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

COST Action TD1105

1ST International Workshop as Open Satellite to *Transducers 2013*

on

New Sensing Technologies and Transducers for Air Quality Monitoring

Barcelona International Convention Centre, Barcelona, Spain, 20 June 2013

GAS SENSOR-SYSTEMS BASED ON HYBRID MATERIALS DEDICATED TO AIR-POLLUTANTS MONITORING

Jérôme BRUNET

French MC Member, involved in WG2, SIG 1 & 3, STSM

brunet@univ-bpclermont.fr

Institut Pascal – University Blaise Pascal **/ FRANCE**

COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

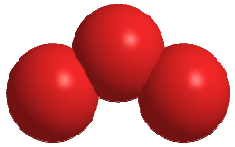
Objectives and motivations

Objectives?

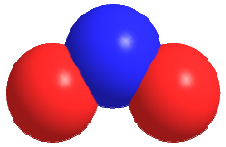
Development of competitive sensor-systems for gaseous pollutants monitoring

Target pollutants?

Oxidizing pollutants



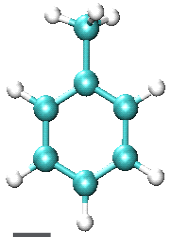
O_3



NO_2

Aromatic hydrocarbons

Benzene



Toluene

Xylene

Motivations?

Hazardous properties, toxic at low concentrations

Monitoring ⇨ safe living and working conditions

Objectives and motivations

Involvements?

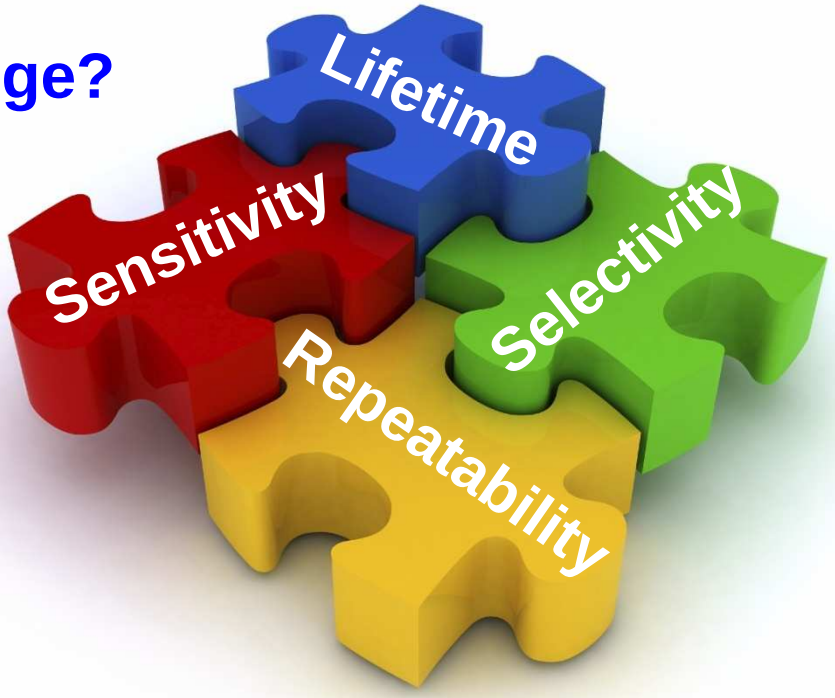
Agence Nationale de la Recherche
ANR

Coordinator of 2 French national projects:

POLL-CAP (2006-2009) : selective detection of oxidizing pollutants

CAPBTX (2010-2013) : efficient and low-cost sensors for BTX

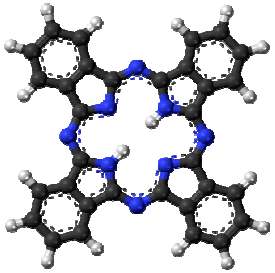
Challenge?

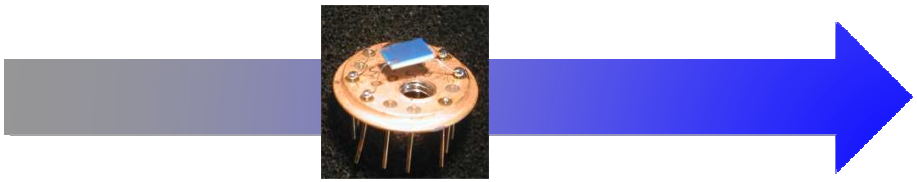


cost
EUROPEAN COOPERATION IN SCIENCE AND TECHN

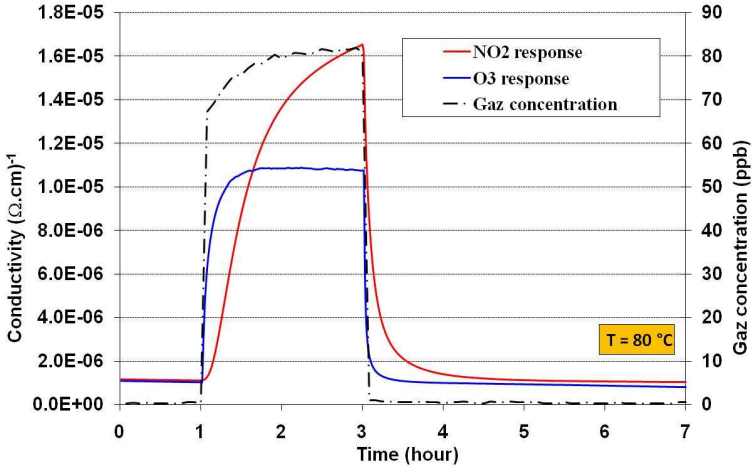
Why phthalocyanines as sensitive material ?

High electronic delocalization

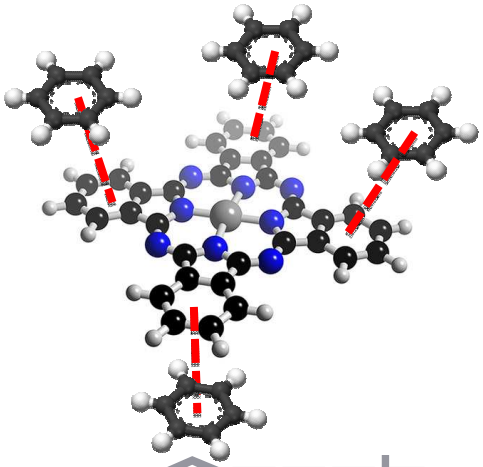


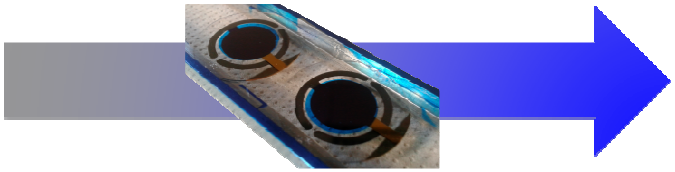


Sensitivity to oxidizing gases
(redox process)

