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

COST Action TD1105

OPEN SESSION COST *EuNetAir* on

New Sensing Technologies for Air Quality Monitoring

CORE-GROUP MEETING at EUROSENSORS-2014 Conference

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Highly Sensitive and Selective VOC Detection for Indoor Air Quality Applications

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Saarland University / Germany

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Why worry about indoor air?

- Safety
  - Gas leak detection (combustible gases, e.g. CH_4)
  - Fire detection (various gases)
  - Hazardous gas detection (e.g. CO)
- Malodor detection (kitchen & bathroom ventilation)
- HVAC systems
  - Reduced air circulation for greatly reduced energy consumption
    - ➢ CO_2 monitoring for fresh air
  - Mold detection / prevention
  - Increased levels of VOCs lead to sick building syndrome
    - ➢ Selective (formaldehyde, benzene etc.) and sensitive (ppb level) detection
  - Systems have to be adapted to the specific room use scenario

Sensor requirements

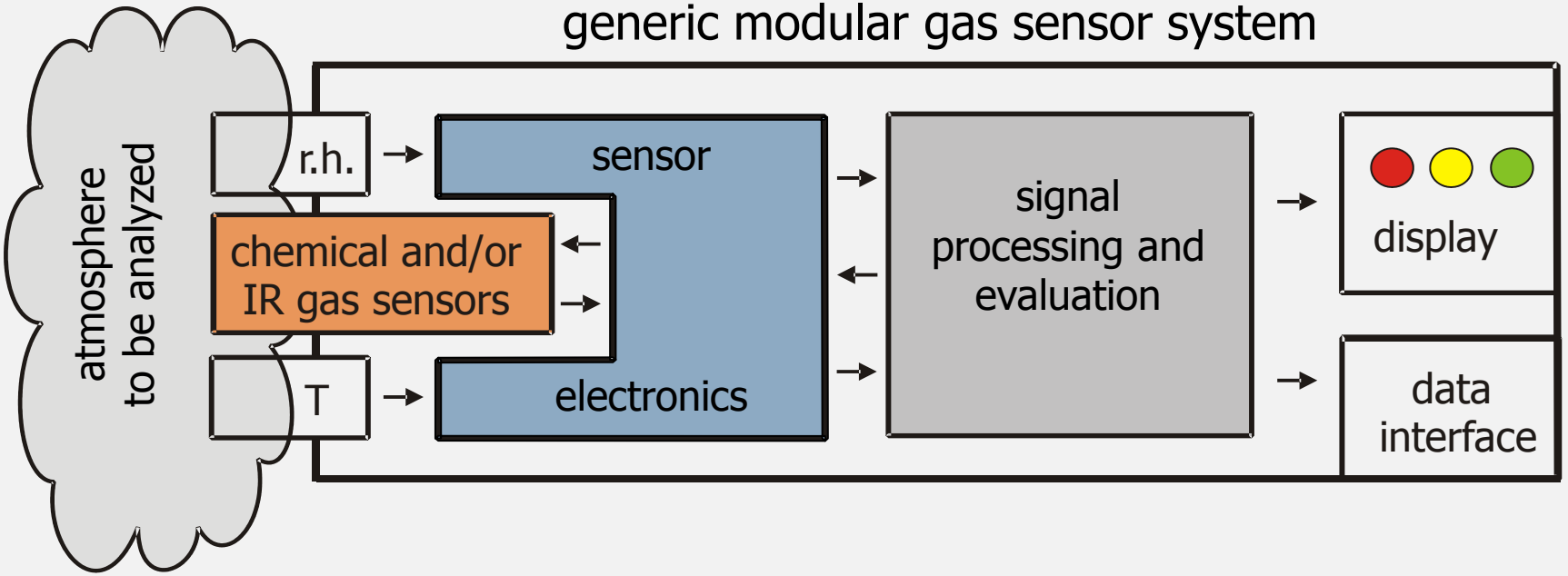
- Low cost
- Networked systems (in major buildings, but also private homes)
- Long lifetime: >10 years without maintenance for private homes

Which sensors are used today?

- Safety
  - Gas leak detection: human nose, Japan: MOS; pellistors: only industrial use
  - Fire detection: various sensors, mostly optical;
    gas sensor systems under development (EC, MOS, GasFET)
  - Hazardous gas detection: EC, MOS
- Malodor detection: MOS
- HVAC systems
  - CO_2 monitoring: NDIR (in major rooms/buildings), EC & GasFET (emerg.)
  - VOCs: MOS (total VOC), GasFET (emerging)

The three "S"

- Sensitivity
  - Broad spectrum
    from below ppb (for malodors, ozone, hazardous VOCs)
    up to 1000 ppm (gas leak, CO_2)
- Selectivity
  - False alarms are primary concern for fire detection (ratio 10:1)
  - VOC detection: hazardous (formaldehyde) vs. neutral (alcohol vapor, cleaning agents) vs. wanted (odorants)
- Stability
  - Industrial applications: maintenance interval < 6 months
  - Public buildings: annual or bi-annual tests (if that)
  - Private homes: 10 years lifetime w/o regular maintenance?

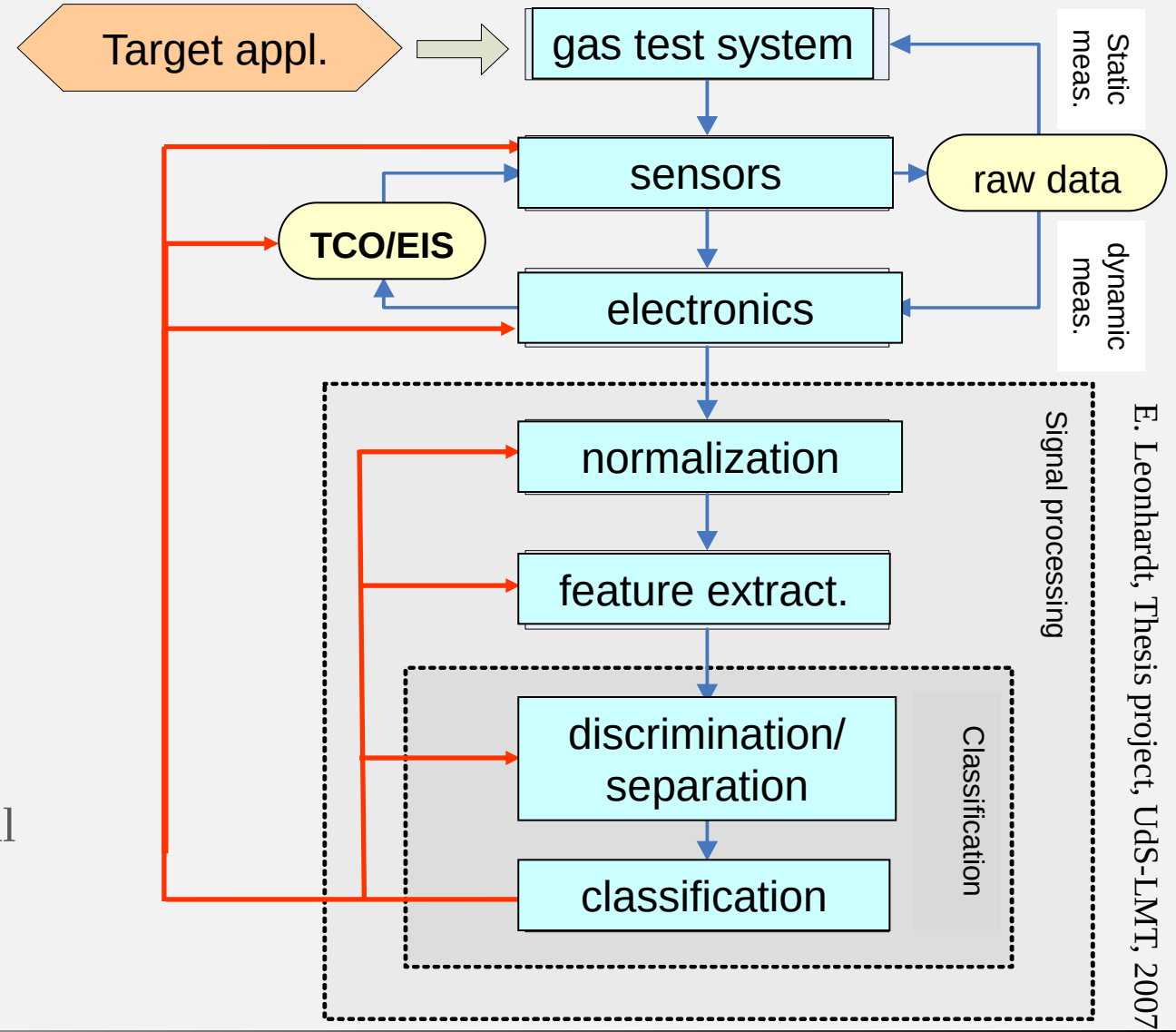

generic modular gas sensor system
atmosphere to be analyzed
r.h.
T
chemical and/or IR gas sensors
sensor
electronics
signal processing and evaluation
display
data interface

