« FROM METAL OXIDE GAS SENSOR TO INTEGRATED SMART NOSE »

by Ph. Ménini

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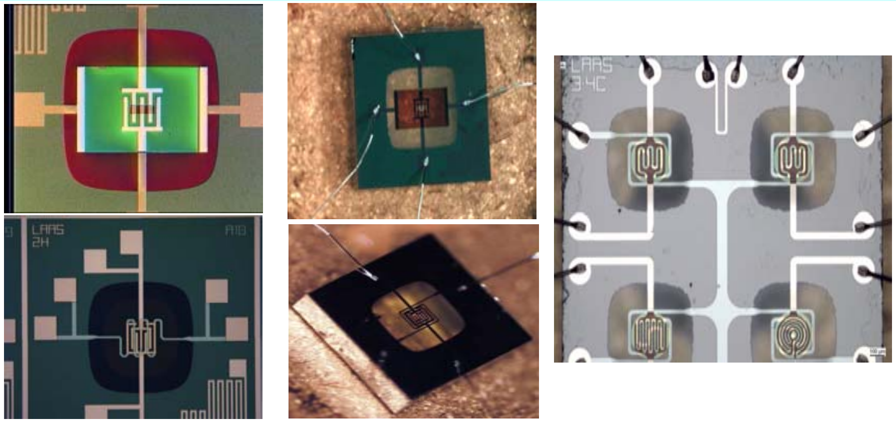
Gas Sensor Activities at LAAS

Ph. Ménini (MCF;100%), A. Martinez (Pr;10%) - E. Scheid (CR1;10%) - H. Chalabi (doct3) - C. Tropis (doct2) – P. Yoboue (doc1)

Microtechnology

Design et Realisation of micro hotplate for SGS

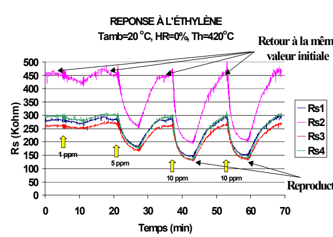


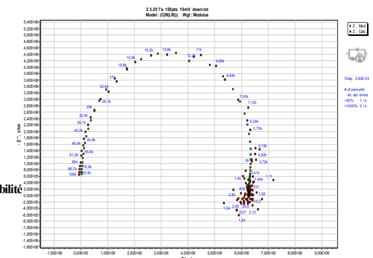
Characterisations

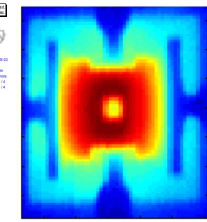
-Rs(t)

-Impedance spectroscopy under controlled atmosphere

-Thermal Characterisation : IR Camera



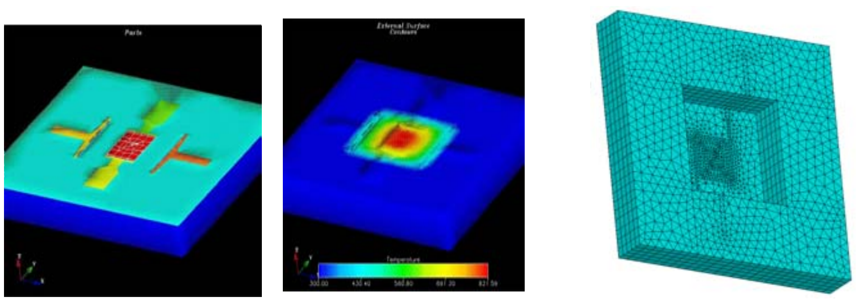




Modelling - Simulation

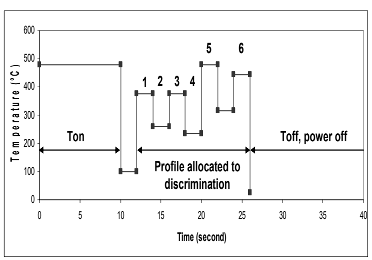
Electro-thermal -Thermo mechanical modelling

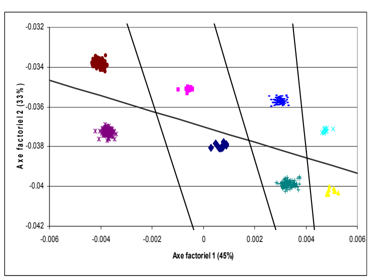
(ANSYS → Comsol)



Operating mode
Data treatment and integration

Fonct. at pulsed T° + mathematical data treatment (FDA, NN)





Introduction

Introduction

Our Objective :

Measuring accurately the concentration of one target gas (CO) in a gas mixture (air, NO_2 and CxHy)…
… with only 1 sensor (SGS)

Knowing that SGS :

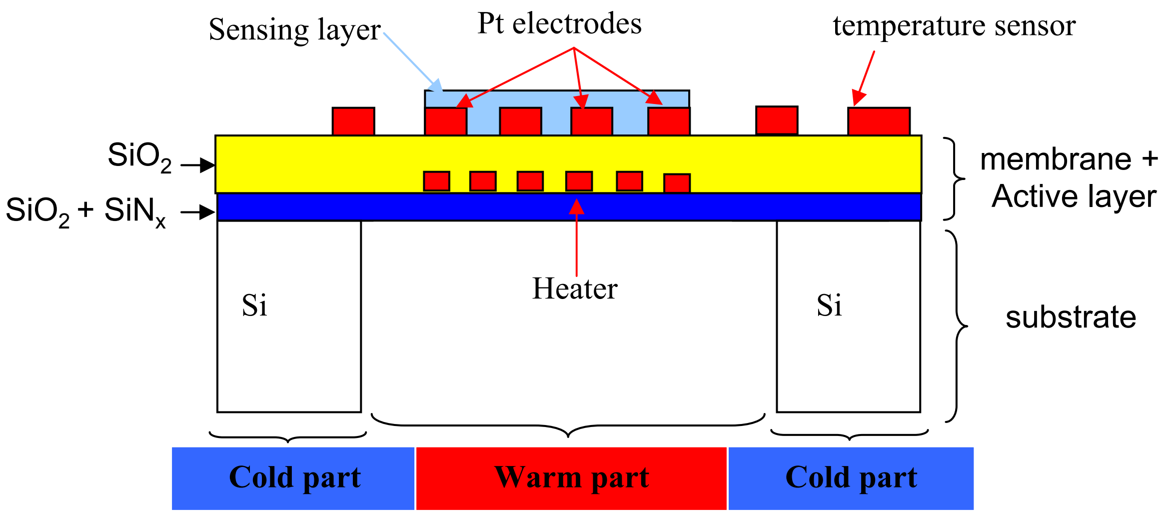
- good sensitivity
- Poor selectivity at constant working temperature
- Great influence of humidity

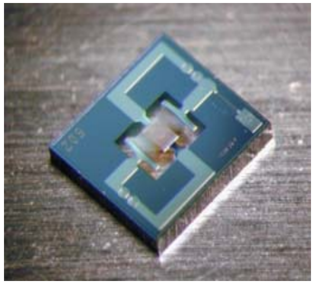
Outline

- Single Sensor technology
- Functioning Method and Data Treatment
- Results
- Conclusion and Outlook