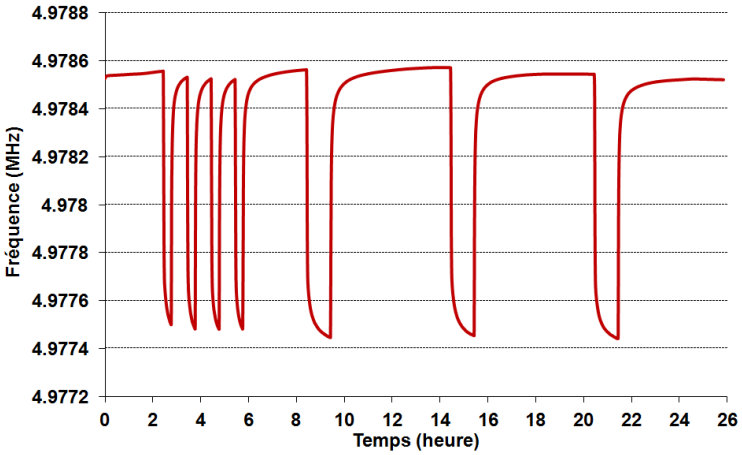


Peripheral aromatic moieties



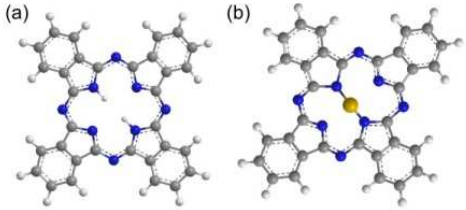


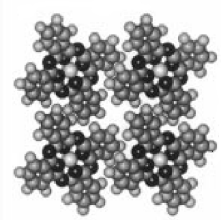
Interactions with BTX
(π-stacking ---)

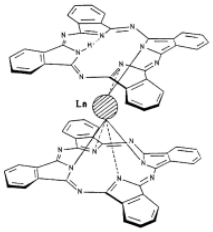


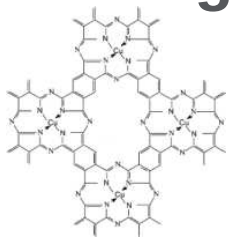
Why phthalocyanines as sensitive material ?

A great diversity of molecule ⇨ shaped material to the target gas

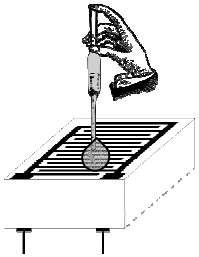




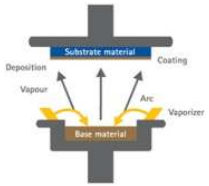




Elaboration of thin/thick films

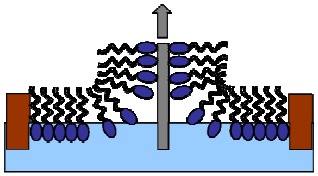


Drop-casting



PVD

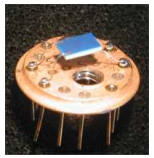
Spin-coating



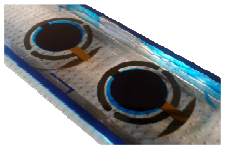
Langmuir-Blodgett

High specific surface area ⇨ **Highly sensitive gas sensors**

Compatibility with several transducers



Conductometry

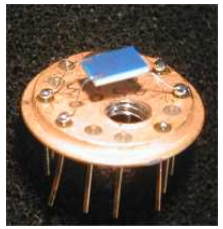


QCM

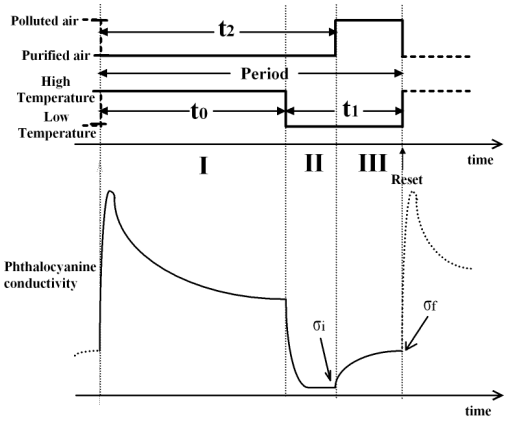
Microwave transduction

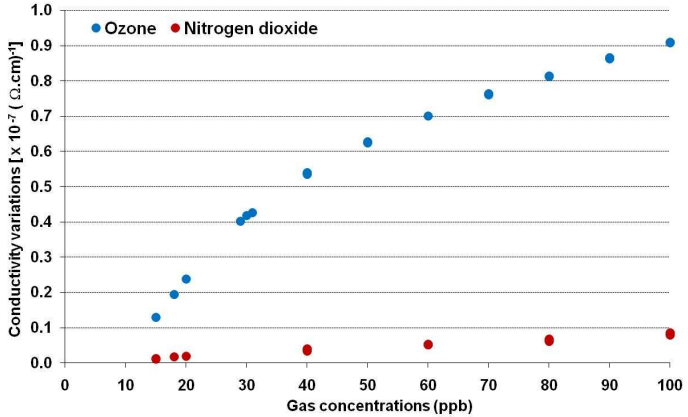
1st App: Selective monitoring of oxidizing pollutants

Ozone monitoring



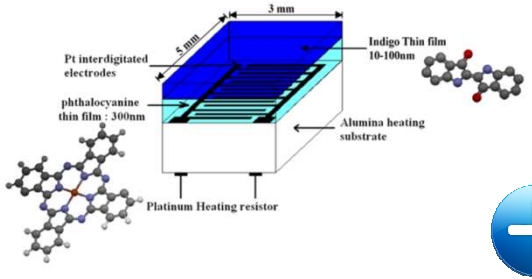
CuPc gas sensor

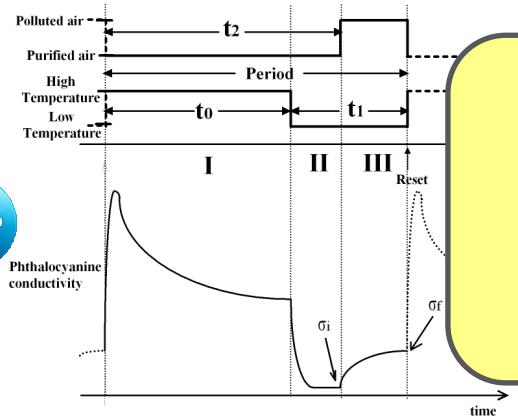




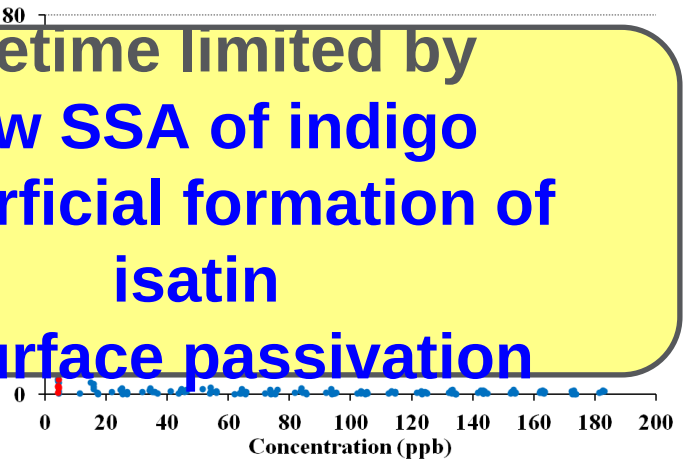
J. Brunet et al., Thin Solid Films 490 (2005)

Nitrogen dioxide monitoring





Lifetime limited by
Low SSA of indigo
Superficial formation of isatin
⇨ surface passivation

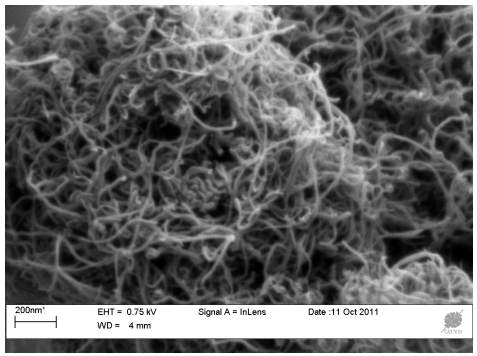


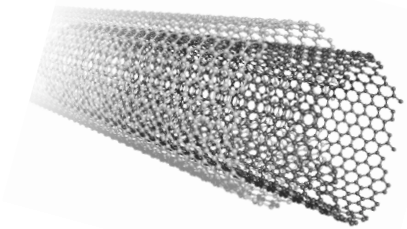
1st App Enhancement of ozone removal

Strategy?

