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

COST Action TD1105

3rd International Workshop *EuNetAir* on

New Trends and Challenges for Air Quality Control

University of Latvia - Faculty of Geography and Earth Sciences

Riga, Latvia, 26 - 27 March 2015

Several ways to get more data out of chemosensing

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Sub-WG 1.3 leader, MC member

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ESF provides the COST Office through a European Commission contract

Scientific context and objectives in the Action

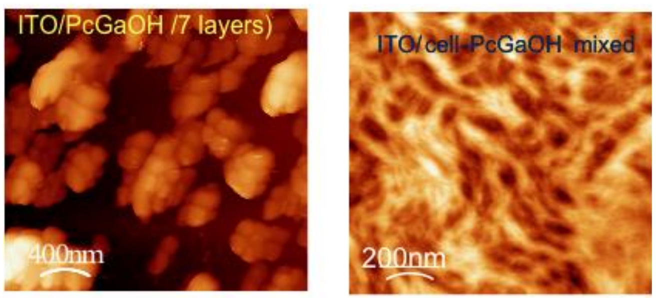
Sub-WG 1.3: Emerging sensor materials for air-pollution detection
molecular materials, organic/inorganic, hybrid, nanocomposites, polymers …

- **Background / Problem statement:**

  - Interest: The tuning of properties by molecular engineering

  morphology, roughness and specific surface, hydrophilicity or hydrophobicity, processability, electrical properties

  - One way: to combine materials for improving chemosensing



AFM images (1 mm x 1 mm) of a pure HOGaPc film (left) and a hybrid film cellulose/HOGaPc film;

Langmuir 23 (2007) 3712-3722

- **Brief reminder of MoU objectives:**

  selectivity, low-cost: solution processing (e.g. printing techniques …)

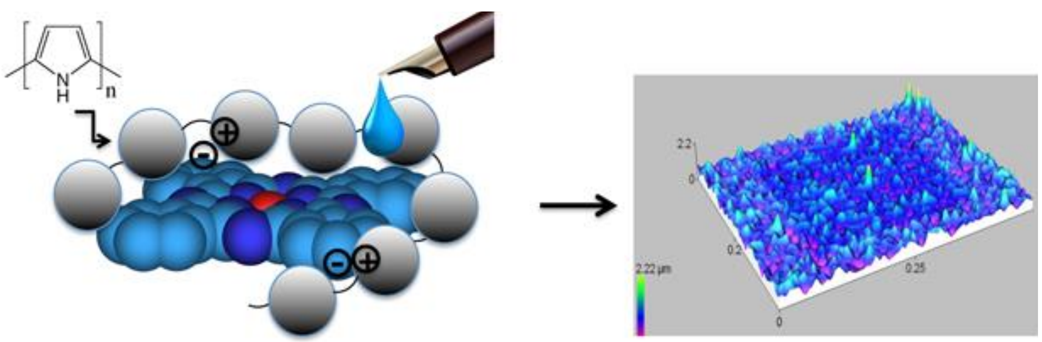
Suggested R&I Needs for future research

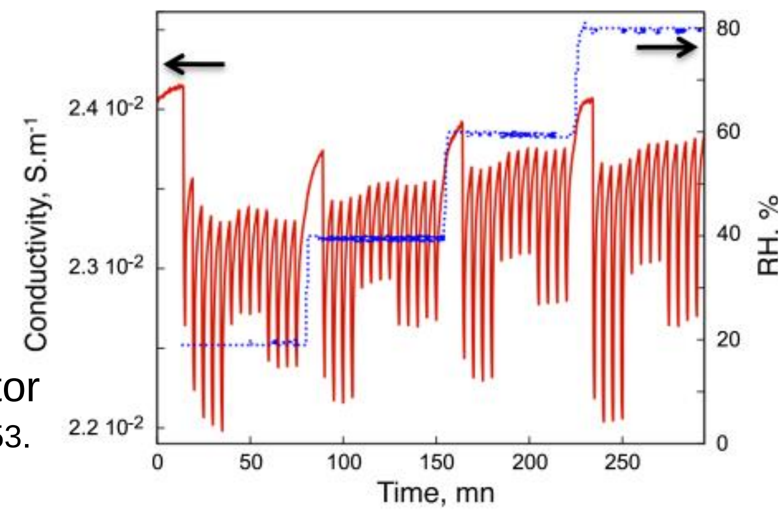
- **Research directions as R&I NEEDS:**

  - to stabilize the structure and morphology of sensing materials for a higher stability of the response of sensors

  - to study the compatibility with humidity (a key species in AQM)

- The effect of RH on the response of sensors must be studied, not only at one particular value, but also in a broad RH range





Response to NH_3 of an electrodeposited s-CoPc-PPy resistor

T. Sizun, T. Patois, M. Bouvet, B. Lakard, J. Mater. Chem. 22 (2012) 25246-25253.

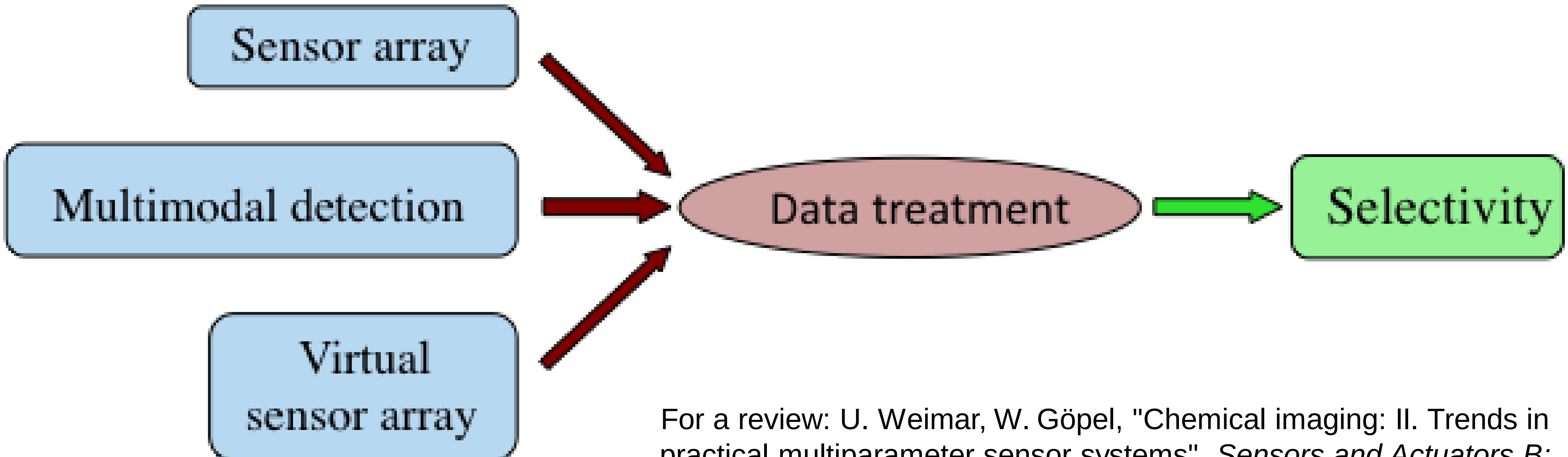
The main drawback of sensors:

Their lack of selectivity

The question is:

How to get a reliable information on a gas concentration?