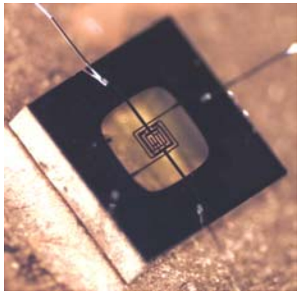
Sensor Technology : SGS

Structure





Mics sensor



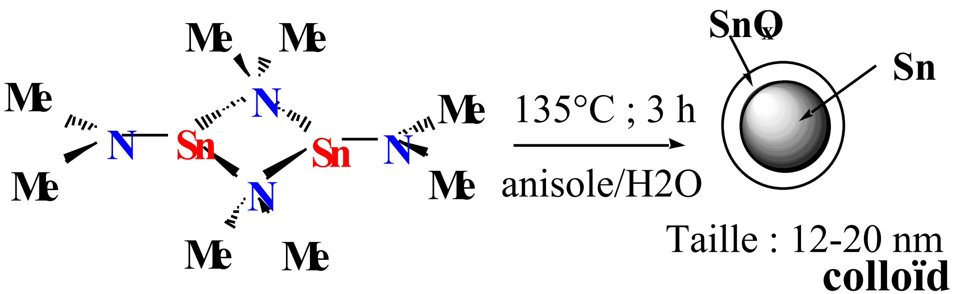
LAAS sensor

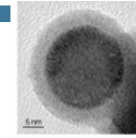
The sensor used

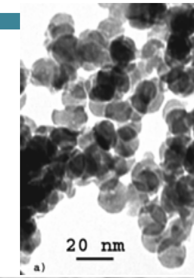
4% Pt-doped SnO_2 sensor

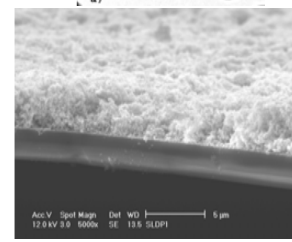
Sensing layers

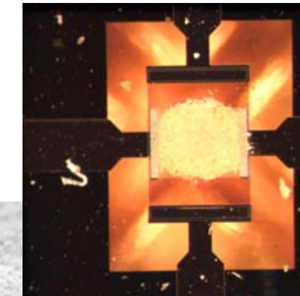
LCC-CNRS : Nanoparticular SnO2







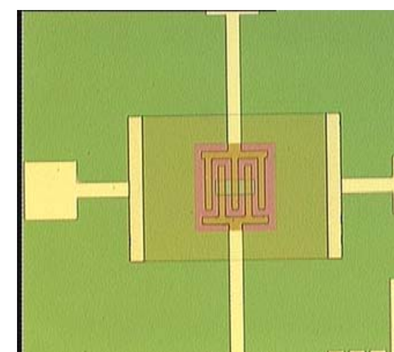




Colloïd Deposited by microinjector (industrialised by MiCS)

Volume controlled (1 nl – Ø400µm – 2 µm of thickness)

L2MP-Marseille : WO_3



Deposited by RF magnetron sputtering

50 nm of thickness

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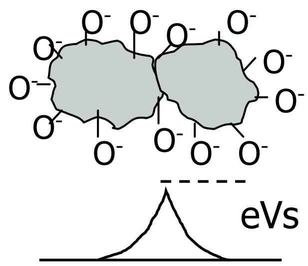
Principle of Detection

Phase 1: Oxygen Adsorption

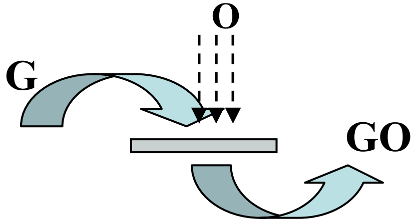
$$\tfrac{1}{2}\, O_2 gaz + SnO_{2-x} + e^- \rightarrow (SnO_{2-x})O_{ad}^-$$



Grain Boundary

Phase 2 : Reaction with reductive gases

$$G + (SnO_{2-x})O_{ad}^- \rightarrow GO + SnO_{2-x} + e^-$$



G : reductive gas

⇨ ρ decreases

(opposite for oxidative gases)

Chemical reactions at the surface occurs at high temperatures (>250°C):

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Functioning Method

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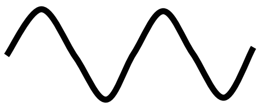
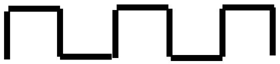
Sensing layer is heated by an integrated resistor

Either powered by constant voltage (T° = Ct)
Or by variable voltage :



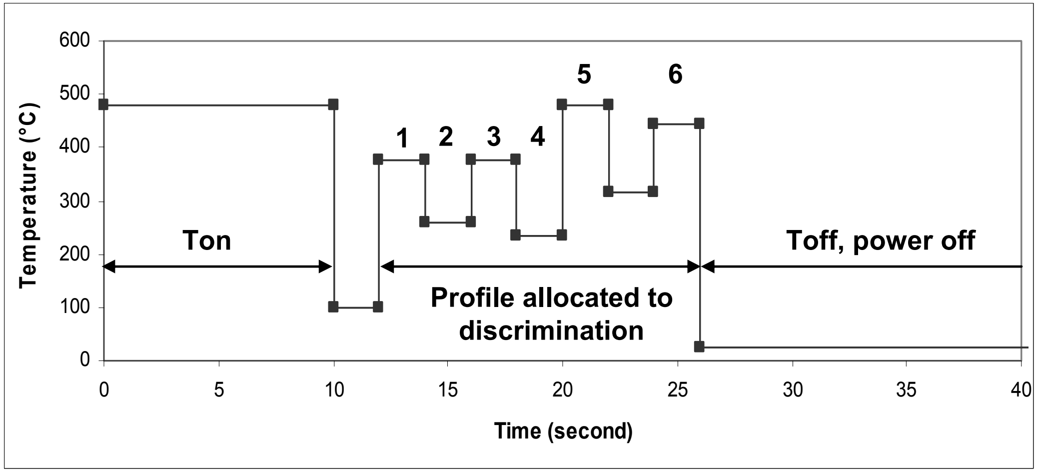
Sinusoïdal

Triangular



Regular pulses

Our choice : profile with fast steps (T_{amb}<T°<500°C):



Cycled Profile :

-T_{on} : for desorbtion (10s)

