09:00 - 10:30
Diagnostics and nanotechnologies for cultural heritage
WS.IV.2 - TT.IX.A

Nano 2019 Innovation Conference & Exhibition
Rome, 11-14 June

Hybrid devices based on nanostructured sensors for gas and VOCs monitoring

Antonella Macagnano, Papa Paolo, Emiliano Zampetti, Andrea Bearzotti, Joshua Avossa, Fabrizio De Cesare

INSTITUTE OF ATMOSPHERIC POLLUTION RESEARCH-NATIONAL RESEARCH COUNCIL

Via Salaria km 29,300,

00016 Monterotondo (Rome) Italy

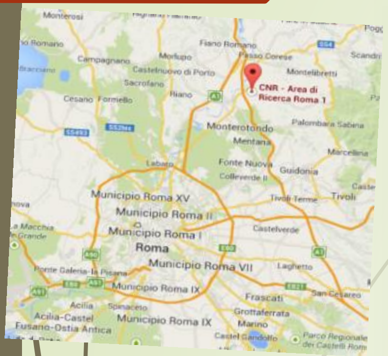
REGIONE LAZIO

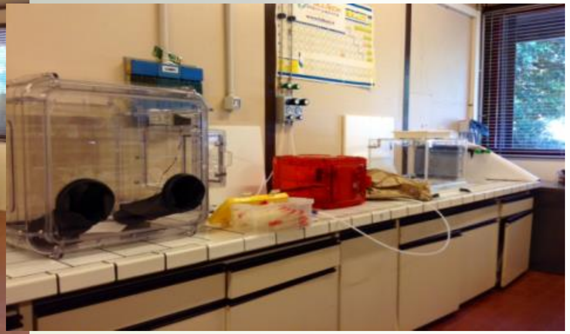
ADAMO

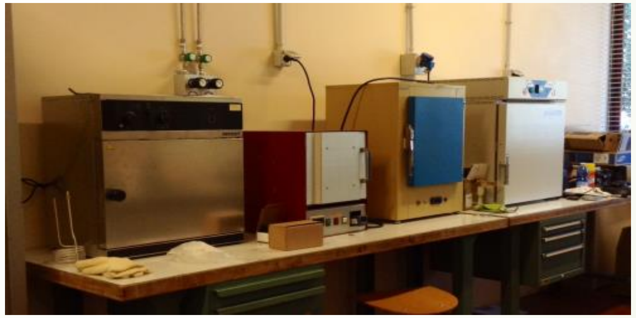
DTC LAZIO CENTRO DI ECCELLENZA

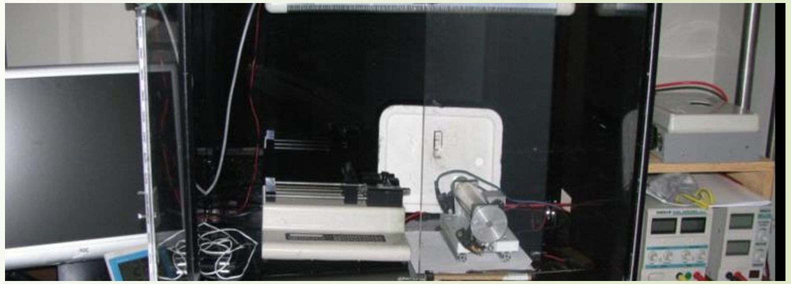
CNR-IIA

CNR - Consiglio Nazionale delle Ricerche
Istituto sull'Inquinamento Atmosferico



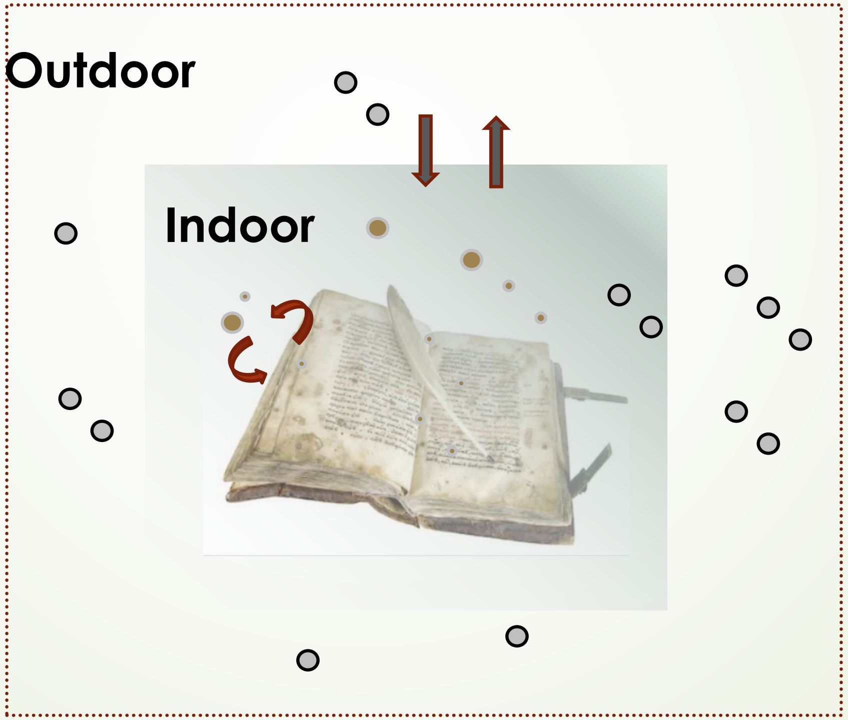




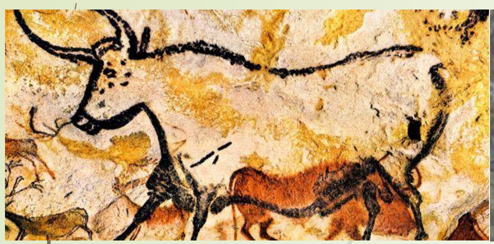


CONTENTS

Defining the scenario:
- Can the monitoring environment surrounding cultural heritage prevent damages?
- Are there pollutants responsible for any damage?

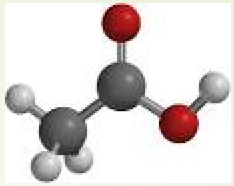


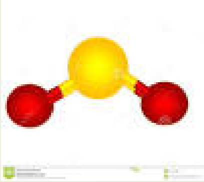
AIR POLLUTION AND ITS EFFECT ON ARTS

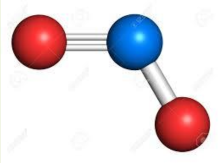


- ✓ **Prehistoric era: smoke from cave fires** obscured the details of art applied to cave walls.
