MACPoll Workshop

Gas Sensors and Sensor Systems for Air Quality Monitoring

JRC Ispra, November 19, 2013, Ispra, IT

Andreas Schütze
Saarland University, Lab for Measurement Technology

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

mnt-era.net
VOC-IDS

SENSIndoor

> Outline

- **Background: indoor air quality**
- Gas sensors for air quality
  - Electrochemical cells
  - Semiconductor gas sensors
  - Other technologies: mass sensitive devices, GasFETs
- Gas measurement systems – more than just sensors
  - The three "S"
  - Gas measurement systems incl. signal processing and evaluation
  - Calibration and field testing
  - Performance example: ppb-level VOC identification
- Novel developments
  - Novel sensor technologies: nanomaterials and integrated GasFETs
  - System self monitoring
  - Multifunctional multisensor systems
- Conclusions

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
  - 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

> Background: Indoor Air Quality

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 industr.
  - 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
  - VOCs: MOS (total VOC), GasFET (emerging)

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

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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

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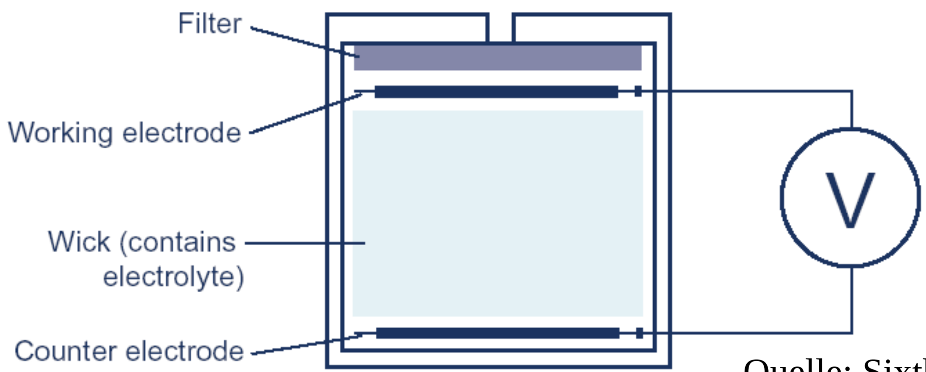
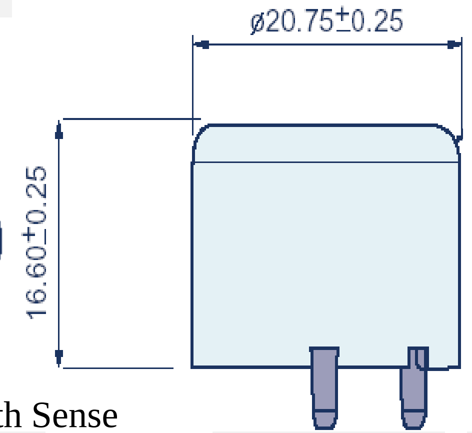
- Electrochemical cells: amperometric gas sensors
  - Gas molecules are ionized at sensing electrodes
  - Ions are conducted through the electrolyte cell
  - Current is proportional to gas concentration (diffusion limited)
- Sensitivity typically down to ppm, for some reactive gases sub-ppm
- Partial selectivity achieved, but still relevant cross-sensitivities
- Poor long term stability (especially at high temperature, low humidity)
- Plus: baseline drift, sensitivity change, poisoning

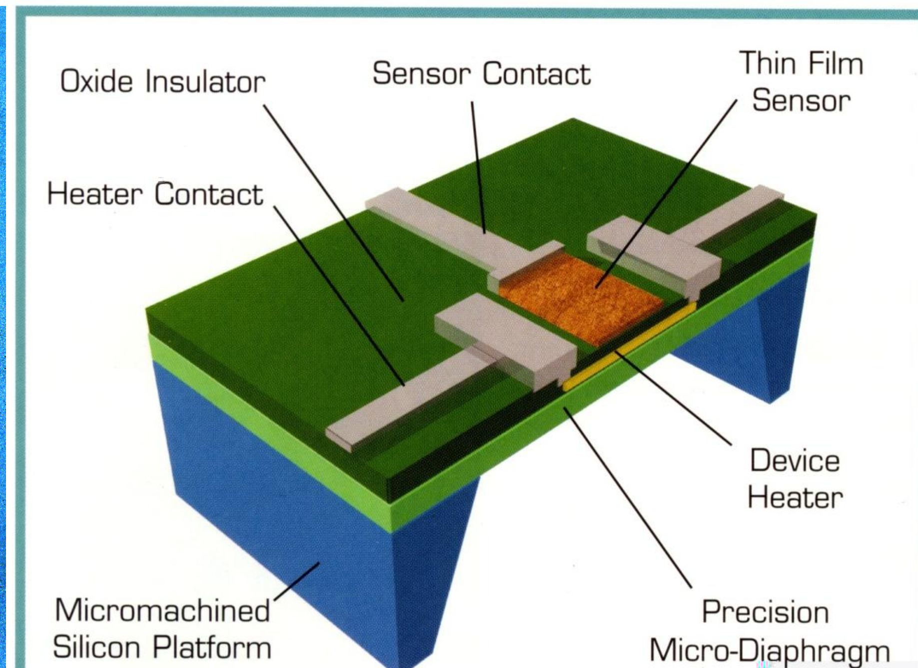
Source: Alphasense Ltd.





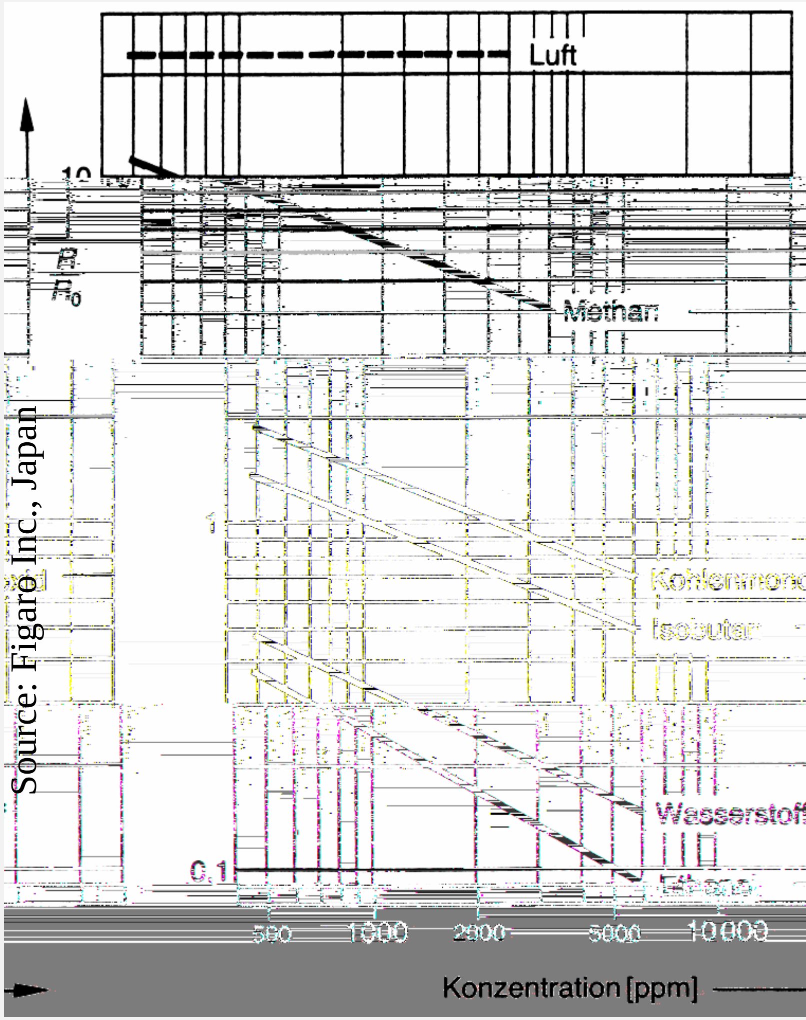
Quelle: Sixth Sense

- Metal Oxide Semiconductor (MOS), e.g. SnO_2, Ga_2O_3, WO_3
  - Oxygen adsorption leads to energy barrier at grain boundaries
  - Gas adsorption or reaction with O^- influences energy barrier
- Very high sensitivity (exponential effect of energy barrier on resistance)
- Very low cost: manufacturing based on MEMS and screen printing



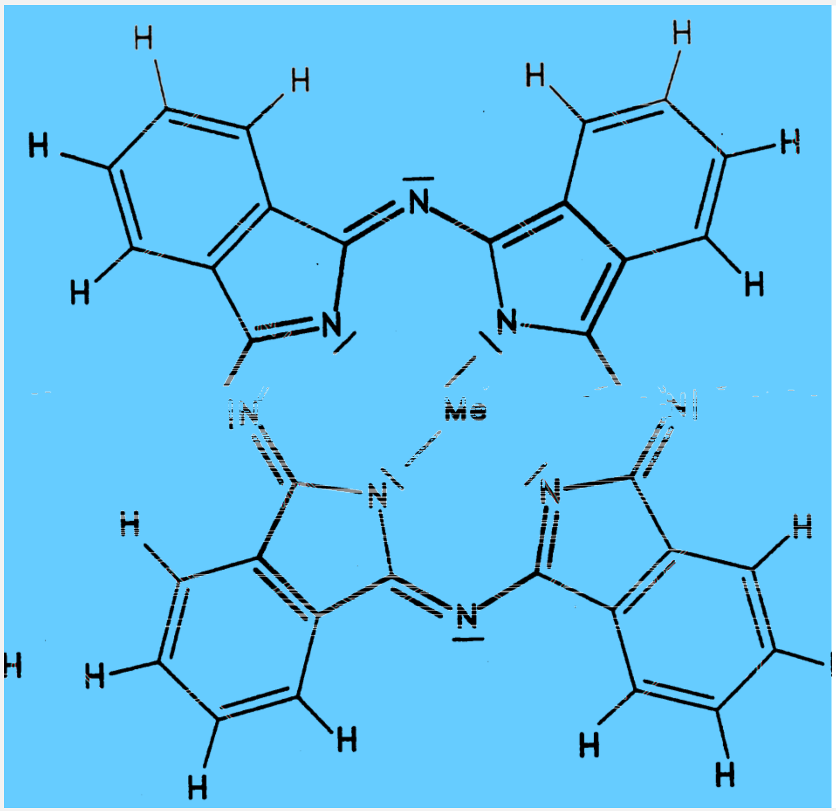
Source: MicroChemical Systems S.A., Corcelles, CH

- Metal Oxide Semiconductor (MOS), e.g. SnO_2, Ga_2O_3, WO_3
- Great robustness (> 10 years lifetime in applications)
- Poor stability
  - Sensor drift due to poisoning etc.
  - Influence of background, esp. humidity
  - ➢ **quantitative meas. difficult**
- Poor selectivity
  - Response is mainly due to changing oxygen coverage
  - "Its surprising if the MOS sensor does not show a reaction!"
  - ➢ **greatest challenge for R&D**

