

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

COST Action TD1105

Third Scientific Meeting – Istanbul, December 3-5, 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016

Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)

Plenary Session 1: Indoor Environment Quality Applications Selective VOCs Detection in the ppb Range for Demand Controlled Ventilation



UNIVERSITÄT
DES
SAARLANDES



Andreas Schütze

WG2 leader, MC member

Saarland University / Germany

schuetze@LMT.uni-saarland.de

 **cost**
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY





Why worry about indoor air?

- Safety
 - Gas leak detection (combustible gases, e.g. CH₄)
 - 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
 - CO₂ 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



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

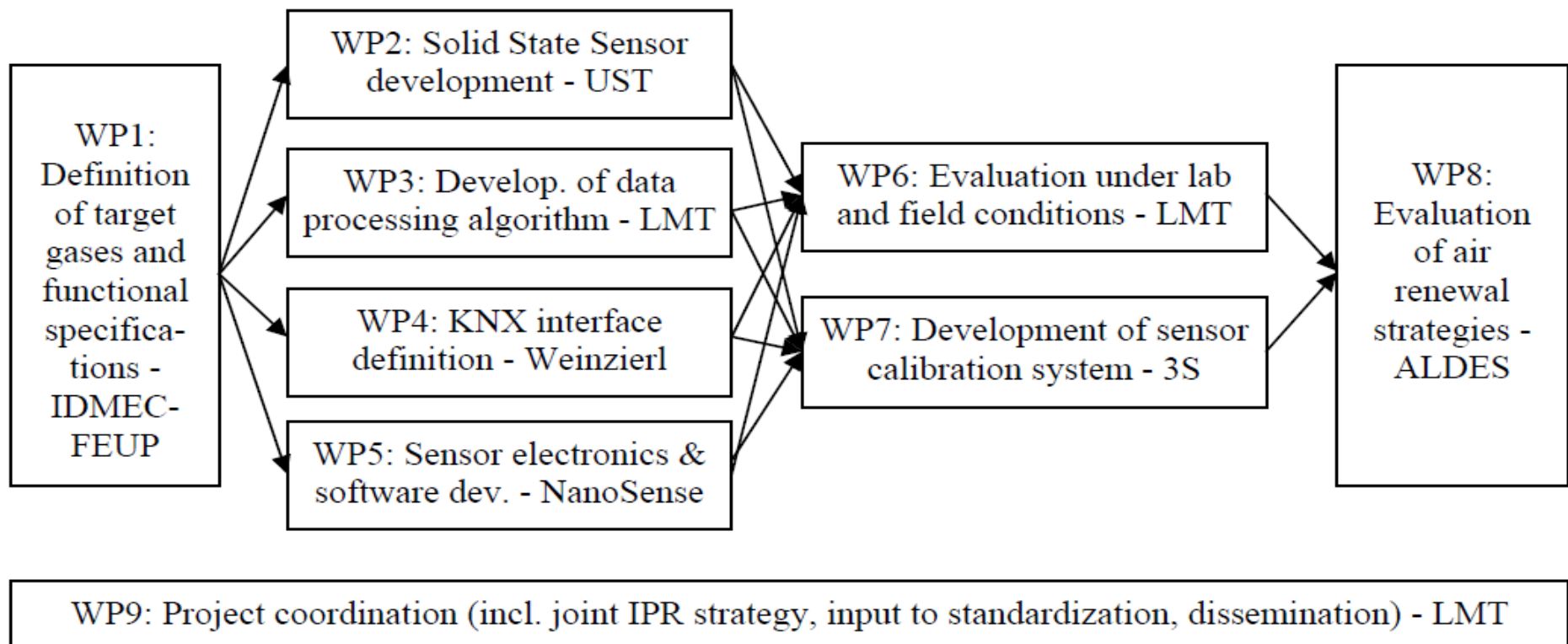


> Indoor Air Quality monitoring

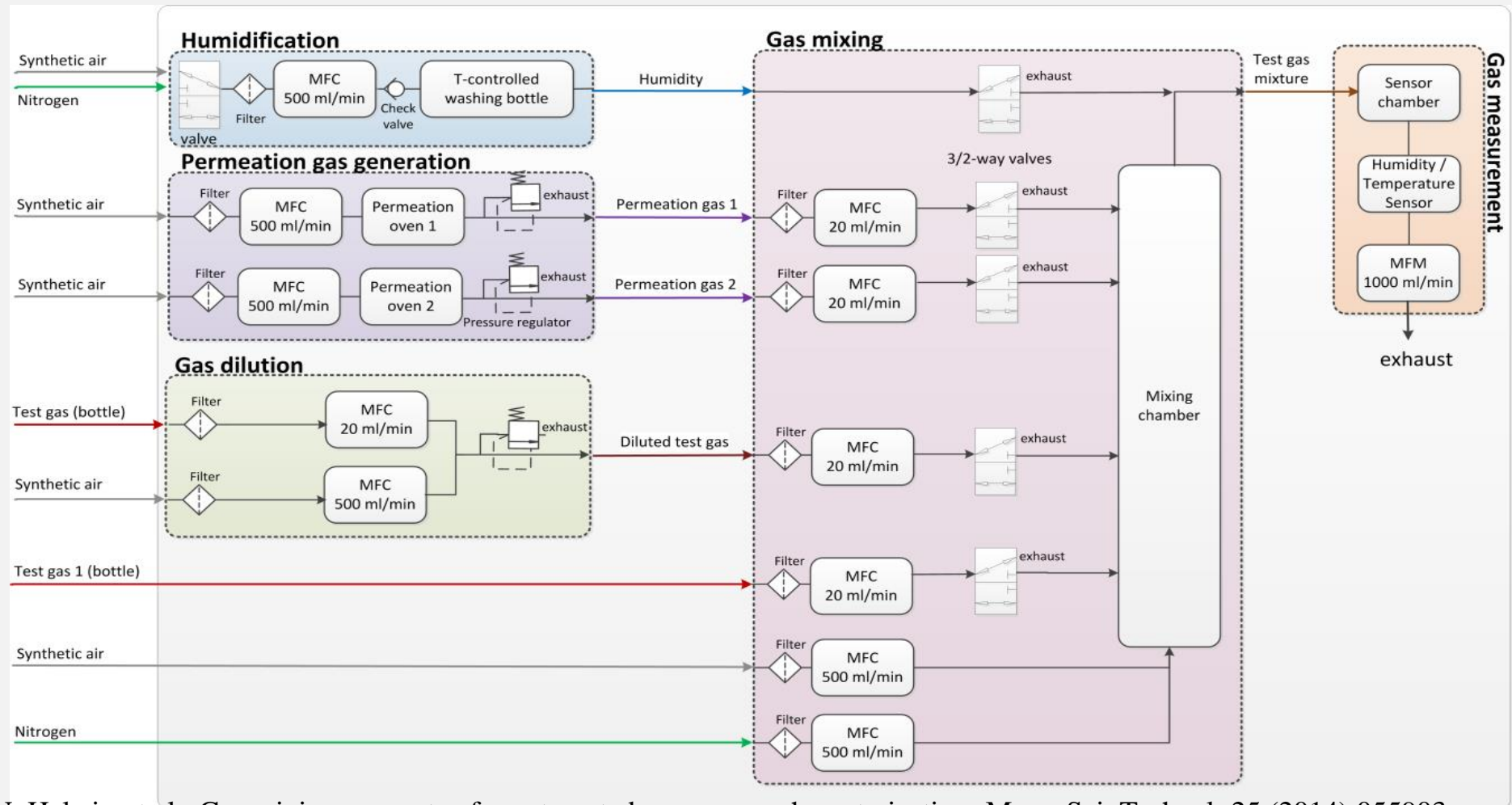


MNT-ERA.net project VOC-IDS

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



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 measurement systems – more than sensors