- ✓ Wall paintings in the Chapels were dulled by **smoke from centuries of burning candles**
- ✓ New chemicals from **industrial revolution** damaged both statues (marble, metal..), buildings, paintings, frescoes, textiles, books….
- ✓ **Global wind currents spread pollutants far from their sources**.

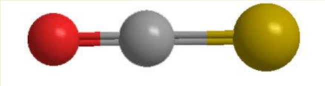
INDOOR POLLUTION

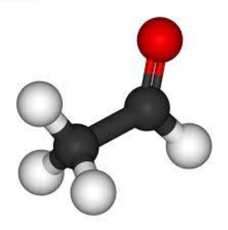

Acetic acid

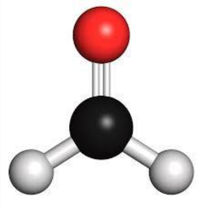

Sulfur dioxide

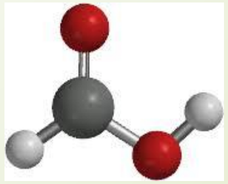

Nitrogen dioxide

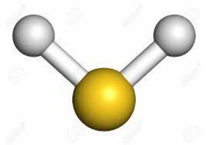
- **Dangerous outdoor pollutants: sulfur dioxide, nitrogen dioxide, nitrogen oxide, ozone, and reduced sulfur gases such as hydrogen sulfide**
- ✓ **Naturally ventilated buildings =indoor pollutants concentrations = outdoor levels.**
- ✓ Buildings with filtering systems (**heating, ventilation, and air-conditioning) reduce the indoor level up to 5% of the outdoor concentration**.
- **Indoor-generated** gases that pose a serious risk to cultural property are **acetic acid, formic acid, acetaldehyde, formaldehyde, hydrogen sulfide, carbonyl sulfide, and ozone** (*paints, boards, carpets, and cleaners, plastics, as well as many other materials and products)*