The answers can be:

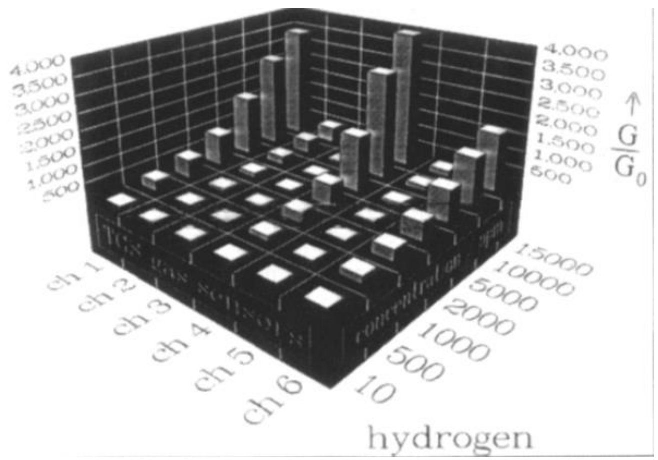


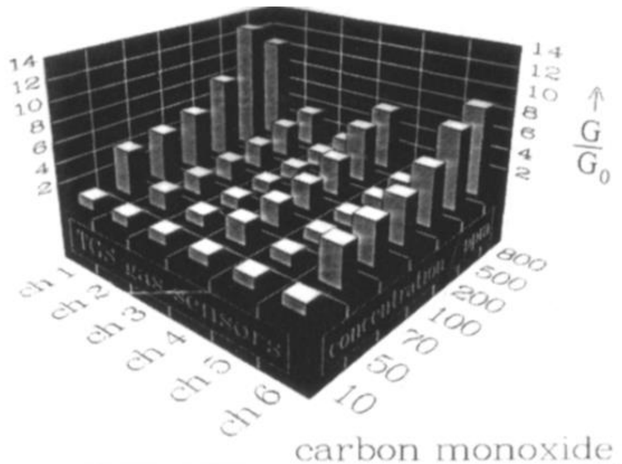
For a review: U. Weimar, W. Göpel, "Chemical imaging: II. Trends in practical multiparameter sensor systems", *Sensors and Actuators B: Chemical* 52 (1998) 143–161.

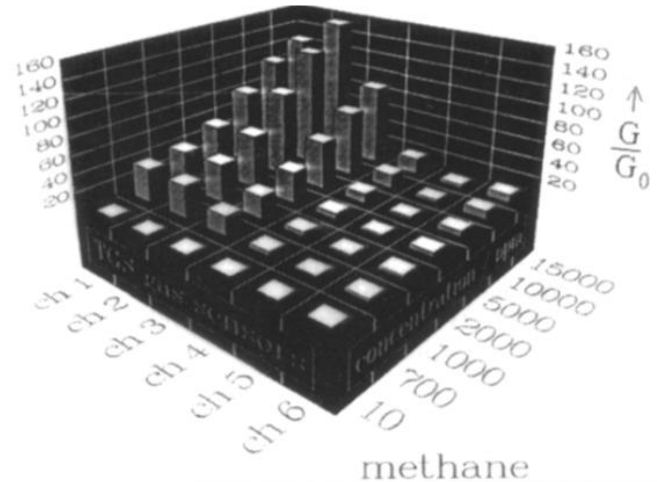
Sensor arrays

Several identical transducers are coated with different sensing materials

Ex.: 6 sensors TGS (conductometric SnO_{2-x} sensors, Figaro),
exposed at 3 pure gases at different concentrations, the conductance G was measured







Each sensor exhibits a response different from each other.

The relative responses G/G0 are different for the different gases,
These responses lead to patterns specific to each gas.

U. Weimar, K.D. Schierbaum, W. Göpel, R. Kowalkowski, "Pattern recognition methods for gas mixture analysis: Application to sensor arrays based upon SnO_2", *Sensors and Actuators B: Chemical* 1 (1990) 93–96.

Sensor arrays

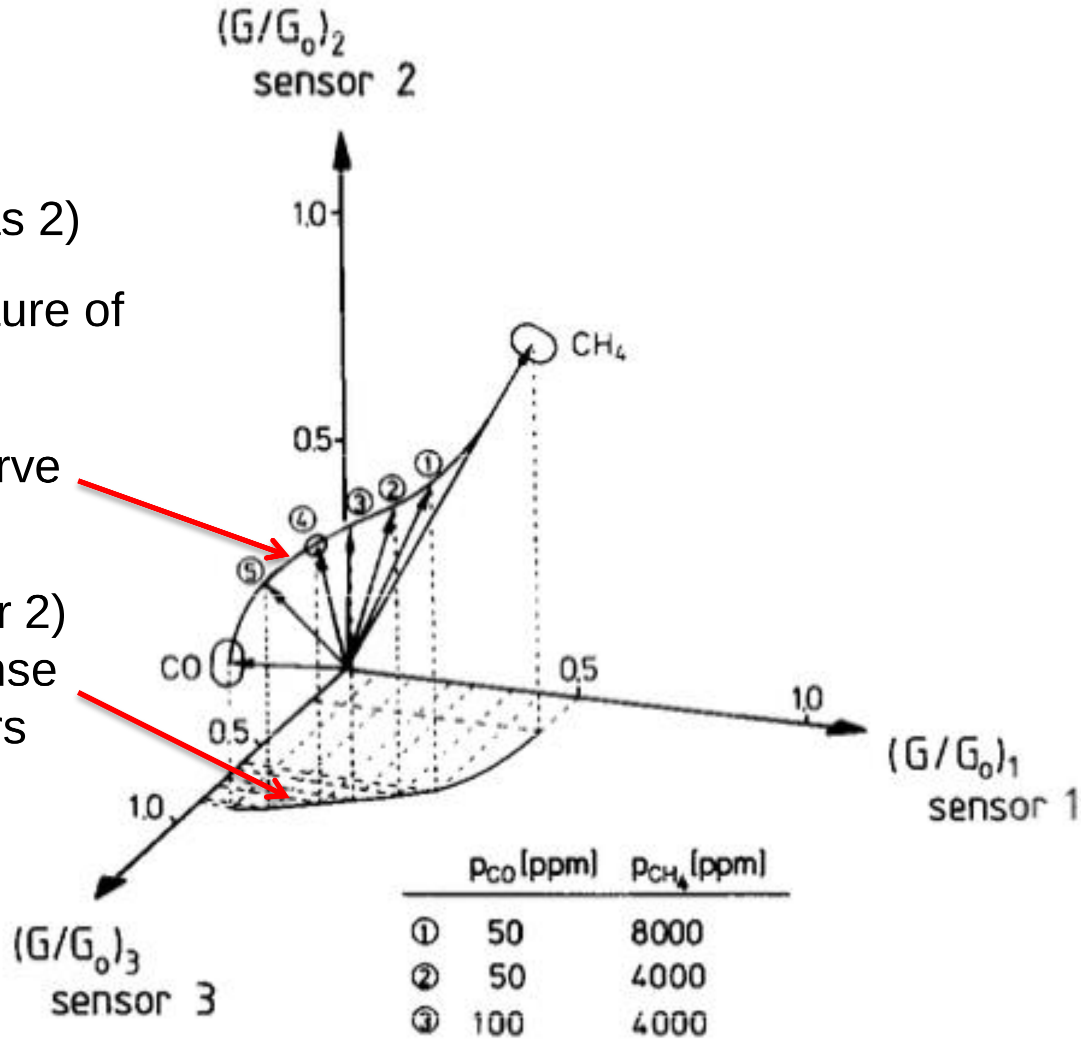
But in a mixture of gases,
it becomes more difficult