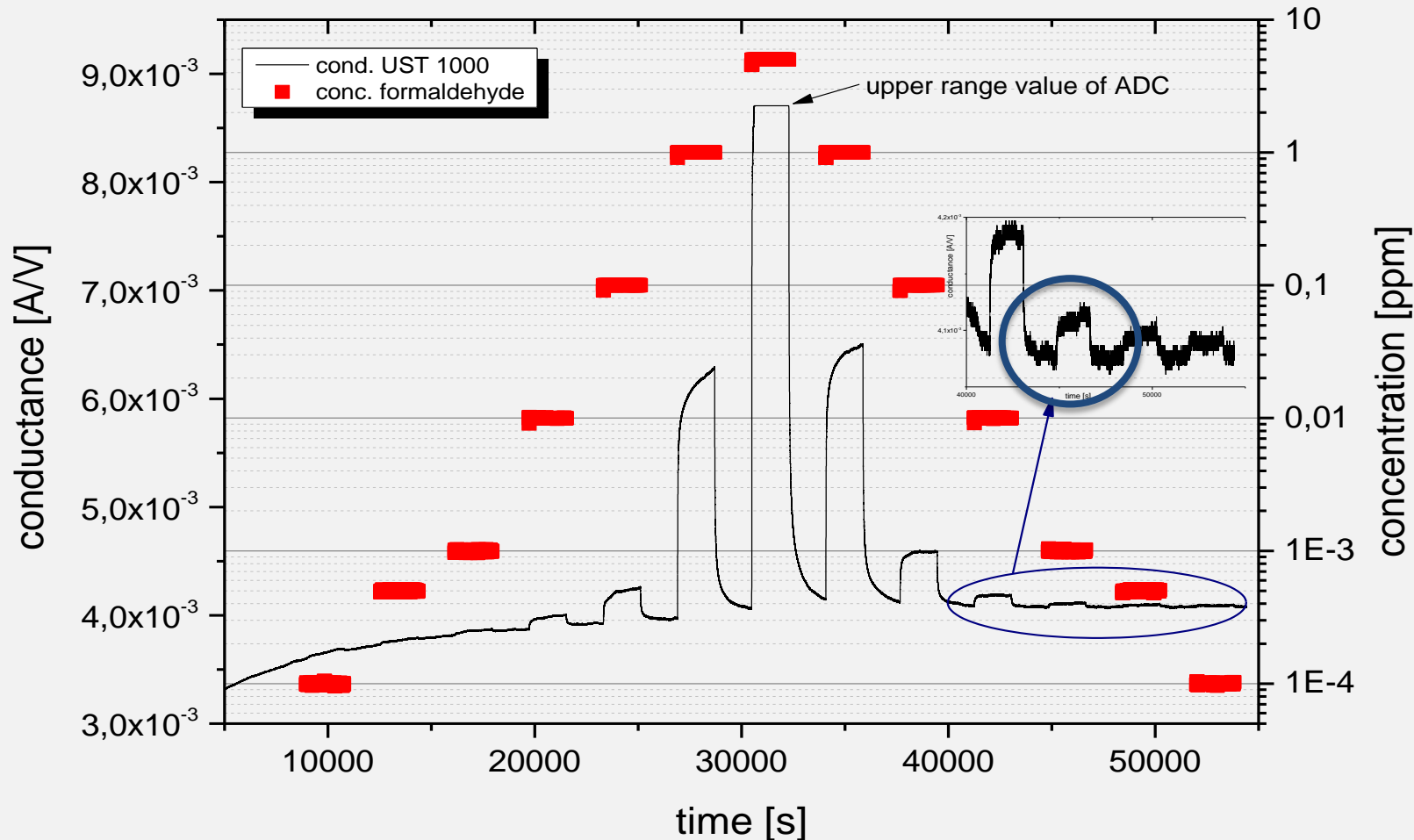
**Gas mixing system:
results of reference
measurements
(zero air)**

compound	CAS no	c [$\mu\text{g}/\text{m}^3$]	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
bicyclo[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

> 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

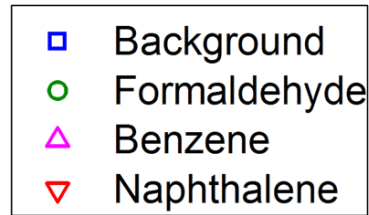
target gas	Concentration (ppb)	humidity	Interferents (EtOH ppm)
Air	NA	40%, 60%	none, 0.4, 2
Formaldehyde	10, 100	40%, 60%	none, 0.4, 2
Benzene	0.5, 4.7	40%, 60%	none, 0.4, 2
Naphthalene	2, 20	40%, 60%	none, 0.4, 2

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

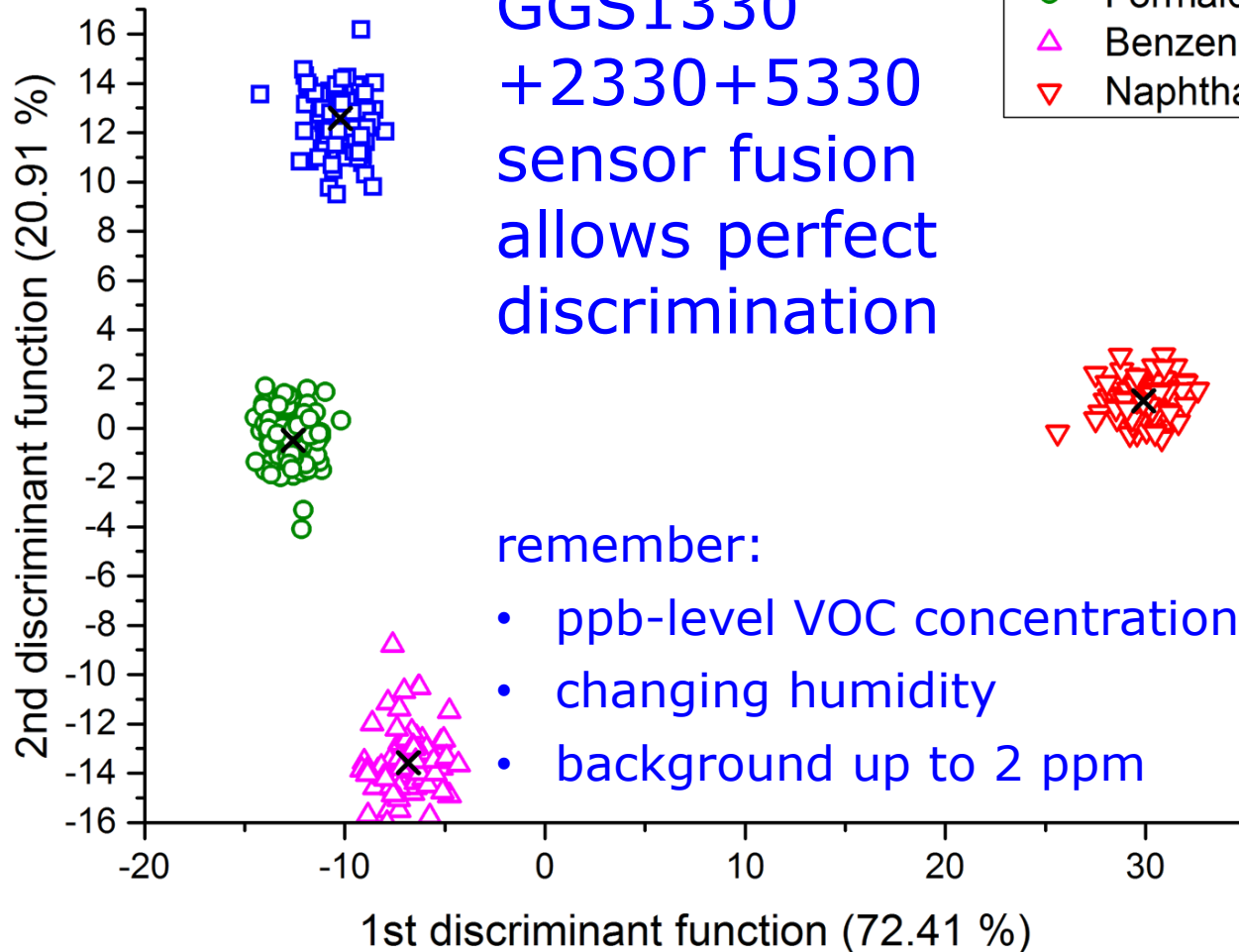
> IAQ monitoring with MOS sensors



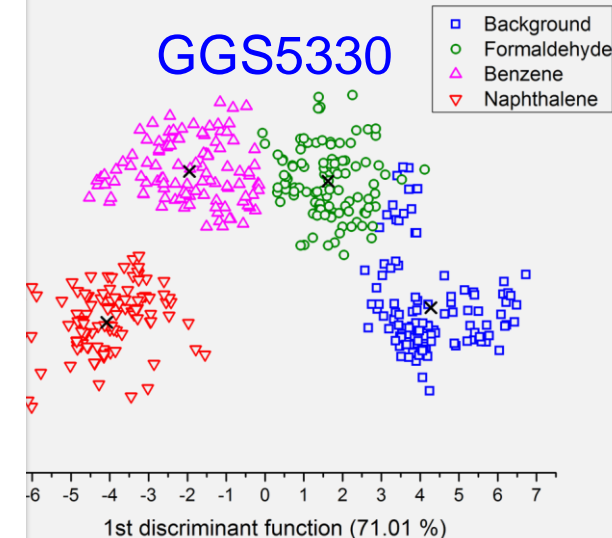
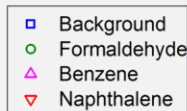
GGG1330
+2330+5330
sensor fusion
allows perfect
discrimination