Increase in surface/volume ratio of indigo

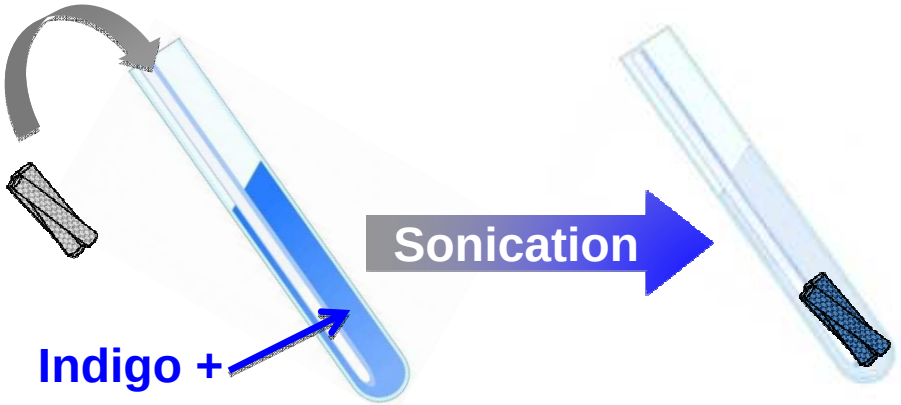
Indigo / carbon nanotubes hybrid material as chemical filter





Arkema Corporation

SSA = 215 m².g⁻¹



Indigo + Acetonitrile

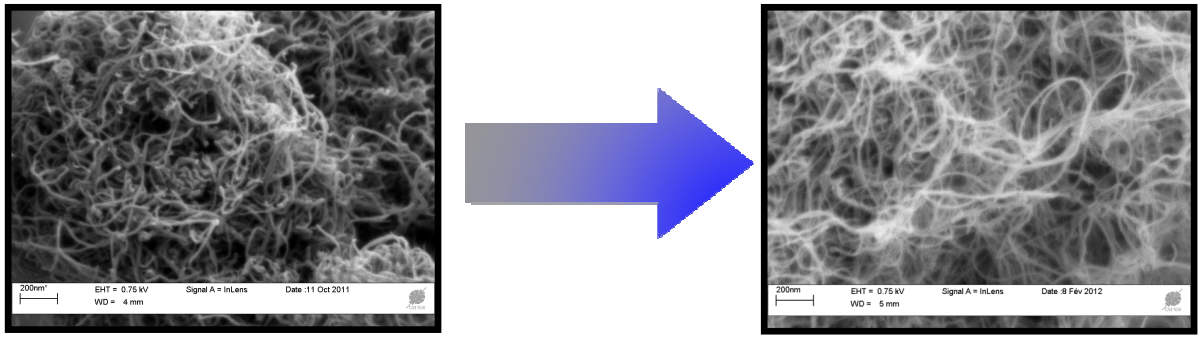
At saturation :

144 mg of indigo / 1 g of MWCNTs

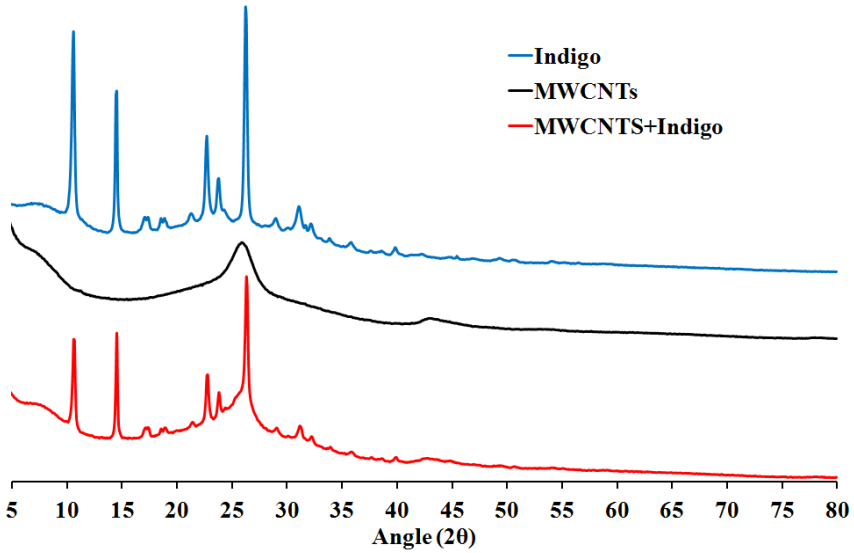
(UV-vis spectroscopy)