R(gas 1 + gas 2) ≠ R(gas 1) + R(gas 2)

Ex.: 3 sensors TGS exposed to a mixture of 2 gases

The response lies on the CH_4 ➔ CO curve

The projection on the (Sensor 1, Sensor 2) plane shows the evolution of the response from pure CH_4 to CO for these 2 sensors

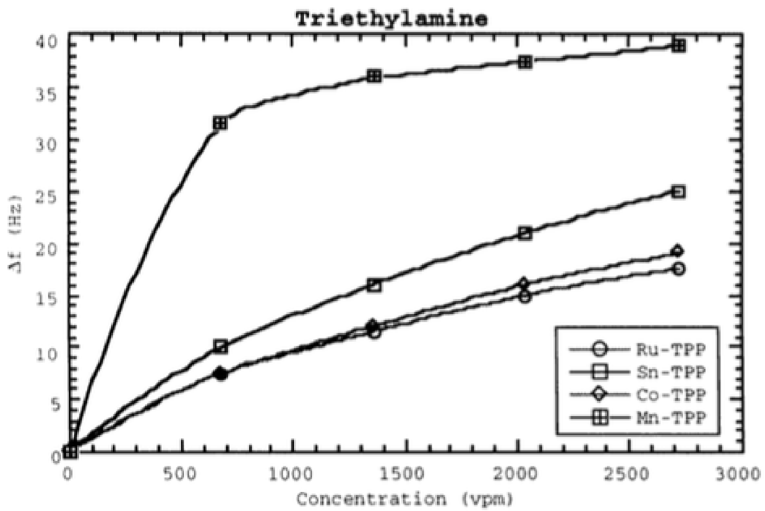


	p_{CO} [ppm]	p_{CH_4} [ppm]
①	50	8000
②	50	4000
③	100	4000
④	100	2000
⑤	200	1000

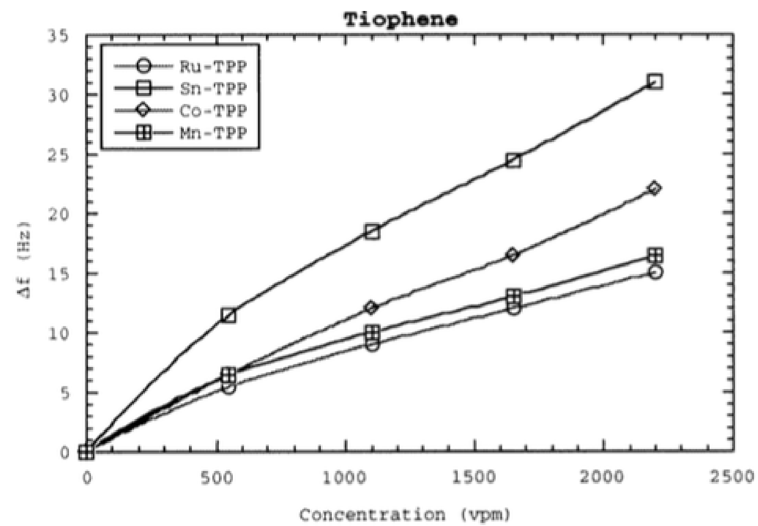
U. Weimar, K.D. Schierbaum, W. Göpel, R. Kowalkowski, "Pattern recognition methods for gas mixture analysis: Application to sensor arrays based upon SnO_2", *Sensors and Actuators B: Chemical* 1 (1990) 93–96.

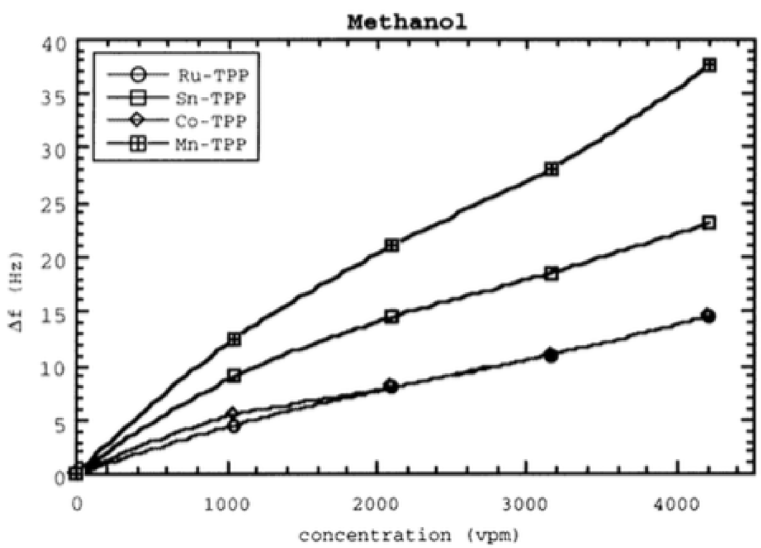
Another example of sensor array

4 quartz microbalances coated by different metalloporphyrins



$$\Delta f\ (Hz) = f_{gas} - f_0 \propto \Delta m$$



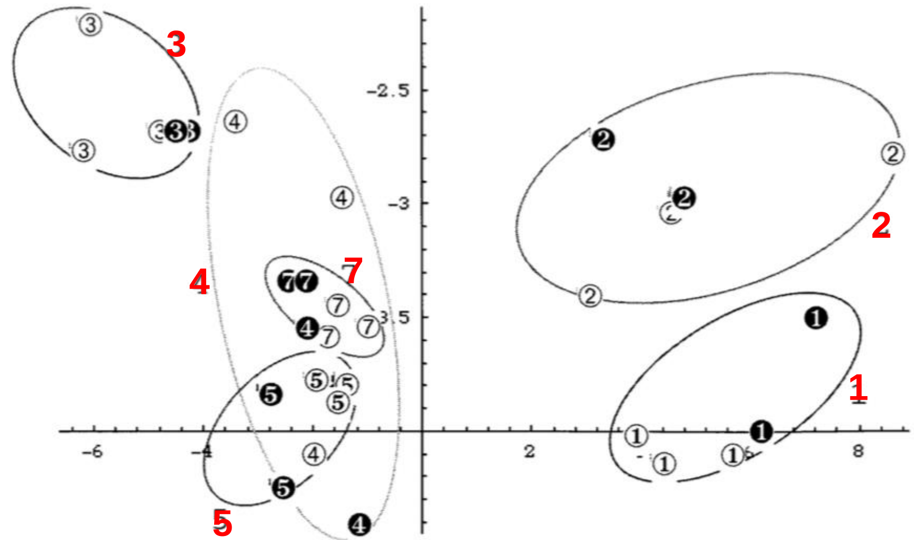


C.D. Natale, J.A.J. Brunink, F. Bungaro, F. Davide, A. D'Amico, R. Paolesse, T. Boschi, M. Faccio, G. Ferri, "Recognition of fish storage time by a metalloporphyrins-coated QMB sensor array", *Meas. Sci. Technol.* 7 (1996) 1103–1114.