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



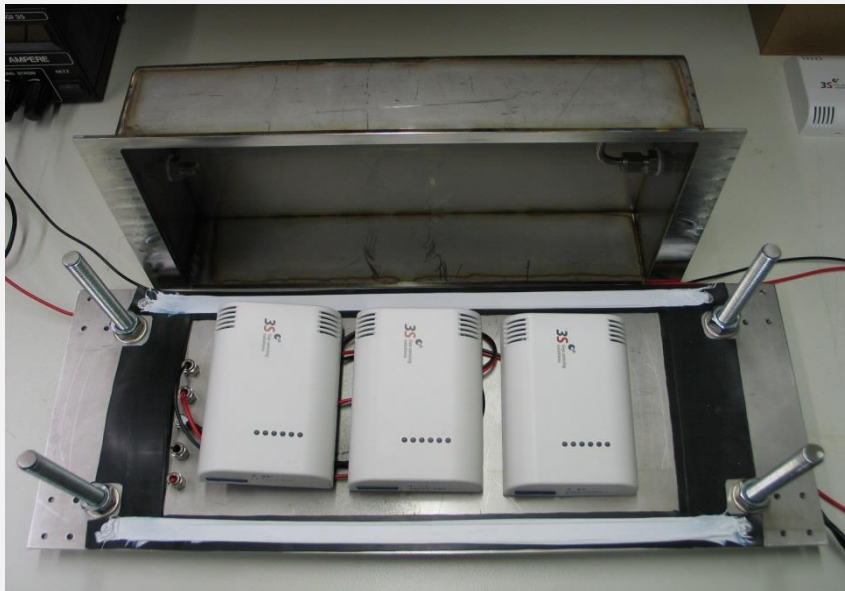
GGG5330



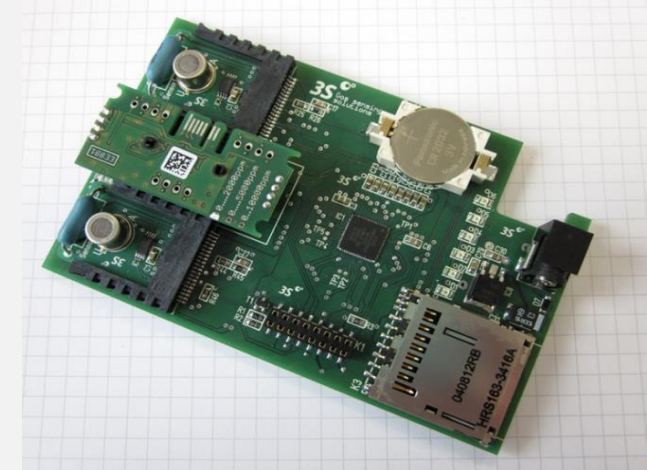
> IAQ monitoring: field test systems



- Stand-alone field test systems by 3S GmbH (Saarbrücken, Germany)
- 2 MOS gas sensors (+ CO₂ + humidity) with independent temperature control
- Data storage on SD card
- Same test gas profile as for sensors only

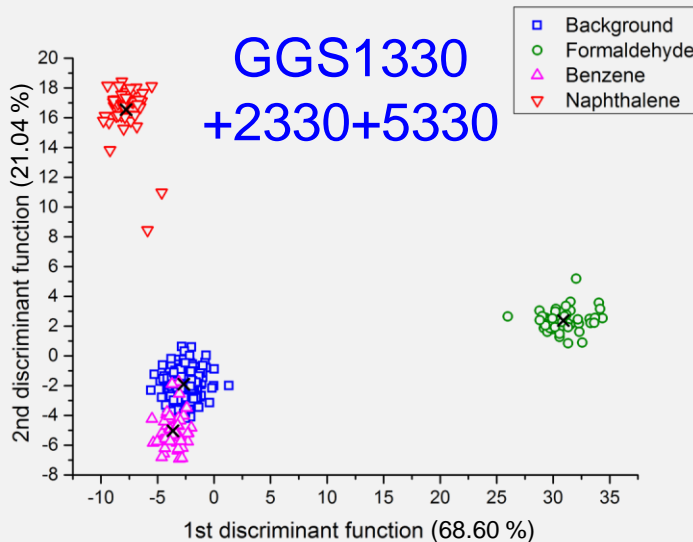
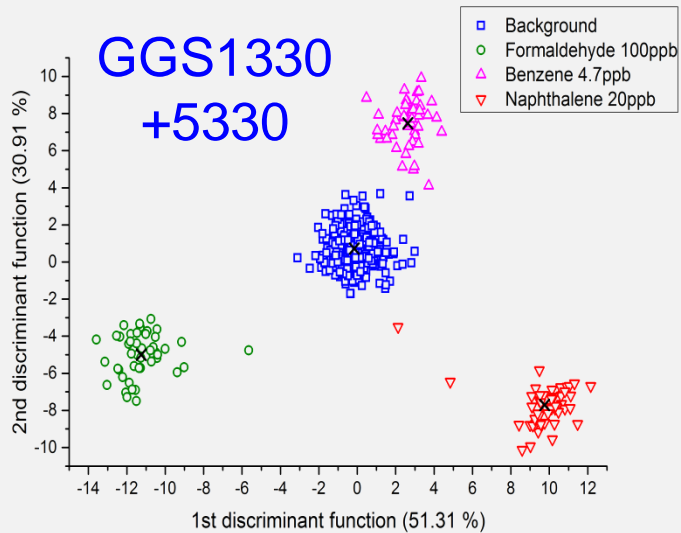