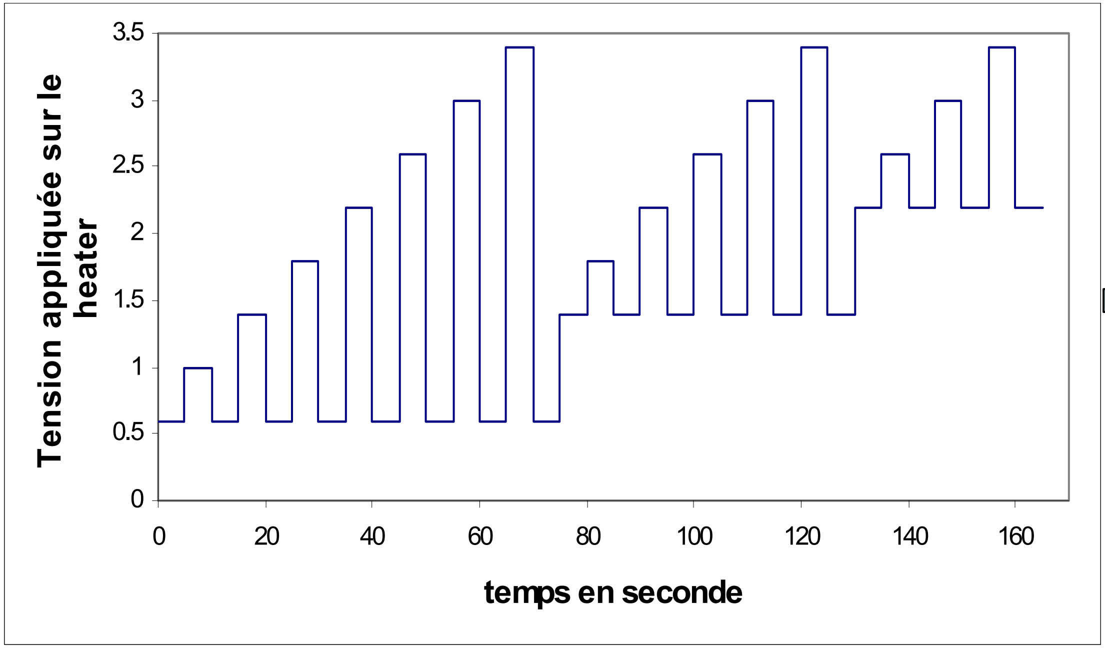
-Toff : power minimizatio

-Steps (2s): for discriminat

Operating mode : Dynamic thermal profile

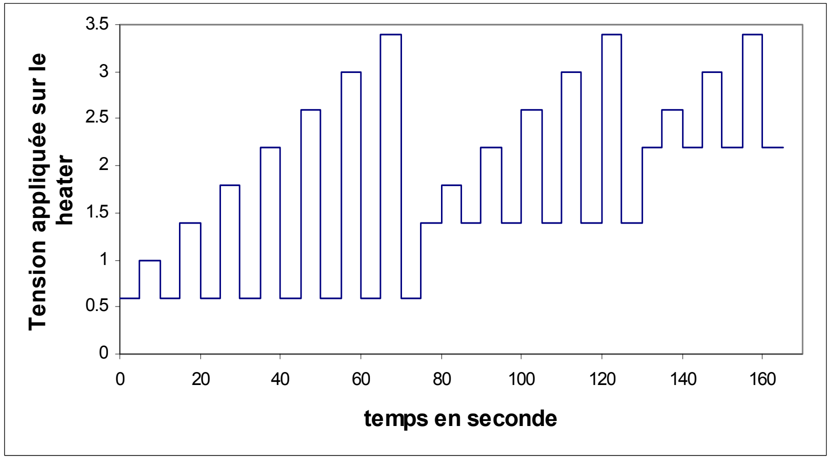
(PhD of F. Parret ➨ C. Tropis)

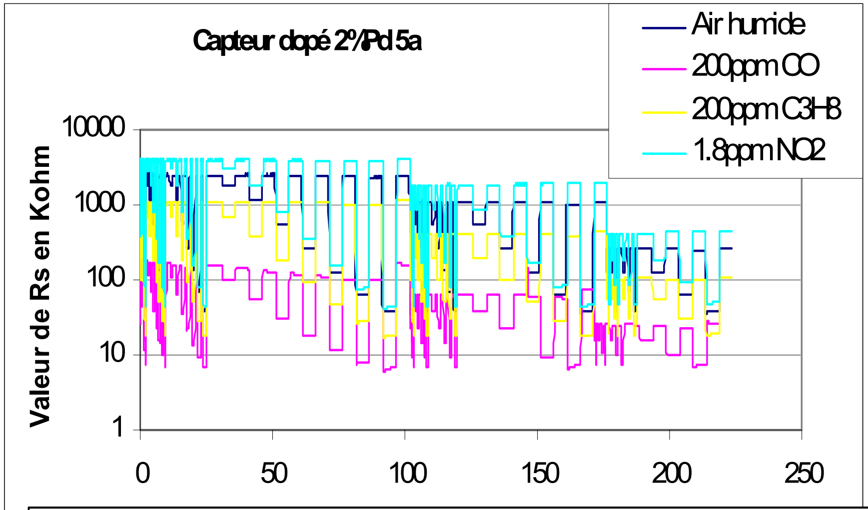
Example of test profile applied on the heater :

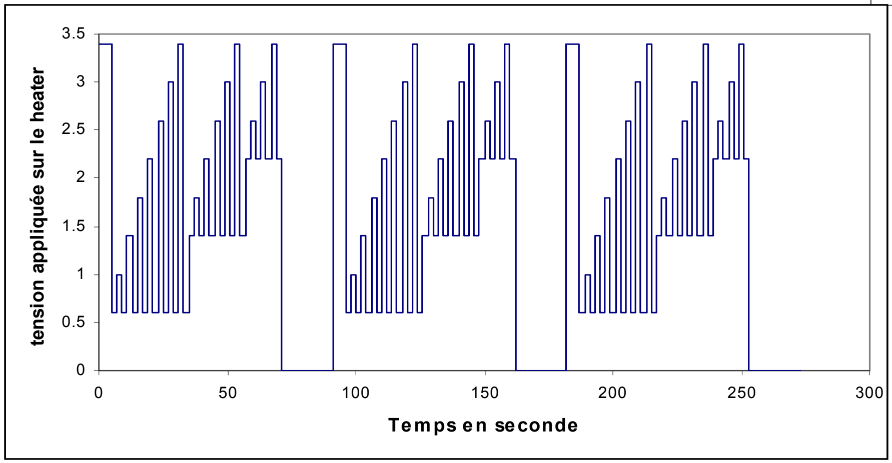


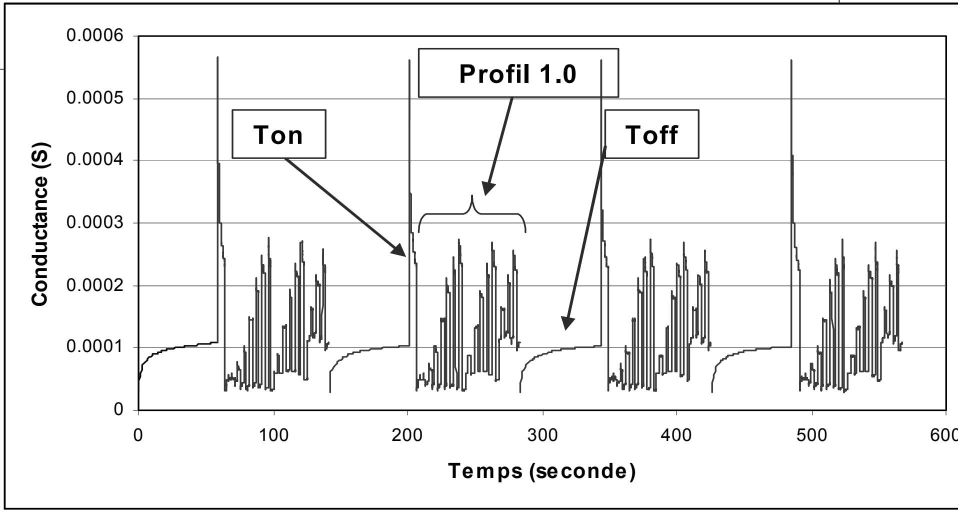
Goal : to determine most efficient steps (with significant discrimation) for one application

