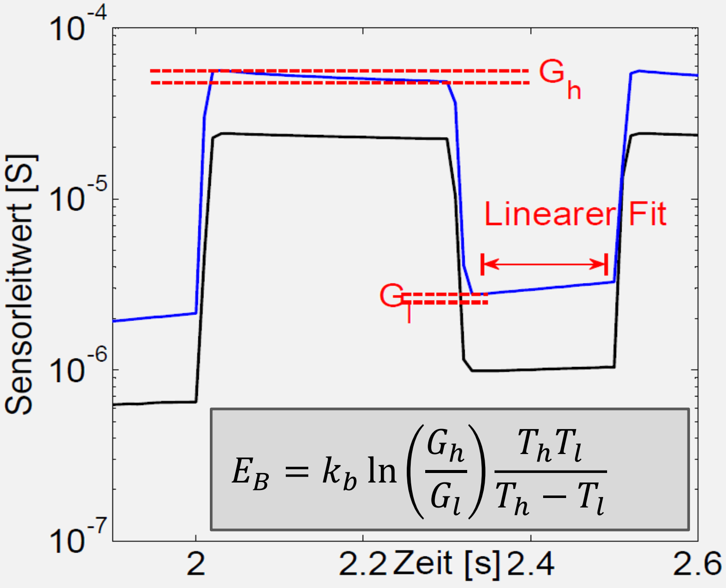
Improved quantification using MOX sensors



- **Sensor model (Tilman Sauerwald, Tobias Baur)**
  - G_{Sensor} is influenced by many parameters (mainly base conductance G_0, energy barrier E_B)
  - Change of E_B vs. time is evaluated (rate constants)
  - Expectation: different effects add up and linear dependence on concentration

$$\frac{d\ln(\mathrm{G})}{dt} = \frac{2 \cdot E_B(0)(k_{-A} + k_{gas})}{k_B T}$$





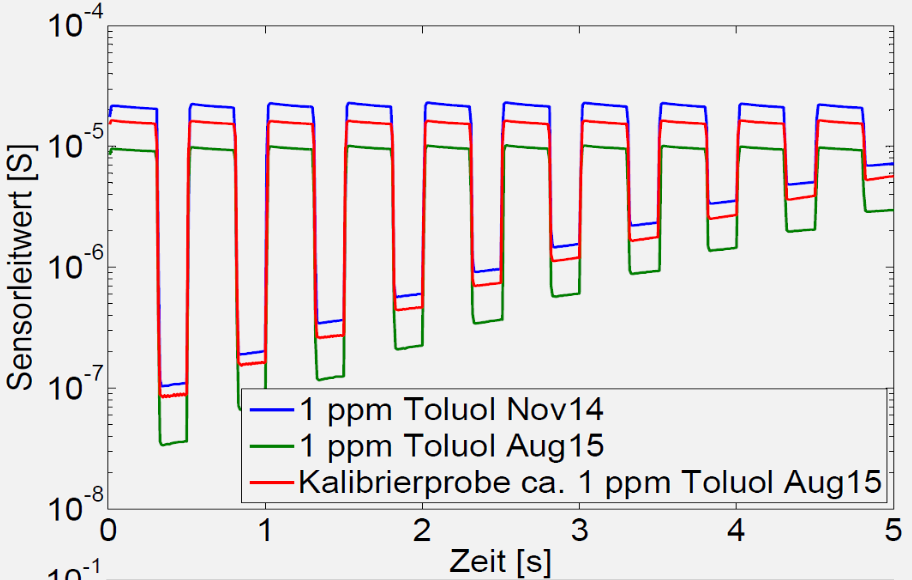
$$E_B = k_b \ln\left(\frac{G_h}{G_l}\right)\frac{T_h T_l}{T_h - T_l}$$