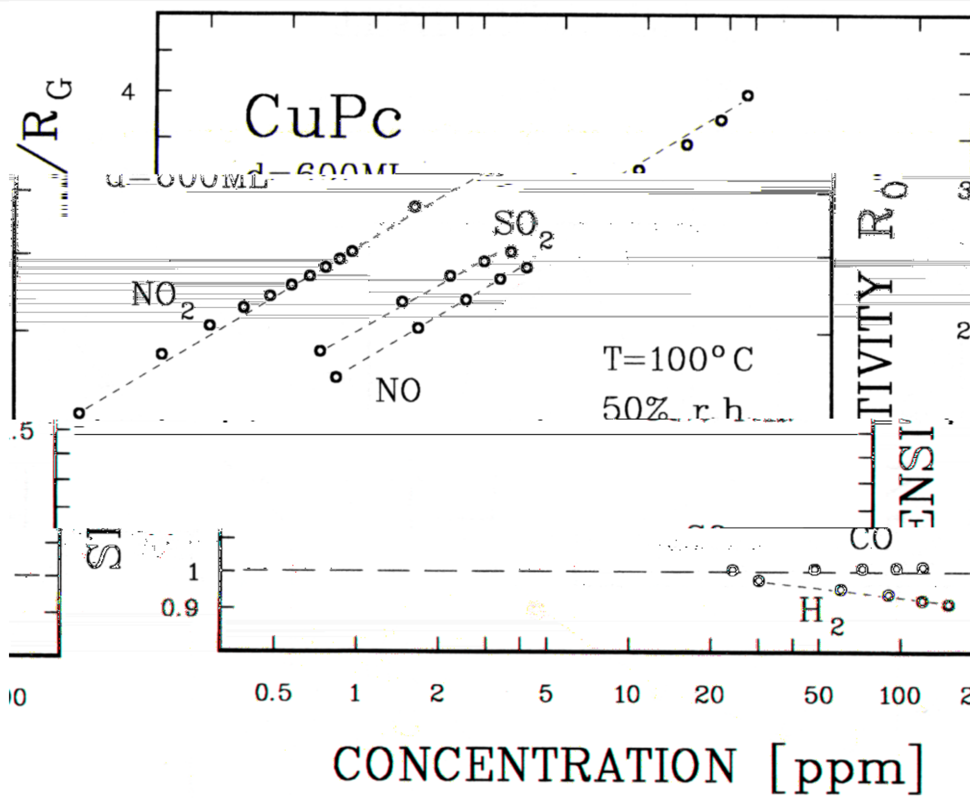


Source: Figaro Inc., Japan

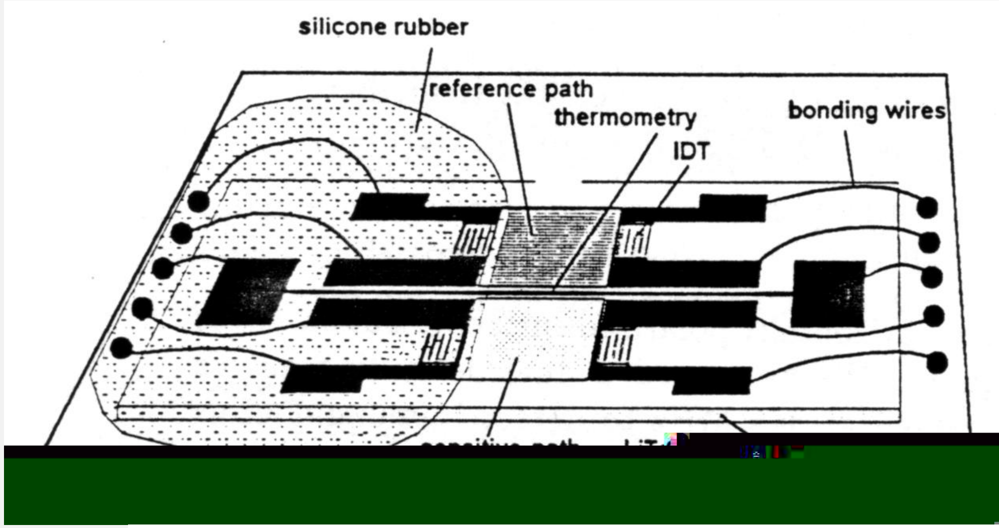
- Organic semiconductor materials, i.e. Phthalocyanine
  - p-type semiconductor esp. suitable for oxidizing gases, i.e. NO_x, O_3
  - robust, low-cost, stability and selectivity similar to MOS



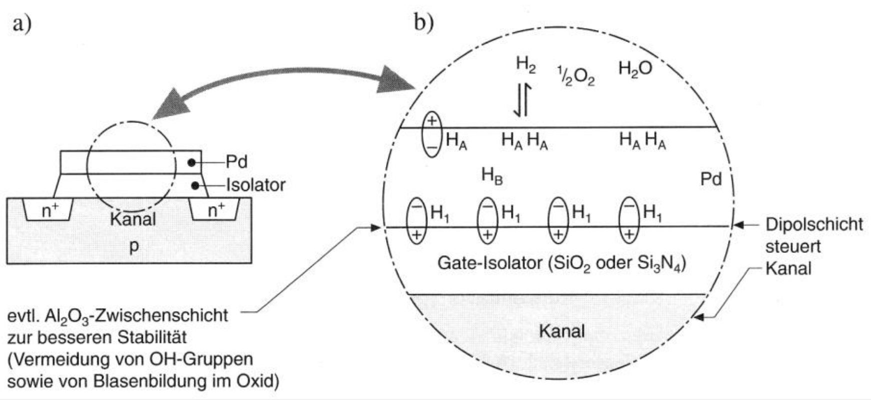
Source: A. Schütze, Dissertation, JLU Gießen, 1994



- Other sensor technologies? Mostly still under development
- Pellistors: detection of combustible gases at higher conc.
- Mass-sensitive devices
  - Bulk or surface acoustic
  - Mass change on surface leads to change of f_{res}
  - High sensitivity: SAW
  - GHz: complex electronics
  - high temp. stability req.



- GasFET
  - Gas-sens. Field Eff. Transistor
  - Classic Lundström FET: Hydrogen diffusing thru Pd
  - Only H-containing gases



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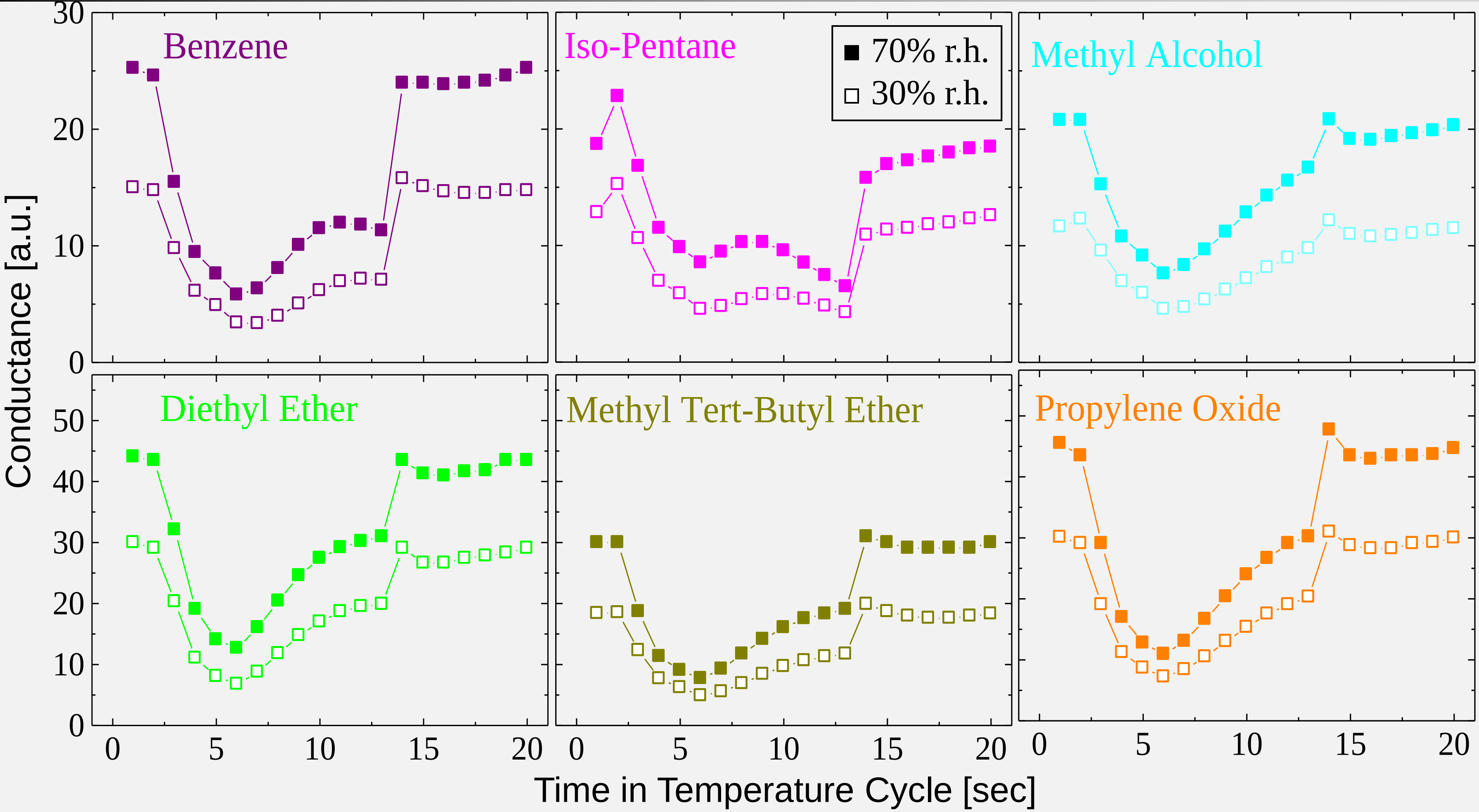
The three "S"

- 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?

Temperature Cycled Operation (TCO)



A. Schütze, A. Gramm, T. Rühl
IEEE Sensors Journal, Vol. 4, No. 6, 2004

Signal evaluation:

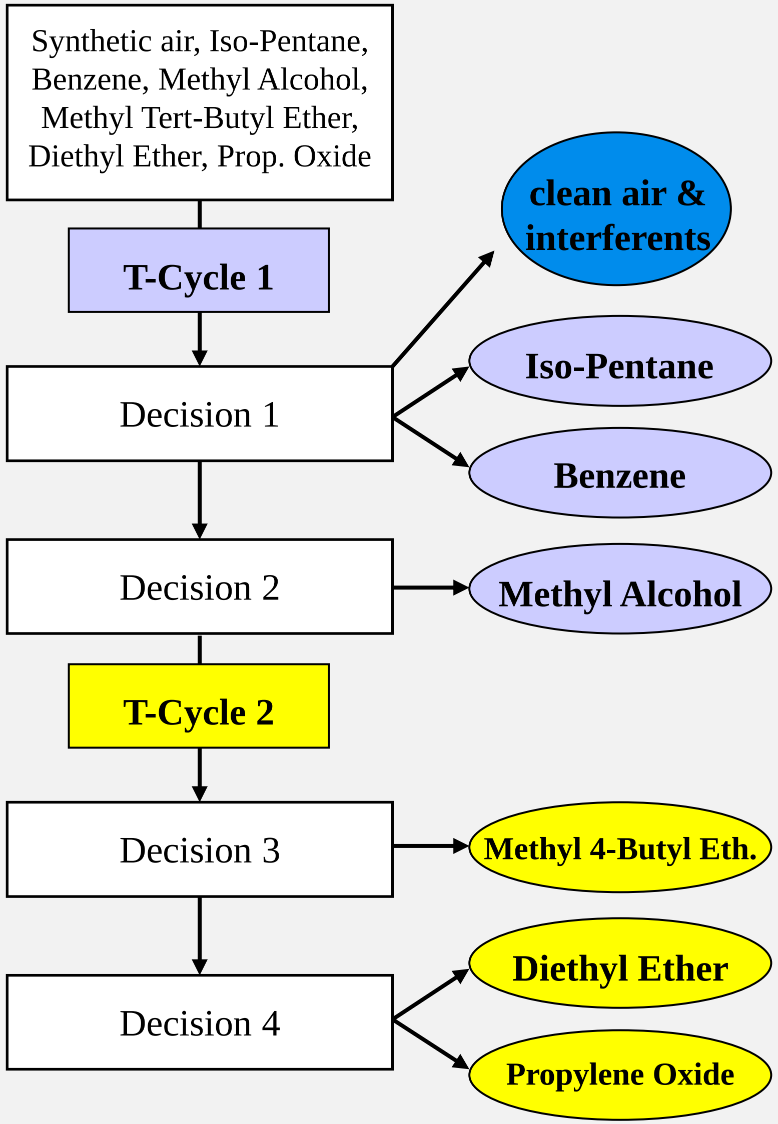
1. Normalization of the response curves ⇒ reduces sensor drift
2. Generation of secondary features, i.e. levels, slopes etc.
3. Suitable patterns are extracted for further evaluation