Test Profile









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Transient sensor responses

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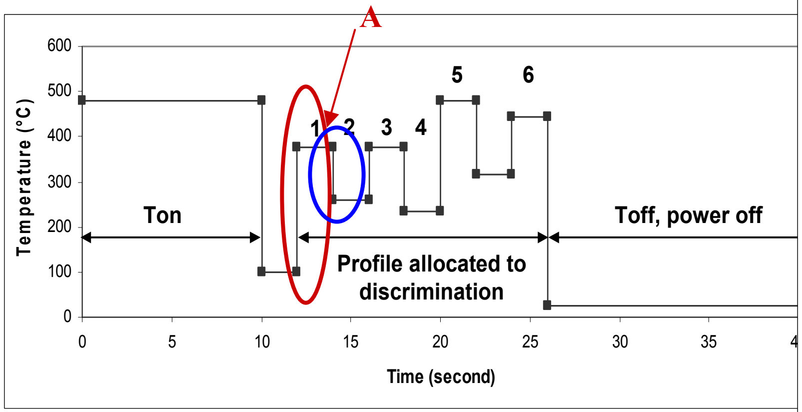
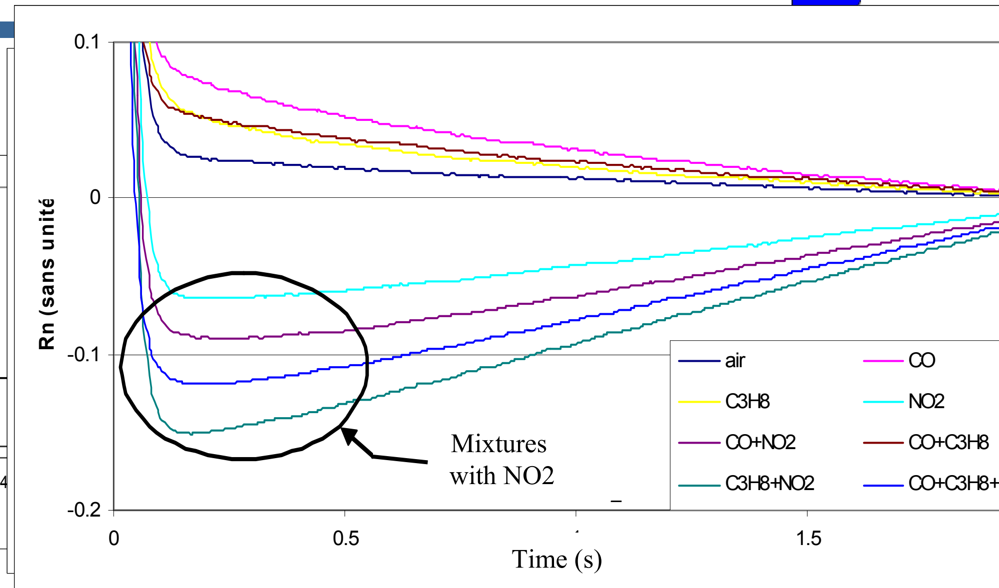
1. Normalisation



Profile of temperature



Sensor response

$$\Delta R_n = \frac{(R_i - R_f)}{R_f}$$

Transient response depends on :

- Temperature variation
- ambient gas mixture

Correlation to kinetic chemical reactions

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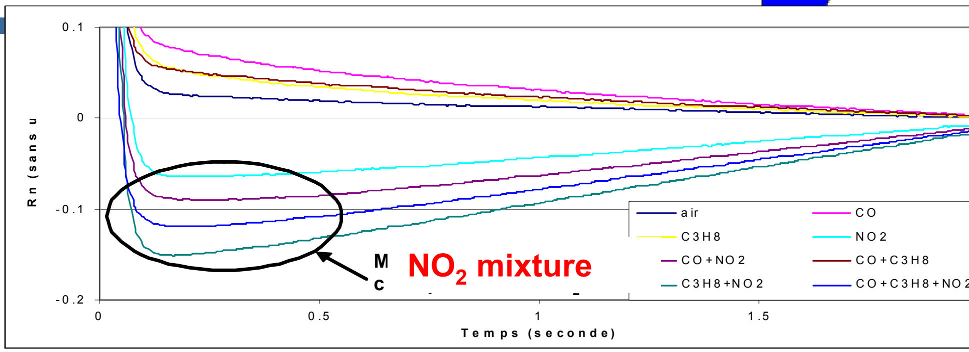
Typical sensor responses

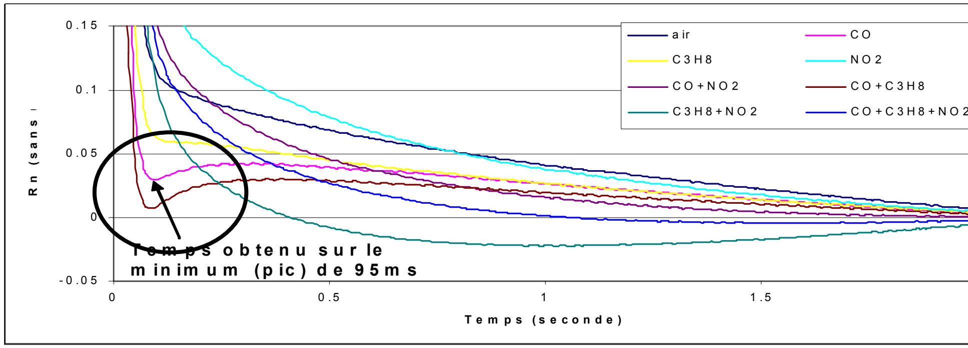
Low temperature step (dT = 110 – 185°C):

- Distinction of NO_2 & mixture from other gases



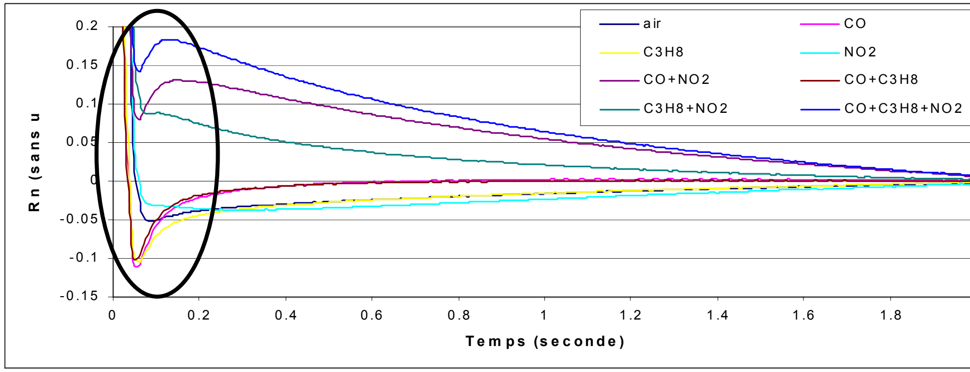
Around 250°C (dT = 110 – 285°C):

- Beginning of CO & C_3H_8 detection
- Good distinction from mixtures with NO2



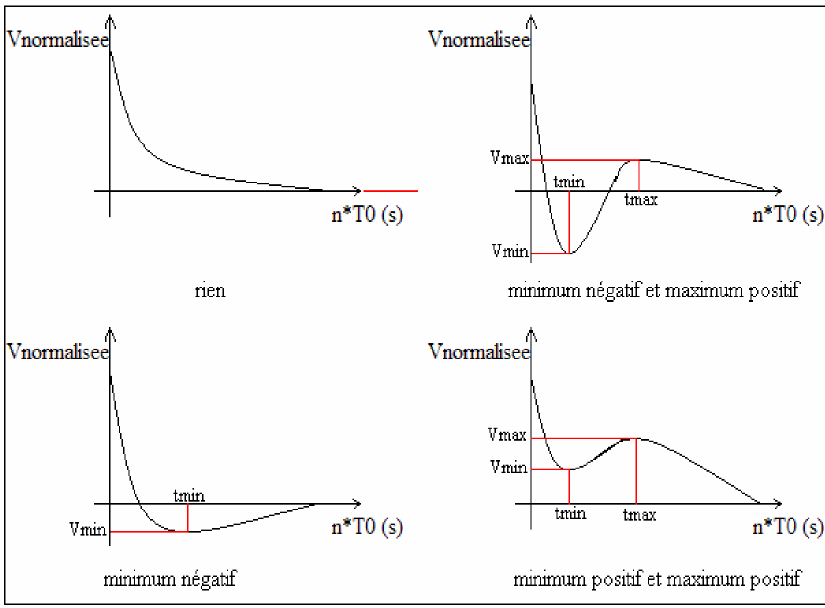
High temperature (dT = 110 – 480°C):

- All mixtures with CO create an overshoot & similar position time.