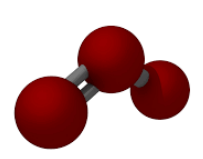

Carbonyl sulfide

Acetaldehyde



Formaldehyde

Formic acid


Hydrogen sulfide



Ozone

FOR INSTANCE: MUSEUM ENVIRONMENT MONITORING

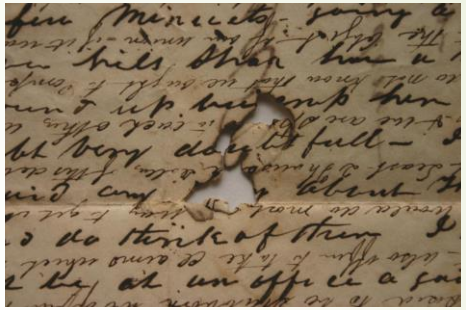
- **Common sensors in museums: relative humidity and temperature** (play a role in the chemical reactions).
- Low concentration of pollutants to make **irreversible chemical changes**
- Sensors should have extremely **low detection limits**, typically on the order of parts per billion (**ppb**)
- Sensing devices should be able to detect **a mixture of pollutants**




Indoor monitoring: the first step for preventing chemical EFFECTS (acid compounds)

Designing sensors highly selective and ultra-sensitive to the main common chemical agents in deterioring:

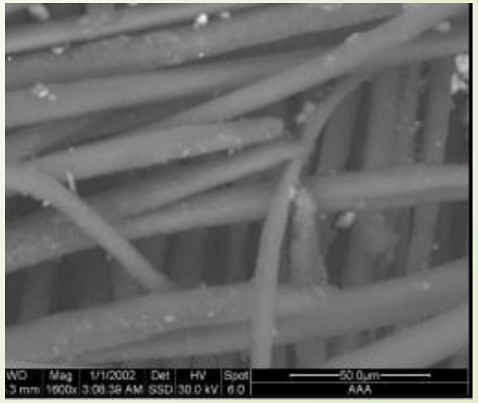
Paper is caused by many factors (molds, insect and bacteria) such as acid hydrolysis (**ACETIC ACID**), oxidative agents (**NO_2**, ozone), light, air pollution, or the presence of microorganisms.



Metals :very small amounts of acetic acid (500 ppb. or less) can promote corrosion of **metals** at moisture levels of 80% R.H. and above.

Calcareous materials (acceptable damage concentration (ADC)) (**NO_2 and organic acids**)

Textiles are deteriorated by heat, exposure to ultra-violet light, dye photochemical degradation, exposure to noxious gases (e.g. **formaldehyde converted to acid**), microorganisms.



Sensors array or ENOSE: could be useful for cultural heritage monitoring?

- The concept of the electronic nose as a tool made up of sensors used to classify odors was introduced for the first time by Persaud and Dodd in 1982
- Usually the **electronic nose** does not recognize the individual odor-generating compounds, but rather **provides an olfactory signature** (fingerprint) of the analyzed air. To do this, the instrument must be trained, *i.e.*, it must be provided with a database of olfactory fingerprints relating to the odors to which it may be exposed to during the analysis
- Depending on the type of application involved, various types of systems have been developed and are used to deliver gas samples to the inside of the electronic nose
- **ENOSE COMPOSITION**:
- (I) a **matrix of sensors to simulate the receptors** of the human olfactory system;
- (II) a **data processing unit** that would perform the same function as the olfactory bulb;
- (III) **a pattern recognition system** that would recognize the olfactory patterns of the substance being tested, a function performed by the brain in the human olfactory system

CNR-IIA

HYBRID PROTOTYPE for INDOOR MONITORING BASED ON COMMERCIAL AND NANOSTRUCTURED SENSORS: from EXPO to ADAMO PROJECT

Interchangeable Modular Systems:

- ✓ QCMs
- ✓ IDEs
- ✓ Electrochemical sensors

(CO, NO_x, SO_2, H_2S)