Evaluation of sensor data based on temperature cycling (example)
→ **Virtual multisensor**

Characteristic features of the curve shapes (i.e. ***slope at the end of the high temperature phase*** and ***curvature during the low temperature phase***) are evaluated, to discriminate between different gases in several steps.

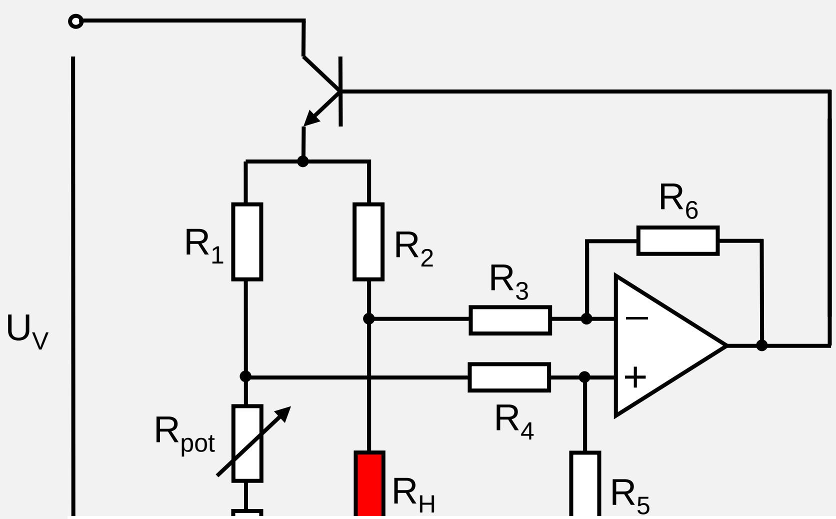
Note: the decision tree reflects the chemical composition of the solvents starting with the alkane pentane and the aromatic benzene (both pure CH-compounds), then the alcohol (R-COH) and finally the three ether compounds (R1-O-R2). This indicates that an expansion might be possible to classify many different molecules.

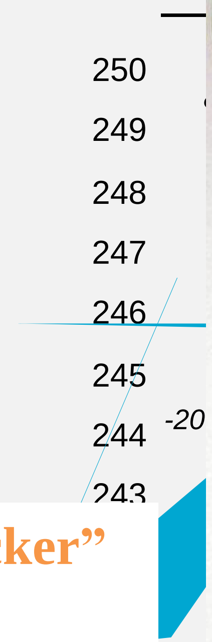
Source: A. Schütze, A. Gramm, T. Rühl
IEEE Sensors Journal, Vol. 4, No. 6, 2004

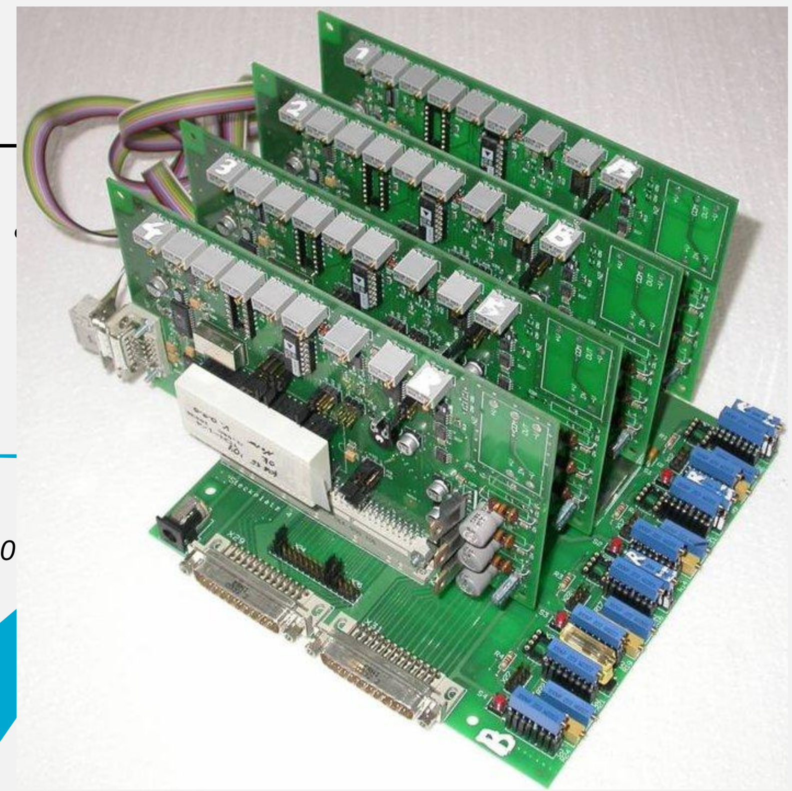


Hardware platform GasTON for exact temperature control and large dynamic range data acquisition – Gas sensor T-cycle Operating uNit

- 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





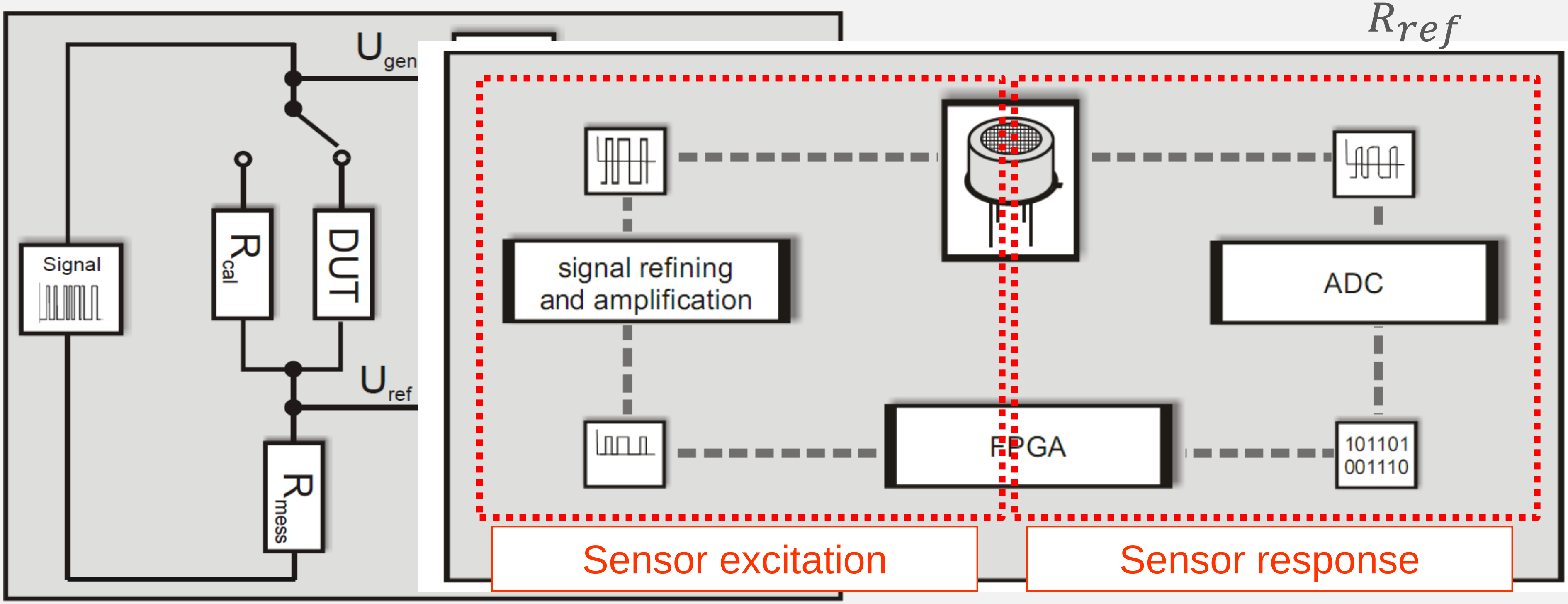


➢ **now commercialized "OdorChecker"**
by 3S GmbH (spin-off of LMT)

Hardware platform for Electrical Impedance Spectroscopy

E F T E

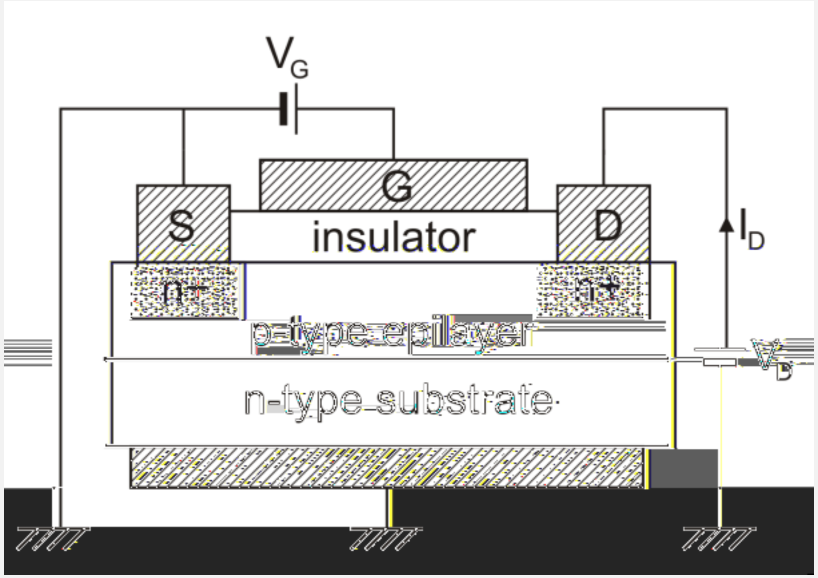
$$Z(\omega) = \frac{U(\omega)}{I(\omega)} = \frac{U_{Sensor}(\omega)}{\frac{U_{R_{ref}}(\omega)}{R_{ref}}}$$