1st App Characterizations of hybrid material

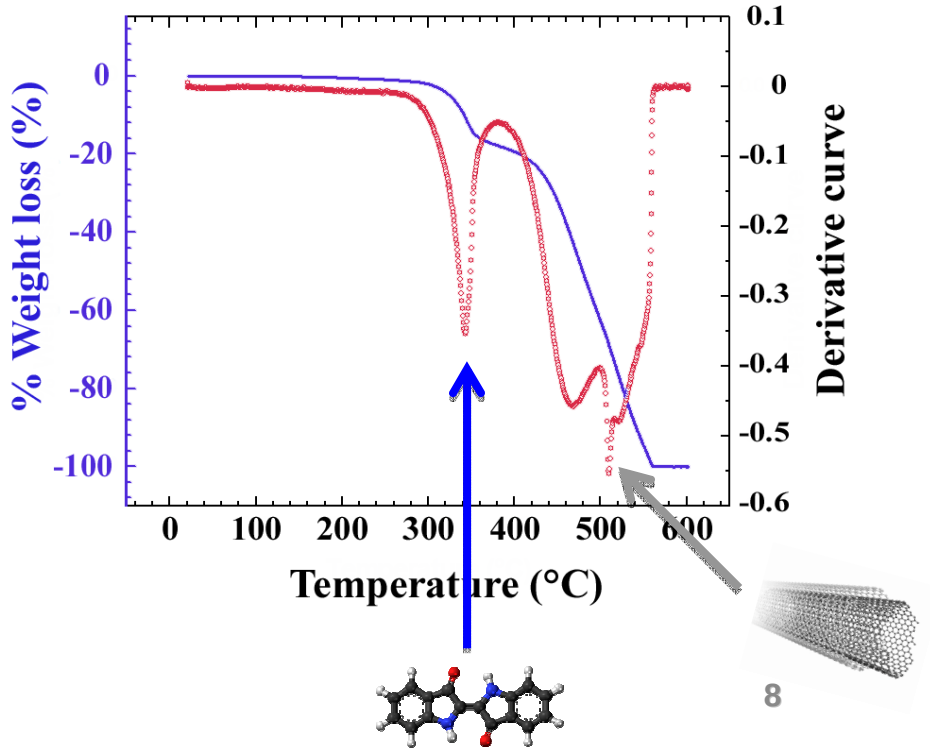
Scanning Electron Microscopy



X-Ray Diffraction

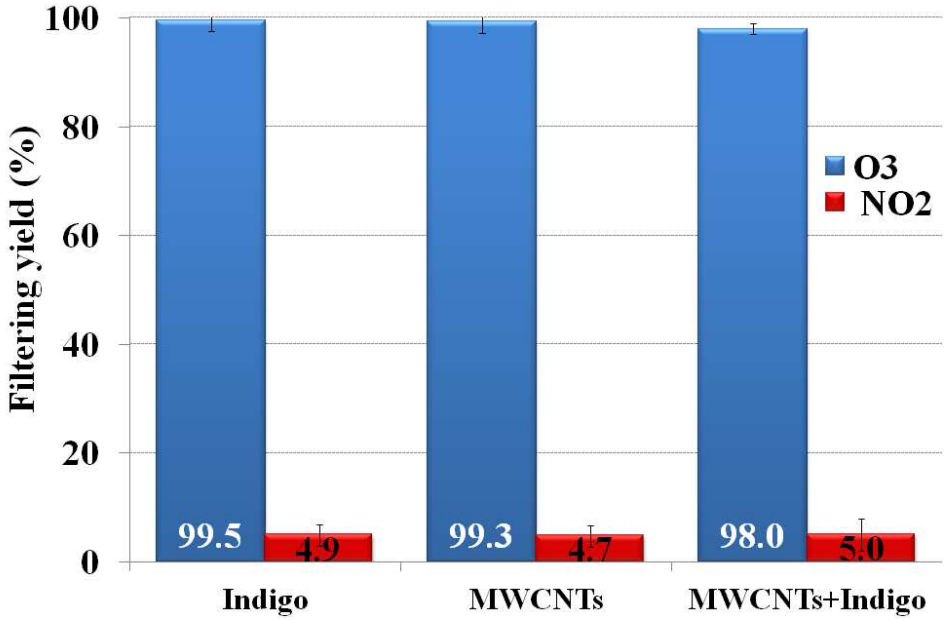


Thermogravimetric analysis



1st App Exposure towards the target gases

[O_3] = 100 ppb Flow = 0.75 l/min T°= RT

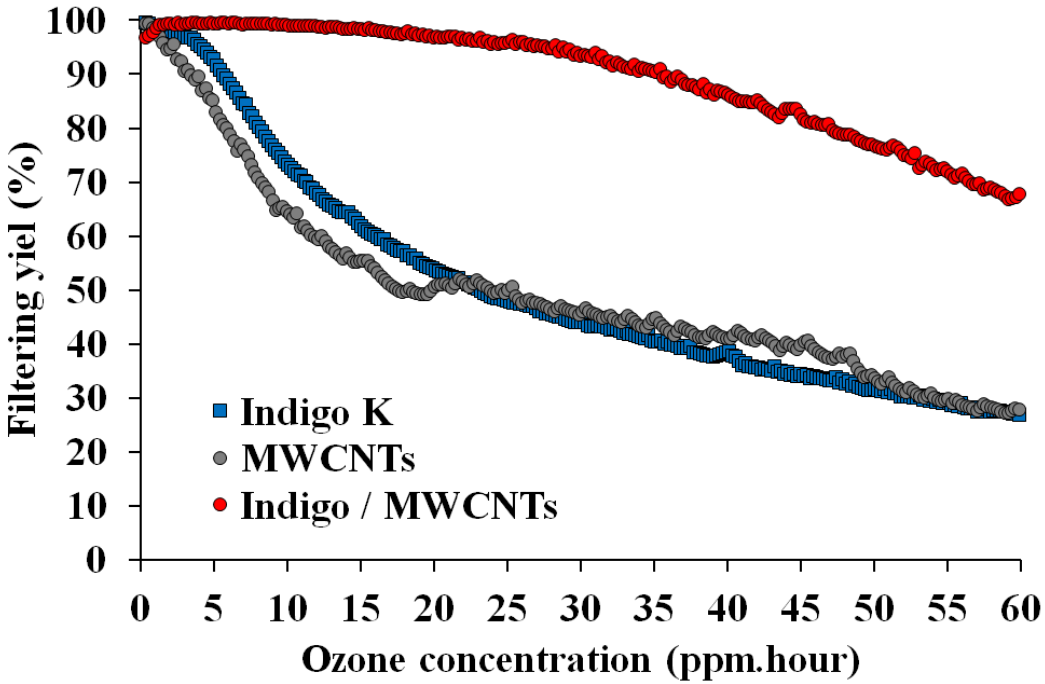


Selectivity ?

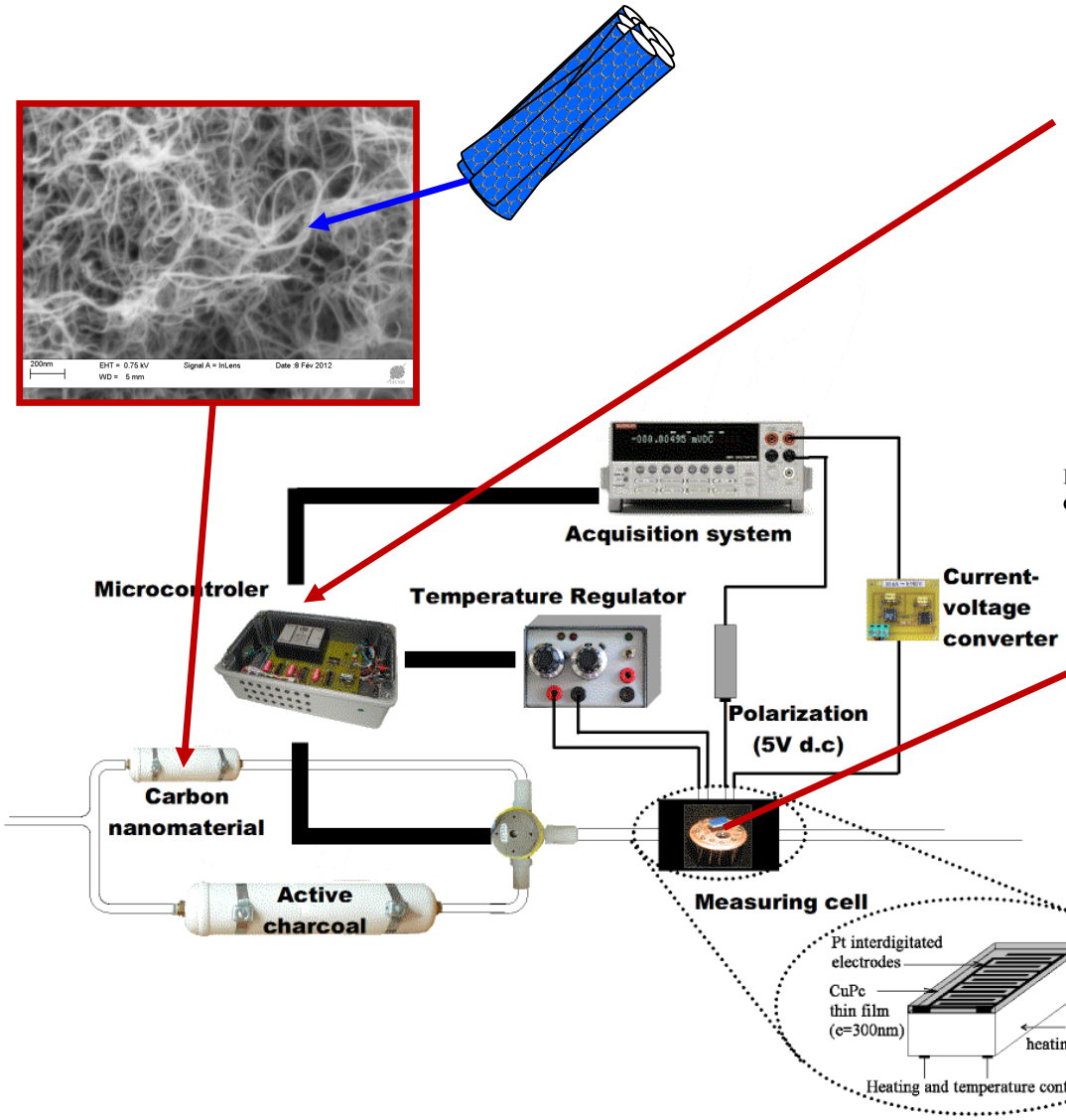
Unchanged !