- ✓ Nondispersive Infrared sensor

CO_2

- ✓ LM35 and HIH406

T and %RH

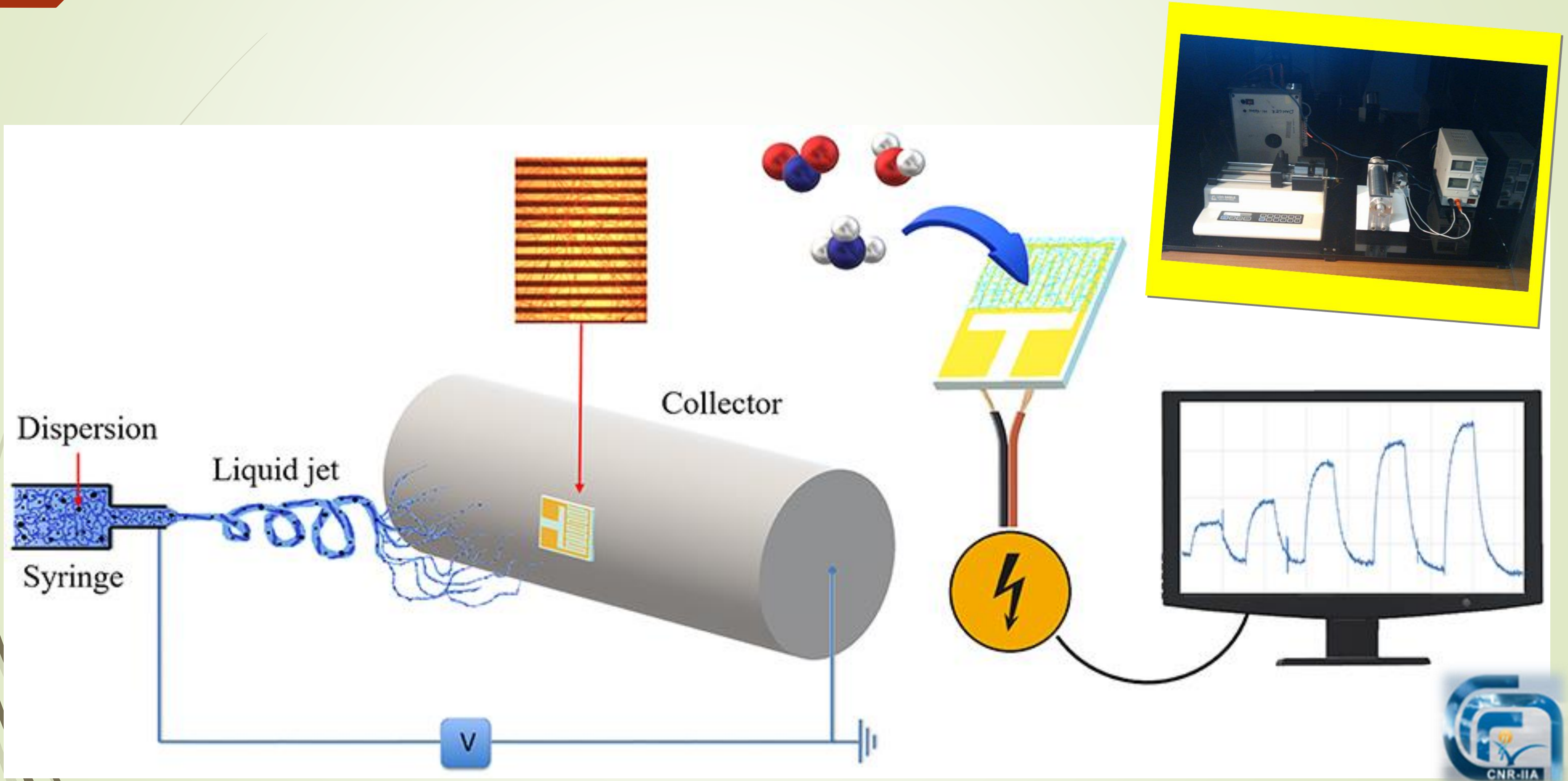
- ✓ Micropump and mass-flow sensor
- ✓ Analog and digital interface circuits

Controller Unit (16 bit A/D, 1 Gb, WiFi)

- ✓ Power supply
- ✓ Controller unit on single board computer
- ✓ OS Linux based

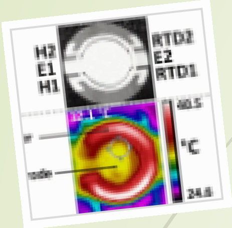
✓ Suitable for: **wireless transmission of data**

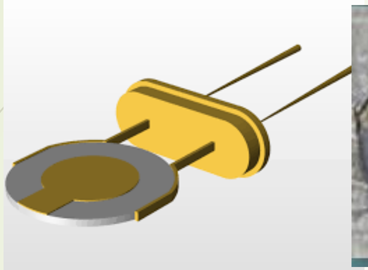
Fabrication of Ultrasensitive Nanostructured Sensors: Electrospinning Technology