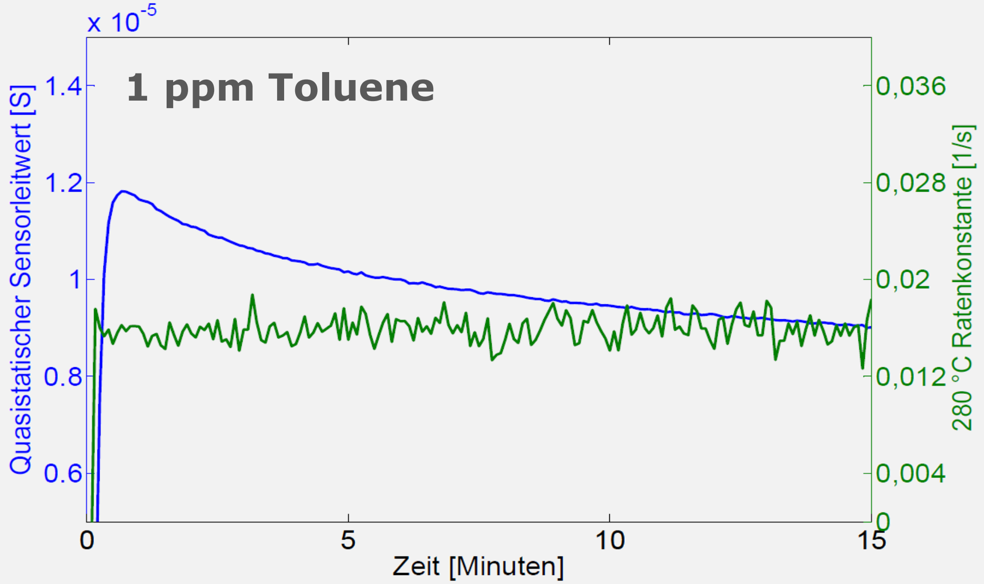
[TB14]

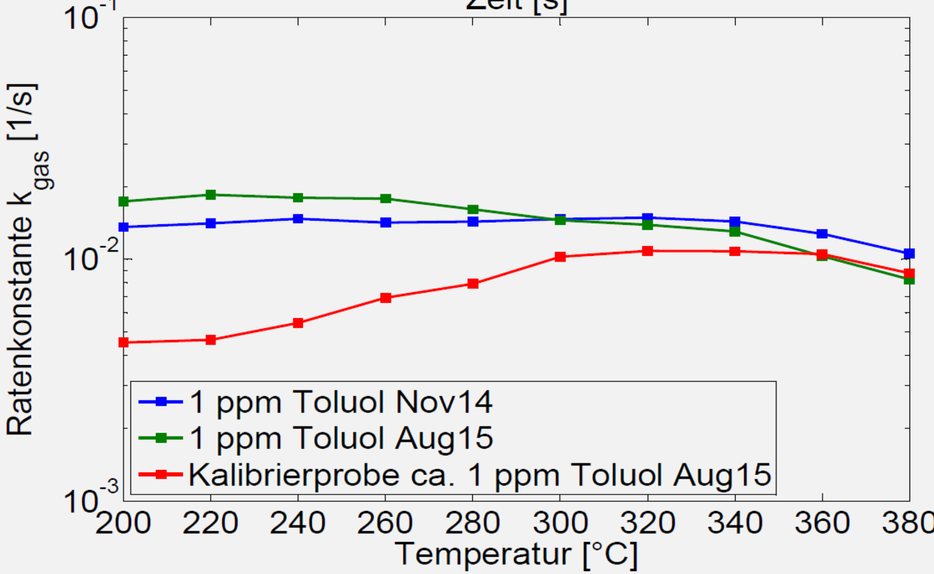
Improved quantification using MOX sensors

- **Comparison model & exp. results**
  - Short term drift (below):
    Overshoot of sensor conductance, constant (noisy) rate constant
  - Long term drift (right):
    Sensor aging & changing ambient conditions, relatively low influence on rate constants

[CS15a]







Realization of mobile calibration standards

- **Purification (!)**
  - Squalane is purified at 80 °C and 500 ml/min flow rate (zero air or nitrogen 5.0) for 72 h

Sensor signal (rate constant k, mean value for all temperatures) Chromatogramm

	Normal room air	Squalane (unpurified)	Squalane (zero air)	Squalane (nitrogen)
former TCO cycle	$1.55 \cdot 10^{-2} \frac{1}{s}$	$3.42 \cdot 10^{-2} \frac{1}{s}$	$1.46 \cdot 10^{-2} \frac{1}{s}$	
new TCO cycle	$1.1 - 1.2 \cdot 10^{-2} \frac{1}{s}$		$0.95 \cdot 10^{-2} \frac{1}{s}$	$0.73 \cdot 10^{-2} \frac{1}{s}$

- **Preparation**
  - Logarithmic dilution series (precision scale & micro pipette)
  - After each step: 15 minutes stirring for equilibration