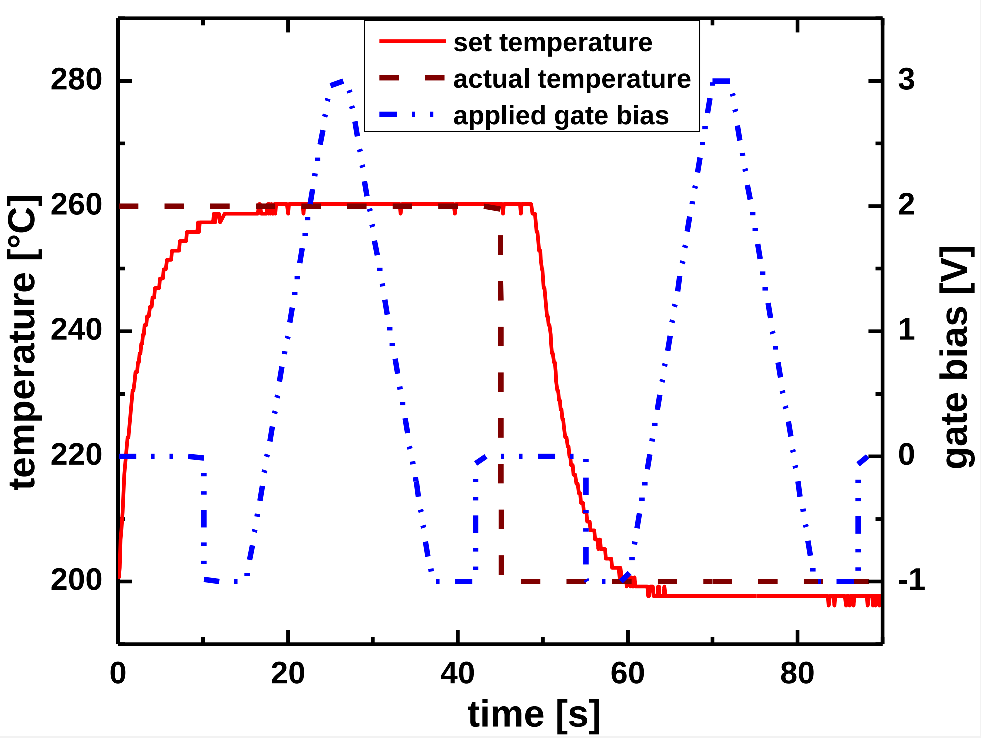


M. Schüler, S. Darsch, P. Reimann, A. Schütze, „Low-cost impedance spectroscopy for semiconductor gas sensors – a hardware concept“ IWIS, Chemnitz, 13.-15. October 2010

TCO hardware platform extended to allow Gate Bias Variation

- Heater temperature control
  Heater resistor $R_H(T)$ controlled for exact temperature control of GasFET
- Sensor read-out: voltage drop V_D measured at constant current I_D
- Gate voltage VG varied to influence the operating point





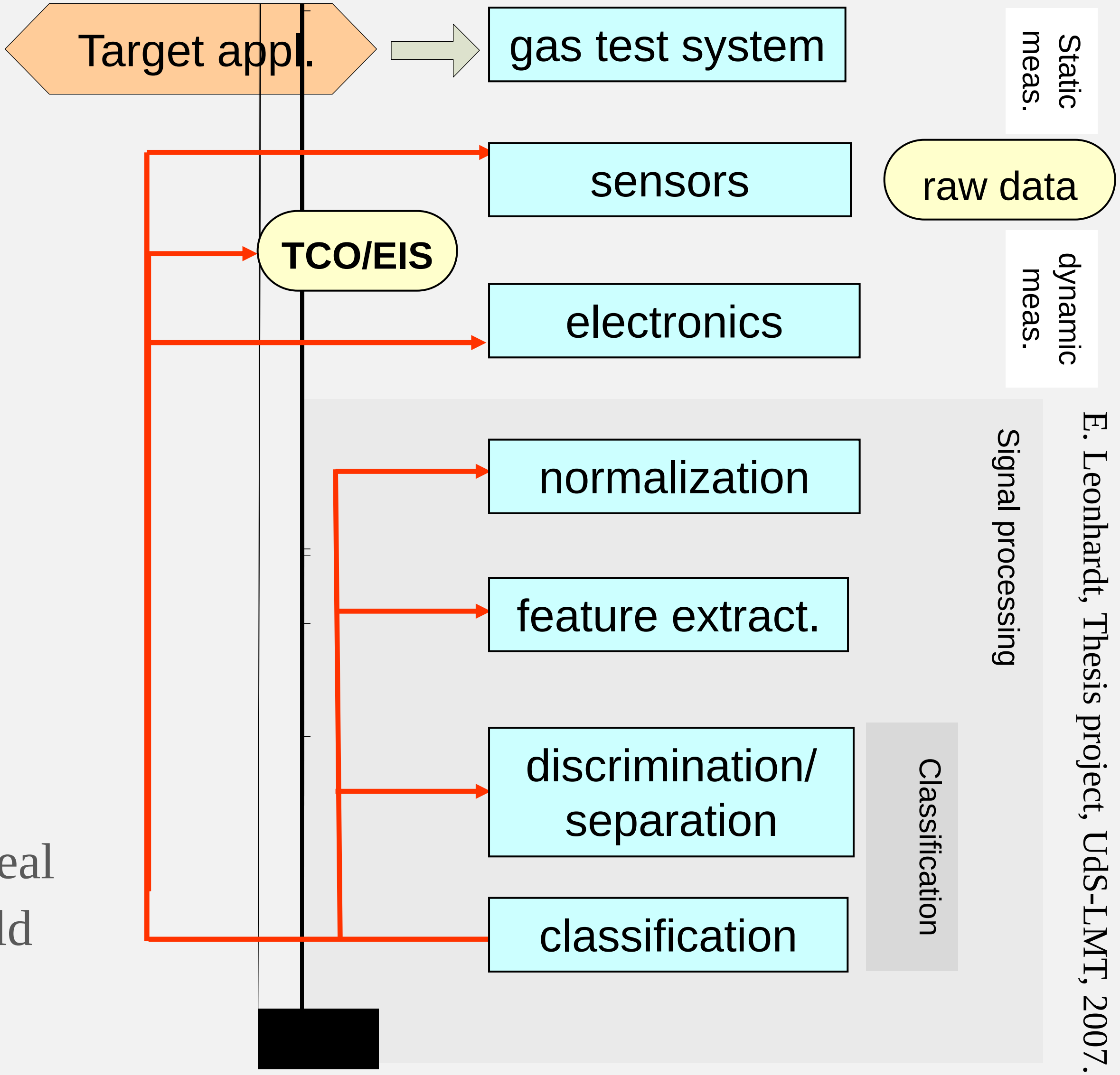
C. Bur et al.: Combination of Temperature Cycled and Gate Bias Cycled Operation to enhance the Selectivity of SiC-FET Gas Sensors, Proc. Transducers 2013 & Eurosensors XXVII; Barcelona, Spain, June 16 - 20, 2013

Temperature Cycled Operation – system design

Many possibilities for optimization:

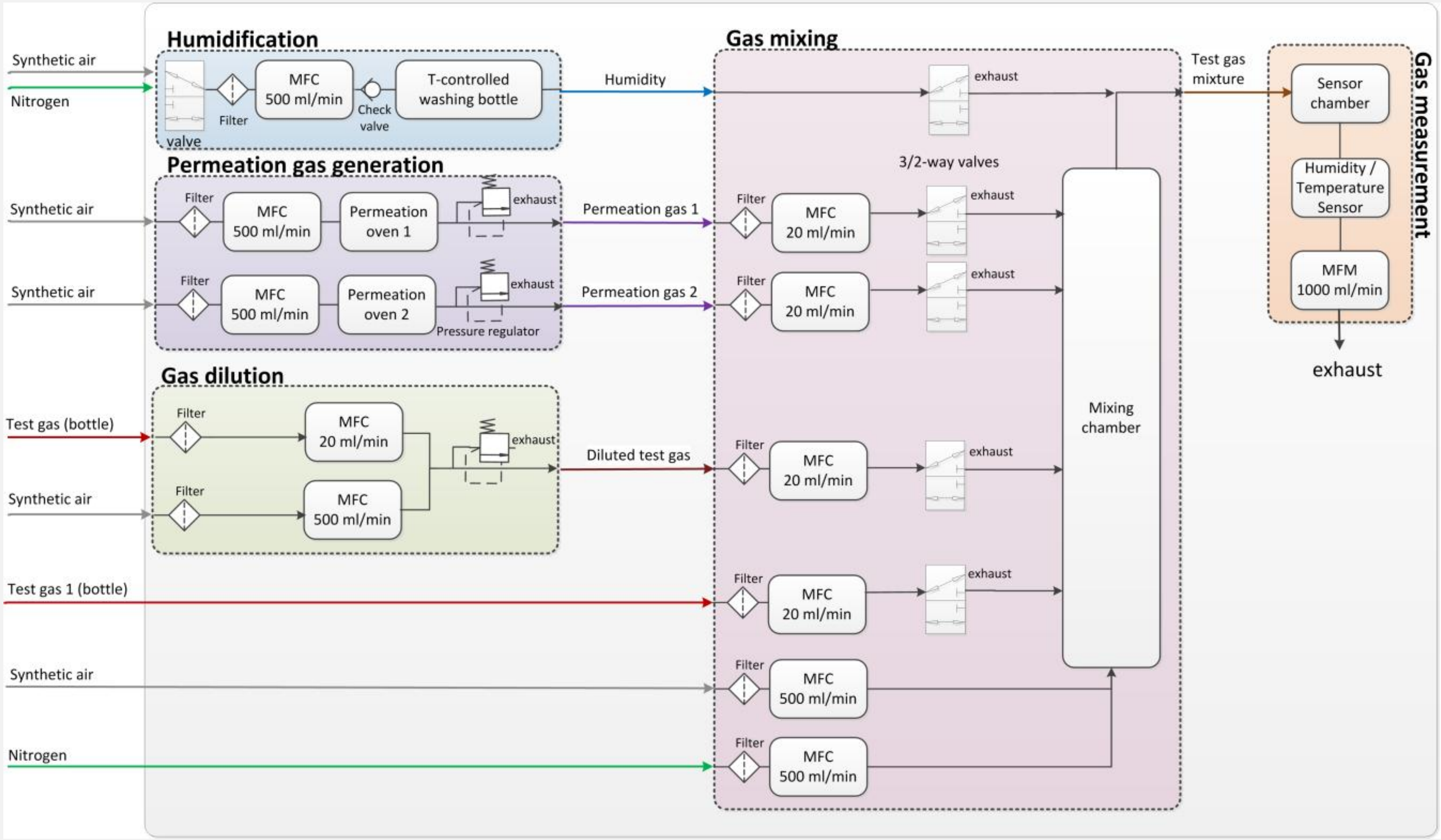
- Sensor selection
- Operating mode
  - TCO
  - EIS
  - GBCO
- Data acquisition
- Signal preprocessing
- Feature extraction
- Separation
- Classification