Setup for system calibration



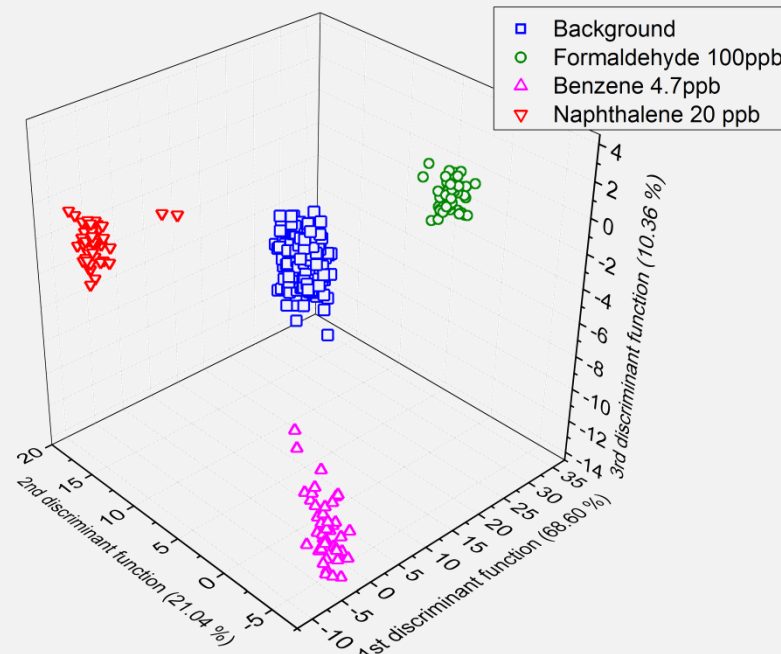
© 3S GmbH, 2013

> IAQ monitoring: field test systems



- 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

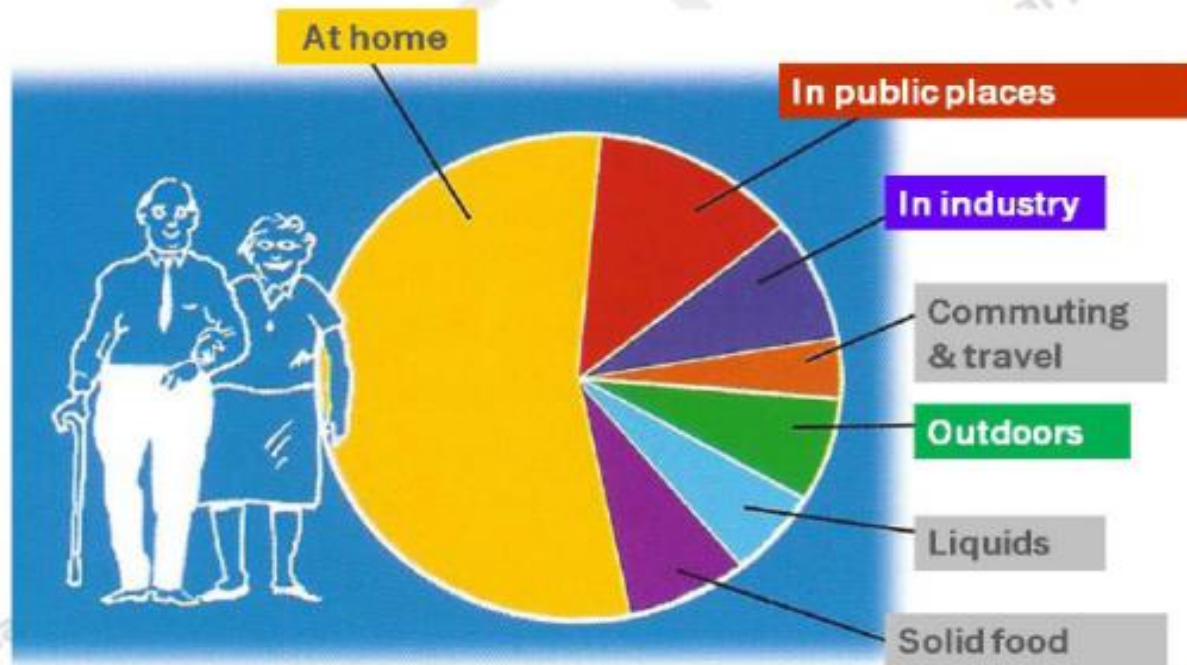
3D
 →



➤ Core motivation for the SENSIndoor project

GUIDELINES FOR HEALTH-BASED VENTILATION IN EUROPE - HEALTHVENT

Indoor air is significant contributor to life-time exposures

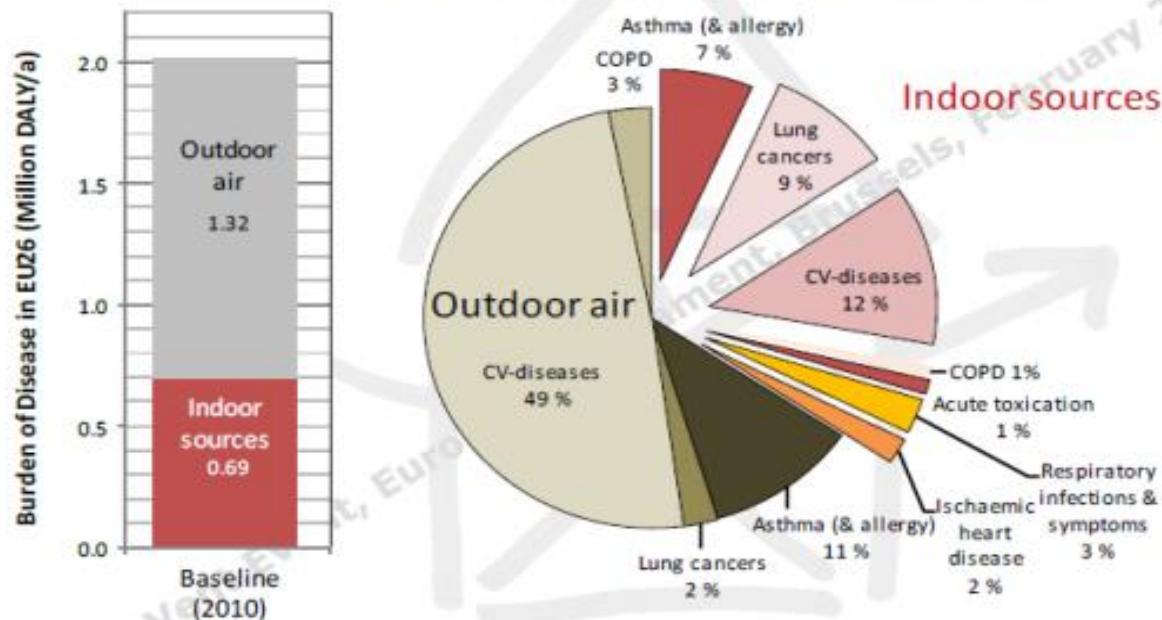


<http://www.healthvent.byg.dtu.dk/>

➤ Core motivation for the SENSIndoor project

GUIDELINES FOR HEALTH-BASED VENTILATION IN EUROPE - HEALTHVENT

Burden of disease due to IAQ



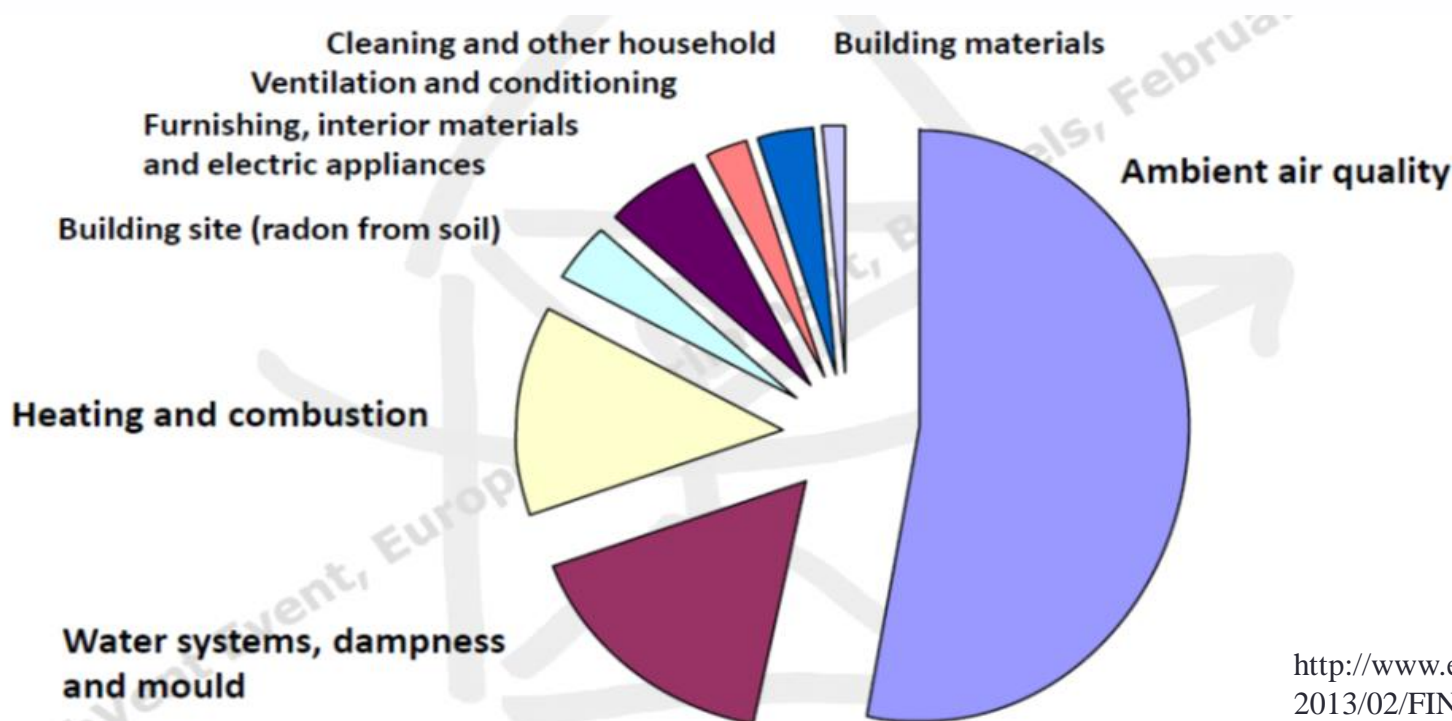
Source: Hänninen, Asikainen *et al.*, 2013: HEALTHVENT Report D8

Figure 1. Burden of disease at the baseline (2010) in EU-26 divided into indoor and outdoor source components (left) and fractions associated with different diseases (right).

http://www.healthvent.byg.dtu.dk/

➤ **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>



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**

Sensor system requirements 1

- Detection of hazardous indoor air pollutants at relevant levels
 - key target pollutants are VOCs, i.e. formaldehyde, benzene,...
 - target concentrations are ppb and sub-ppb level

➤ **extremely high sensitivity required**

	2012							2013			2015			2016			2023		
	MAK work place (8 hours)		TRK work place (15 mn)		Domestic (MAK/3) 24h/24h			French decree n° 2011-1727 of 2/12/2011 long-term guide value for public buildings											
	ppm	mg/m3	ppm	mg/m3	ppm	ppb	mg/m3	ppm	ppb	µg/m3	ppm	ppb	µg/m3	ppm	ppb	µg/m3	ppm	ppb	µg/m3
Formaldehyde	0.5	0.615	1	1.23	0.17	166.67	0.21				0.024	24.39	30.00				0.008	8.13	10.00
Benzene	1	3.25	1	3.25	0.33	333.33	1.08	0.00154	1.54	5.00				0.00062	0.615	2.00			

- In addition: many other interfering gases/VOCs
 - benign, e.g. ethanol, air freshener (much higher concentrations!)
 - unpleasant, but not hazardous, e.g. isovaleric acid
 - other background gases, e.g. CO, O₃, NO_x, ammonia, ...