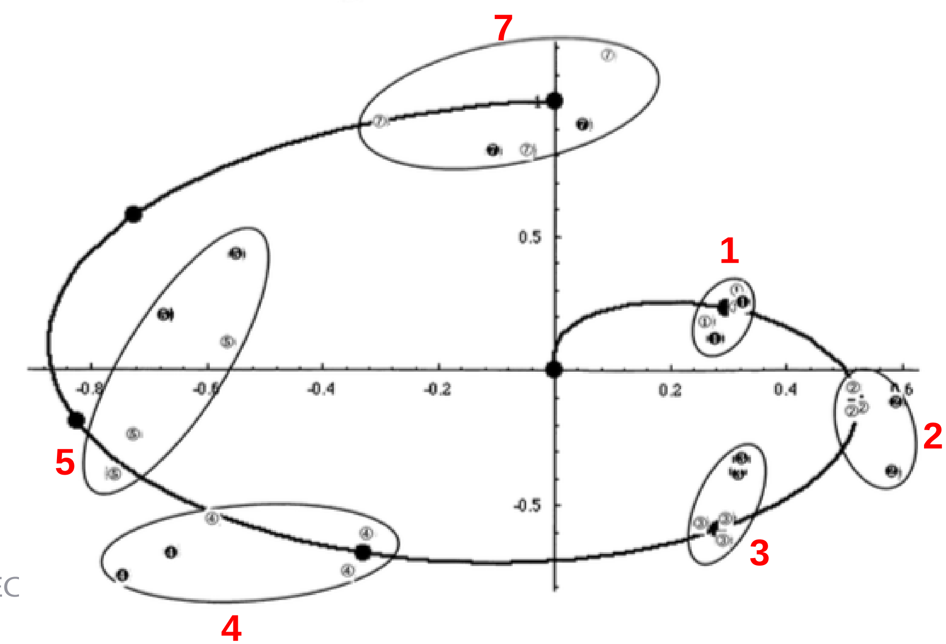
Application to the study of fish freshness

4 quartz microbalances coated by different metalloporphyrins

A score plot of the **principal component analysis** (PCA) of the fish data, from day 1 to day 7.
The white circles correspond to the calibration data and the filled ones to the test data.



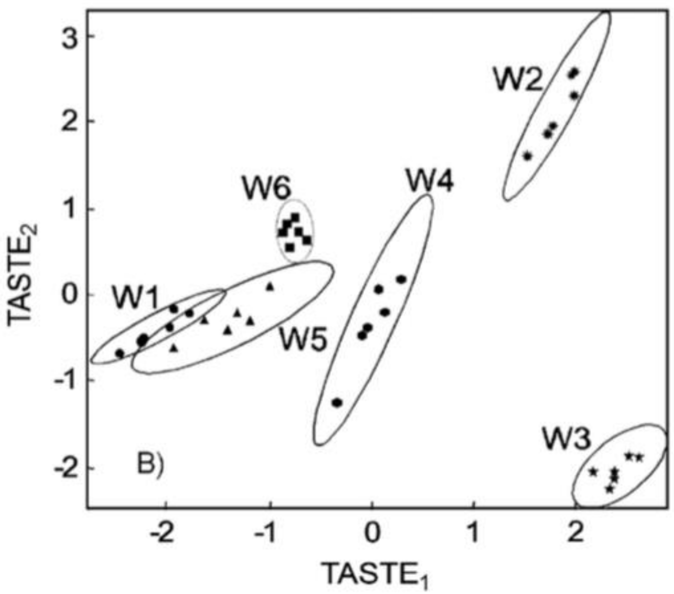
An analysis by a **neural network** leads to this new plot.
As a function of the fish freshness, the sensor array is capable to distinguish between the days 1 to 7.



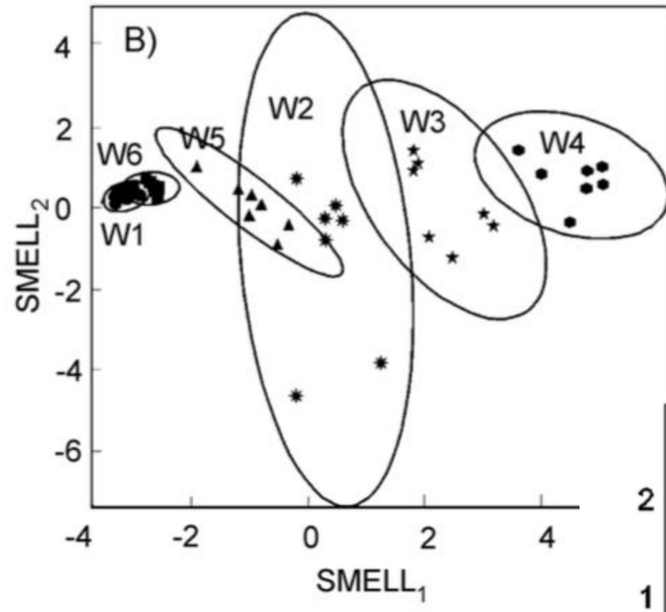
C.D. Natale et al., "Recognition of fish storage time by a metalloporphyrins-coated QMB sensor array", *Meas. Sci. Technol.* 7 (1996) 1103–1114.