2. Variables and mathematical analysis

4 Different transient response shapes



20 points within
the first part of each step

Multi-variable analysis :
Factorial Discriminate Analysi
(FDA)

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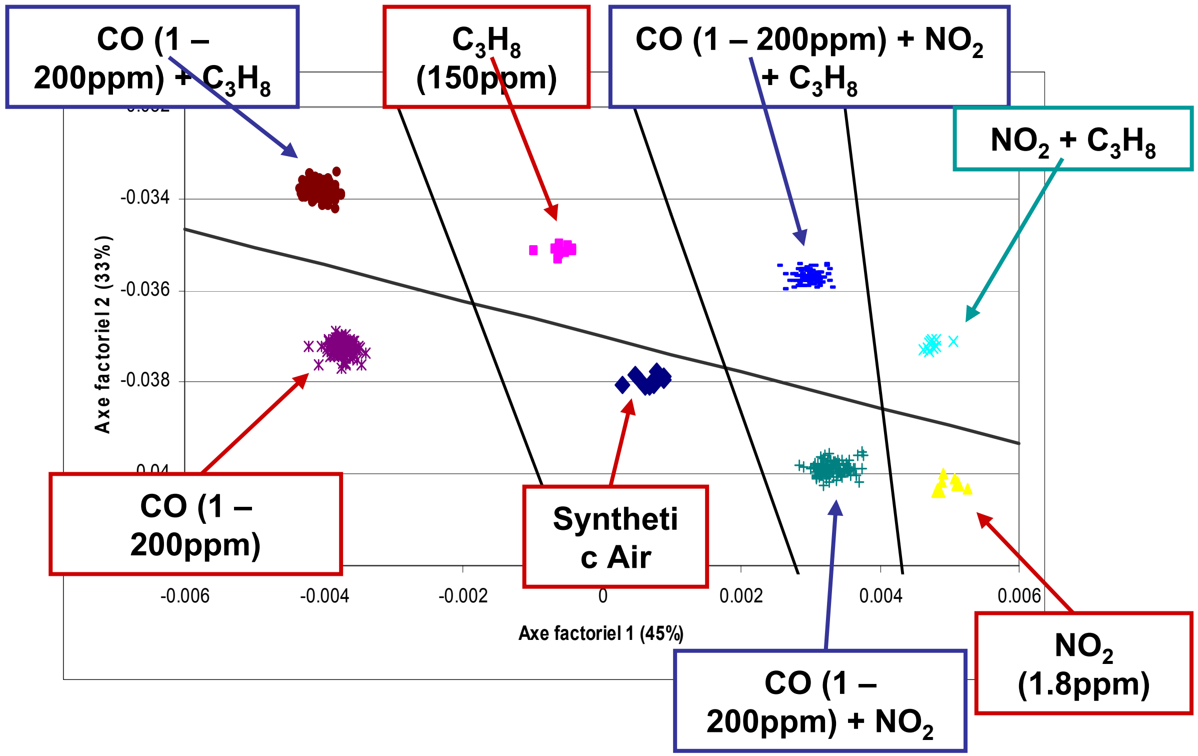
FDA Results