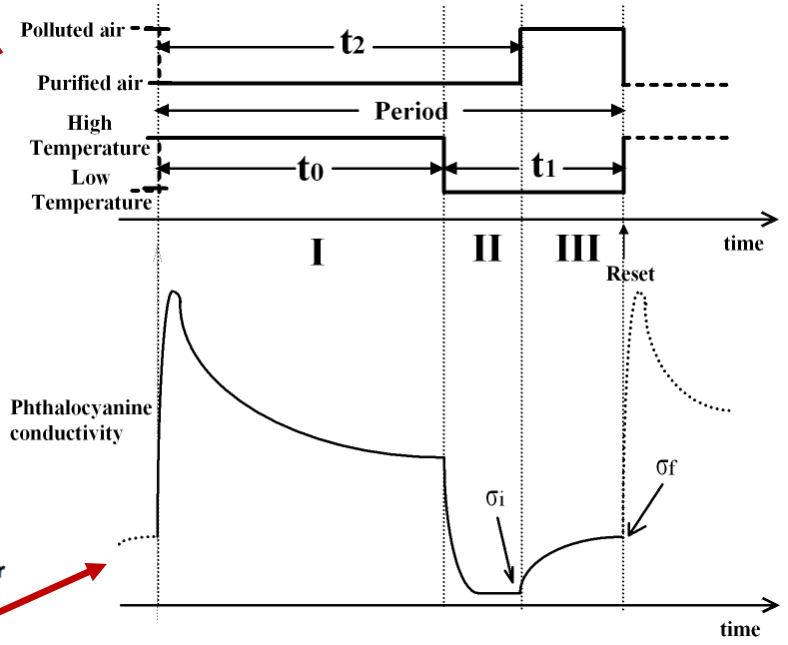
Durability ?

Improved !



1st App Gas sensor-system for NO_2 monitoring

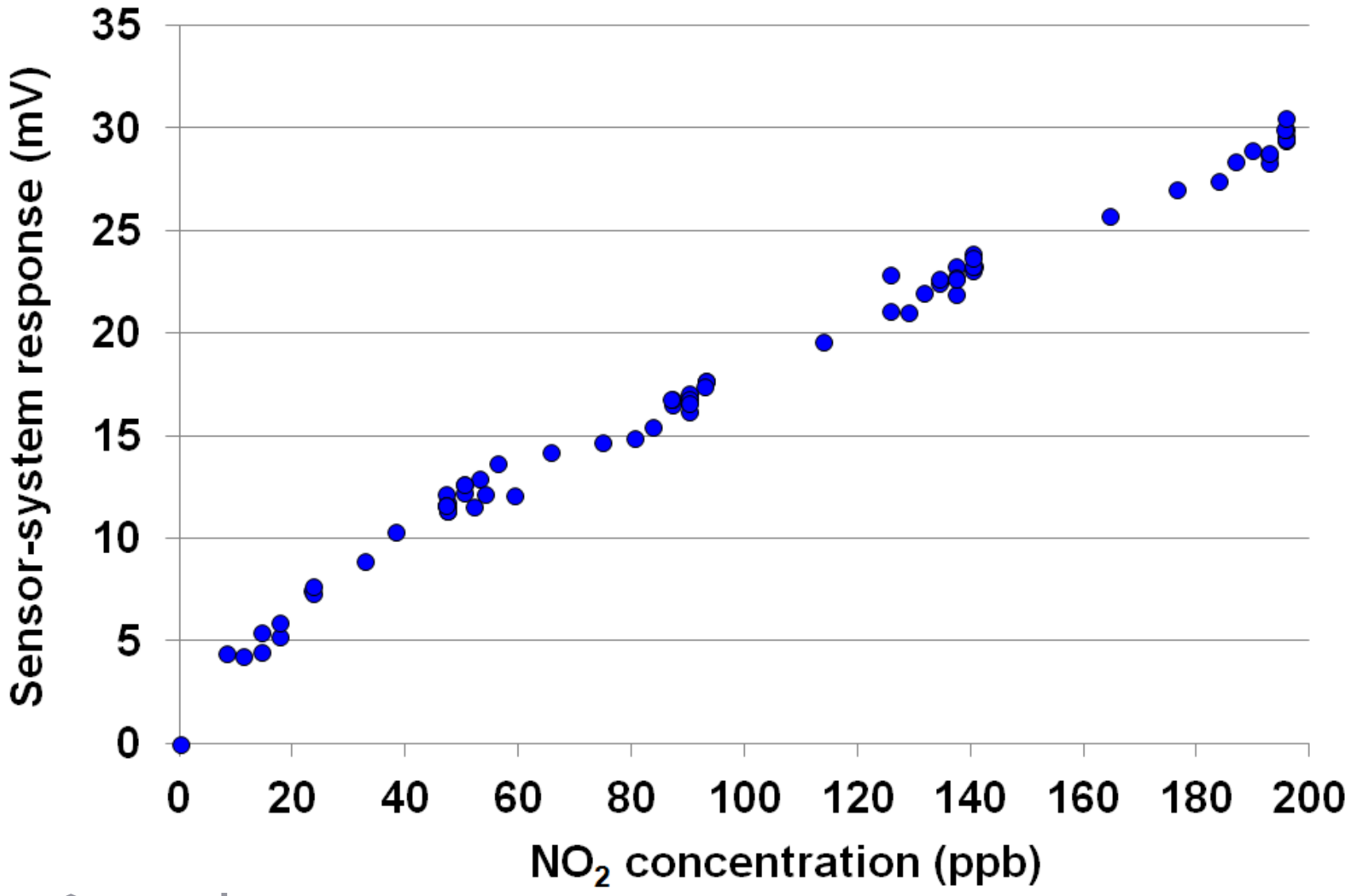




2 minutes of pollutant exposure during one cycle !

One measurement each 15 minutes !

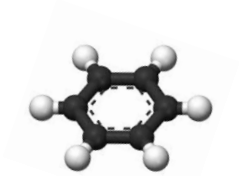
1st App Gas sensor-system for NO_2 monitoring

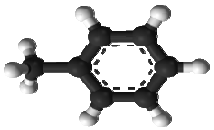


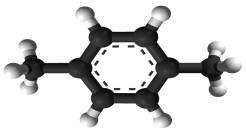
2nd App: sensor-system for BTX detection

Strategy?