Gas measurement systems – more than sensors dynamic operation and system optimization

Many possibilities for optimization:

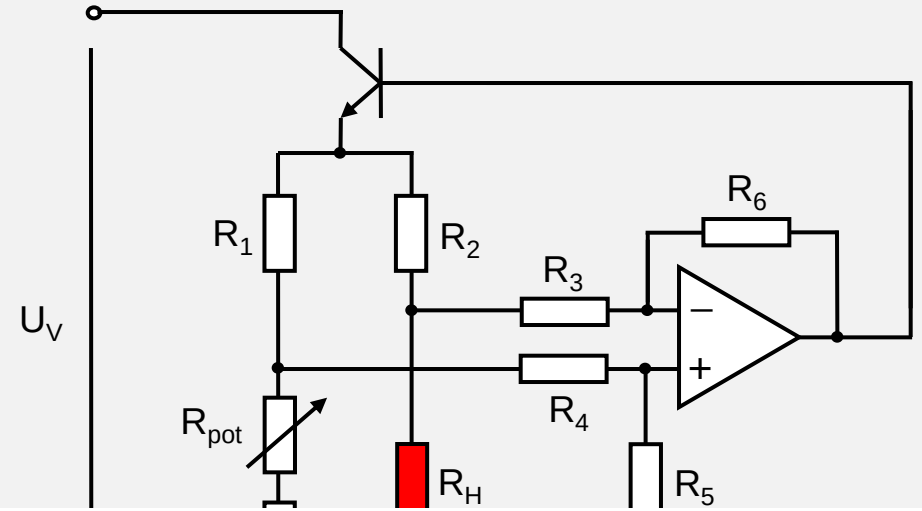
- Sensor selection
- Operating mode
  - TCO
  - EIS
  - GBCO
- Data acquisition
- Signal preprocessing
- Feature extraction
- Separation
- Classification

…and **always** testing under real application conditions (field testing)!



Hardware platform GasTON for exact temperature control and large dynamic range data acquisition – Gas sensor T-cycle Operating uNit

- Heater temperature control
  Heater resistor $R_H(T)$ controlled for exact temperature control of (micro-)hotplates
- Sensor read-out with large dynamic range
  for MOS, GasFET and pellistor type sensors



➢ **now commercialized "OdorChecker"**
by 3S GmbH (spin-off of LMT)

VOC-IDS: Volatile Organic Compound Indoor Discrimination Sensor

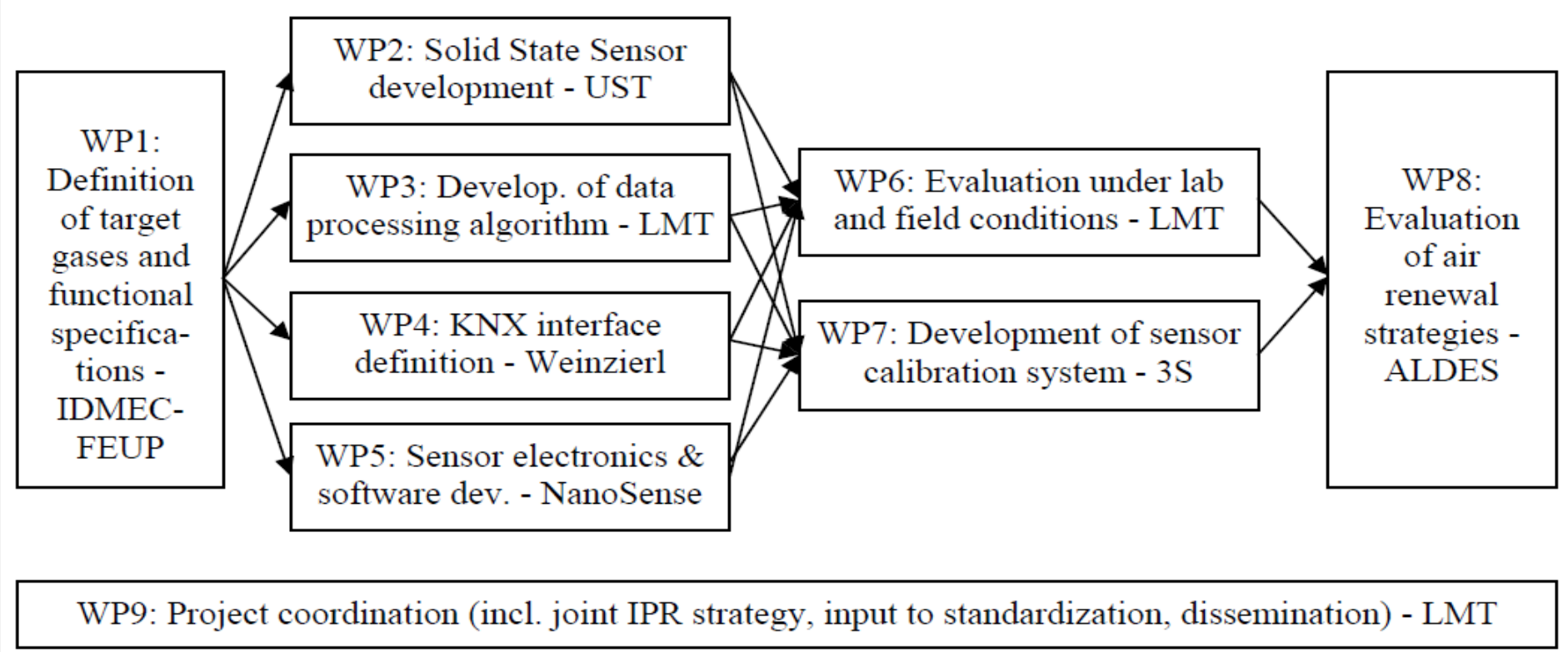
- Transnational project funded within MNT-ERA.net
- Selective VOC detection, primarily formaldehyde, benzene
- Novel ceramic nanomaterial metal-oxide semiconductor gas sensors
- Intelligent signal processing based on temperature cycling
- Networked systems connected to KNX bus