➤ **extremely high selectivity required**

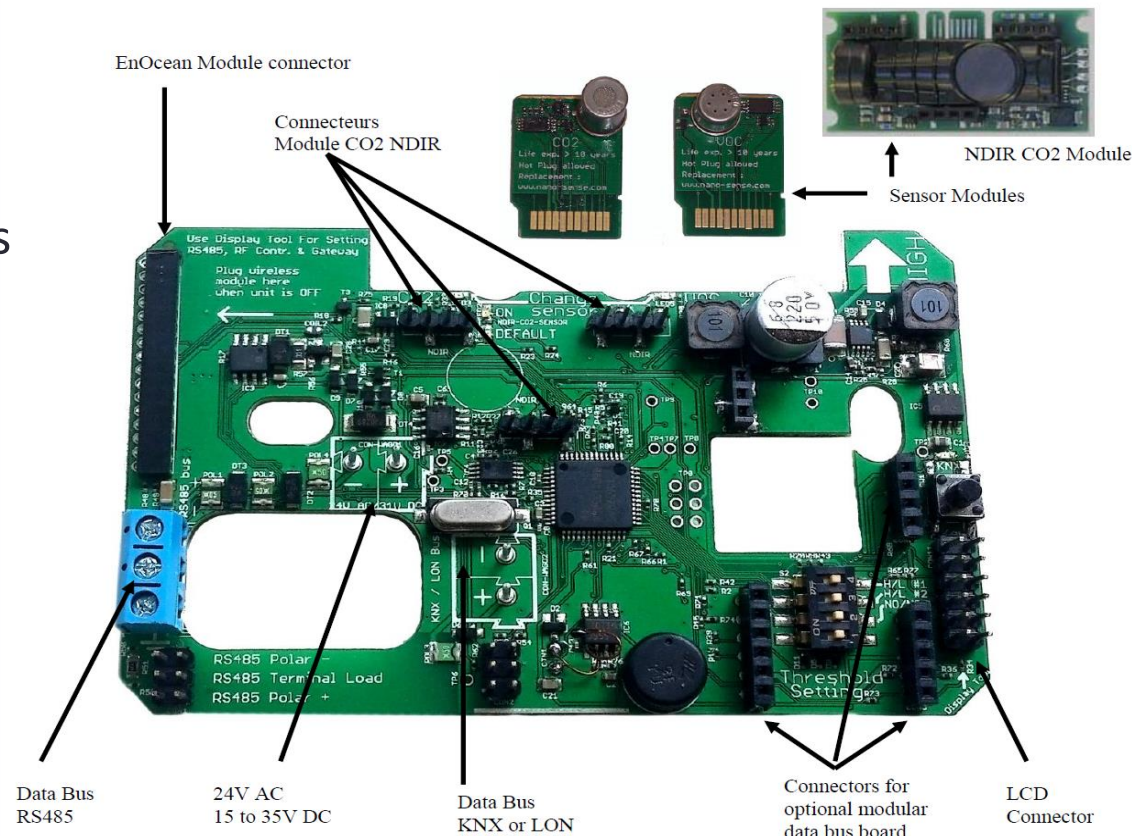
Sensor system requirements 2

- Demand controlled ventilation to achieve optimal compromise between energy efficiency and health benefits adapted to specific application scenarios
 - **room-specific measurements required**
- Significant contribution to EU 20-20-20 goals and health aspects of IAQ targeted
 - **ubiquitous measurements required**
 - **Core challenges addressed with micro- and nanotechnologies**
 - **microtechnologies for low cost mass production (and low power consumption)**
 - **nanotechnologies for unrivalled sensitivity and selectivity**

- Demand controlled ventilation today
 - mostly CO₂ monitoring, at best total VOC (TVOC)
 - CO₂ based on IR absorption or solid state electrolyte
 - TVOC based on metal oxide semiconductor (MOS) sensors



E4000 Air Quality Probe
(NanoSense SARL)



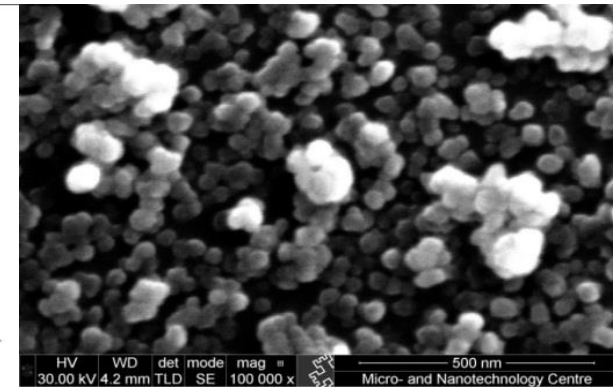
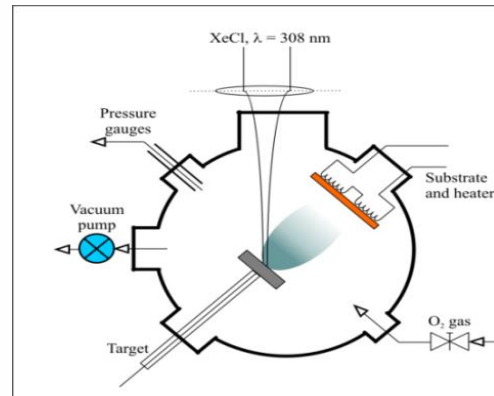


SENSIndoor origins

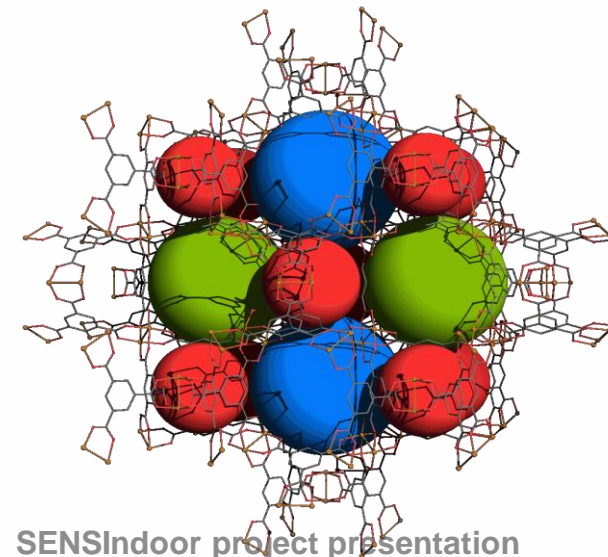
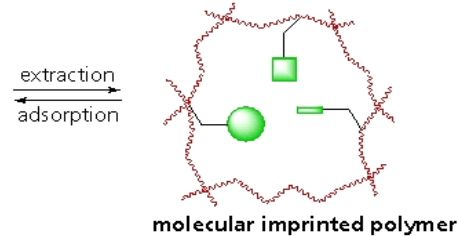
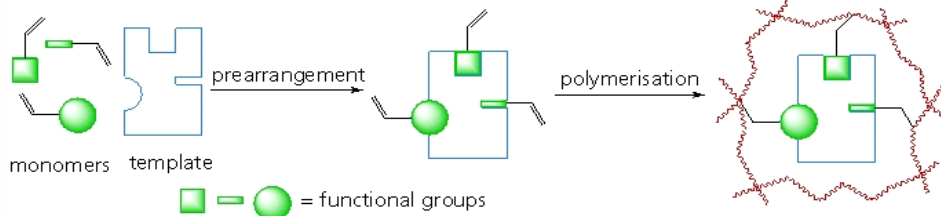
- **VOC-IDS** (MNT-ERA.net collaborative project)
Volatile Organic Compound Indoor Discrimination Sensor
 - Partners: USAAR-LMT, IDMEC-FEUP - Instituto de Engenharia Mecânica, University Porto (P), UST Umweltsensortechnik GmbH (D), 3S GmbH (D), NanoSense SARL (F), Weinzierl Engineering GmbH (D), CIAT - 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**

- Nanotechnology for improved sensor elements

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

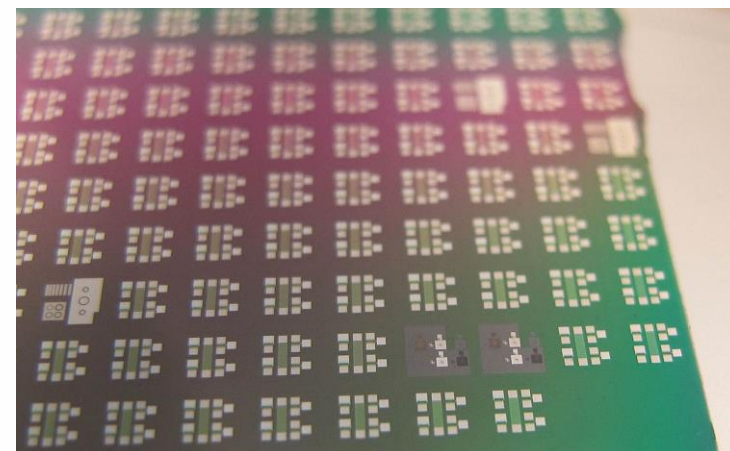
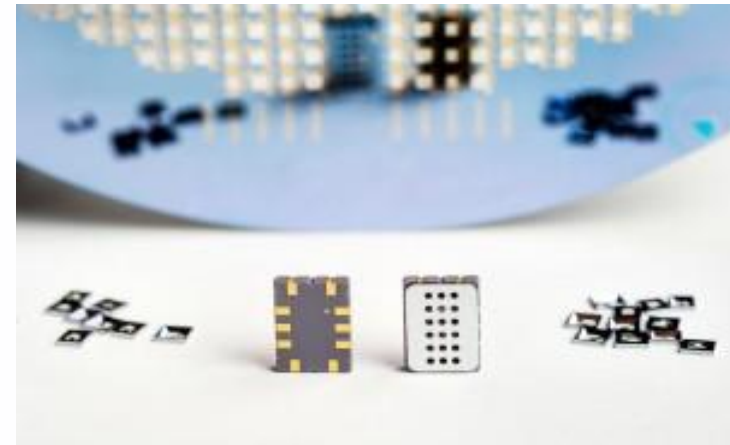