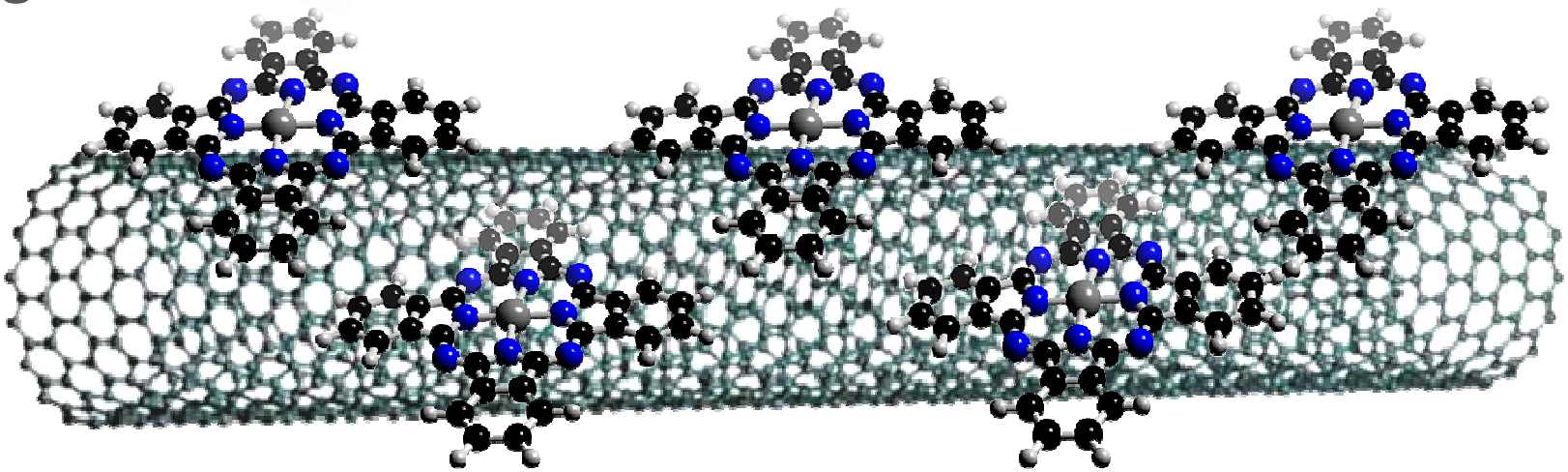
Target pollutants







Sensitive material



Transducing mode

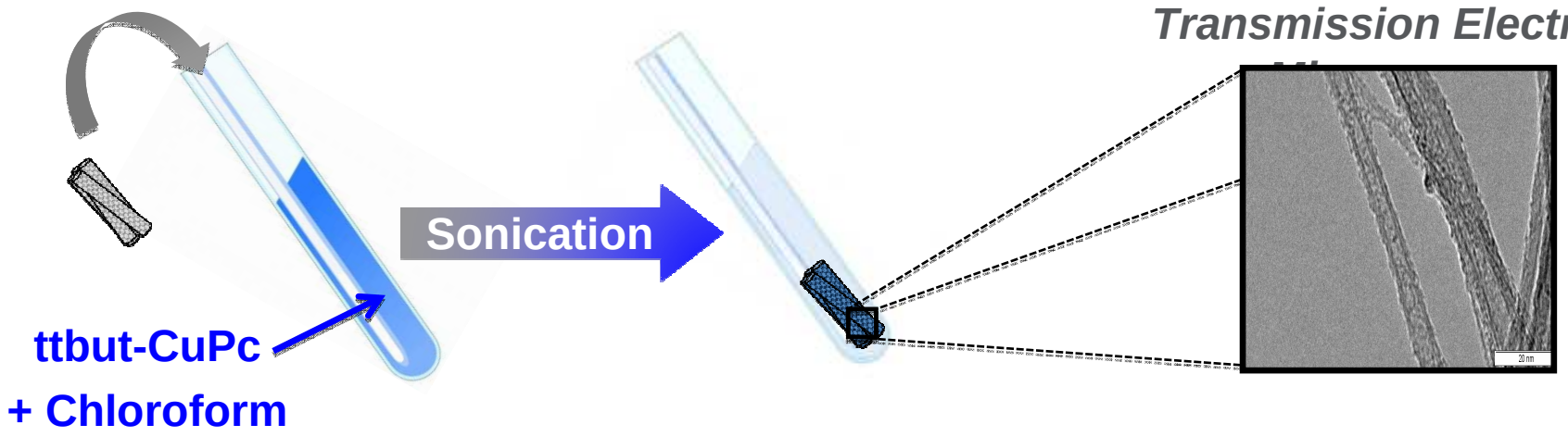
Excepted performances

High sensitivity

Reversibility

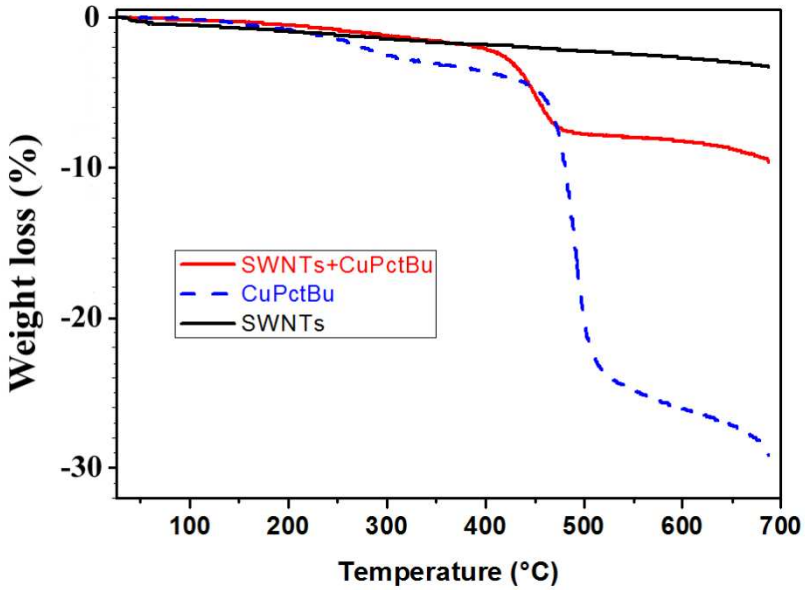
Low response time

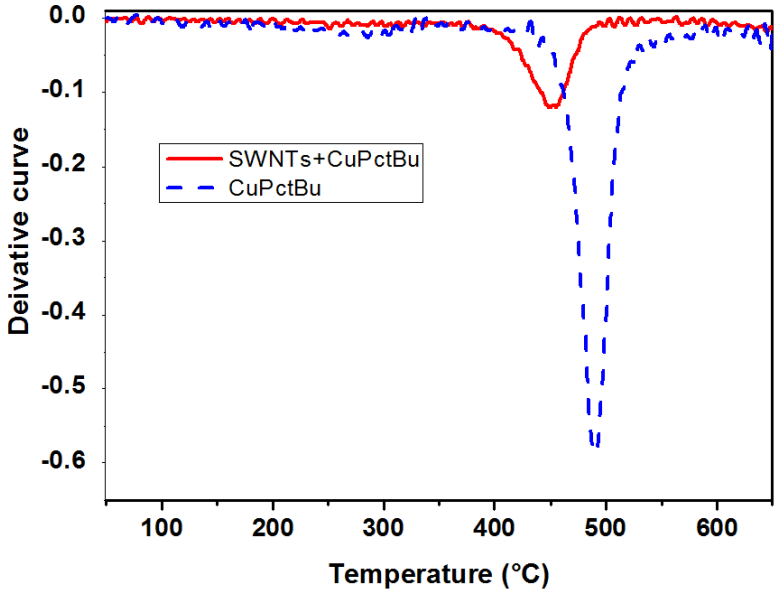
2nd App Elaboration and characterizations