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

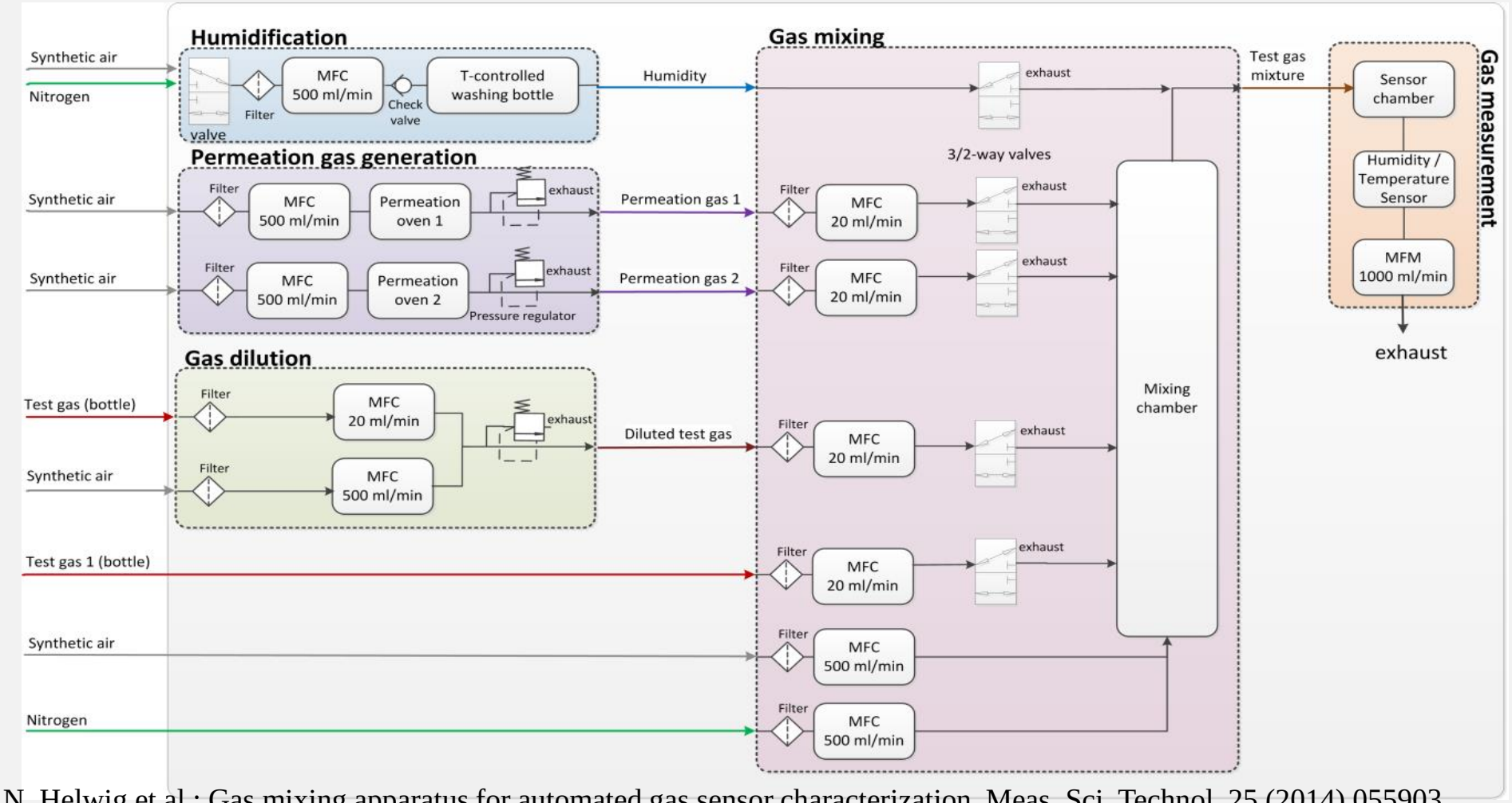
- EU-FP7 project NMP.2013.1.2-1:
  Nanotechnology-based sensors for environmental monitoring
- Microtechnology based approach for MOS and SiC-GasFET sensors
- Pre-concentration to boost sensitivity and selectivity
- Integrated multi-sensor approach
- Application specific priorities and field tests

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



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



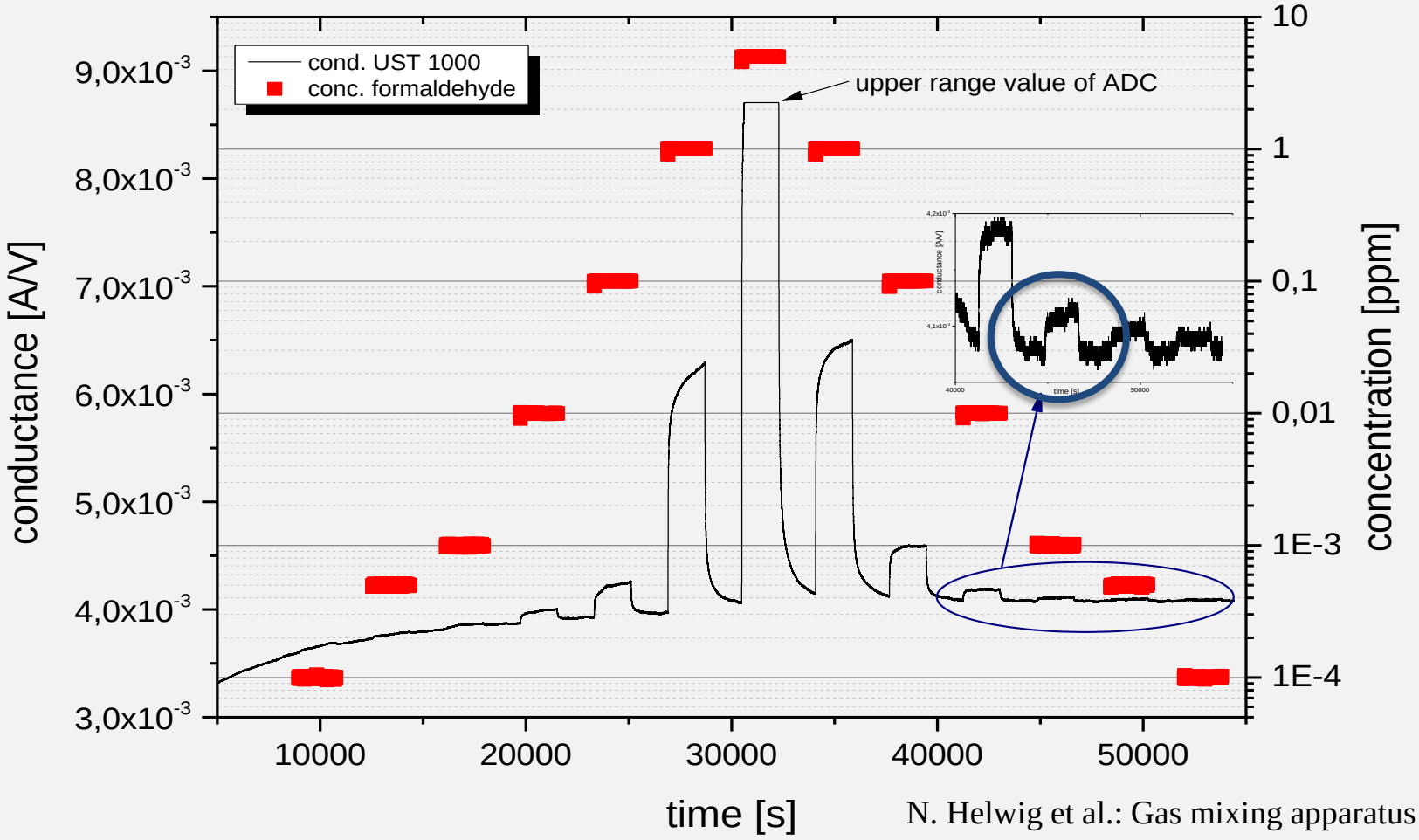
N. Helwig et al.: Gas mixing apparatus for automated gas sensor characterization, Meas. Sci. Technol. 25 (2014) 055903

Gas mixing system: results of reference measurements (zero air)

compound	CAS no	c [µg/m³]	c [ppb]
benzene	71-43-2	0.17	0.053
toluene	108-88-3	0.06	0.016
chlorobenzene	108-90-7	0.26	0.056
camphene	79-92-5	0.29	0.052
benzaldehyde	100-52-7	0.2	0.046
phenol	108-95-2	0.3	0.06
benzonitrite	100-47-0	0.61	0.144
octanal	124-13-0	0.1	0.019
benzyl alcohol	100-51-6	0.19	0.043
acetophenone	98-86-2	0.62	0.126
naphthalene	91-20-3	0.24	0.046
bicyclol[2.2.1]-heptane,2-chloro-2,3,3-trimethyl	465-30-5	16.2	2.6
TVOC		24.3	