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



E. Leonhardt, Thesis project, UdS-LMT, 2007.

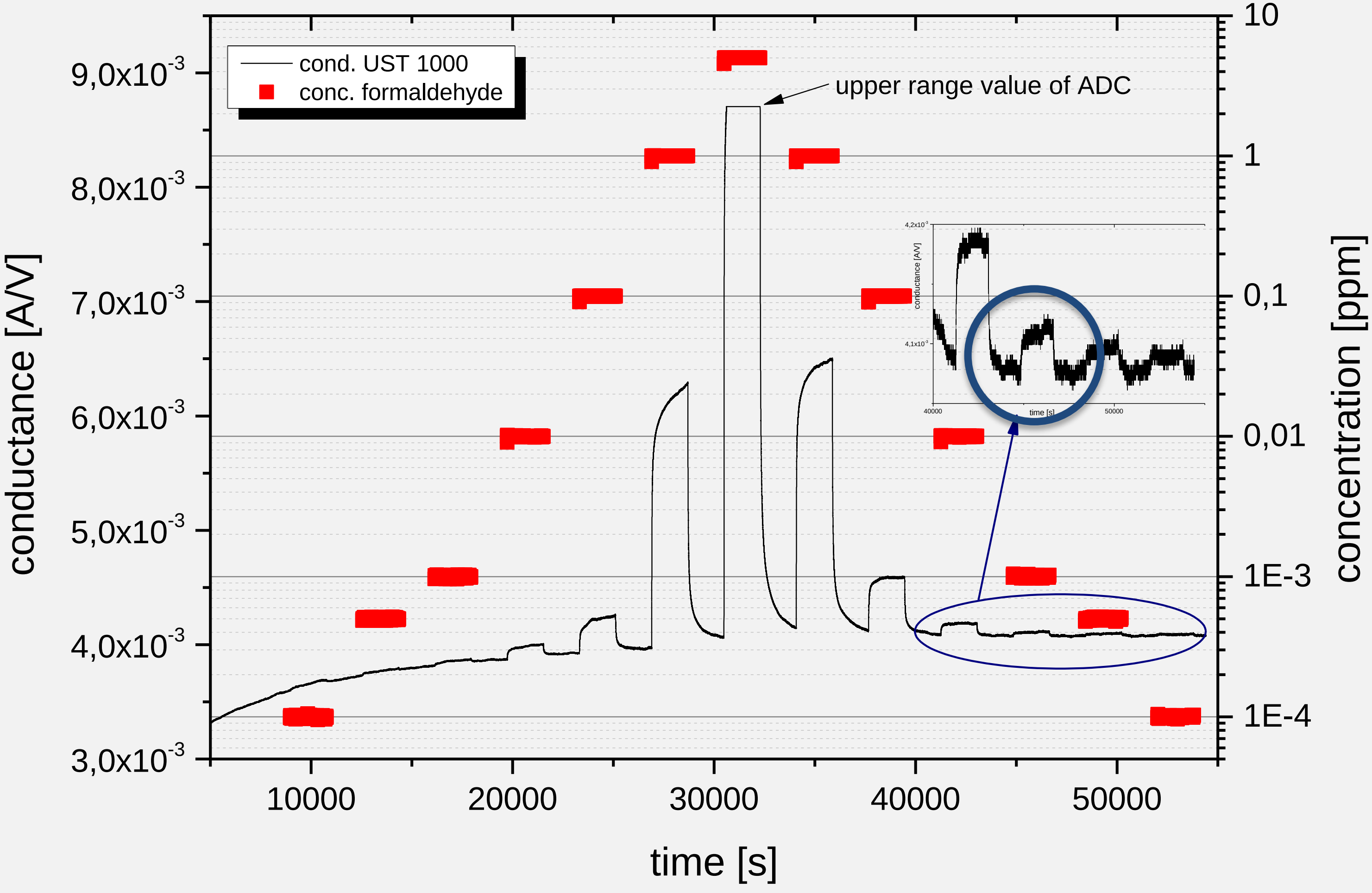
Calibration: novel gas mixing system for VOC testing down to sub ppb-level



Novel gas mixing system: results of reference measurement (zero air)

compound	CAS no	c [µg/m³]	c [ppb]
benzene			

Novel gas mixing system: results of first sensor tests

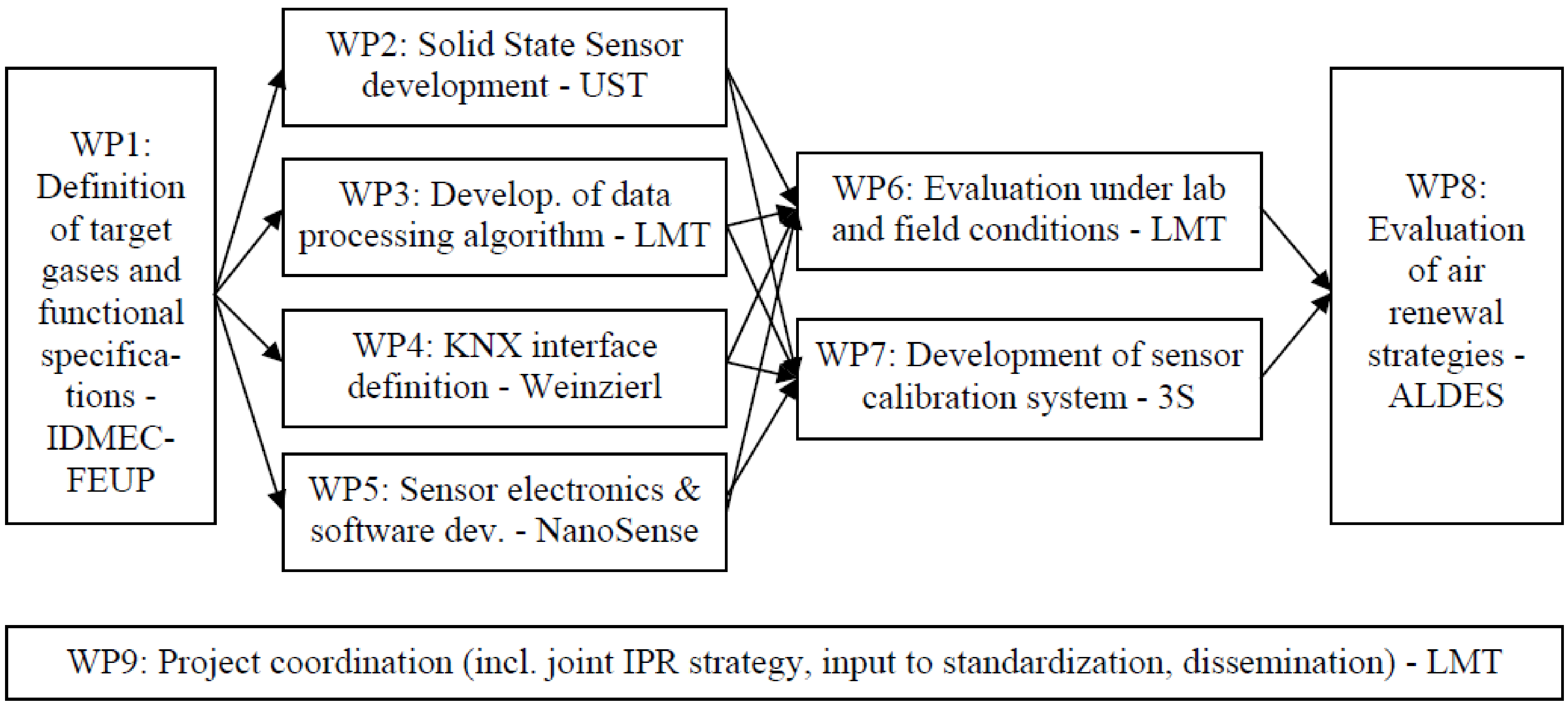


Sensor reaction to **1 ppb formaldehyde**

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

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



MNT-ERA.net project VOC-IDS

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

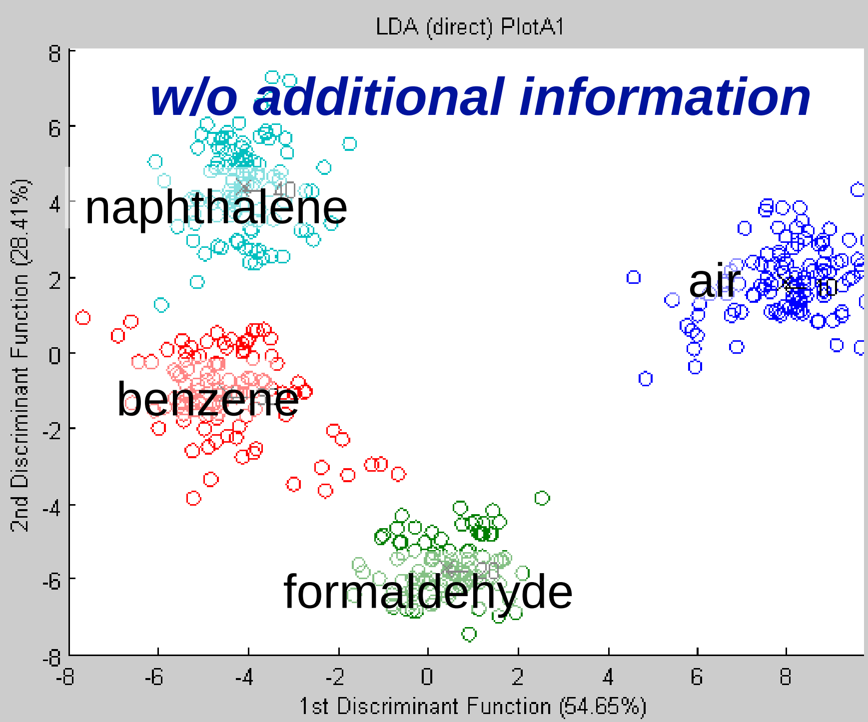
target gas	Concentration (ppb)	humidity	Interferents (EtOH ppm)
Air	NA	40%, 60%	none, 0.4, 2
Formaldehyde	10, 100	40%, 60%	none, 0.4, 2
Benzene	0.5, 4.7	40%, 60%	none, 0.4, 2
Naphthalene	2, 20	40%, 60%	none, 0.4, 2

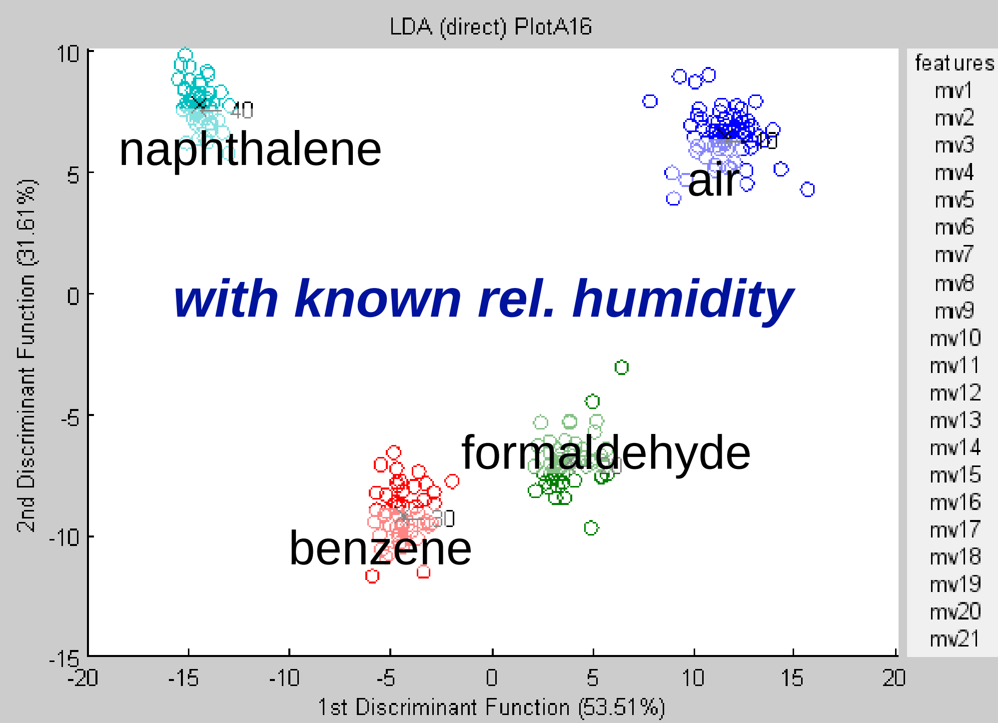
interferent concentrat.	relative humidity	number of LDA steps for charac.	Estimated number of LDAs	
0, 0.4, 2	40%, 60%	1	1	generalized classification
None	40%, 60%	2	1+10(?)*1	classification w known EtOH
0, 0.4, 2	None	1 (2)	(1+) 5*1	classification w known r.h.