- Selective pre-concentration** (*FhG-ICT*)
 based on MOFs (metal-organic frameworks) → and MIPs ↓ (molecular imprinted polymers)

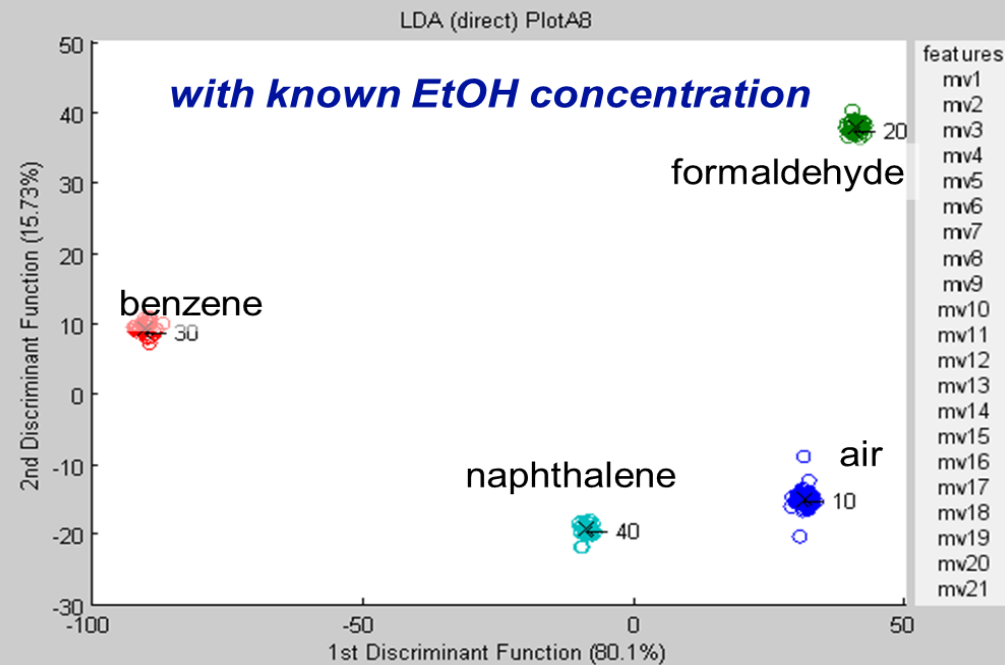
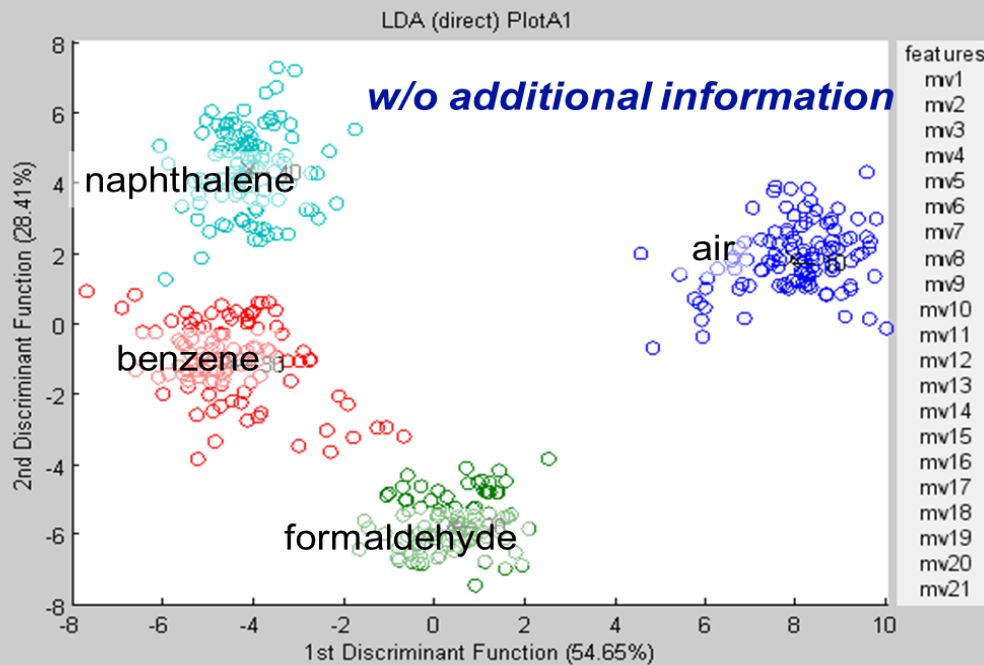


SENSIndoor technologies 2

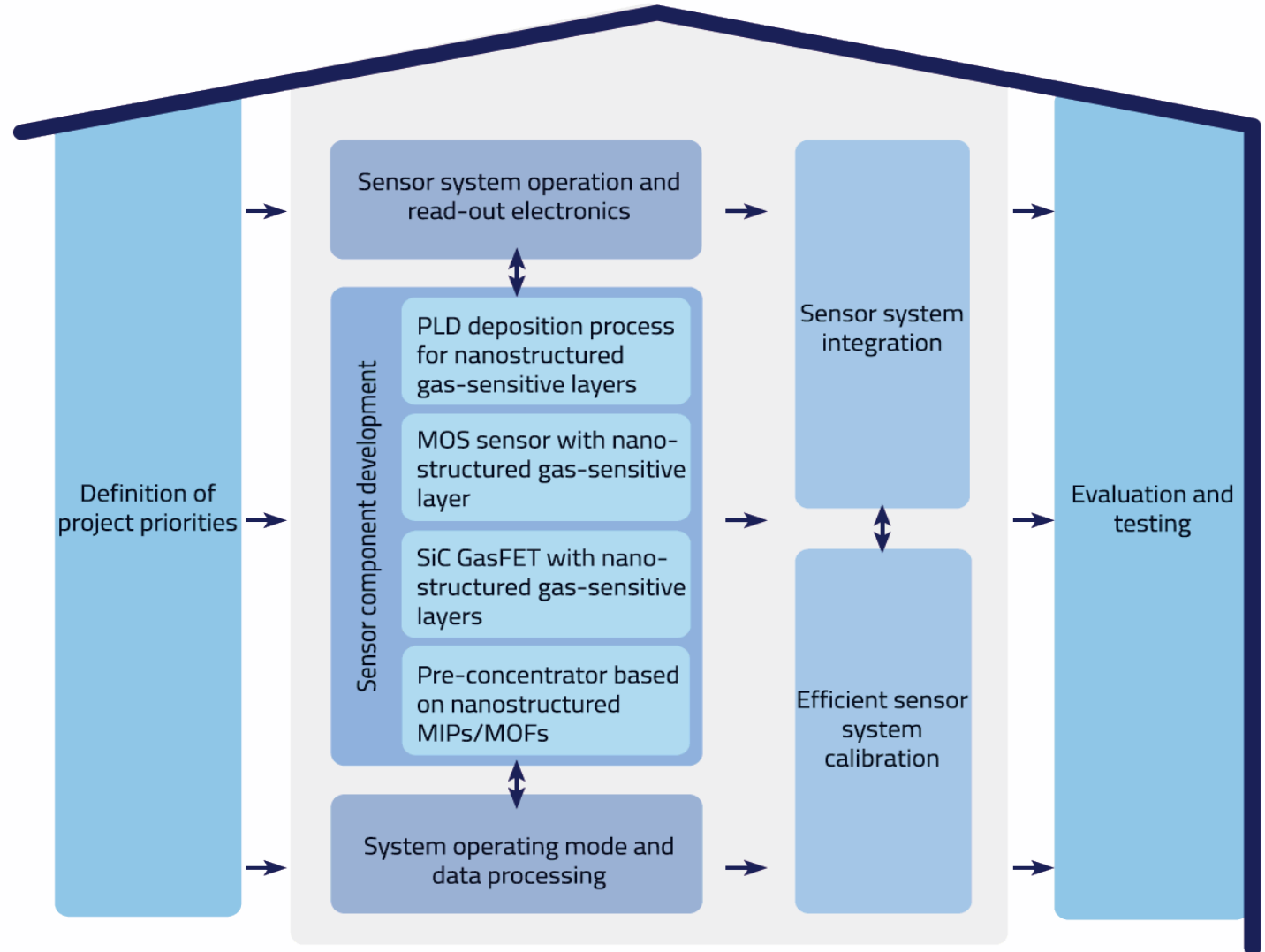
- Sensor technologies
 - **MOS – Metal oxide semiconductor** (*SGX Sensortech, USAAR-LMT*)
 - well known for high sensitivity and robustness @ low-cost
 - MEMS technology for mass production and low power consumption
 - **GasFET – Gas-sensitive Field Effect Transistors** (*LiU, SenSiC*)
 - complementary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