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

Novel gas mixing system: results of first sensor tests



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

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

MNT-ERA.net project VOC-IDS

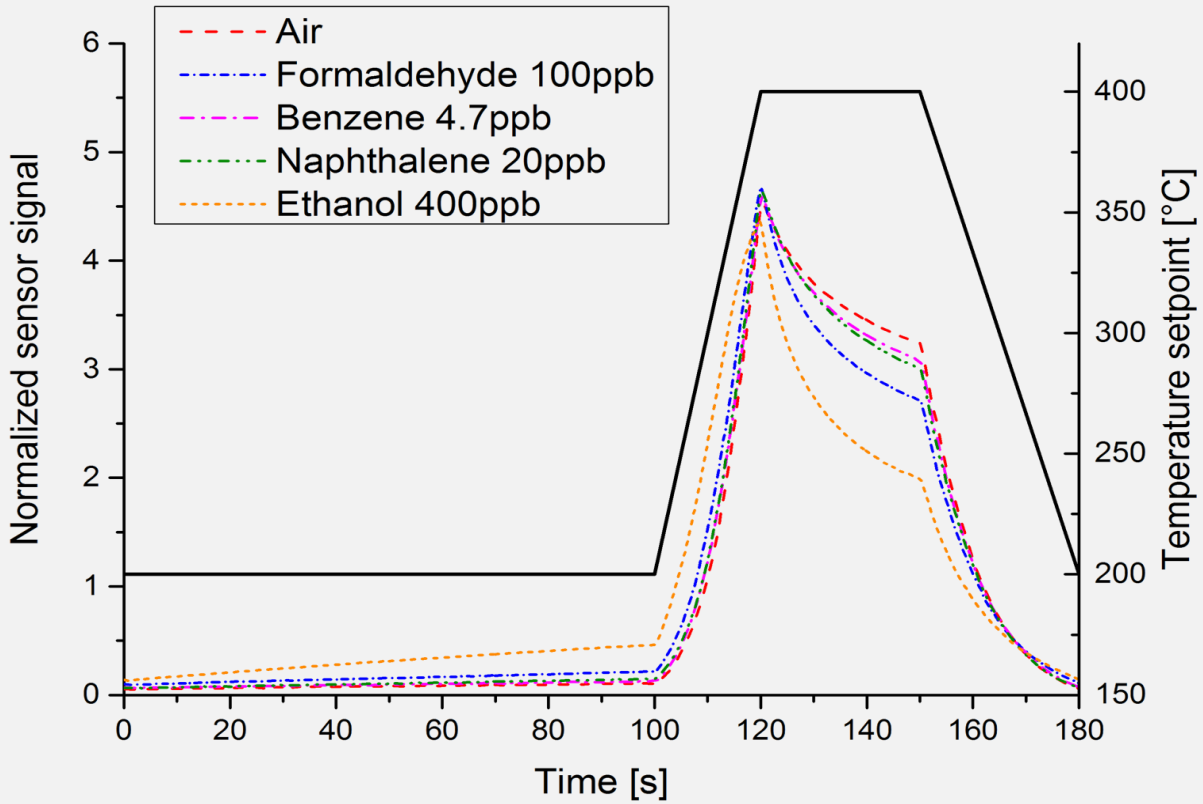
- Example for selective detection of VOCs in interfering background
- Classification of Formaldehydye, Benzene, Naphthalene in presence of ethanol

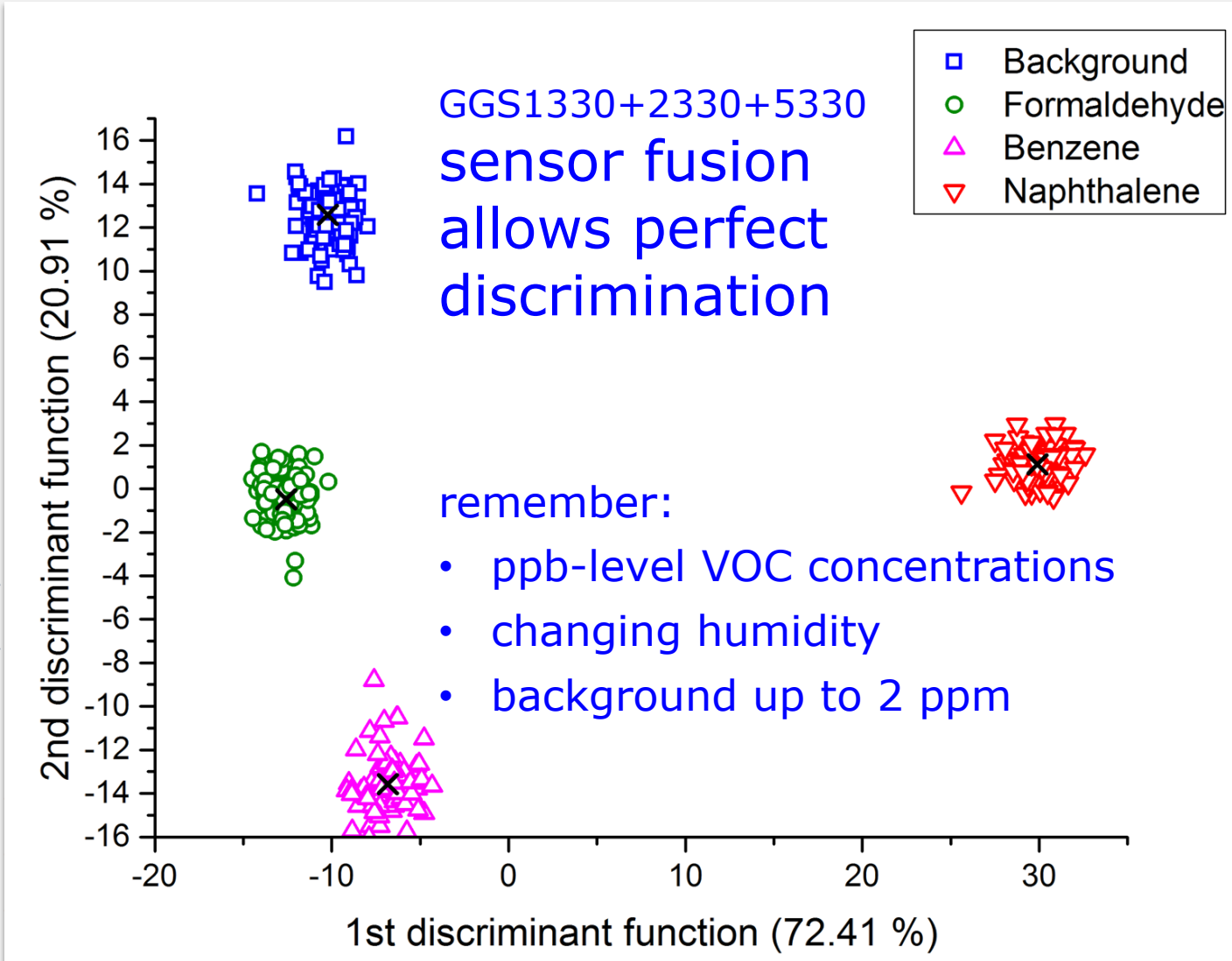
target gas	Concentration (ppb)	humidity	Interferents (EtOH ppm)
Air	NA	40%, 60%	none, 0.4, 2
Formaldehyde	10, 100	40%, 60%	none, 0.4, 2
Benzene	0.5, 4.7	40%, 60%	none, 0.4, 2
Naphthalene	2, 20	40%, 60%	none, 0.4, 2

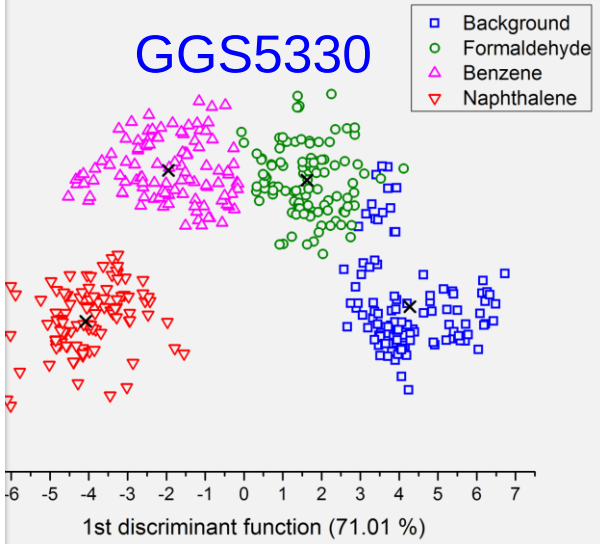
interferent concentrat.	relative humidity	number of LDA steps for charac.	Estimated number of LDAs	
0, 0.4, 2	40%, 60%	1	1	generalized classification
known	40%, 60%	2	1+10(?)*1	classification w known EtOH
0, 0.4, 2	known	1 (2)	(1+) 5*1	classification w known r.h.