Transmission Electron

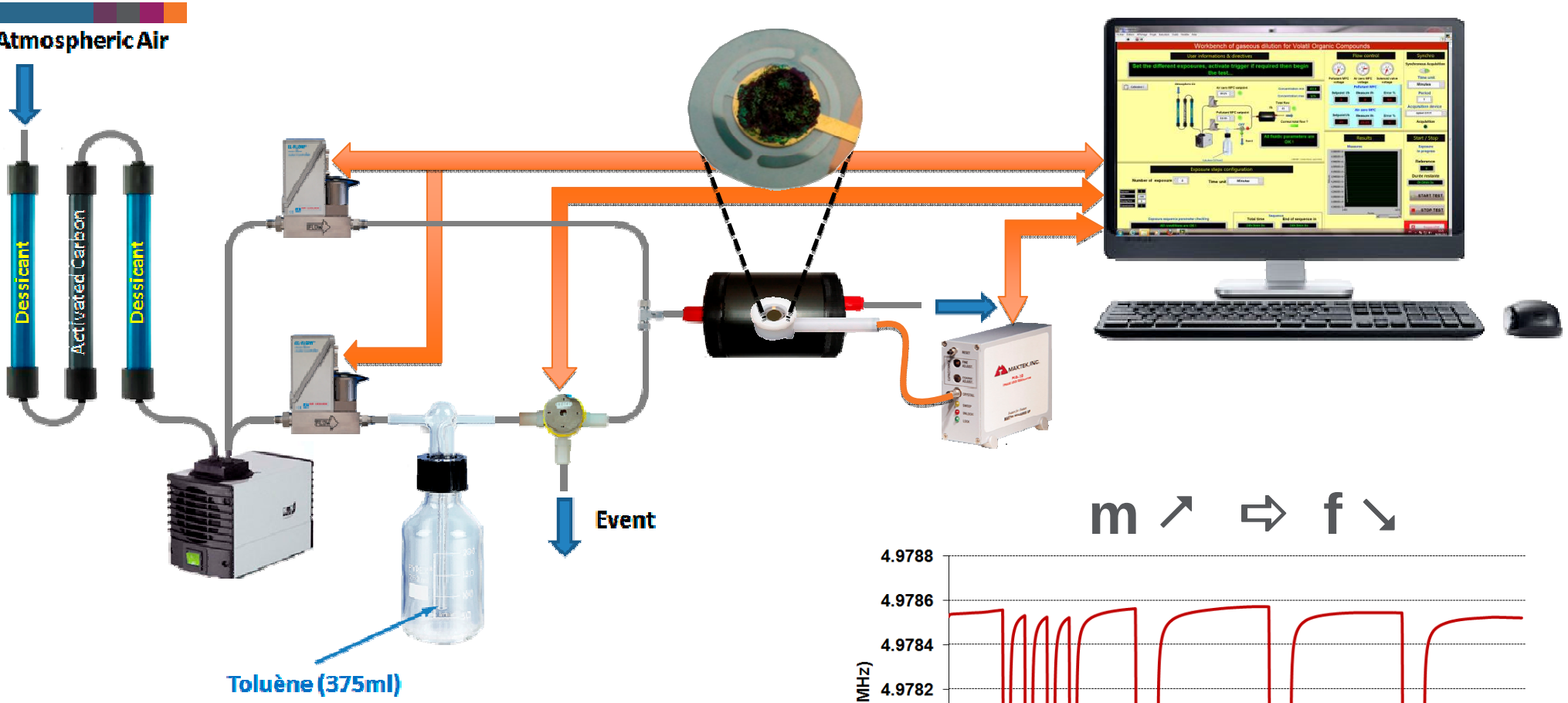
Thermogravimetric analysis





2nd App

Experimental setup

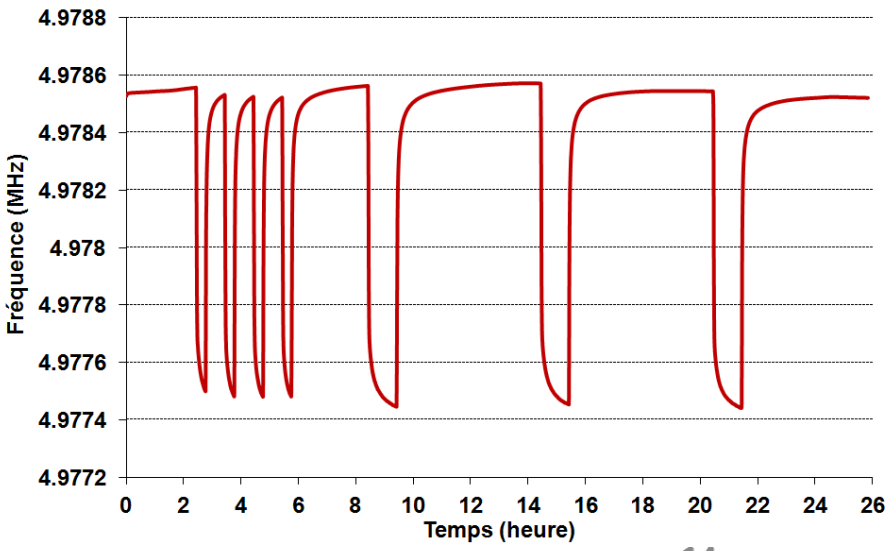


Sauerbrey Equation

$$\Delta f = - C_f \times \Delta m$$

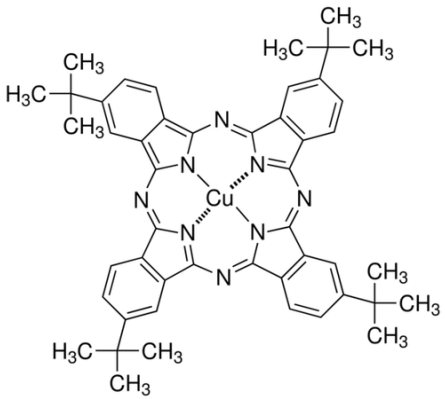
C_f : sensitivity
= 0.056 Hz/ng/cm² (@ 5 MHz)