A multimodal detection, with several sensor arrays

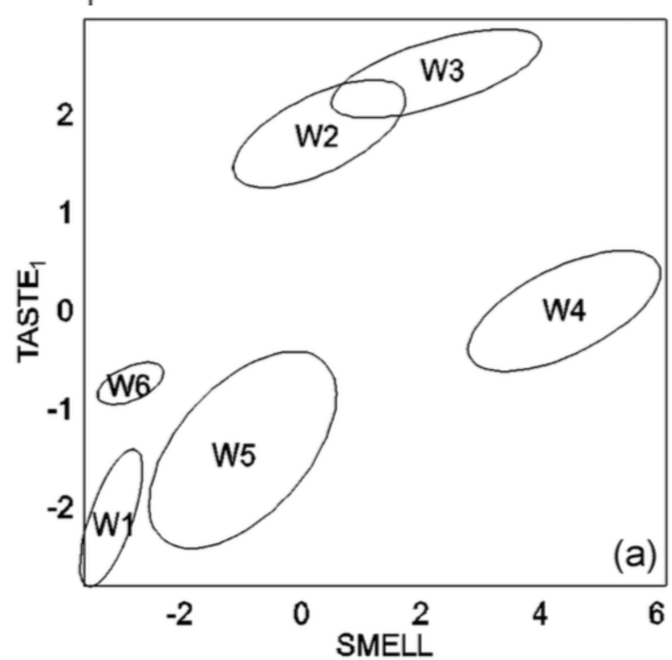
Combination of conductometric, optical and electrochemical transducers



An array of
6 electrochemical sensors

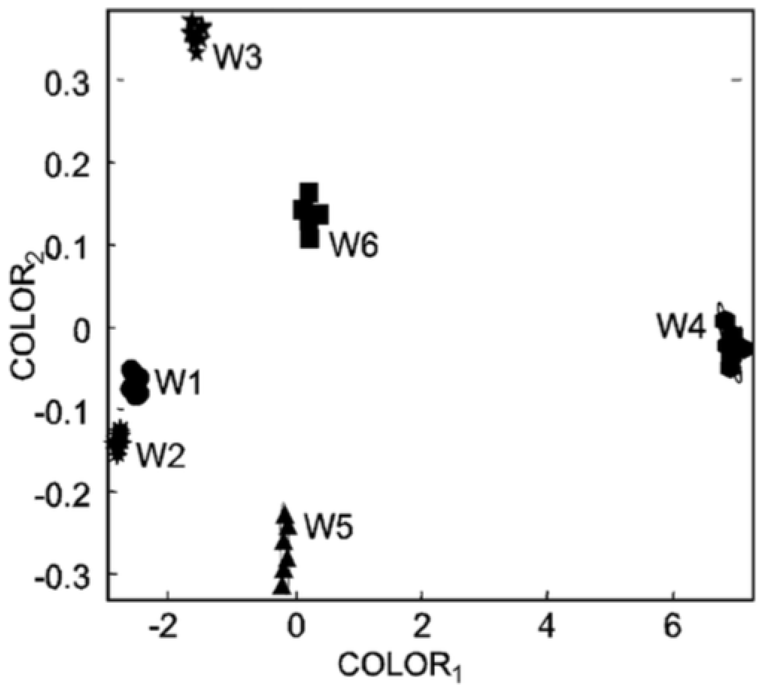


An array of
14 conductometric sensors



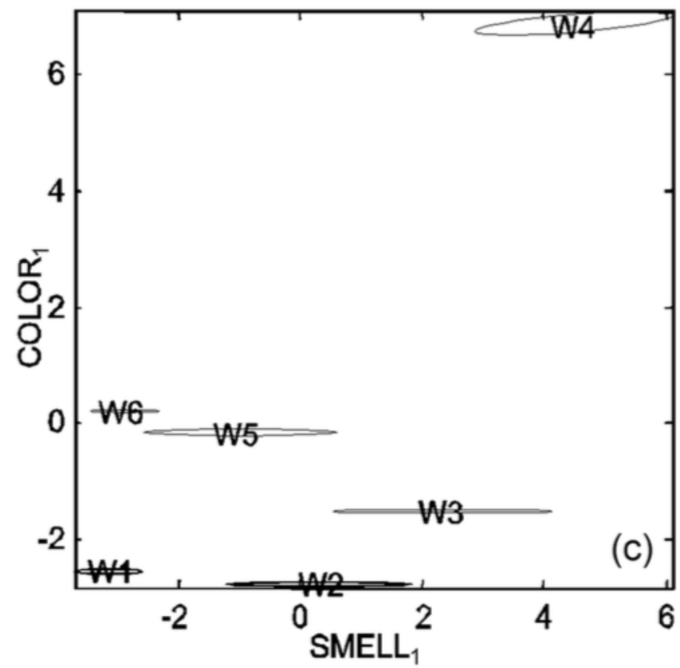
M.L. Rodríguez-Méndez, A.A. Arrieta, V. Parra, A. Bernal, A. Vegas, S. Villanueva, R. Gutierrez-Osuna, "Fusion of Three Sensory Modalities for the Multimodal Characterization of Red Wines", *IEEE Sensors J.* 4 (2004) 348–354.

A multimodal detection, with several sensor arrays



An array of 11 LED

Fusion of color with conductometric data



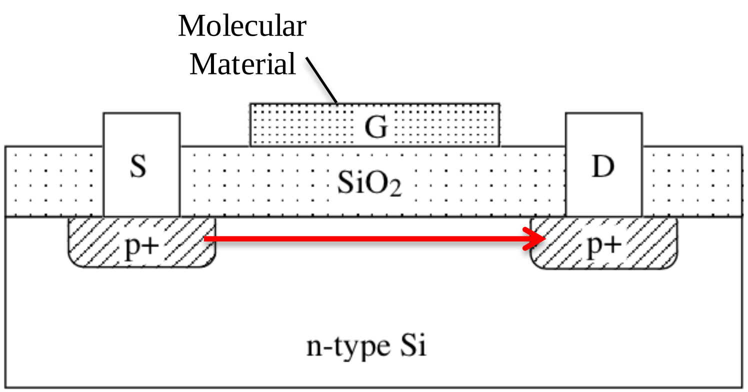
The discrimination capabilities of the system are significantly improved when signals from each module are combined to form a multimodal feature vector

M.L. Rodríguez-Méndez, A.A. Arrieta, V. Parra, A. Bernal, A. Vegas, S. Villanueva, R. Gutierrez-Osuna, "Fusion of Three Sensory Modalities for the Multimodal Characterization of Red Wines", *IEEE Sensors J.* 4 (2004) 348–354.

A multimodal detection

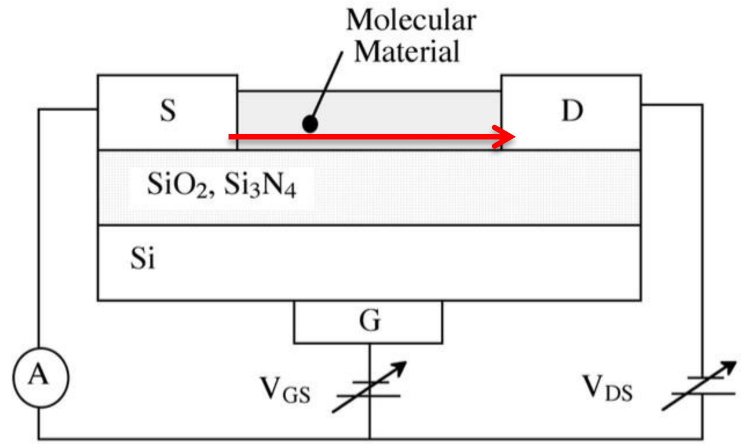
The interest is to be sensitive to the variation of several physical parameters

Example 1: To the surface potential and to charge carrier density



Si FET: The gate is covered by a molecular material

= GateFET, sensitive to the surface potential



OFET: The semiconductor is a molecular material

OFET is sensitive to the density of charge carriers

J. Janata, M. Josowicz, "Organic semiconductors in potentiometric gas sensors", *Journal of Solid State Electrochemistry,* 13 (2009) 41–49.