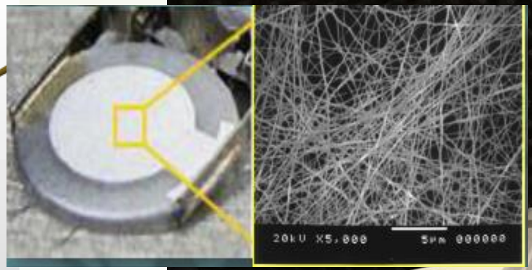


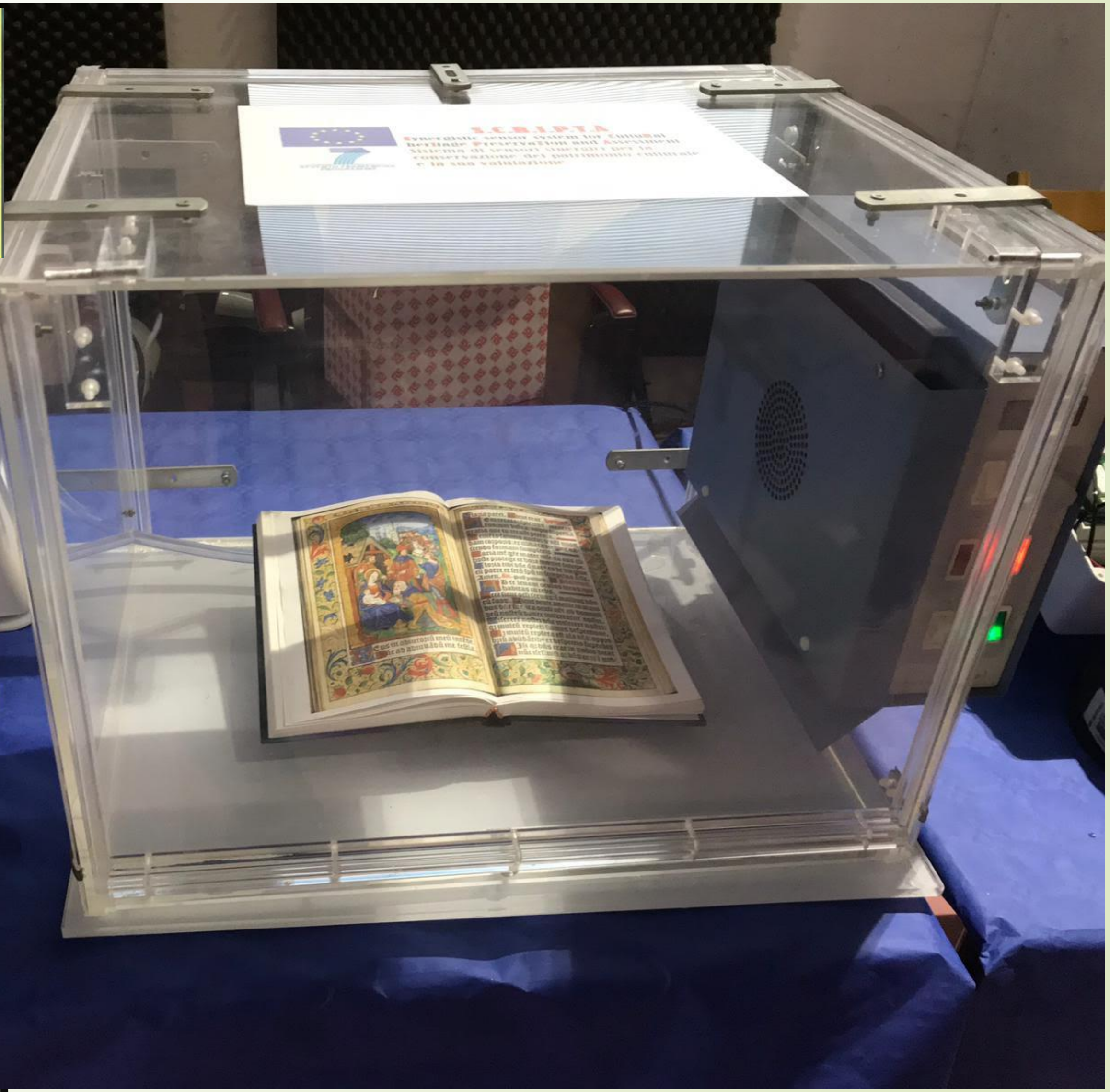
CUSTOMIZATION TO A CULTURAL HERITAGE MICROCLIMATE