> Indoor Air Quality monitoring

MNT-ERA.net project VOC-IDS

- Example for selective detection of VOCs in interfering background
- Classification of Formaldehydye, Benzene, Naphthalene in presence of ethanol
- General classification possible, but noisy
- Improved performance with known rel. humidity (from additional sensor)
- This proves VOC identification at levels below future thresholds!

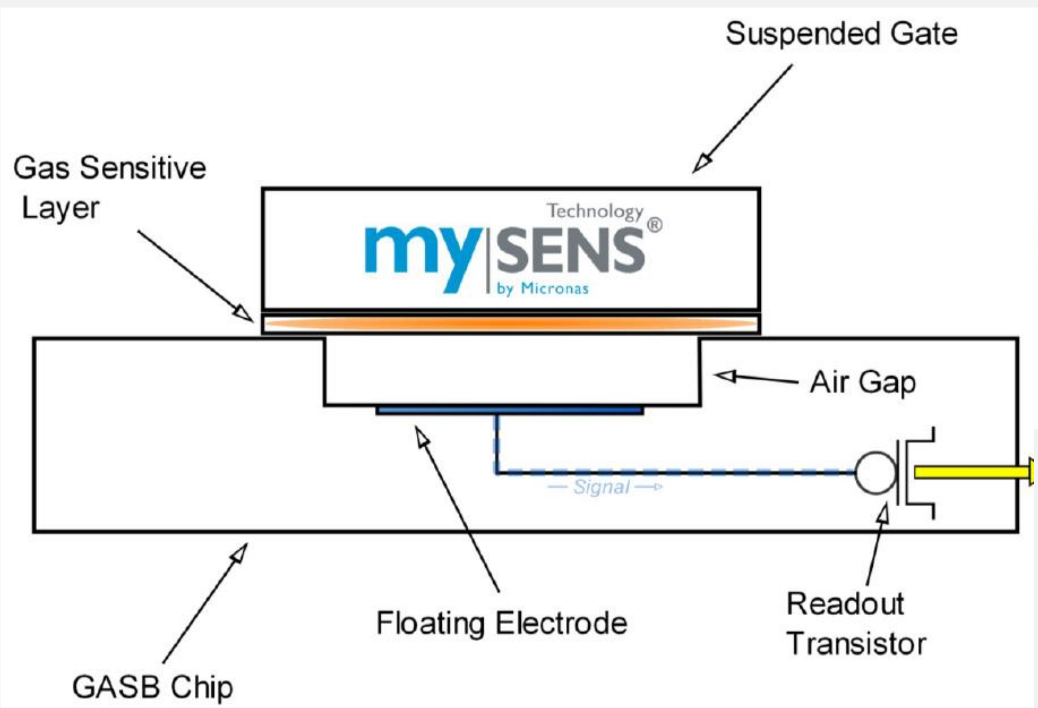


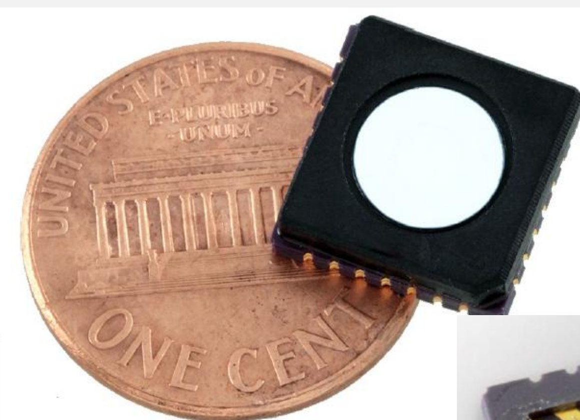


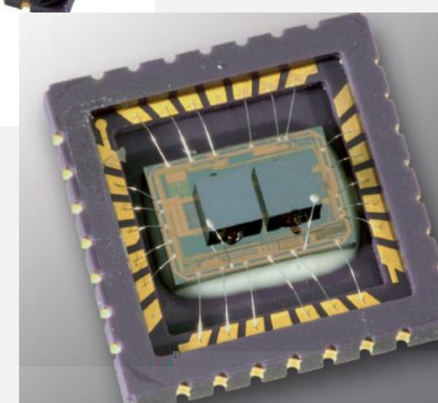
> Novel developments

Novel sensor materials and transducer principles

- Nanotechnology for improved gas sensitive layers
- Novel transducer principles
  - Gas ionization (can be electronically controlled!)
  - GasFETs commercially available





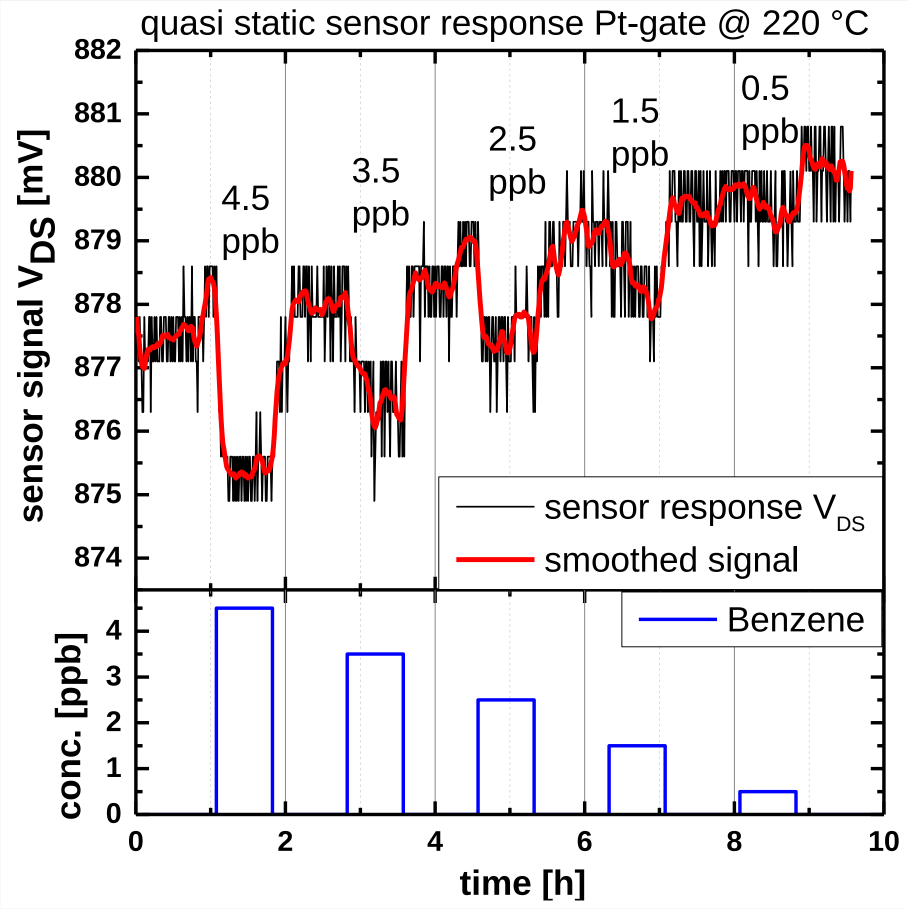


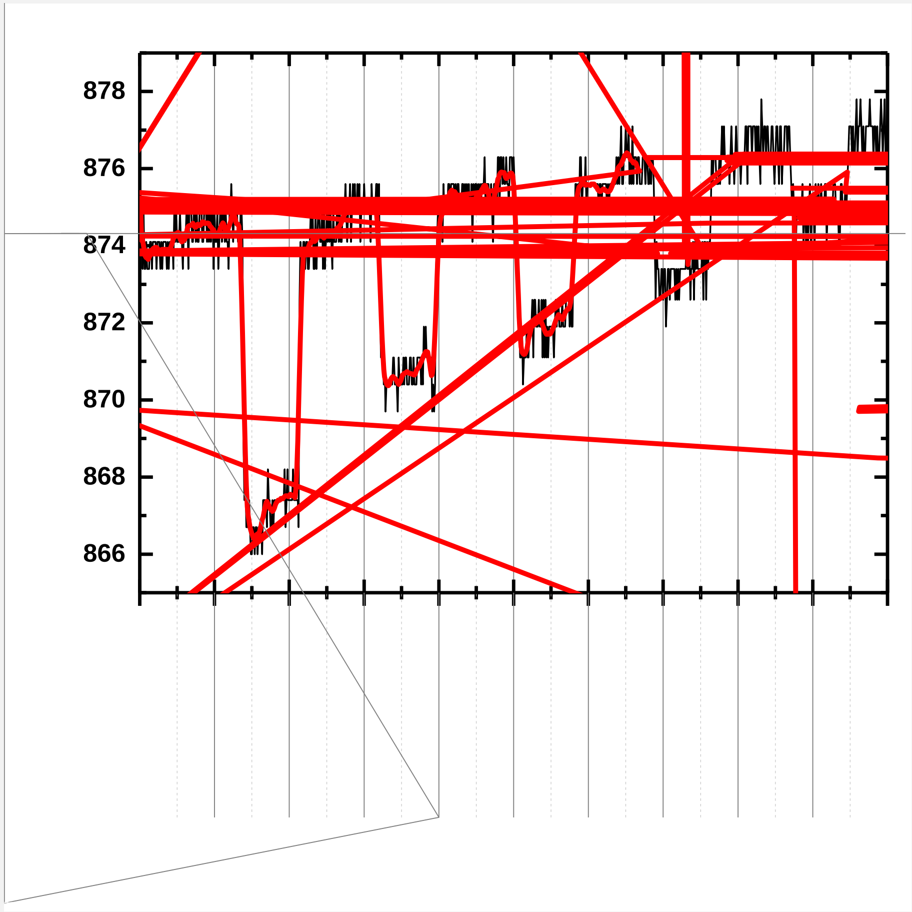
Source: Micronas

SiC Gas-sensitive Field Effect Sensors (Linköping U, SenSiC)

- high temperature operation
- allows temperature cycled operation as for MOS
- (nano-)pi0 usstnupimU,n ani iridium(