M. Bouvet, A. Pauly, "Molecular Semiconductor - Based Gas Sensors" in The Encyclopedia of Sensors, ed. by C.A. Grimes, E.C. Dickey, M. V. Pishko, American Scientific Publishers, vol 6, 227-270, 2006.

Research Goals in Air Quality Control

- **Background / Problem statement:** What is the scientific context and what research goals are the Action SIG3 addressing?

Pollutant
SO_2
NO_x
O_3
CO
CO_2
NH_3
H_2S
VOCs (BTX)
PM
Mould

Multi modal sensor arrays:

- # materials
- # transducers
- # operation modes

How a pollutant affects the physical parameter measured by the transducer?

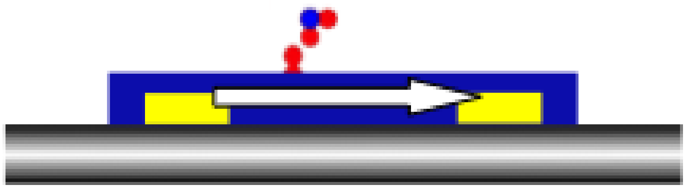
Transducer	**Physical parameter**
Conductimetric (resistor, ChemFET)	Conductivity, Gate work function, Impedance spectroscopy
Resonant sensors (SAW, QCM, cantilever)	Mass, stiffness
Electrochemical	Redox process
Optical	Absorption, Emission, Dielectric constant

Eduard Llobet - Marcel Bouvet

A multimodal detection

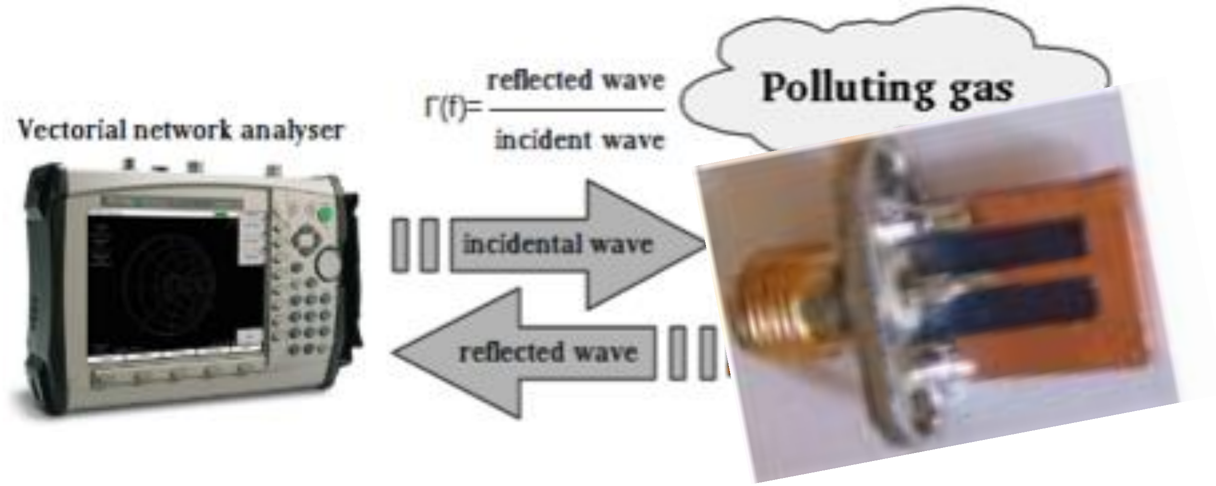
Example 2: To the dielectric constant and to the charge carrier density

Conductometric transduction and microwave transduction



Conductivity: $\sigma = n\ e\ \mu$

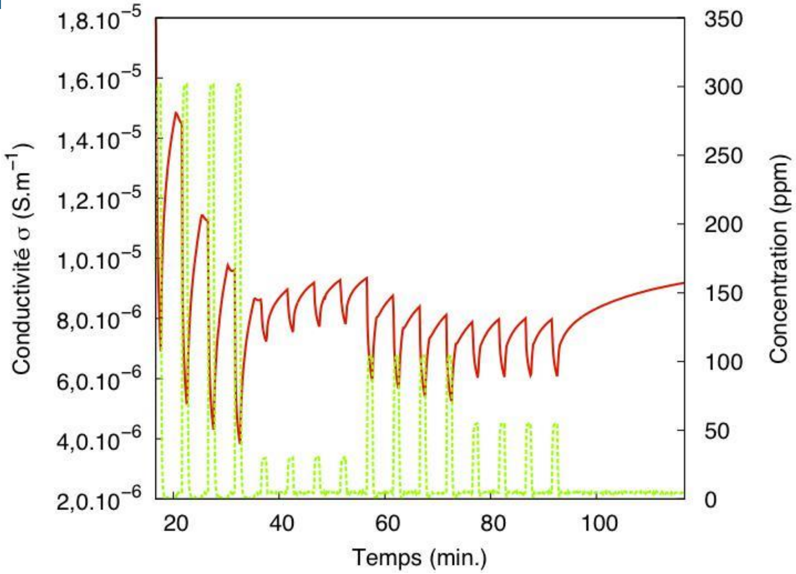
$$\Delta[G] \Rightarrow \Delta n \Rightarrow \Delta\sigma$$