QCMs

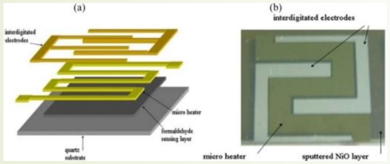


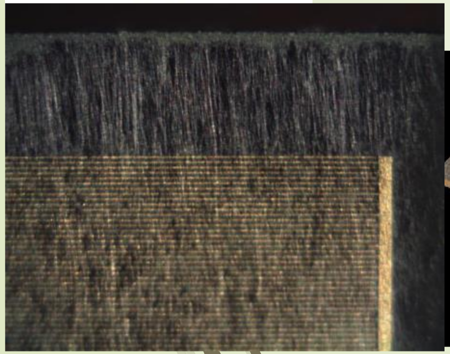


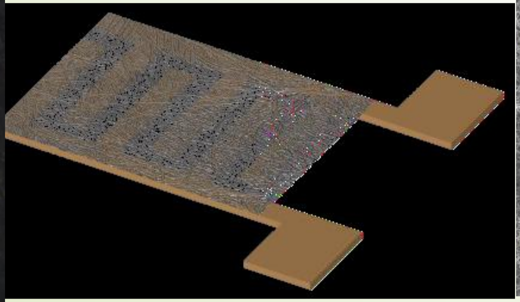


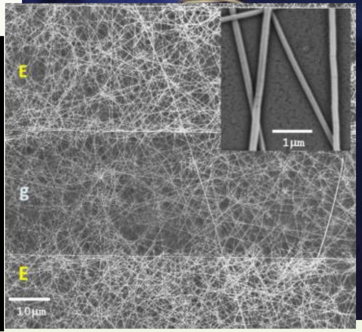


IDES









ENOSE FEATURES

- The **number and type of sensors** in an electronic nose is generally selected on the basis of the **specific application**

(indoor monitoring).

- First and foremost, the **sensors have to be partially selective** *i.e.*, sensitive to the substance of interest

(selective to acids but taking into accounts all the surrounding environment).

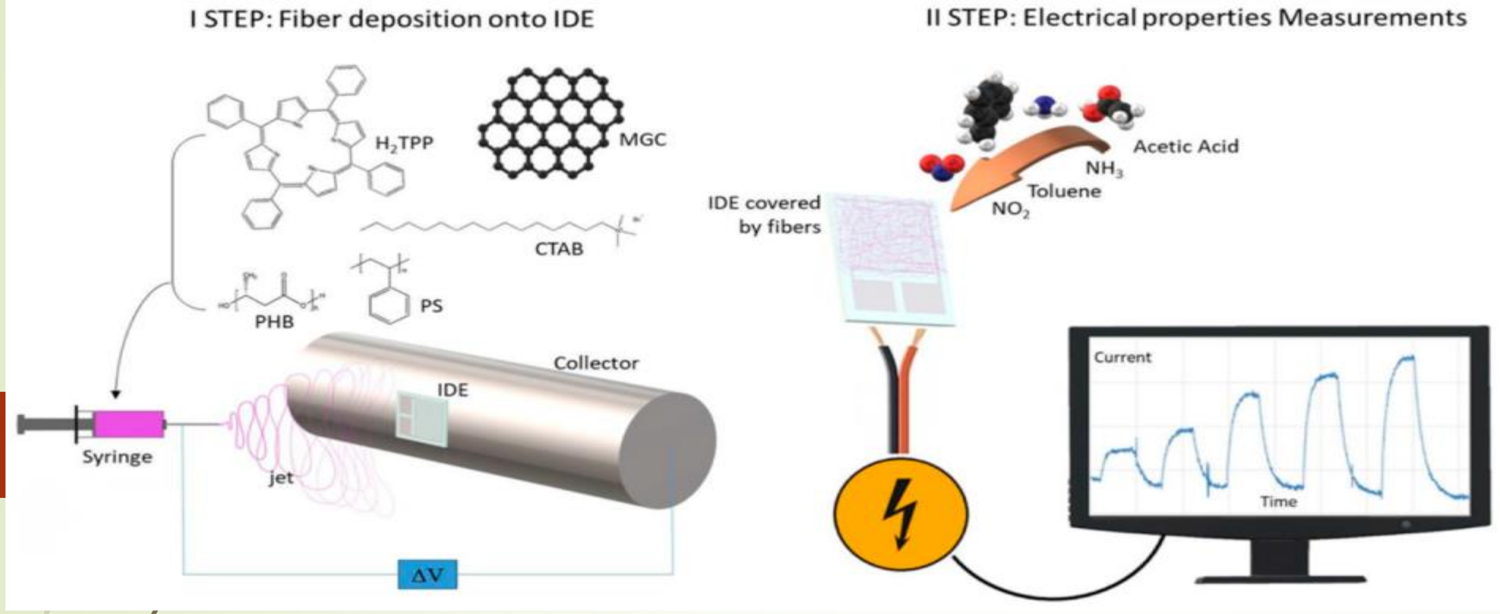
- Sensors have to be **ultra sensitive**