- Used sensors are slow but sensitive (types 1330, 2330 and 5330; UST Umweltsensortechnik GmbH, Germany; thick film ceramic substrate MOS sensors)

- Many gas-specific effects occur during and after transition between temperatures (relaxation effects)
- Optimized operation
- Application specific signal processing




Background
Formaldehyde
Benzene
Naphthalene
GGS1330+2330+5330
sensor fusion
allows perfect
discrimination
remember:
• ppb-level VOC concentrations
• changing humidity
• background up to 2 ppm
2nd discriminant function (20.91 %)
1st discriminant function (72.41 %)
2nd discriminant function (36.7 %)

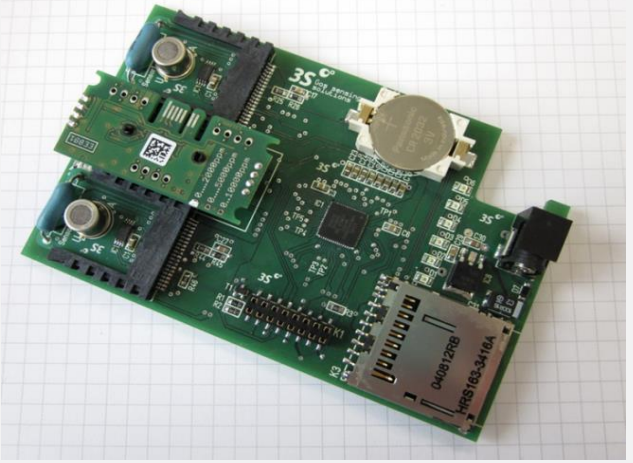

GGS5330
Background
Formaldehyde
Benzene
Naphthalene
1st discriminant function (71.01 %)

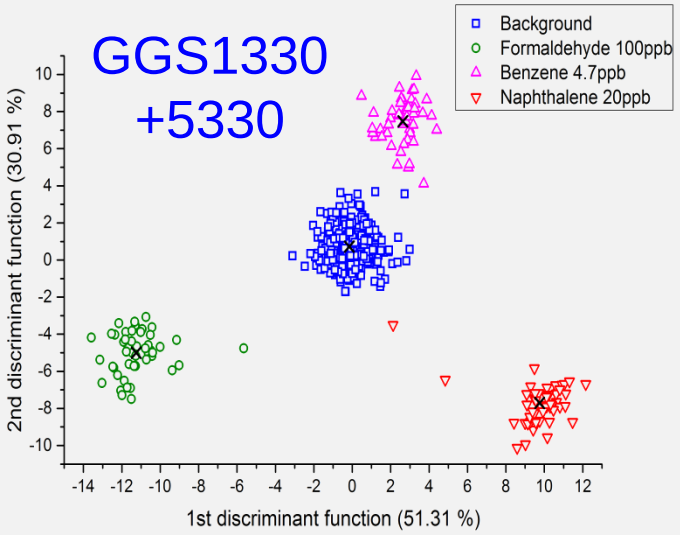
LEHRSTUHL FÜR MESSTECHNIK

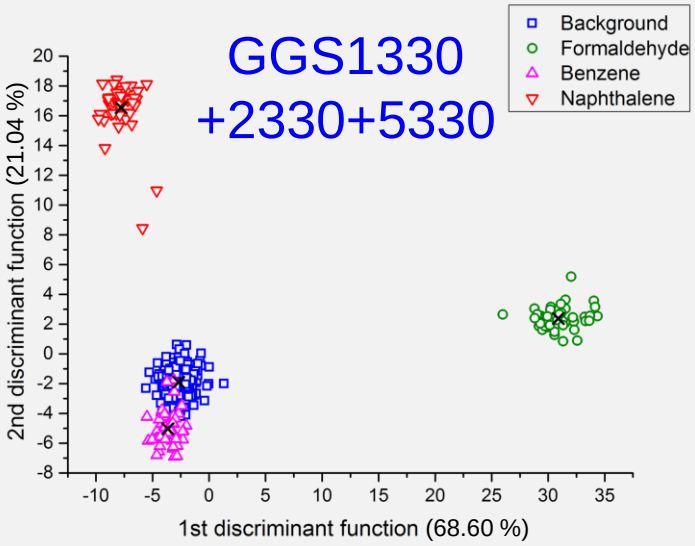
mnt-era.net

- 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
- Same test gas profile as for sensors only

Setup for system calibration

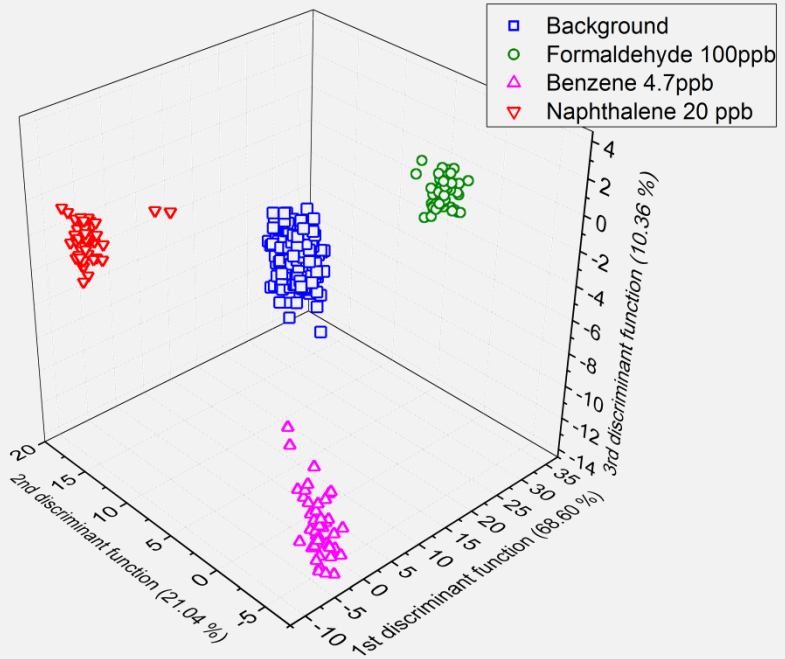






- Reduced discrimination due to VOC background from sensor systems, i.e. PCB, plastic housing
- Good discrimination of higher VOC concentrations
- Sensor fusion improves results considerably
- Further improvement with 3D LDA
- Promising results of initial field tests