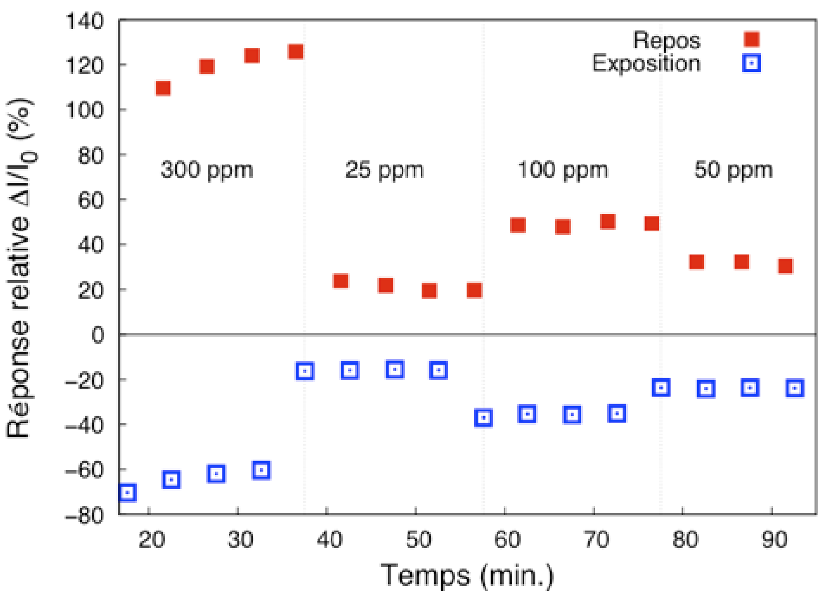


$$\Delta[G] \Rightarrow \Delta\varepsilon \Rightarrow \Delta\Gamma$$

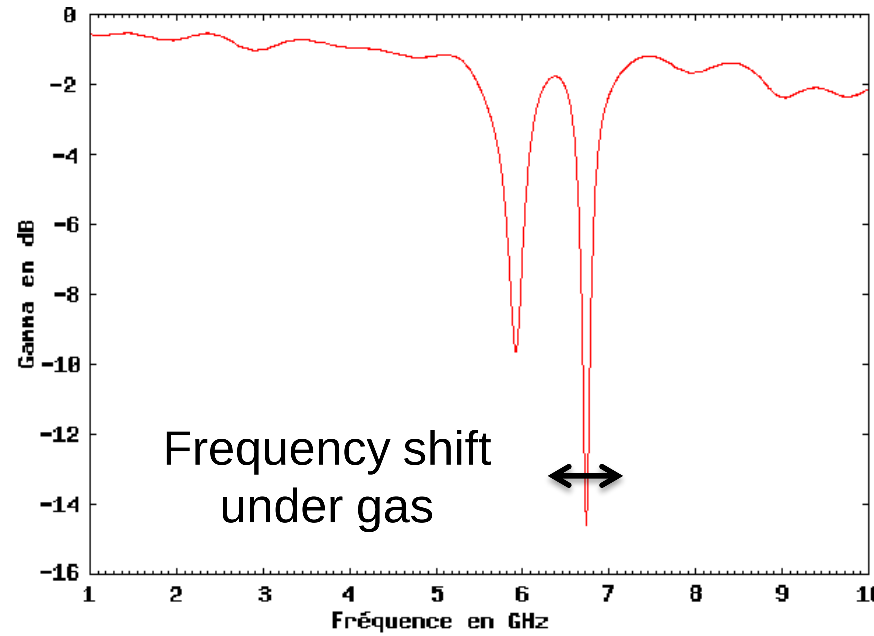
M. Bouvet, J.M. Suisse, T. Sizun, A. Kumar, G. Barochi, B. de Fonseca, J. Rossignol, "The multimodal detection as a tool for molecular material-based gas sensing", *Sensors and Actuators B: Chemical* 187 (2013) 204–208.

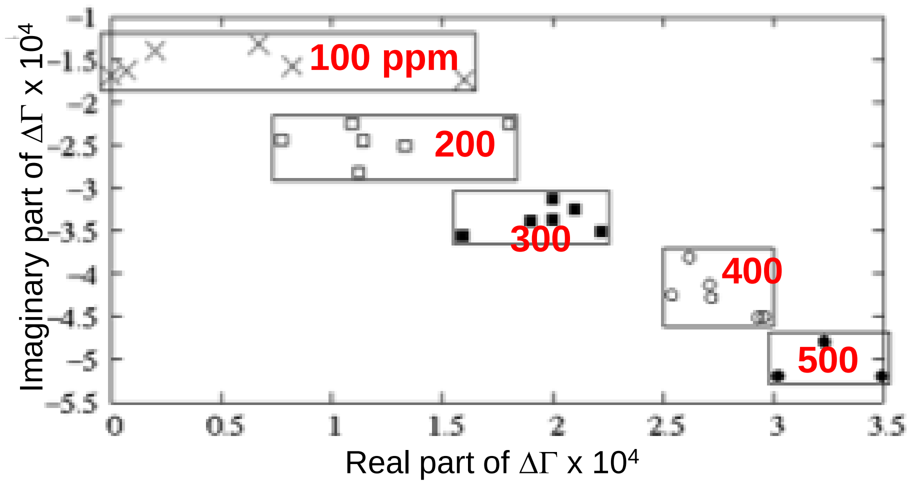
Resistor





Microwave transducer



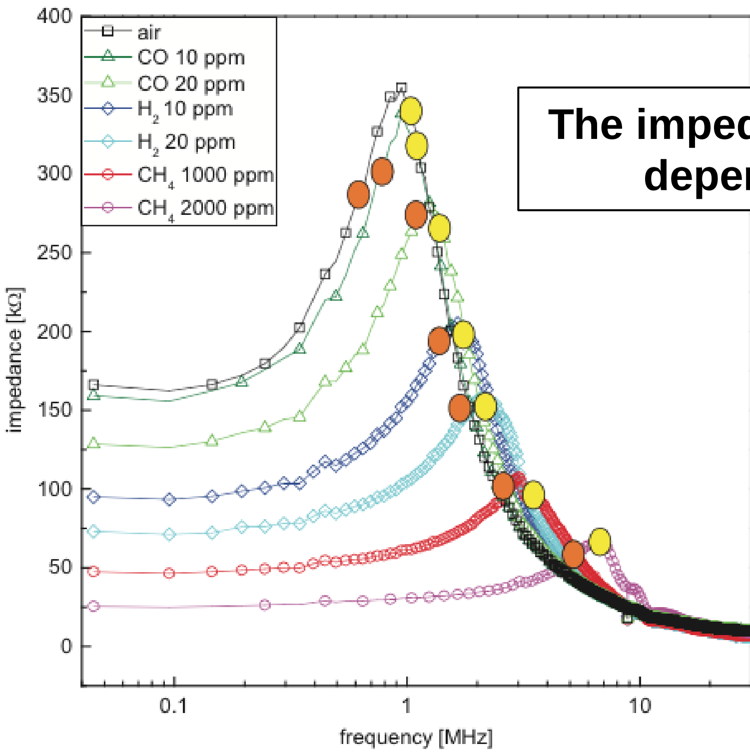


A virtual sensor array

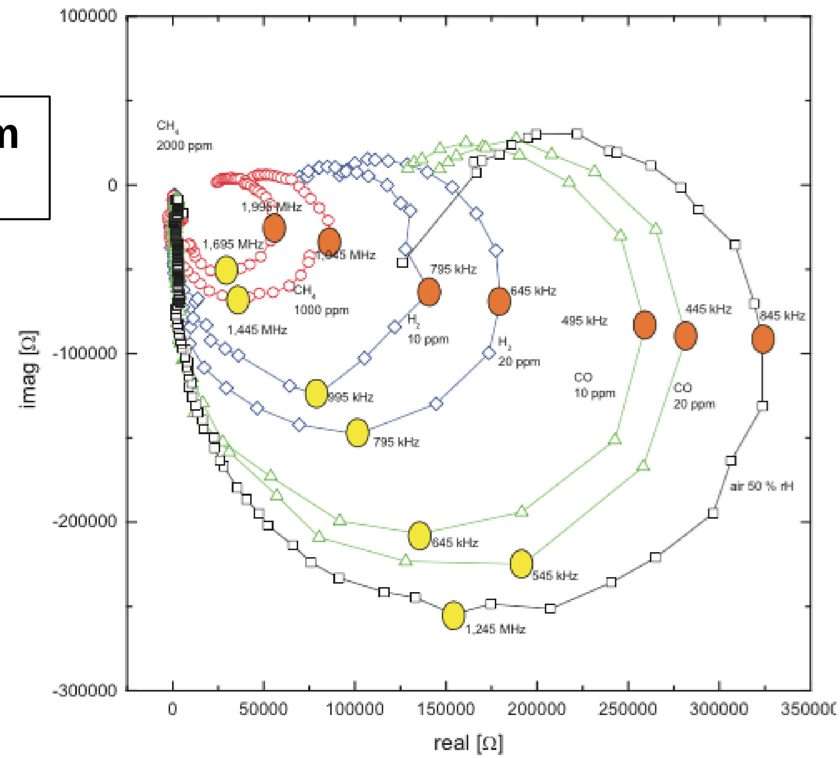
A unique sensitive layer investigated by a unique transducer, but operating in different conditions