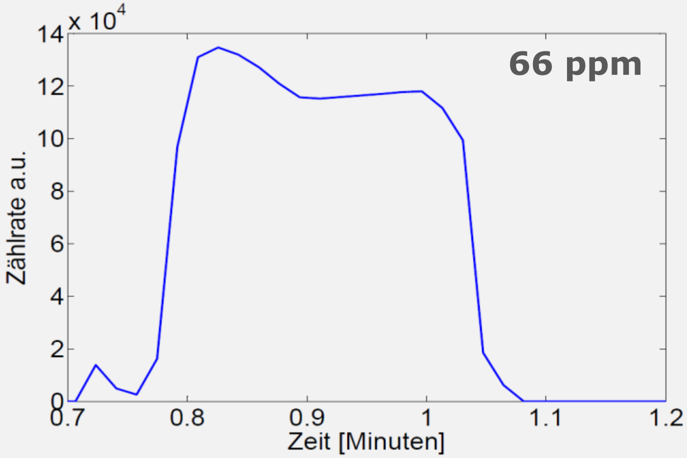
Lower than normal background?!

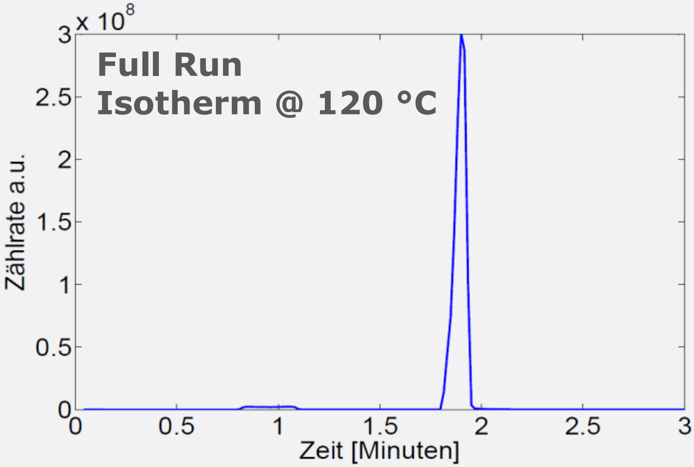
Fraction of Toluene in the liquid phase (concentration based on UNIFAC model at 20 °C in the headspace)

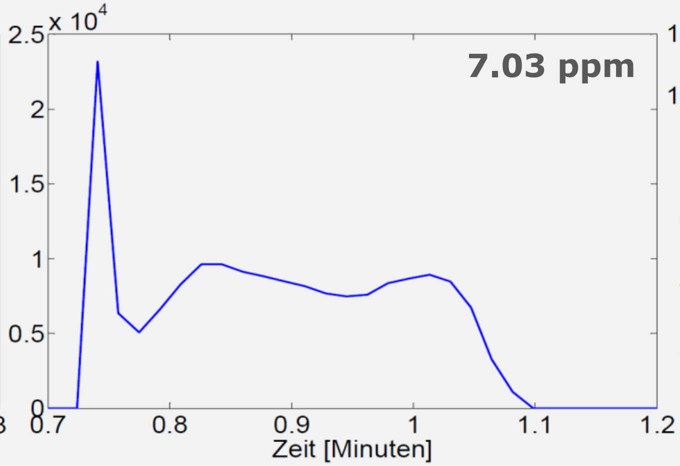
	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7
Dilution series 5	35.1 ‰ $(658\ ppm)$	3.52 ‰ $(66.0\ ppm)$	0.355 ‰ $(7.03\ ppm)$	0.0397 ‰ $(0.744\ ppm)$		
Dilution series 6	$190\ ppm$ $(3.13\ ppm)$	$64\ ppm$ $(1.11\ ppm)$	$19\ ppm$ $(0.325\ ppm)$	$6{,}6\ ppm$ $(0.114\ ppm)$	$2.0\ ppm$ $(0.0344\ ppm)$	$0.67\ ppm$ $(0.0117\ ppm)$

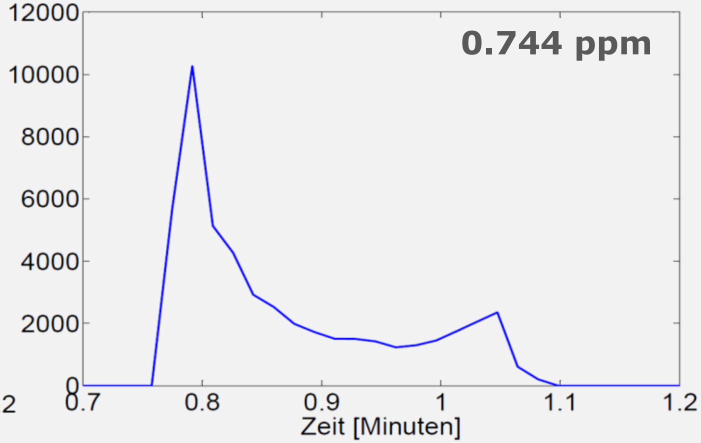
Realization of mobile calibration standards