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



Project structure:
A clear road from
application
requirements to
field evaluation



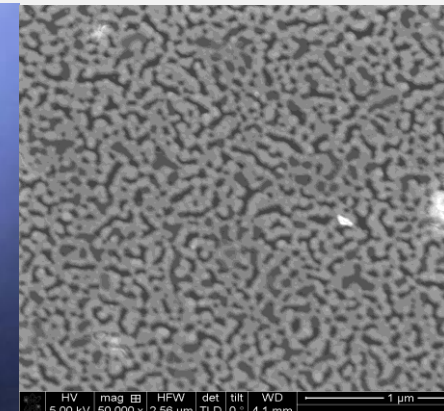
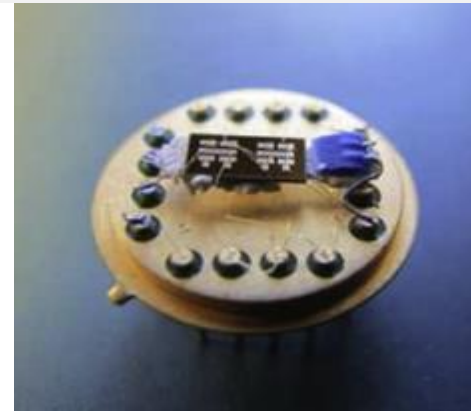
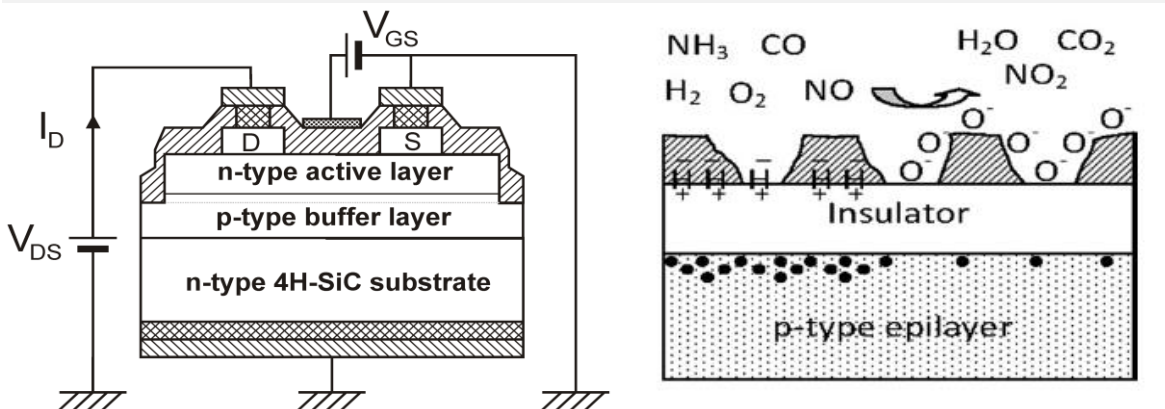
> IAQ monitoring w GasFET sensors



- 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



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



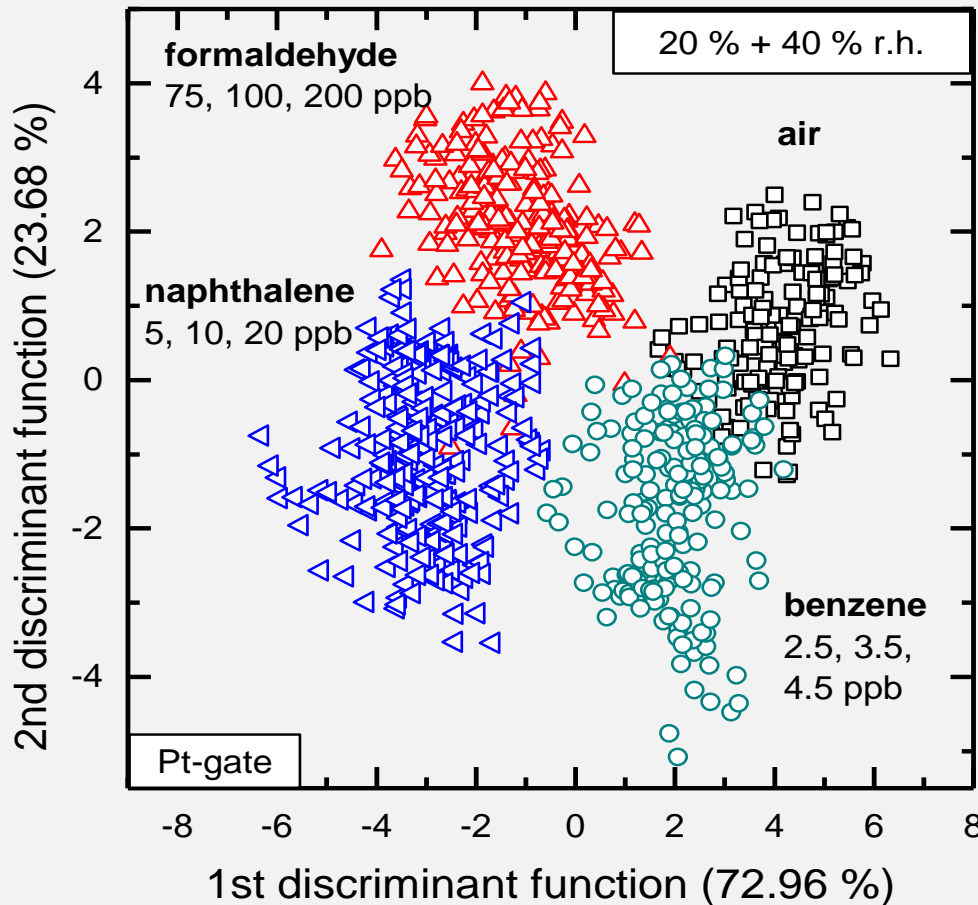
> IAQ monitoring w GasFET sensors



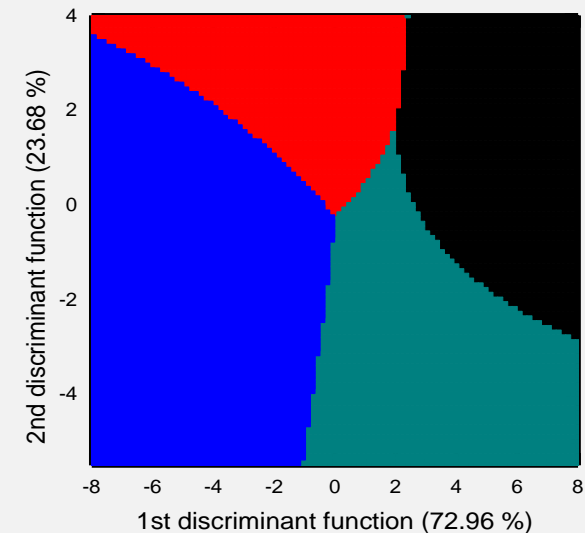
- **Discrimination** tested with 3 concentrations per VOC
- Tests performed at 20 % + 40 % r.h.