(a few ppm to ppb concentration)

- Furthermore, their response has to be:

fast, **stable**, **reproducible** and **reversible**

FABRICATION OF A BATCH OF ULTRA SENSITIVE SENSORS TO ORGANIC ACIDS



POLYMER BLEND + MESOPOROUS GRAPHENE+ Me-H2TPP

POLYMER BLEND

- ✓ **Thermally resistant**
- ✓ **Low environmental impact (biodegradable and recyclable)**
- ✓ **Low cost**
- ✓ **Widely used**

Polystyrene + Polyhydroxybutyrate

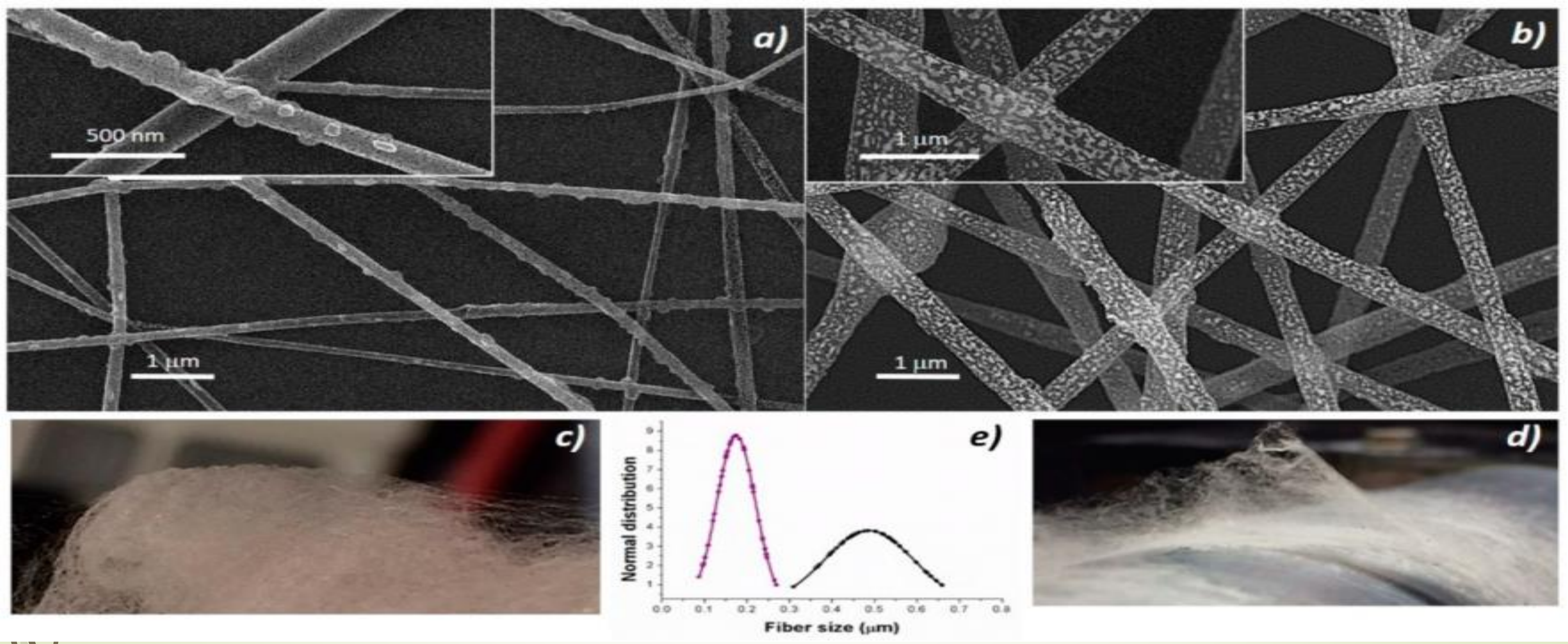
PORPHYRIN

The **sensitivity** of PORPHYRINS is usually correlated with their structure and in particular with the kind of **metal ion**, **aromatic system**, and **peripheral substituents**.