3D →



SENSIndoor overview

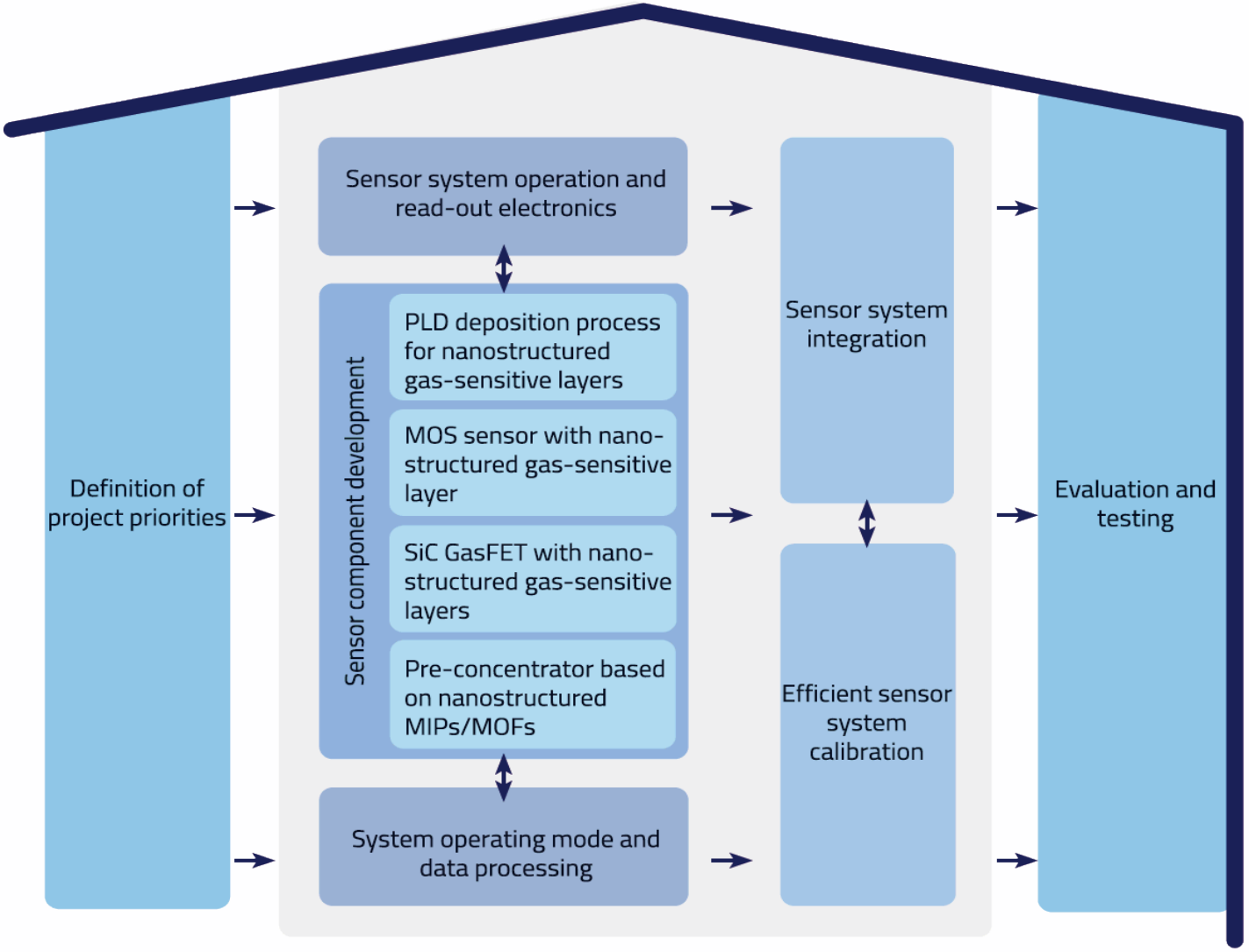
Project

SENSIndoor

Funded by EU-FP7 grant agreement No 604311

For more information visit

www.sensindoor.eu

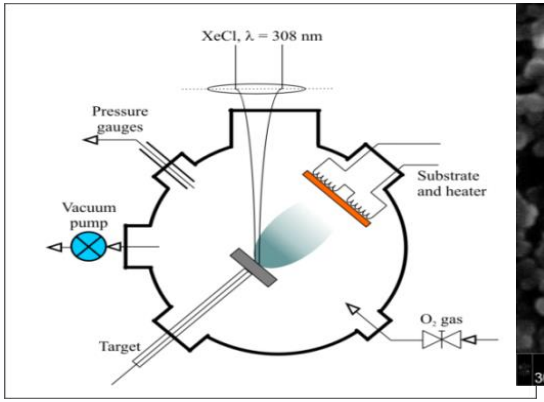


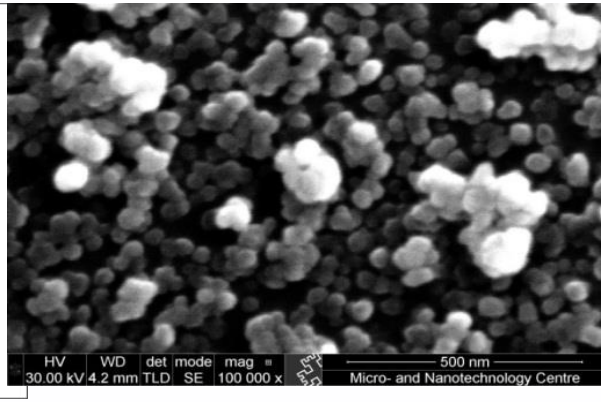
SENSIndoor origins

- **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., Eurice
  - Several topics identified to be addressed in call **NMP.2013.1.2-1 Nanotechnology-based sensors for environmental monitoring**

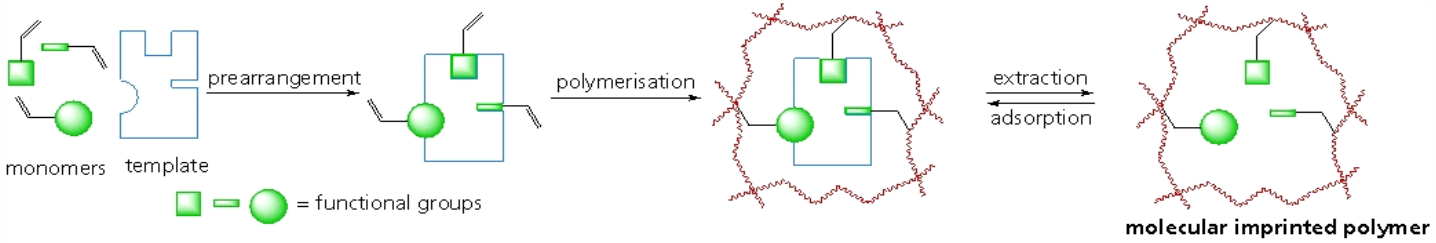
SENSIndoor technologies 1

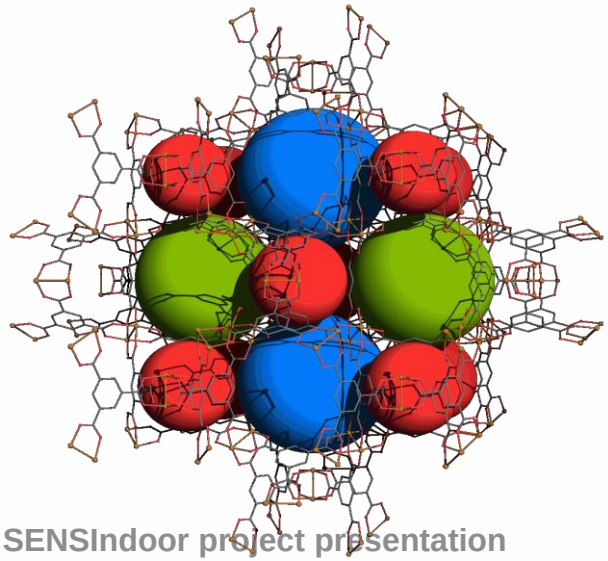
- Nanotechnology for improved sensor elements
  - **Pulsed Laser Deposition** (*U Oulu, Picodeon*)
    for novel, highly sensitive gas-sensitive layers suitable for wafer level mass production





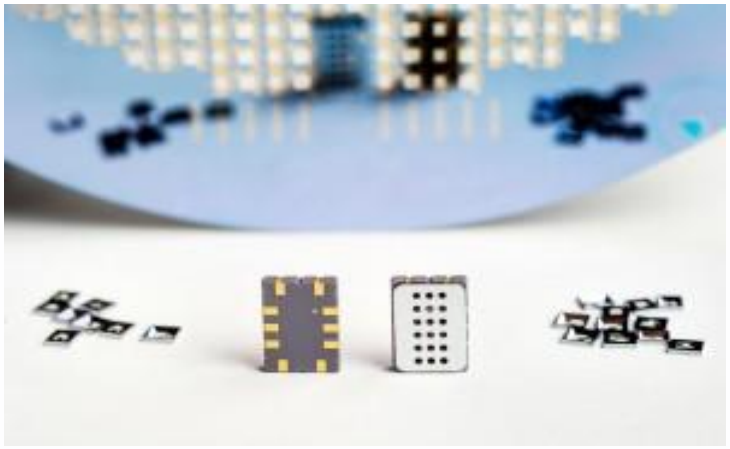
  - **Selective pre-concentration** (*FhG-ICT*)
    based on MOFs (metal-organic frameworks) → and MIPs ↓ (molecular imprinted polymers)