IberN

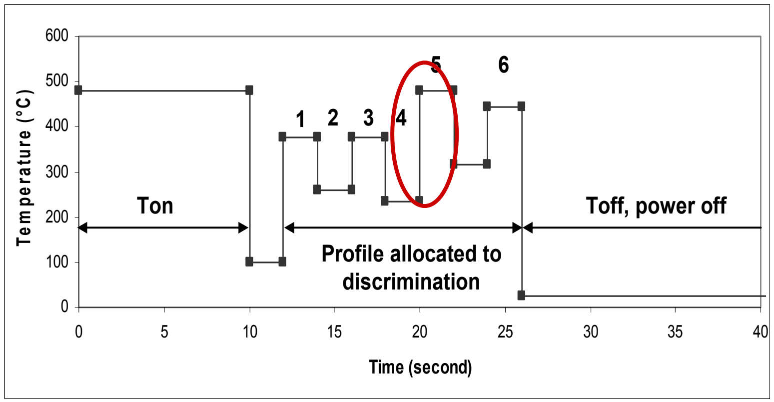
1. Selectivity

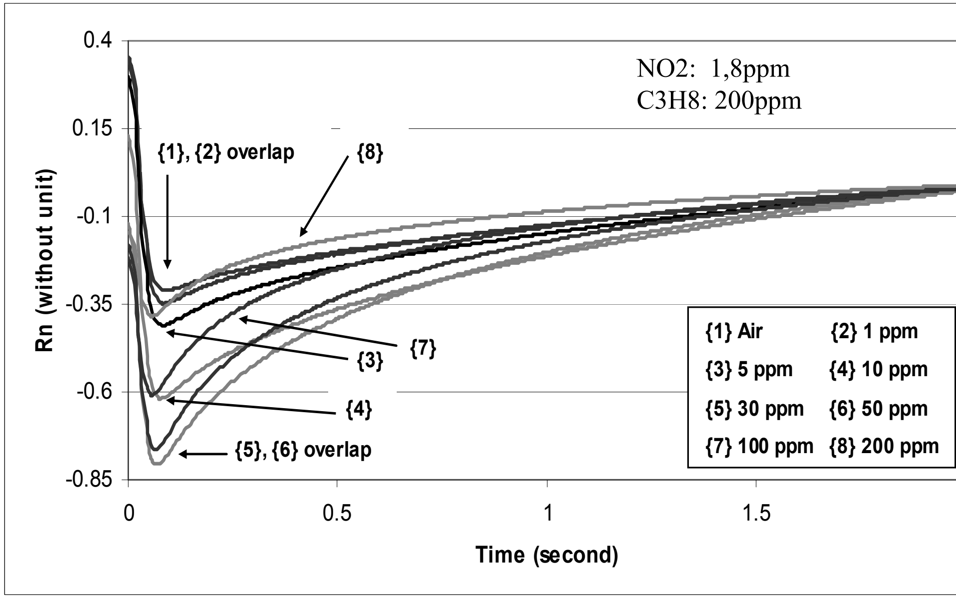


⇨ **Good selectivity… In Humid atmosphere… With only 1 sensor**

2. Determination of CO Concentration

What is the influence of different CO Concentrations on the transient resp



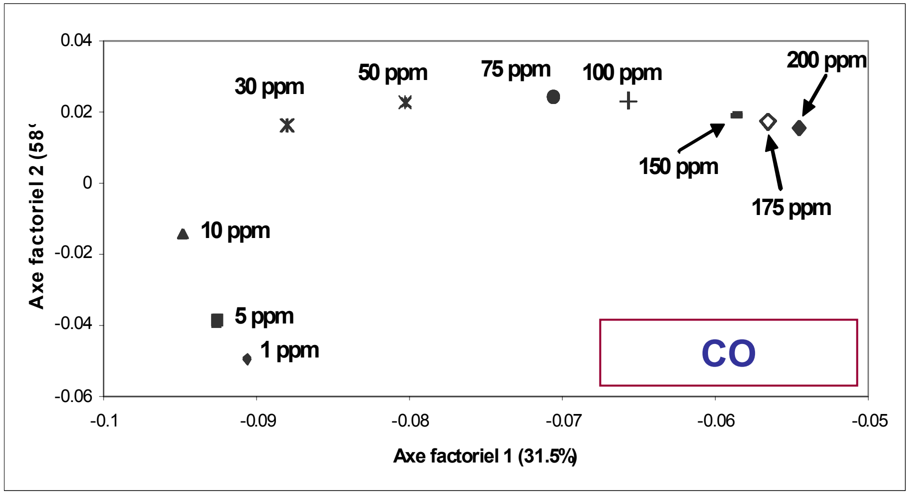


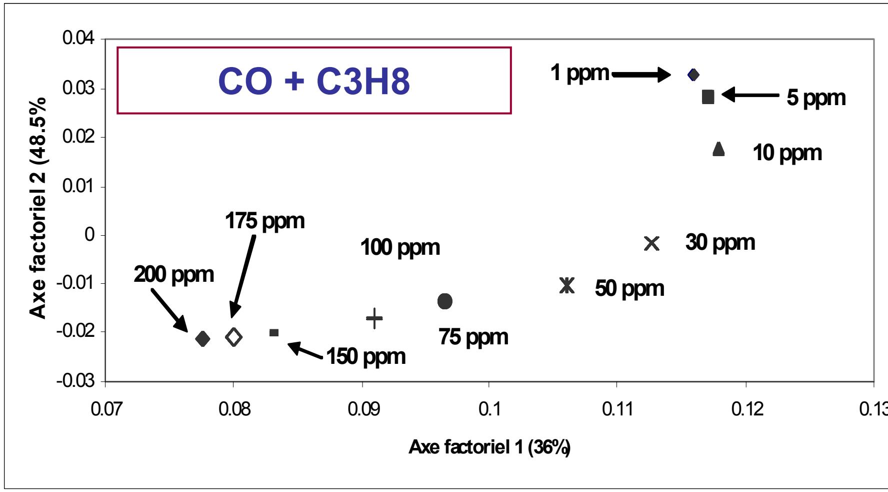
Important variables : over-shoot coordinates

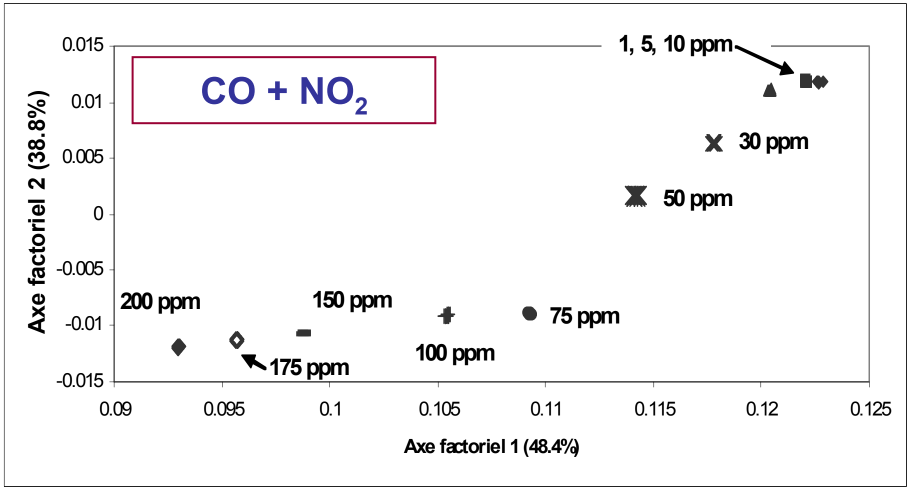
2nd FDA to separate different CO concentrations