- **Analytical reference**
  - Injection of 5 ml vapor in GC injector
  - Internal standard: 1 µl liquid Toluene to compensate instrument variations
  - Reference for quantification: headspace of pure Toluene









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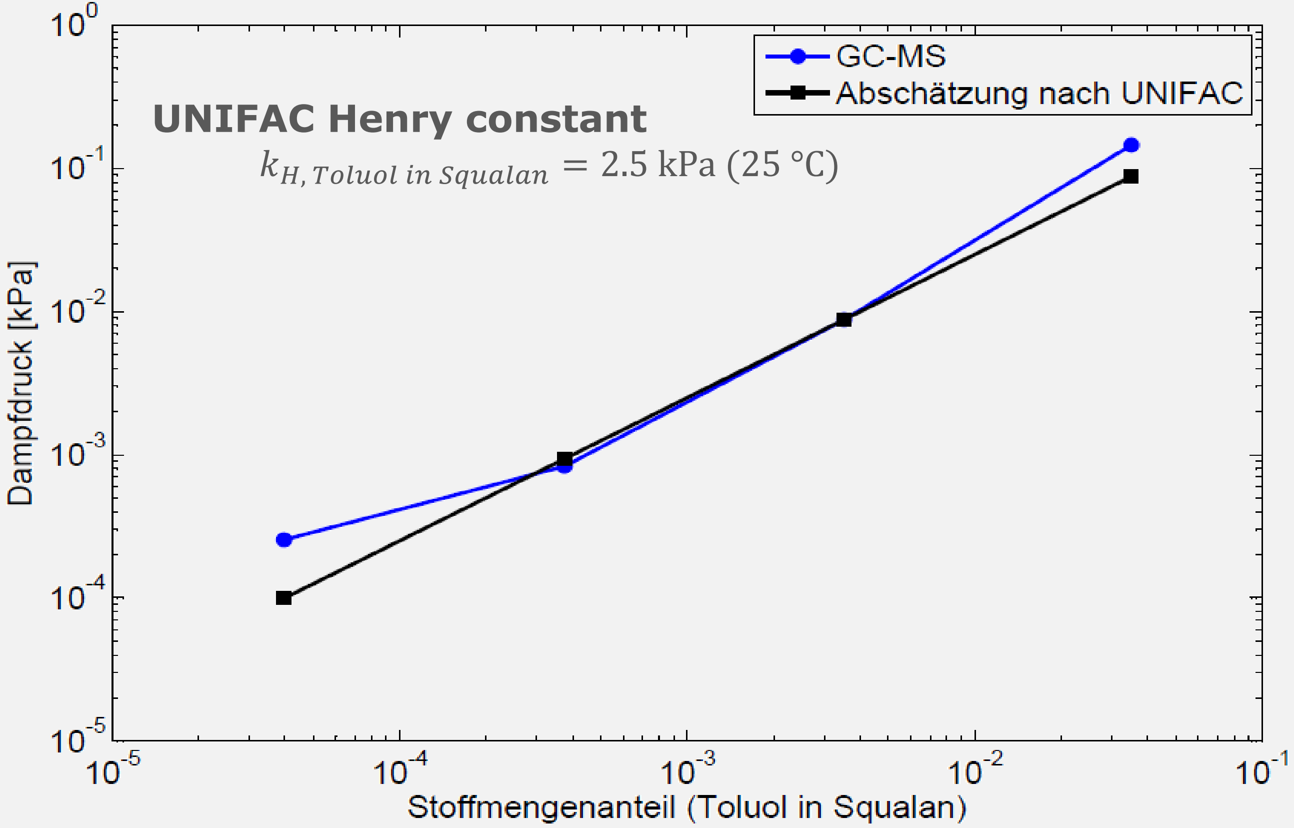
Realization of mobile calibration standards