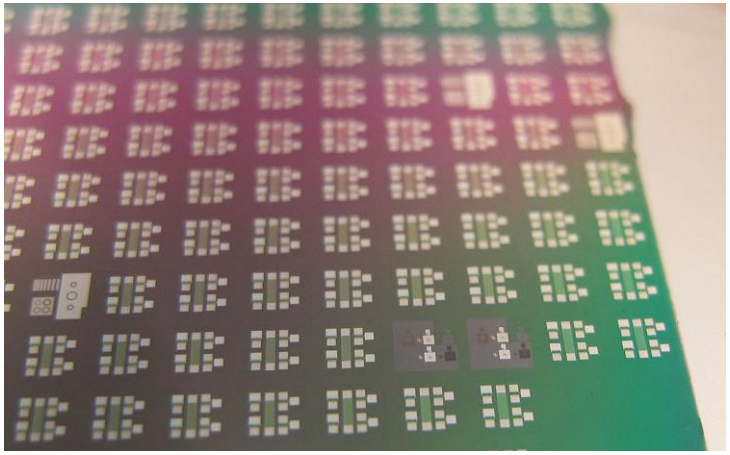




SENSIndoor technologies 2

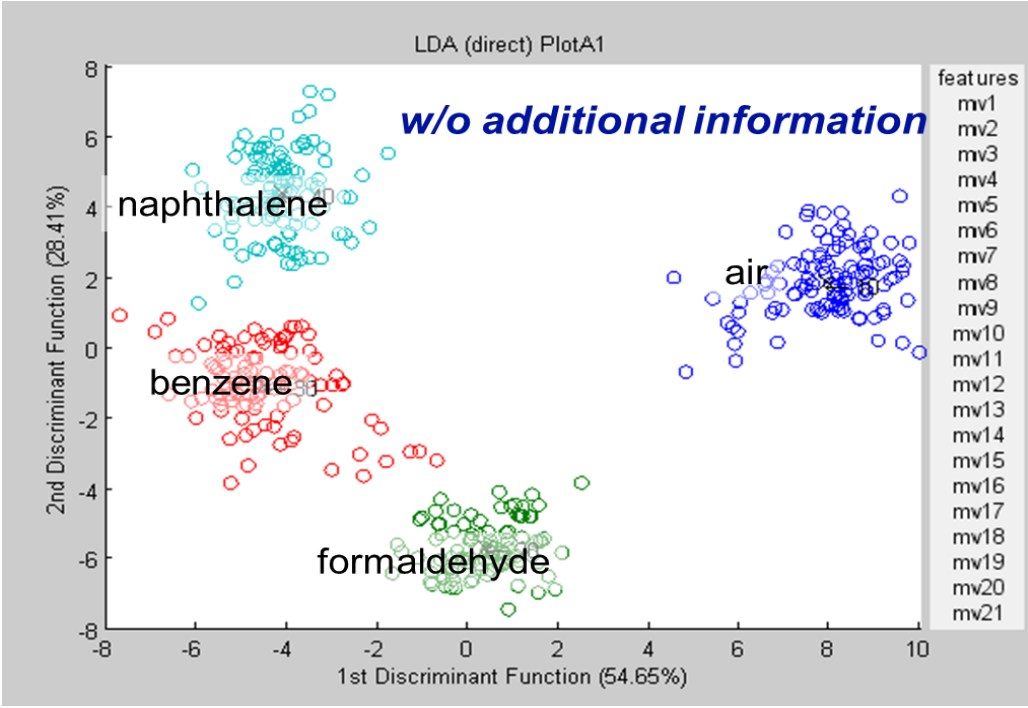
- Sensor technologies
  - **MOS – Metal oxide semiconductor** (*SGX Sensortech, USAAR-LMT*)
    - well known for high sensitivity and robustness @ low-cost
    - MEMS technology for mass production and low power consumption
  - **GasFET – Gas-sensitive Field Effect Transistors** (*LiU, SenSiC*)
    -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

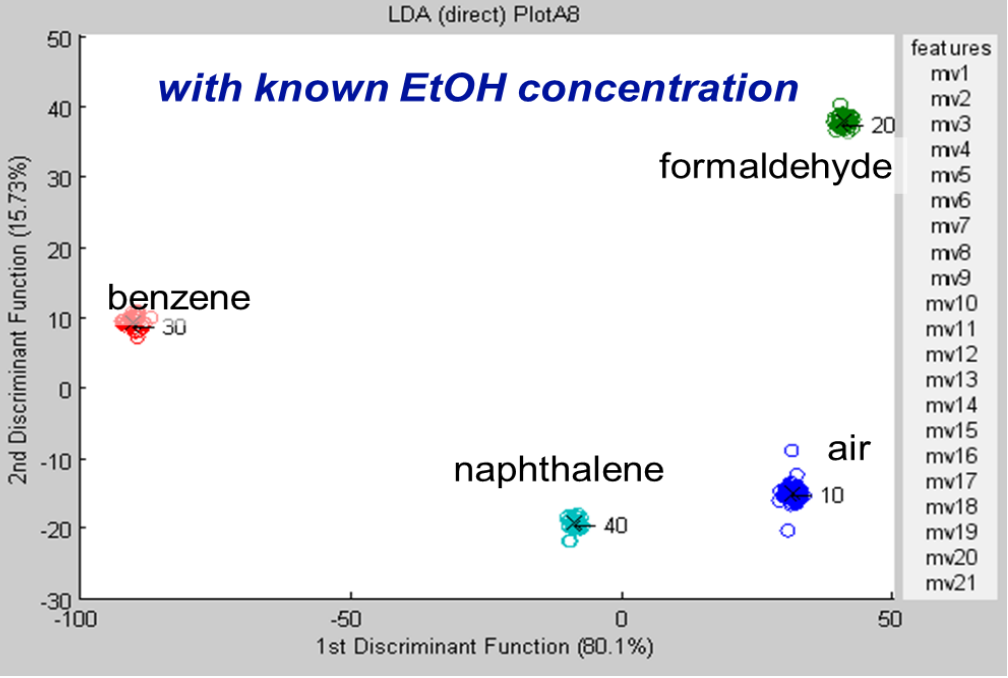




SENSIndoor technologies 3

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





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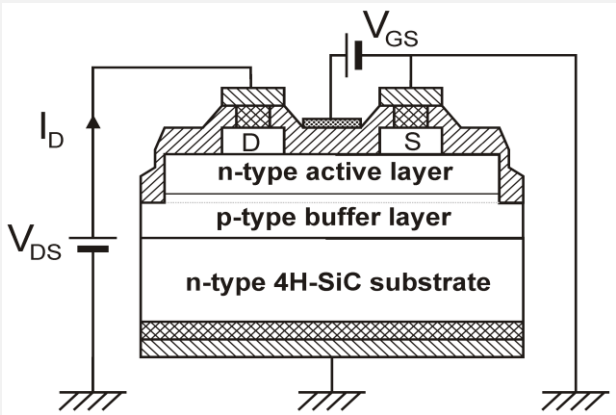
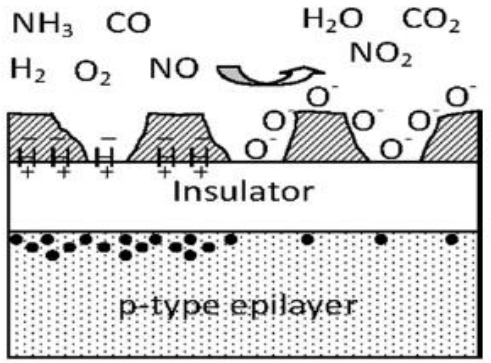
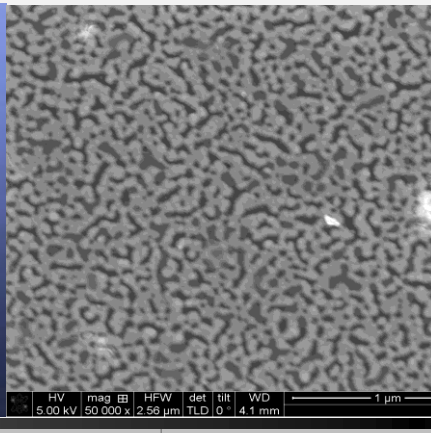
- SiC – Field Effect Transistors
  - Porous gate contacts (Pt, Ir)
- Gas interaction with the gate and insulator
  - Additional (internal) gate bias
- Shift in IV curve
  - Measured at constant current I_D or voltage V_{DS}
- Selectivity enhancement by dynamic operation
  - Temperature Cycled Operation (TCO)
- Goals: VOC discrimination and quantification

SENSIndoor

Joint PhD project of Christian Bur in collaboration with Linköping University, Prof. Anita Lloyd Spetz







LEHRSTUHL FÜR MESSTECHNIK

- **Discrimination** tested with 3 concentrations per VOC
- Tests performed at 20 % + 40 % r.h.