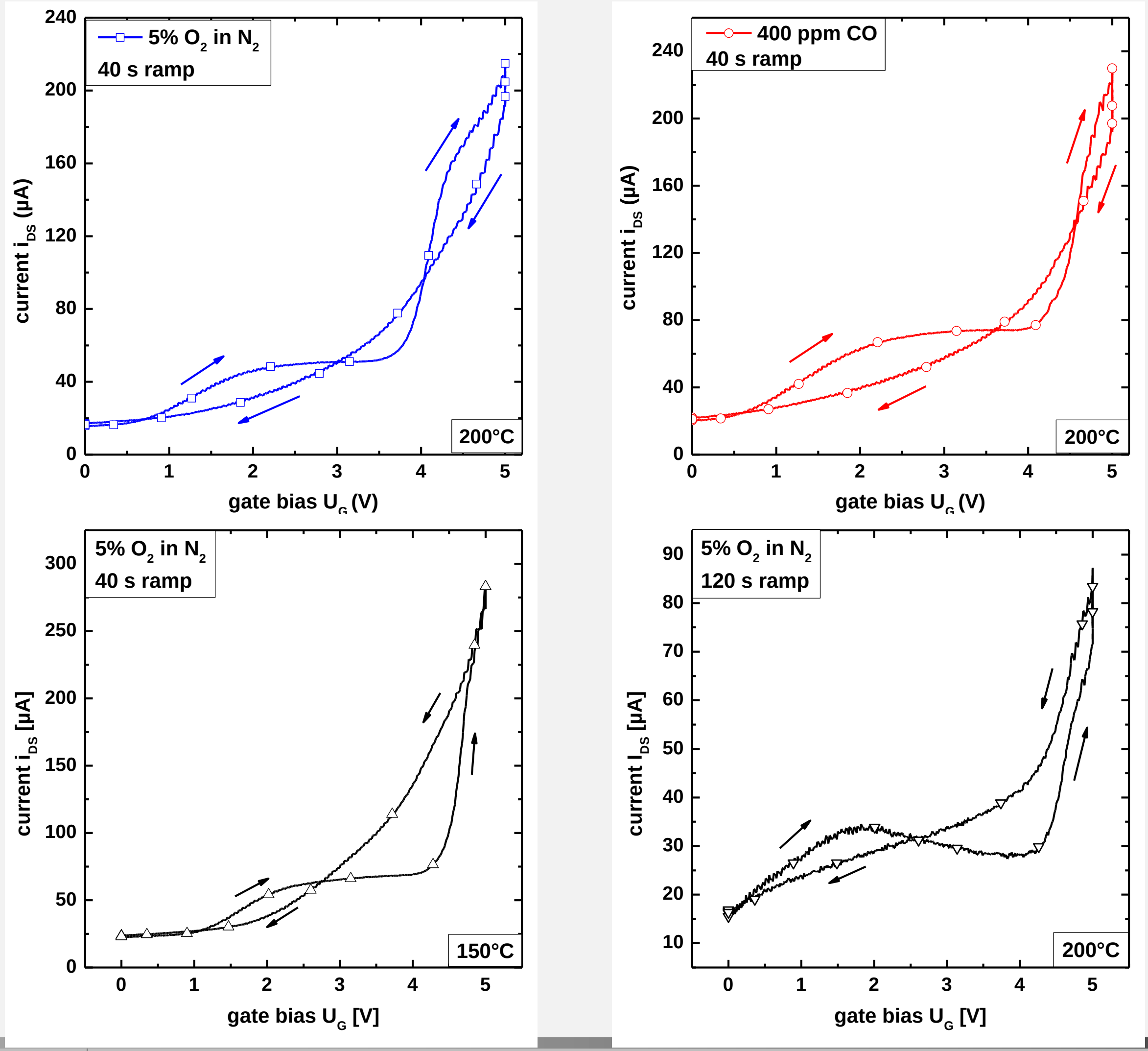
Highly sensitive VOC detection with SiC GasFETs (SenSiC AB)

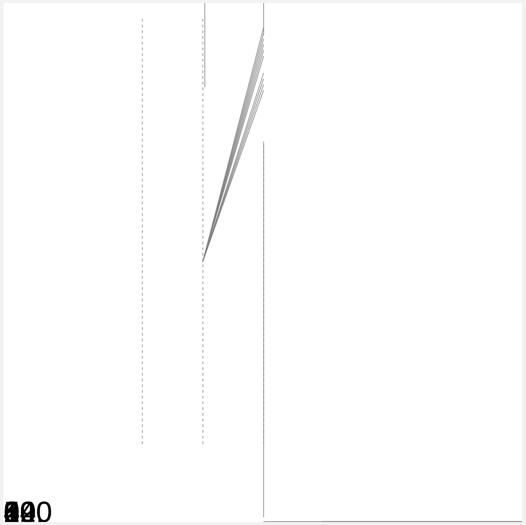




C. Bur et al.: Detecting Volatile Organic Compounds in the ppb Range with Pt-gate SiC-Field Effect Transistors, Proc. IEEE Sensors 2013; Baltimore, USA, Nov. 3-6, 2013