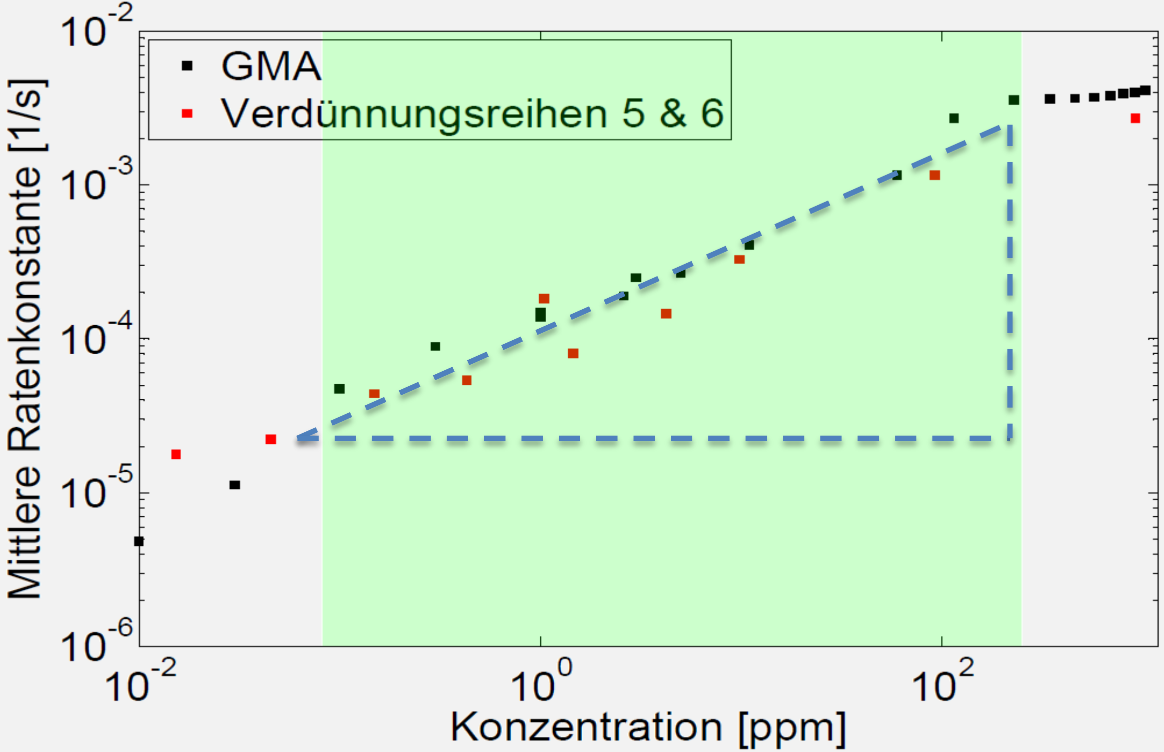


[CS15a]

- **Estimate of sample concentration uncertainties**
  - **Weighing and pipetting errors during preparation: < 5 %**
  - **Vapor pressure changes due to temperature: 5 % / °C**
  - **Lifetime of calibration standard up to 5 % error: 30 – 35 calibrations**
  - ➢ **Sufficient for TVOC field calibration**

Improved quantification using MOX sensors

- **Calibration curve using rate constant approach**
  - Nearly linear dependence in double logarithmic plot (i.e. $\mathrm{k_{gas}} = a \cdot c^{b}$) over wide concentration range
  - Quantification over nearly 5 orders of magnitude, saturation for high concentrations (limit of method/model), for low concentration electronic hardware needs to be improved
  - Sometimes large differences between gas mixing app and calibration standards, but: general trend is similar although backgrounds (zero air, room air) are quite different



[CS15a]

CONCLUSIONS

- Improved quantification with MOX sensors based on TCO and rate constant determination (model based approach)
  - Suitable especially between 100 ppb and 100 ppm
  - More stable compared to resistance → suppression of baseline effects
- Novel approach for on-site calibration based on two-phase equilibrium and liquid mixtures
  - Also **provides on-site zero air** when pure Squalane is used (VOCs from the ambient dissolve in Squalane, greatly reducing concentration)
  - Temperature dependence of vapor pressure limits the overall accuracy under normal ambient conditions

OUTLOOK

- Improved measurement hardware
  - Able to accurately measure up to GOhm in milliseconds (!)
  - Low noise
- Novel adaptive measurement methods
  - Instead of fixed temperature steps adjust temperature to control E_B
  - Wait for specific relaxation and determine necessary time as signal
- Experiments with further VOCs (benzene, formaldehyde, naphthalene for IAQ) and VOC mixtures
- Temperature stabilized calibration standards
- Gel or membrane based calibration standards for easier handling

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Tobias Baur (bachelor thesis sensor model)

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Tilman Sauerwald (idea and thesis supervision)

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the whole team at LMT

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