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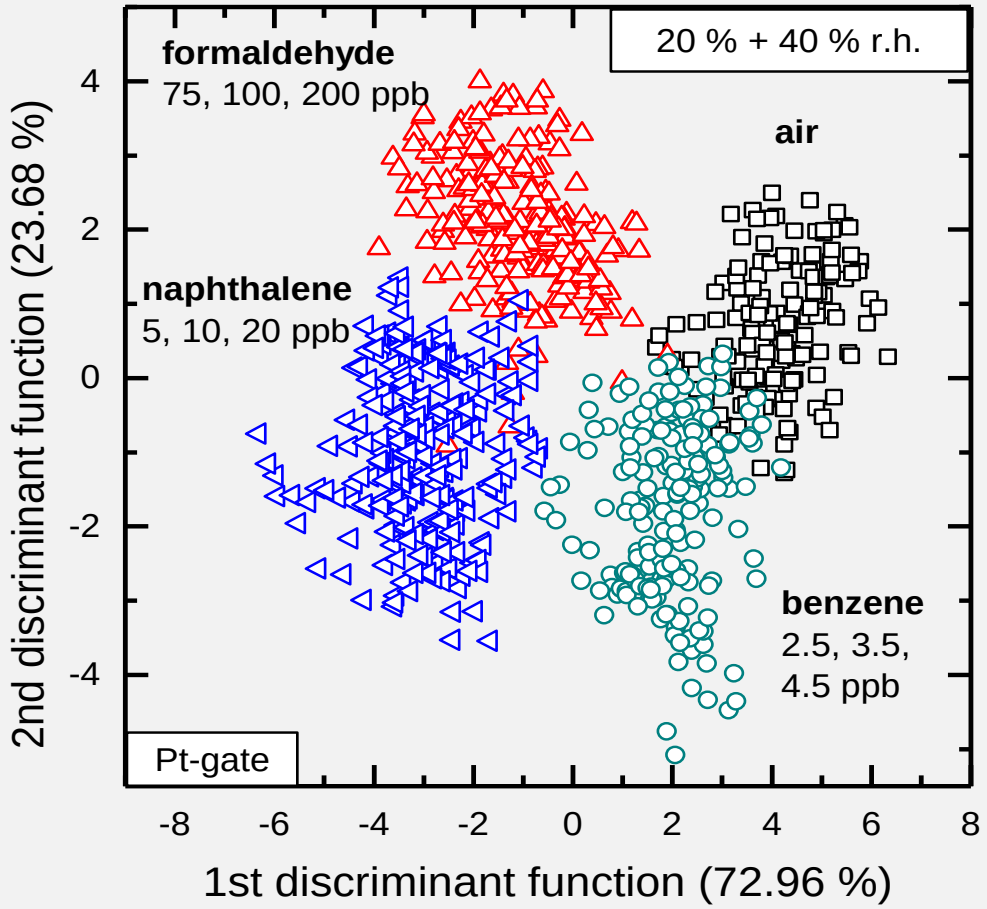
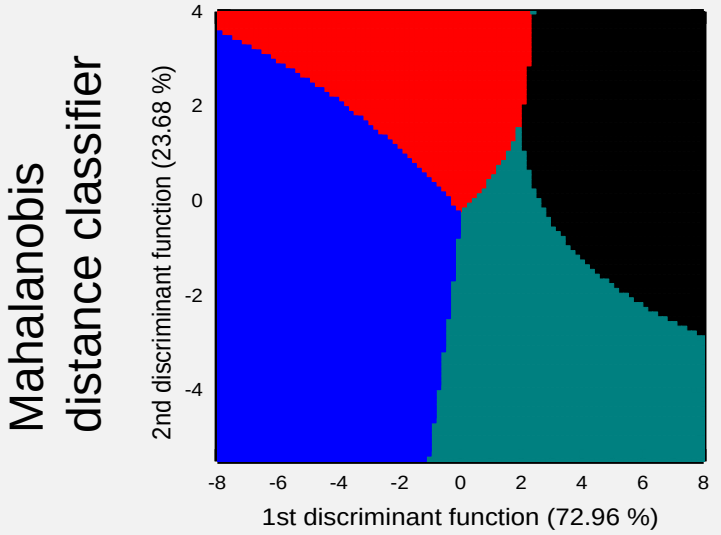


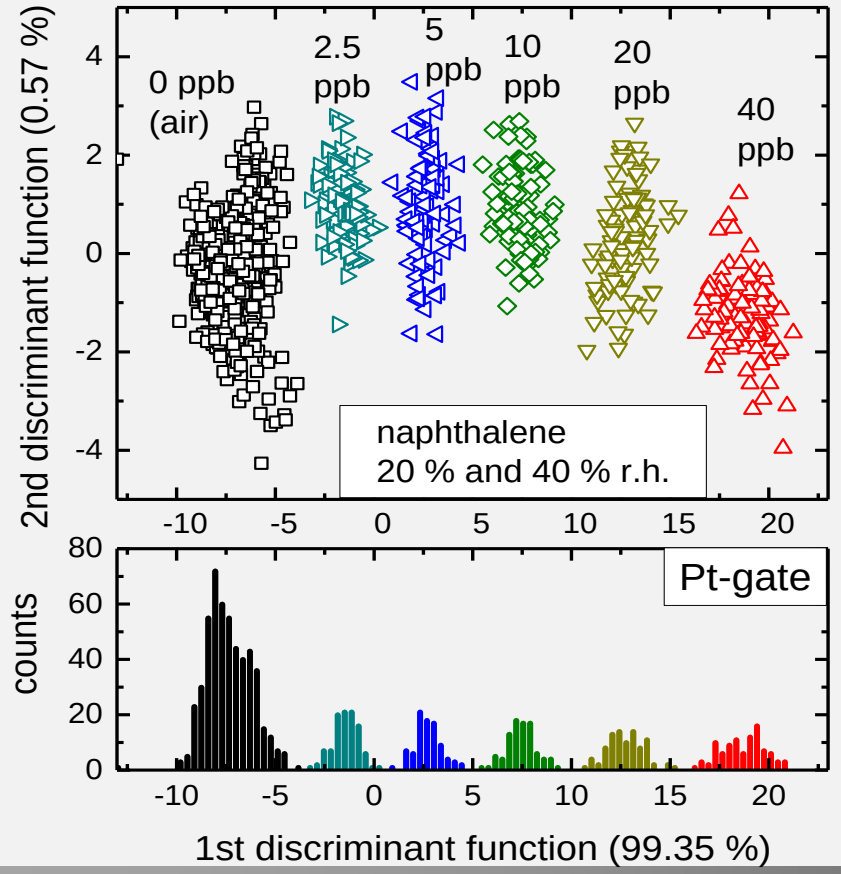
10-fold cross validation yields an overall classification rate of 94.7%

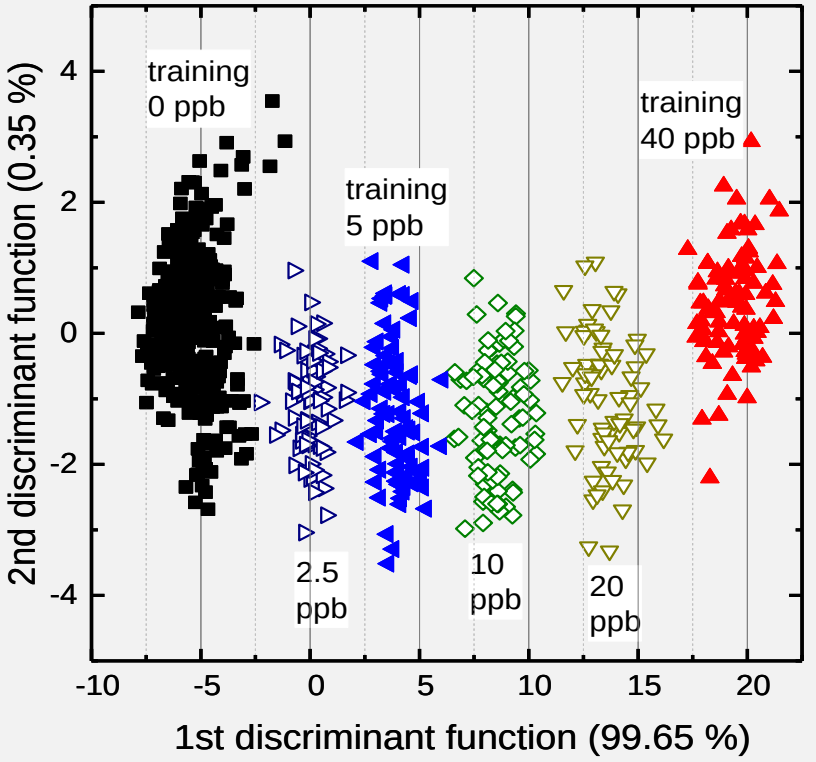


LEHRSTUHL FÜR MESSTECHNIK

- **Quantification** tested with Naphthalene
- 5 concentrations 2.5 to 40 ppb @ 20% and 40% r.h.
- Calibration based on 2 conc., evaluation with 3 others

SENSIndoor





CONCLUSIONS

- **CONCLUSIONS:**
- Both MOS and GasFET sensors highly sensitive for VOC
- TCO allowing discrimination and quantification
- Ubiquitous low-cost sensor systems for IAQ realistic

- **OUTLOOK:**
- Further improvement: nanotechnology, micro-analytical approach
- Extensive field testing required: calibration and reliable operation
- Priority target application scenarios: schools/kindergarten, refurbished homes