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



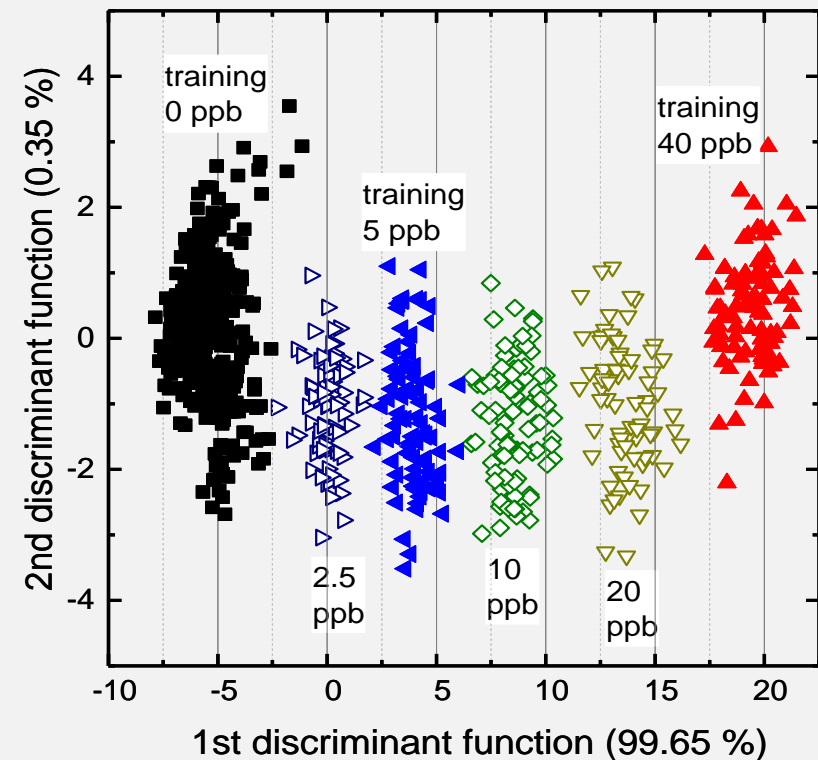
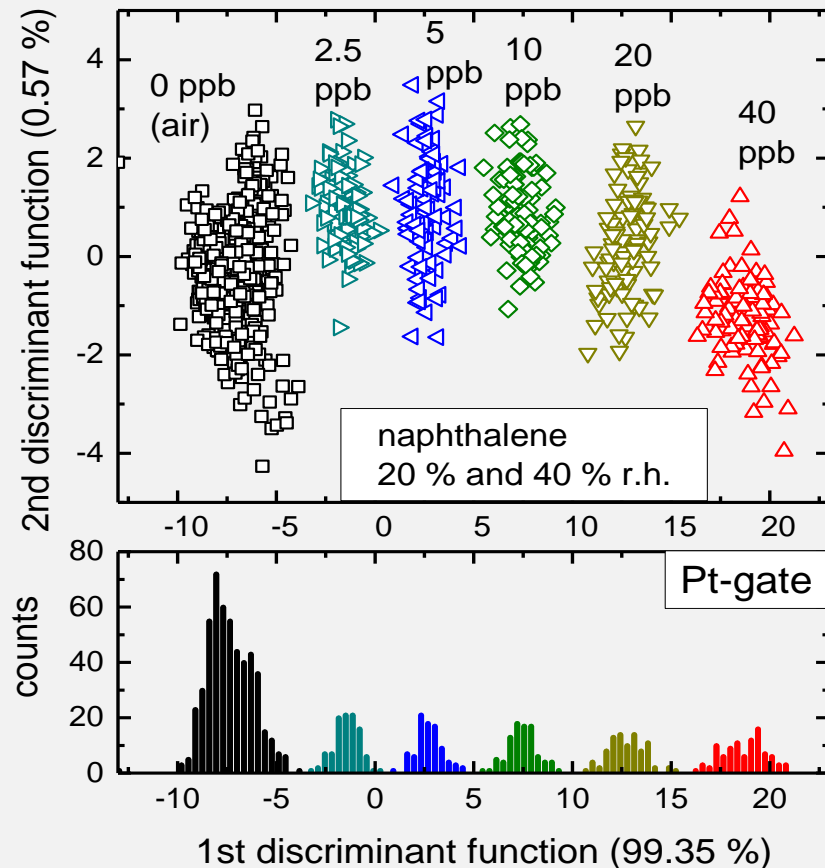
Mahalanobis distance classifier



> IAQ monitoring w GasFET sensors



- **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

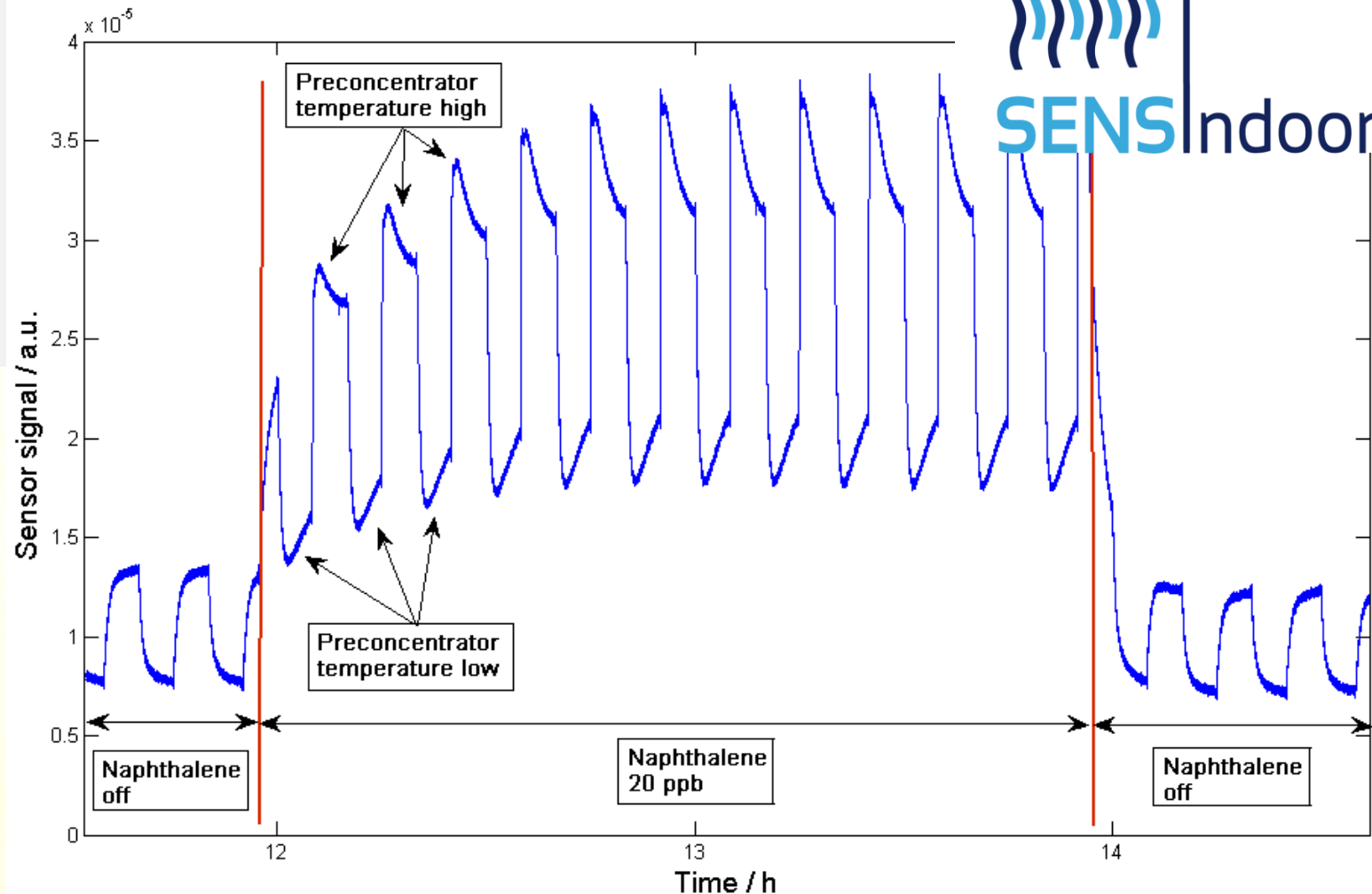
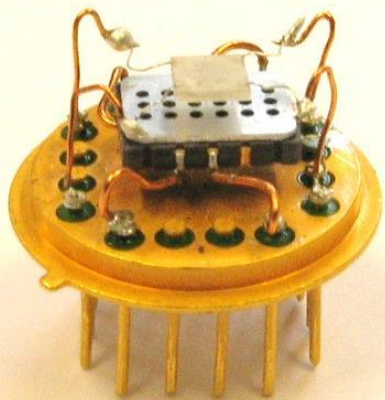


> μ -pre-concentrator: proof of concept



First proof-of-principle measurements

- preconc. off: signal low, then increases
- preconc. on: signal high, then decreases



CONCLUSIONS

- **CONCLUSIONS:**

- Both MOS and GasFET sensors highly sensitive for VOC
- TCO allowing discrimination and quantification
- Micro- and nanotechnologies for excellent functionality at low cost
- μ -pre-concentrator promising concept for IAQ applications
- Ubiquitous low-cost sensor systems for IAQ realistic

- **OUTLOOK:**

- Extensive field testing required: calibration and reliable operation
- Priority application scenarios: schools/kindergarten, refurb. homes

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

COST Action TD1105

Third Scientific Meeting – Istanbul, December 3-5, 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016

Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)

Selective VOCs Detection in the ppb Range for Demand Controlled Ventilation



UNIVERSITÄT
DES
SAARLANDES



Andreas Schütze

WG2 leader, MC member

Saarland University / Germany

schuetze@LMT.uni-saarland.de

 **cost**
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