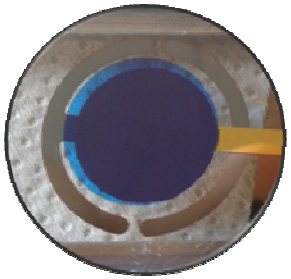
m ↗ ⇨ f ↘

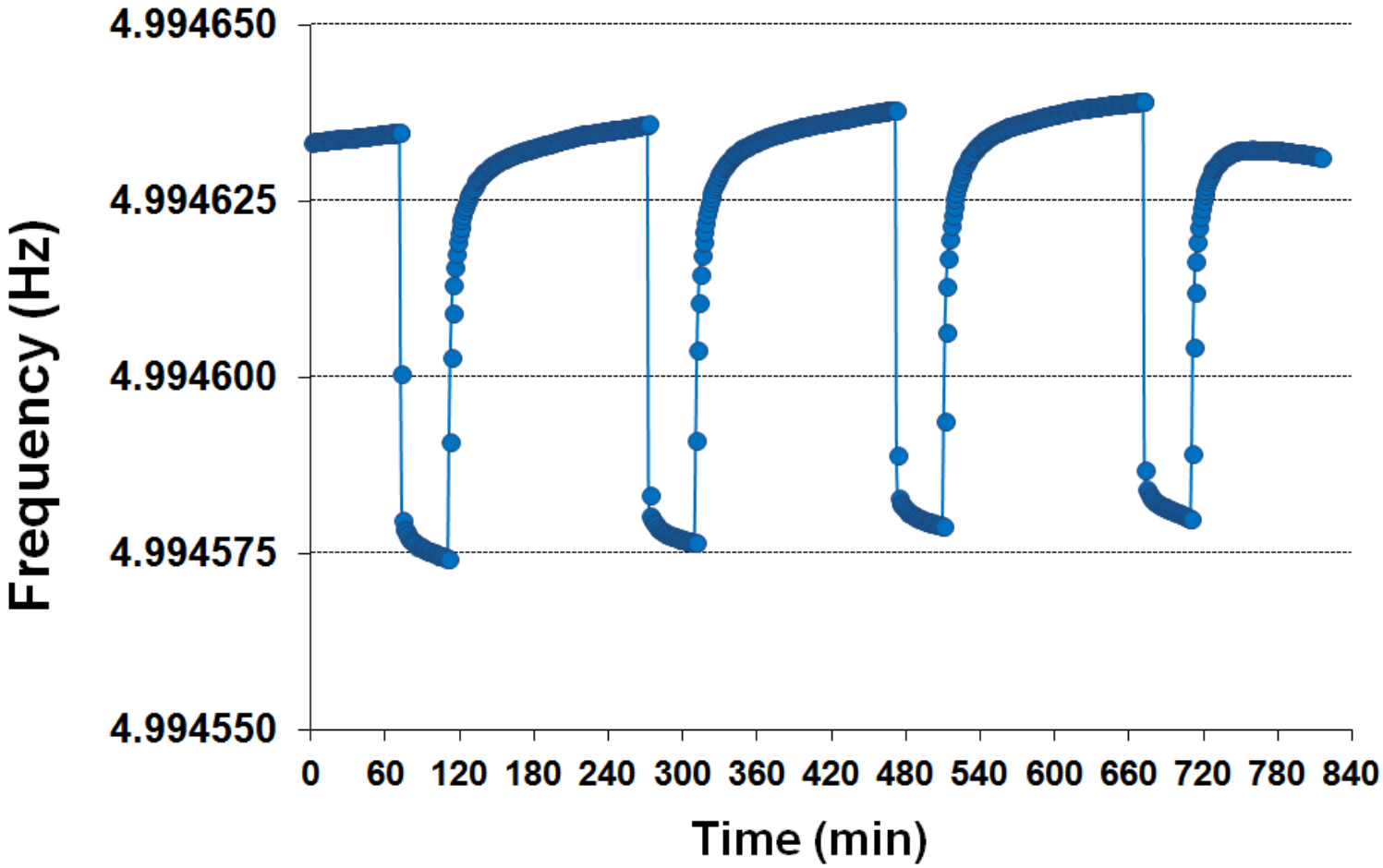


2nd App Gas sensitivity of phthalocyanine

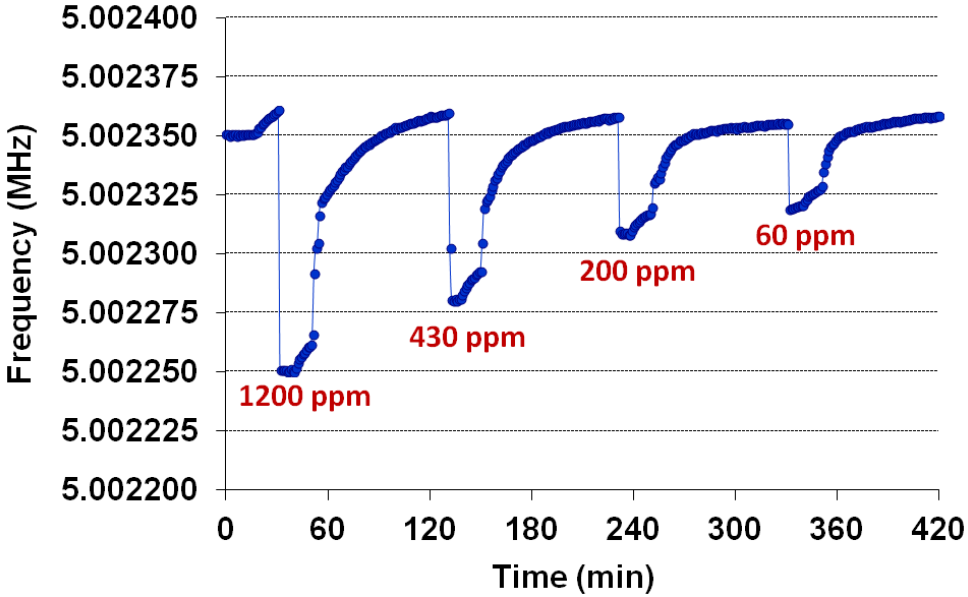
[C_7H_8] = 375 ppm Flow = 0.50 l/min T°= RT Thickness$_{ttb\text{-}CuPc}$ = 400 nm







2nd App Gas sensitivity of hybrid material

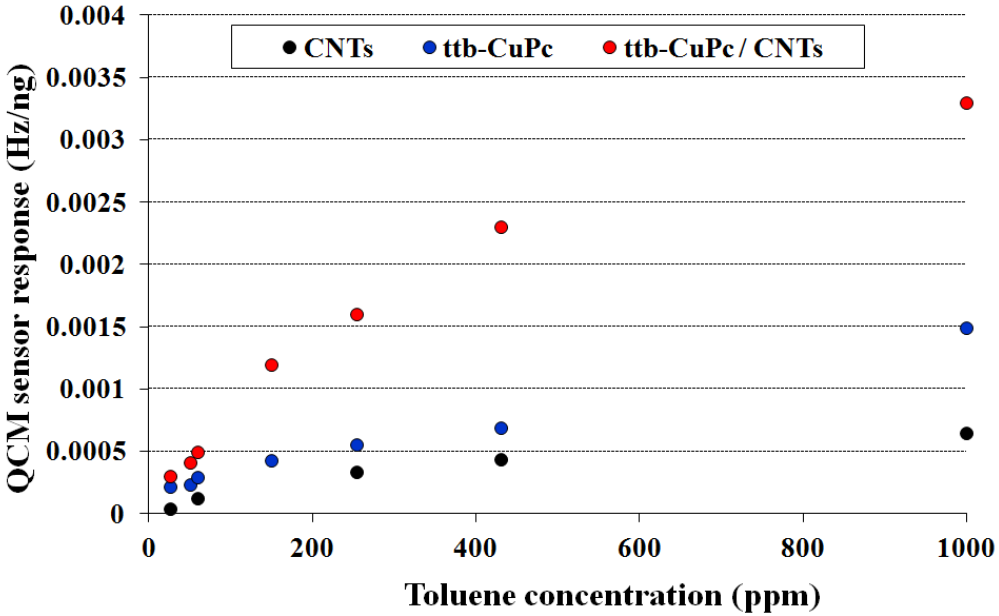


Reversibility ?
Response time ?

Satisfying !

Sensitivity ?

Enhanced !



CONCLUSIONS

- Hybrid materials ⇨ enhanced sensitivity to the target gases
  - Filtering materials ⇨ **improvement of selectivity**
  - Sensing materials ⇨ **improvement of sensor sensitivity**
- Strategy based on the most relevant material-transducer couple

⇨ **SIG3 - Guidelines For Best Coupling Air-Pollutant and Transducer**

Open problems and ongoing activities

- Discrimination between aromatic hydrocarbons
- Effect of interfering analytes
- Reproducibility of sensing devices


obrigado
Dank U
Merci
mahalo
Köszi
спасибо
Grazie
Thank you
mauruuru
Takk
Gracias
Dziękuję
Děkuju
danke
Kiitos