Frequency modulation: Electrical Impedance Spectroscopy applied to semiconductor gas sensors

The impedance spectrum depends on gas



Bode plot: Impedance =f(frequency)

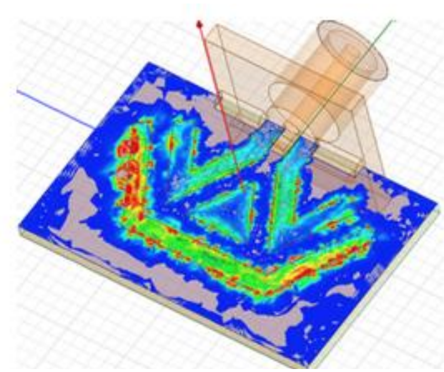


Nyquist plot: Imaginary part = f(Real part)

A. Schütze et al. SENSOR+TEST Conferences 2011.

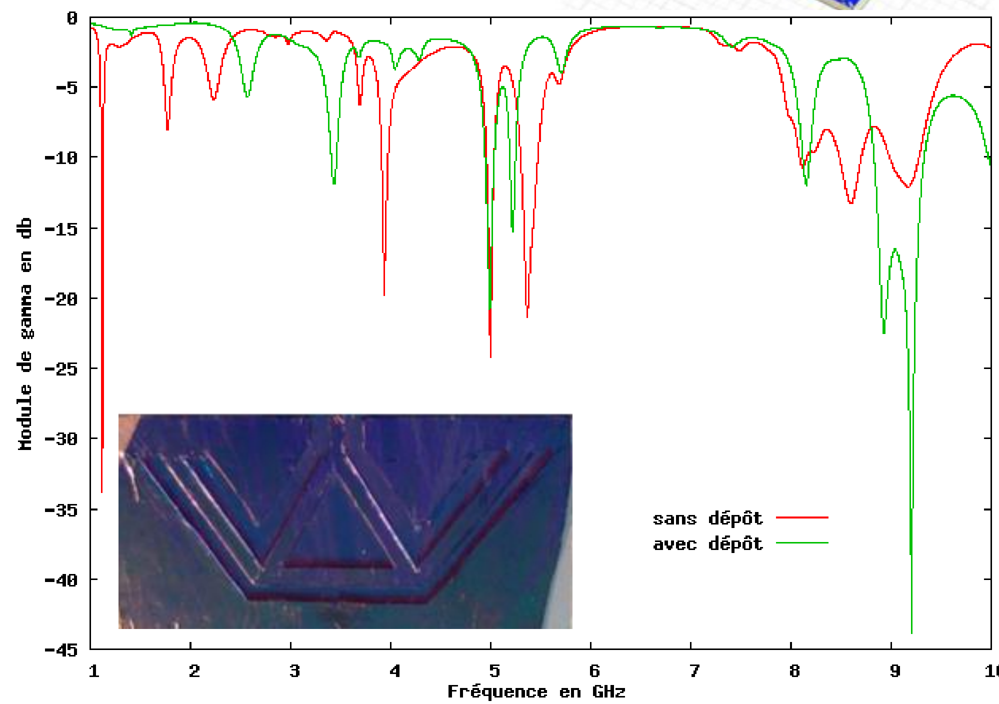
A virtual sensor array

Frequency modulation in the microwave range



Instead of one value, we got a spectrum

A frequency shift is observed with and without the sensing layer, and under gas



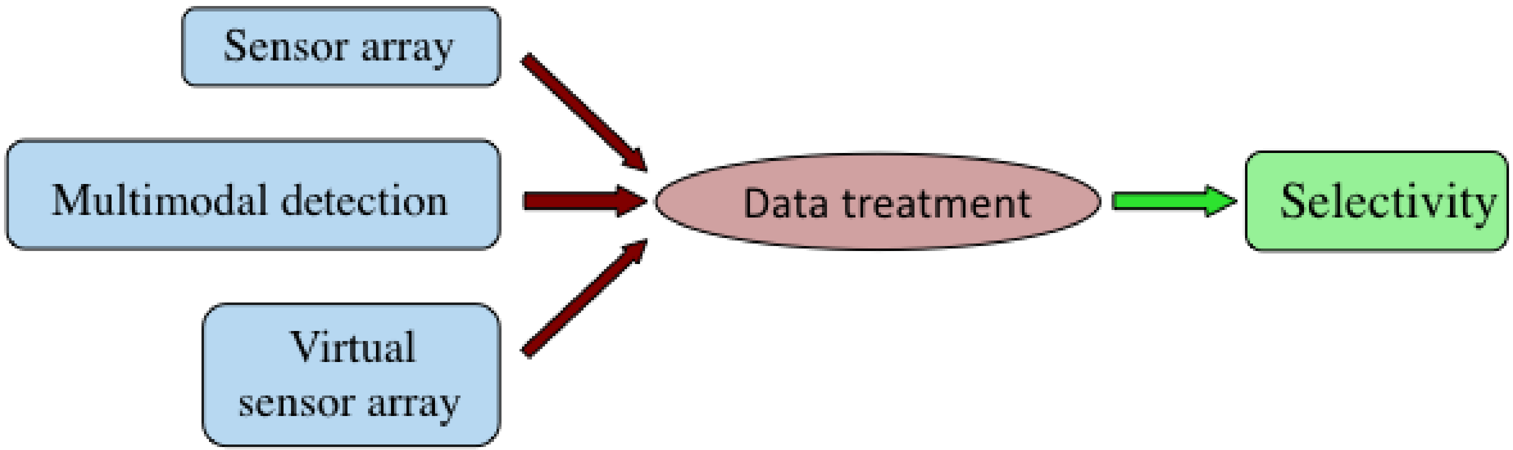
J. Rossignol, G. Barochi, B. de Fonseca, J. Brunet, M. Bouvet, A. Pauly, L. Markey, "Microwave-based gas sensor with phthalocyanine film at room temperature", *Sensors and Actuators B: Chemical* **189** (2013) 213–216.

CONCLUSIONS

The question was:

How to get a reliable information on a gas concentration?

The answers can be:



- All these methods give more data than individual sensors
- They are analytical systems
- They give reliable information not only on one gas,

  but also on complex atmospheres

Paldies