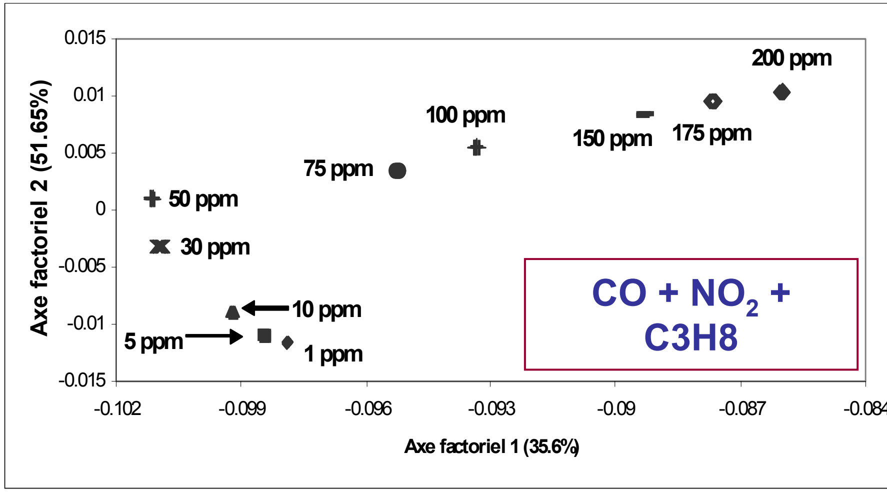
2nd FDA Results

2. Determination of CO Concentration









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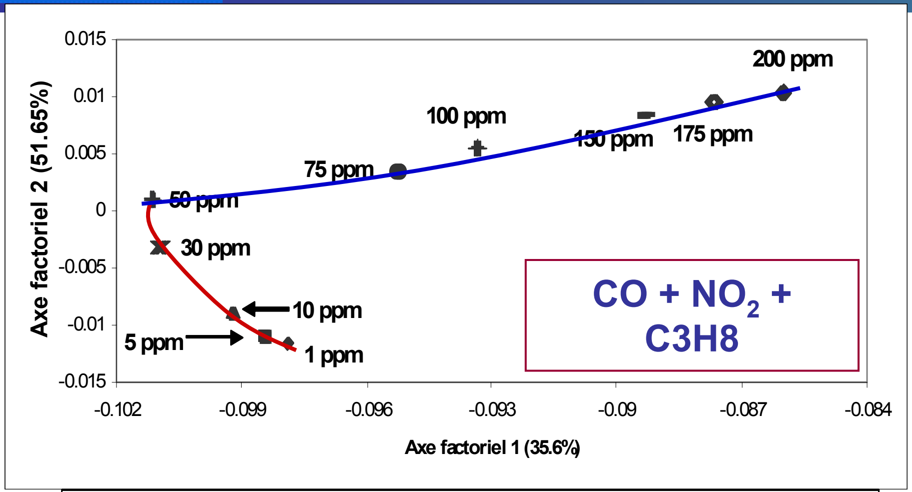
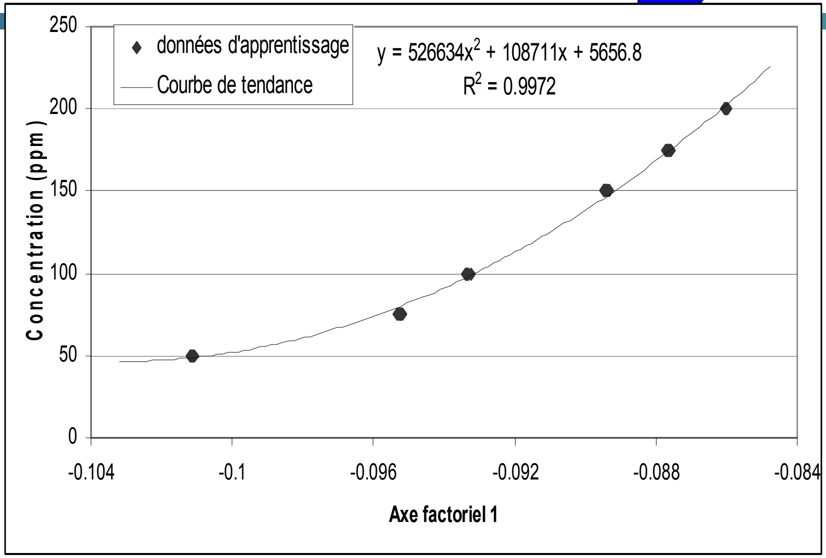
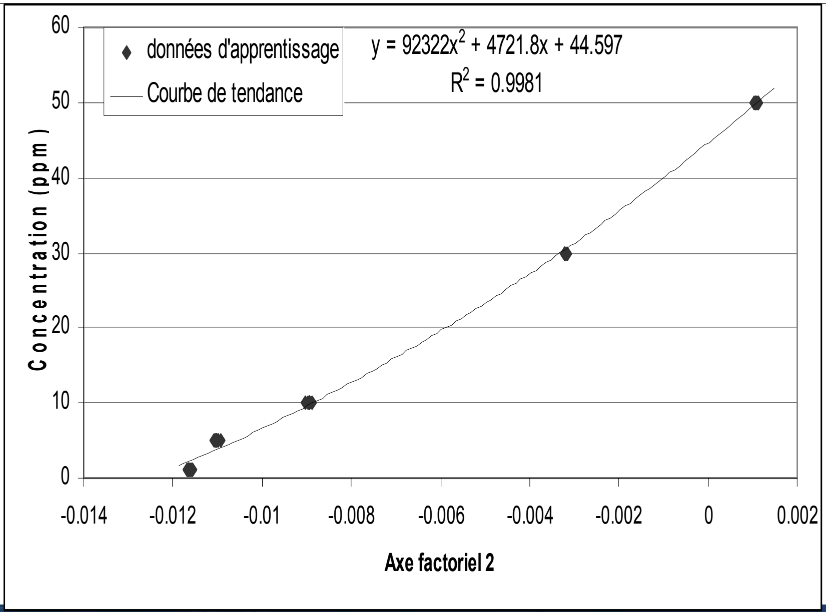
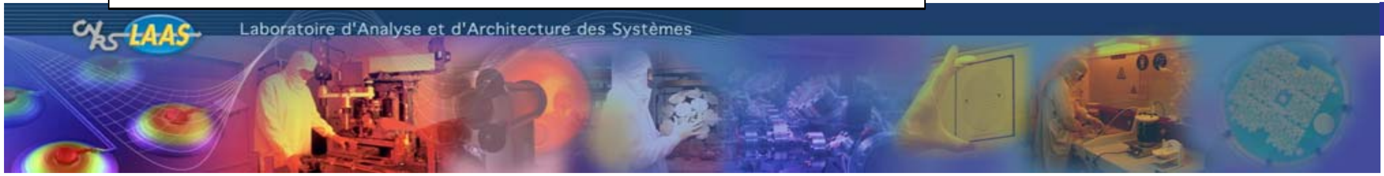
Determination of CO Concentration