System integration: Gate Bias Cycled Operation for SiC-GasFETs

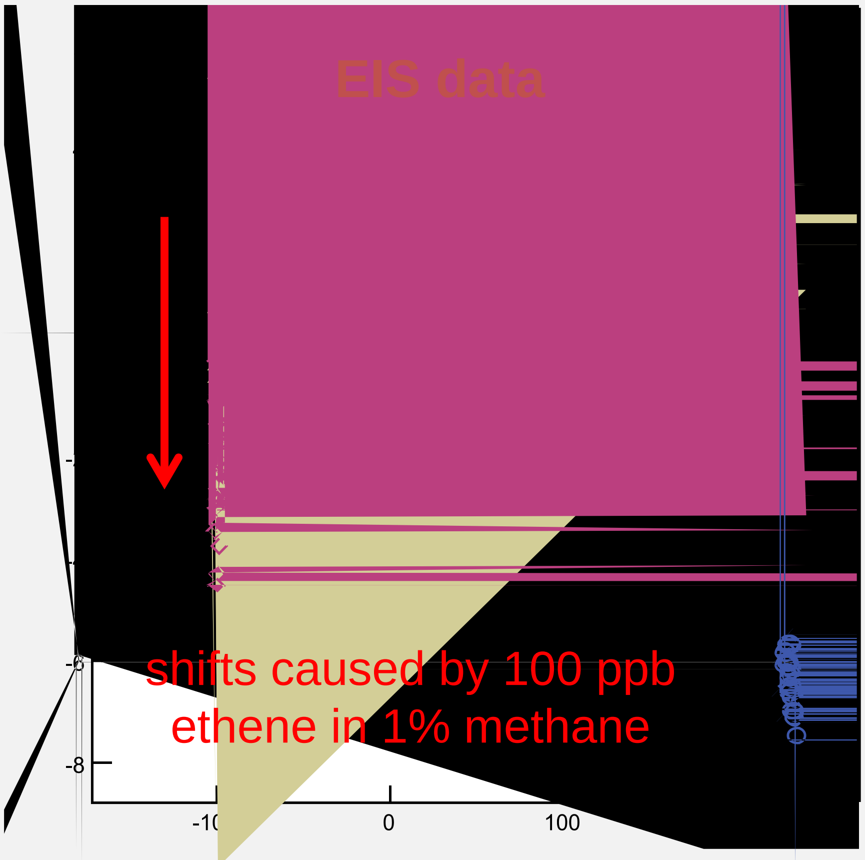


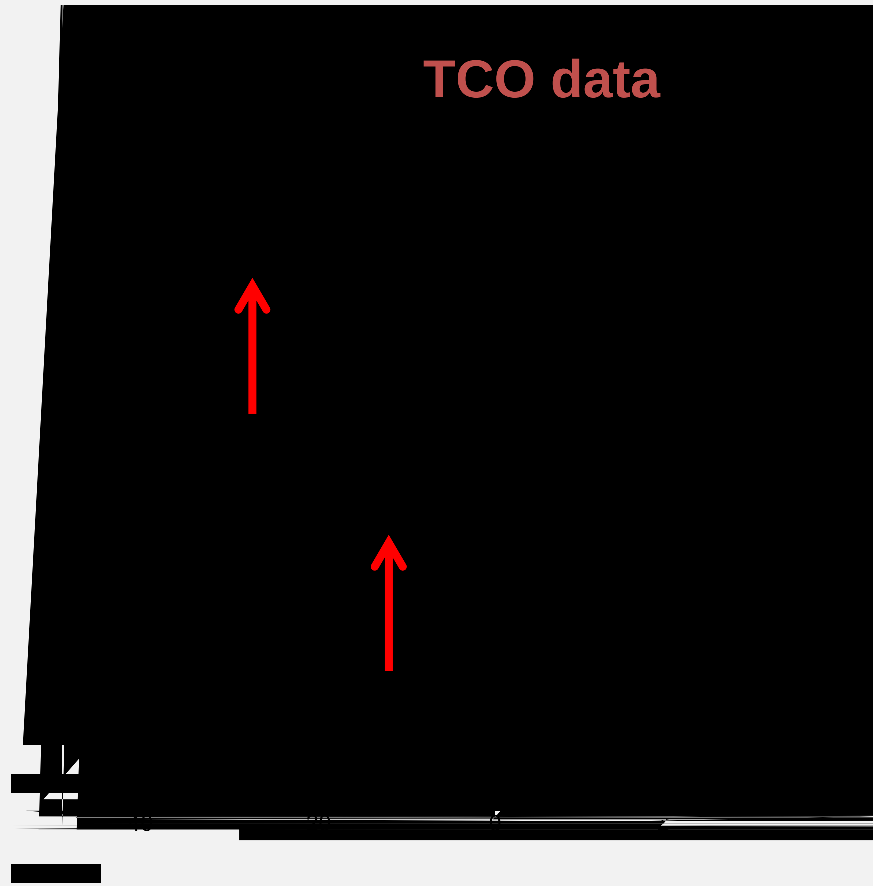


C. Bur et al.: Influence of a Changing Gate Bias on the Sensing Properties of SiC Field Effect Gas Sensors, IMCS 2012

> Novel developments

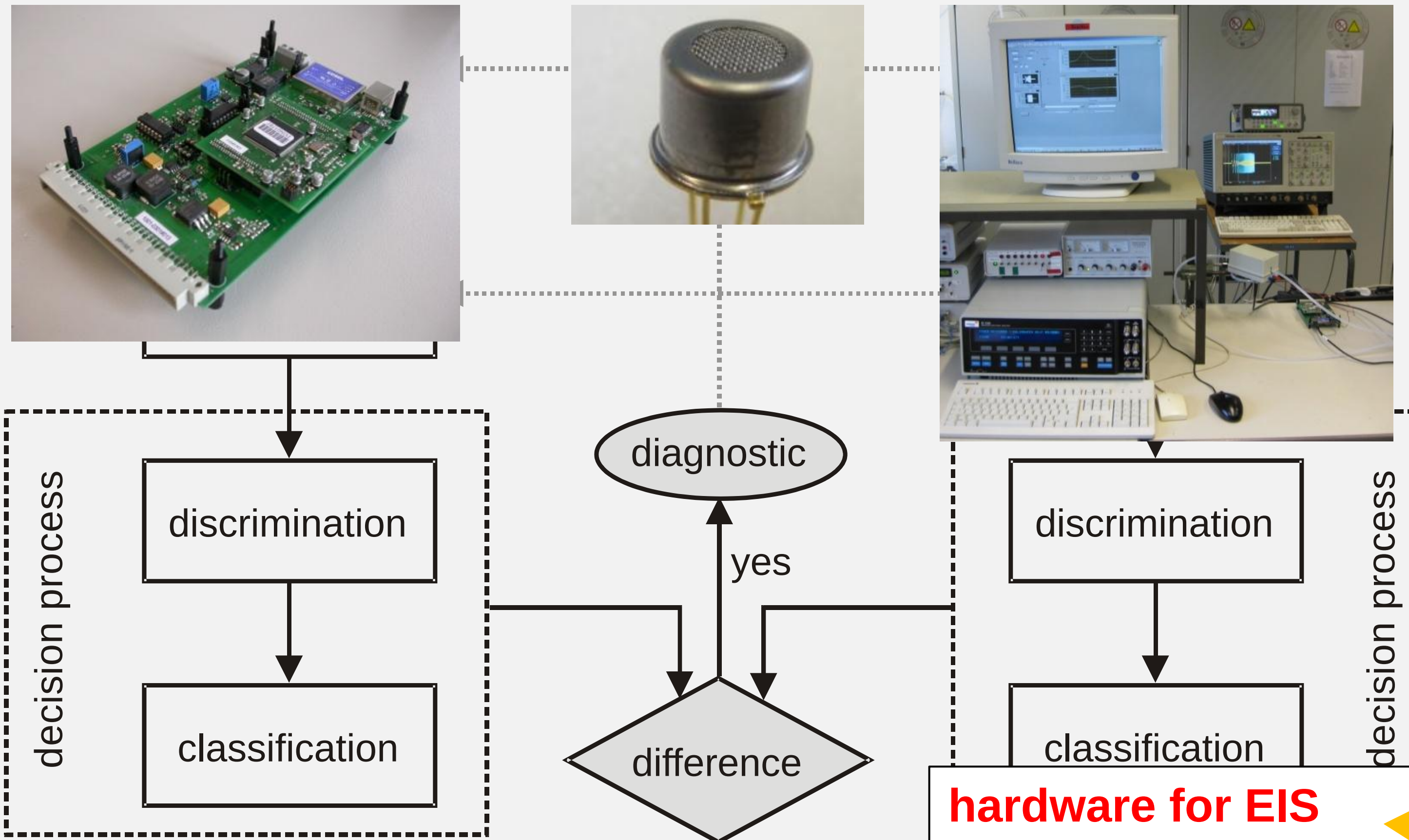
- **Electrical Impedance Spectroscopy** achieves similar improvement in selectivity as Temperature Cycled Operation – but time scale is completely different!





A. Schütze et al.: Improving MOS Virtual Multisensor Systems by Combining Temperature Cycled Operation with Impedance Spectroscopy, ISOEN 2011

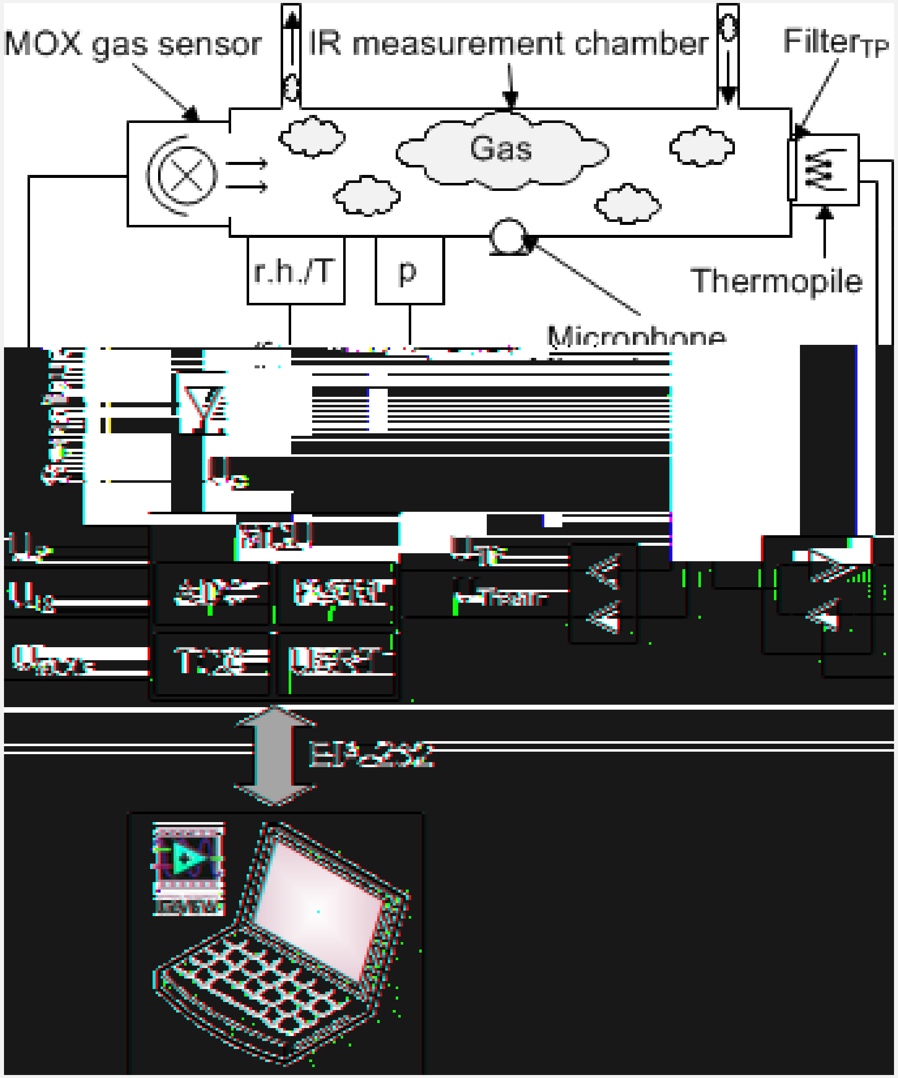
Sensor self-monitoring with combination of TCO and EIS



hardware for TCO operation available at reasonable cost

hardware for EIS
- **poor mobility**
- **high cost**
- **long acquisition time**

A. Schütze et al.: Improving MOS Virtual Multisensor Systems by Combining Temperature Cycled Operation with Impedance Spectroscopy, ISOEN 2011

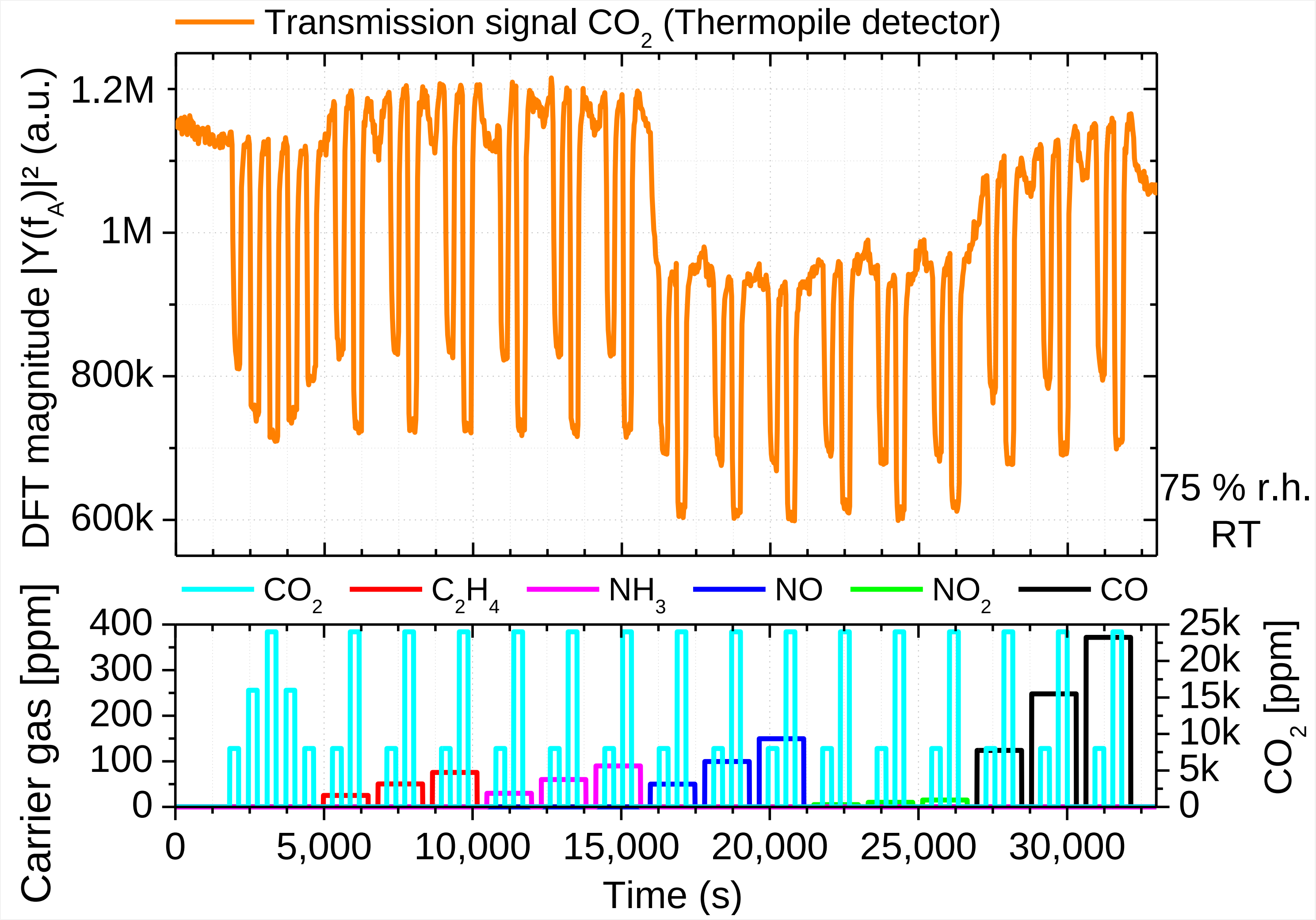


MOS-IR measurement system:

- Gas filled chamber (9 cm length)
- MOS gas sensor (MICS 5131, e2v)
- Transmission: Thermopile (HIS A21 F4.26, Heimann Sensors)
- Ambient condition monitoring (p, r.h./T)
- Electronics controlled by a microcontroller
- Configuration settings set by a GUI (LabVIEW)
- Data evaluation offline using Matlab

K. Kühn et al.: Investigations on a MOX Gas Sensor as an Infrared Source for an IR-based Gas Sensing System, IMCS 2012

Transmission signal, f_A = 6 Hz square wave mod. of the MOS gas sensor (MICS 5131, SGX)



K. Kühn et al.: Investigations on a MOX Gas Sensor as an Infrared Source for an IR-based Gas Sensing System, IMCS 2012

> Conclusions

- Gas sensor systems are more than just sensors
- Sensors are highly sensitive, but often lack selectivity and stability – especially for quantitative measurements
- Intelligent multisensor/dynamically operated sensor systems address existing drawbacks to broaden application spectrum
- Application specific development still required
- Field testing is a must for chemical sensor systems
  - Hardware for combined EIS-TCO currently in field test
  - Field tests of VOC-IDS sensor systems are starting now
- Chemical sensor systems are complementary to analytical techniques for Air Quality Monitoring
- They can become ubiquitous due to low cost and portability

UNIVERSITÄT DES SAARLANDES

LAB FOR MEASUREMENT TECHNOLOGY
Prof. Dr. rer. nat. A. Schütze

Thank you for your attention.

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

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VOC-IDS

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