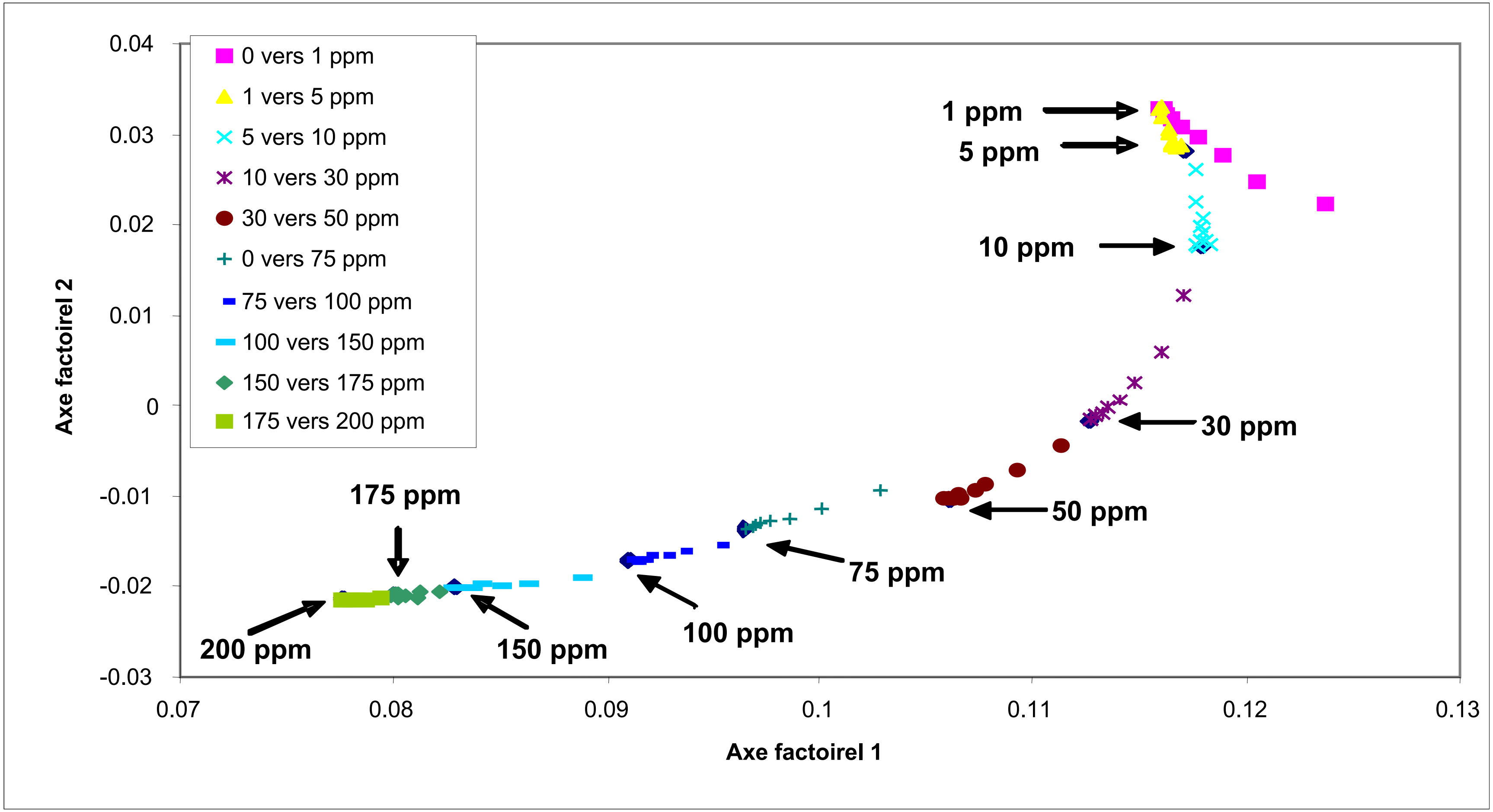


⇨ **Polynomial Regressions**



Exemple of dynamic measurements

New individuals corresponding to the evolution of CO concentration



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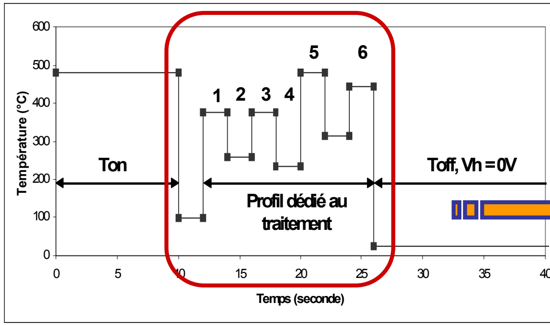
Summary : CO-Sensor description

IberN

Thermal Profile



Algorithm

- Normalisation
- 20 points / step
  0-650 ms
- detection of max and min

Selective analysis

{ Unknown vector } × { Tranfert Matrix From FDA1 }

Determination of the ambient gas mixture by Decision tree

CO ?

no

yes

quantitative Analysis

{ unknown } × { Tranfert Matrix From FDA2 }

Regression (2^{nd} order)

CO Concentration (1 – 200 ppm)

Conclusions

- Development of a new generation of SGS
  - (Microhotplate + Pt-doped Nanoparticular SnO_2 by drop deposition)

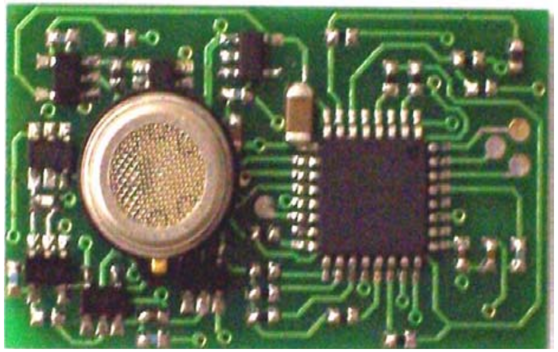
- New Functioning Method :
  - Cycled Temperature profile (Ton, 2s-Steps, Toff)

- Data Treatment :
  - Normalization (to put in evidence the transient response of the sensor)
  - choice of useful variables,
  - FDA method (2 phases)

- Results :
  - Discrimination between 8 different mixtures of gas
  - Determination of CO concentration with 2 ppm of resolution
  - Possibility to measure dynamically

Outlook

- Multi-sensor technology
- Optimization of the profile :
  - Minimum of steps to minimize the response time (<30 s)
  - Use of NN method
- Reproducibility
  - Plug and Play system
- Integrability : portable system



Example : SGS + DSPiC (MC68HC908) developed by NANOSENSE in the frame of Nanosensoflex Project

Acknowledgements to :

- H. Chalabi, F. Parret, C. Tropis, E. Scheid, A. Martinez
- L. Salvagnac, V. Conedera, B. Rousset, L. Bouscayrol, P. Dubreuil
- Ch. Ganibal, D. Lagrange, B. Franck, S. Assié, F. Blanc
- MicroChemical Systems, LCC-CNRS, L2MP-CNRS

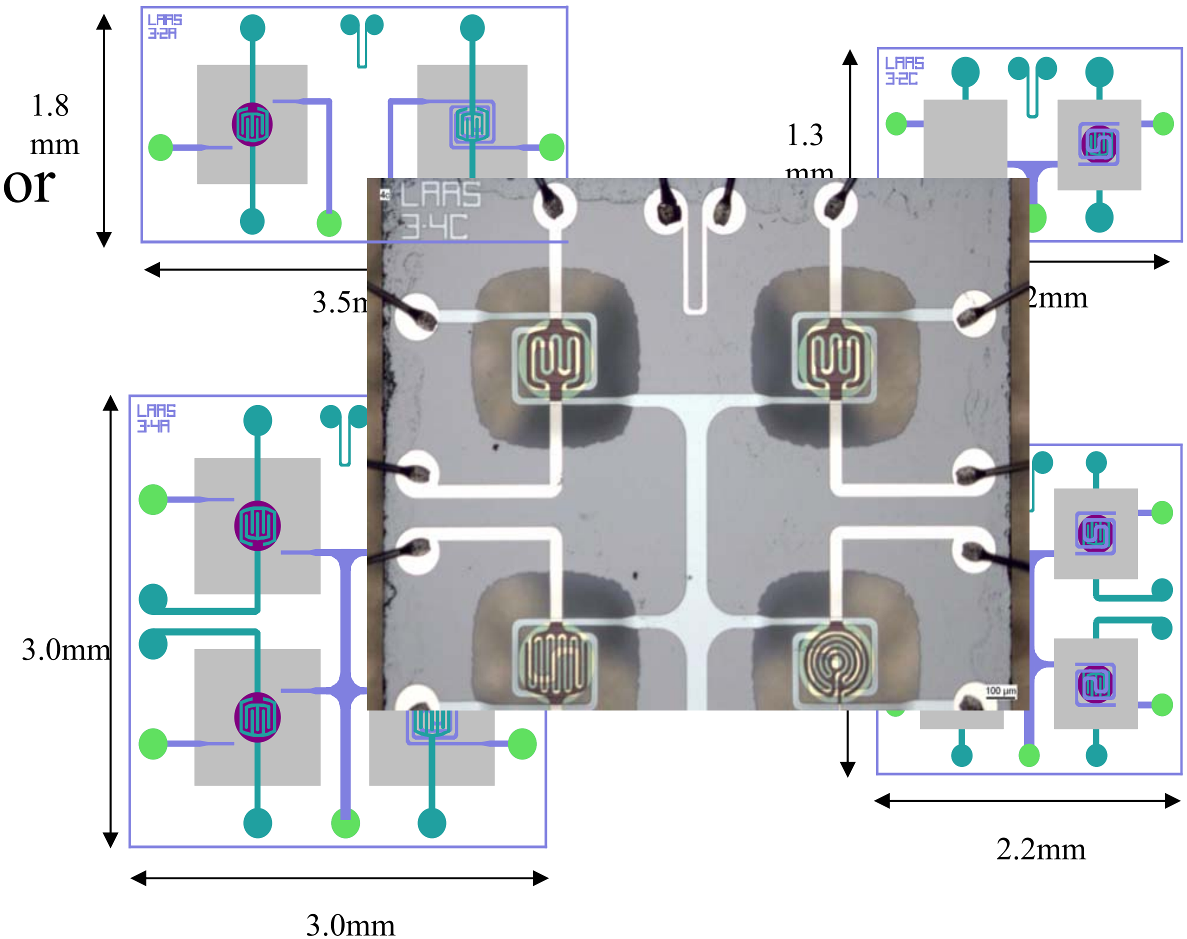
Thank you for your attention !

CMC2

Design of Multisensors
(membranes and heaters independant)

Double sensor

Array of 4 sensors



To go to the smart nose…

Influence of Moisture