MESOPOROUS GRAPHENE

- ✓ G is theoretically a zero-bandgap semiconductor with **excellent r. t. electrical conductivity**, with a charge carrier mobility of about 10^4 cm^2 V^{-1} s^{-1}
- ✓ **Mesopores** make the structure highly **adsorbing small polar and oxidizing molecules**

PS-PHB-G/PS-PHB-G-H2TPP: FIBERS CHARACTERIZATION

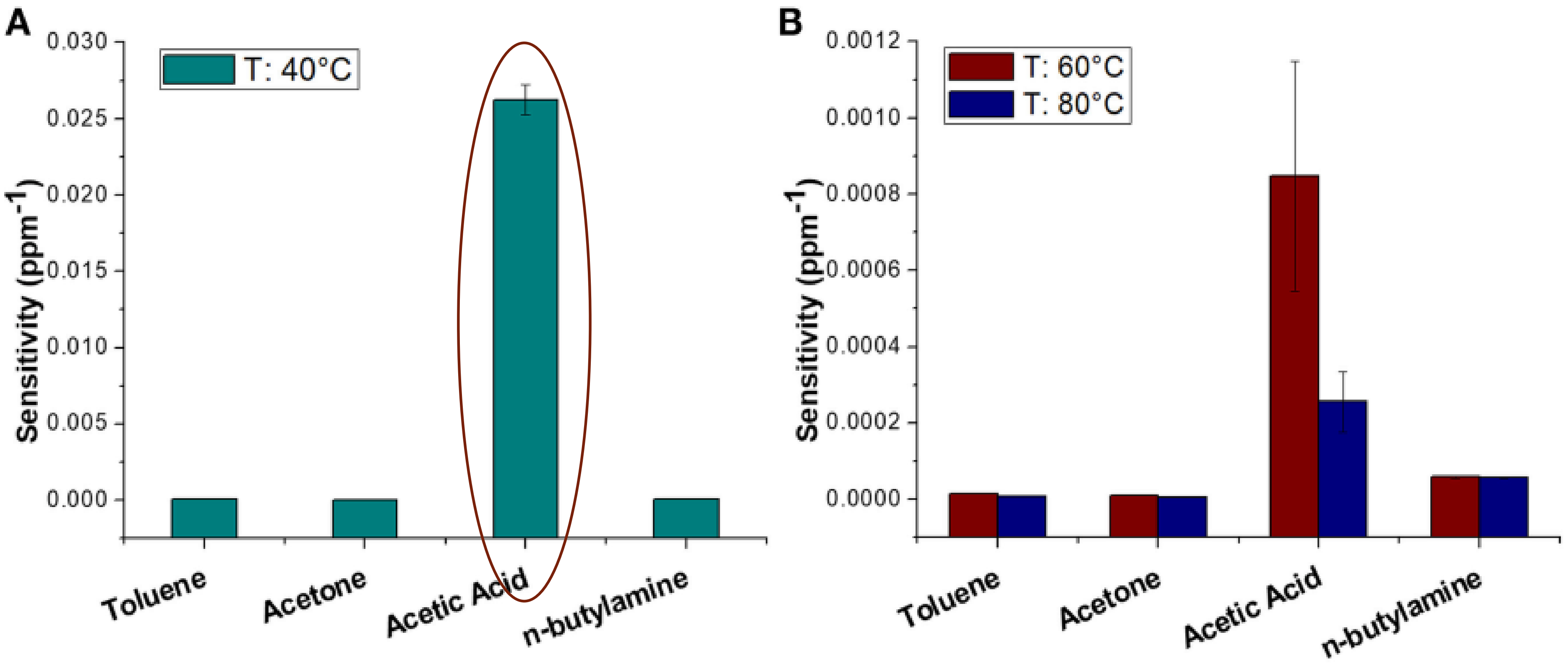


SEM micrographs of H_2TPP-PsB-MGC (**a**) and PsB-MGC (**b**) and their respective pictures placed under (**c**,**d**). Diameter distribution graph (**e**) of H_2TPP-PsB-MGC (purple) (**a**) and PsB-MGC fibers (black) (**b**). (*Avossa et al., Nanomaterials 2019, 9(2),280*)

SENSOR SELECTIVE TO ACETIC ACID (T:40°C)

PHB+PS+G

T increased S decreased

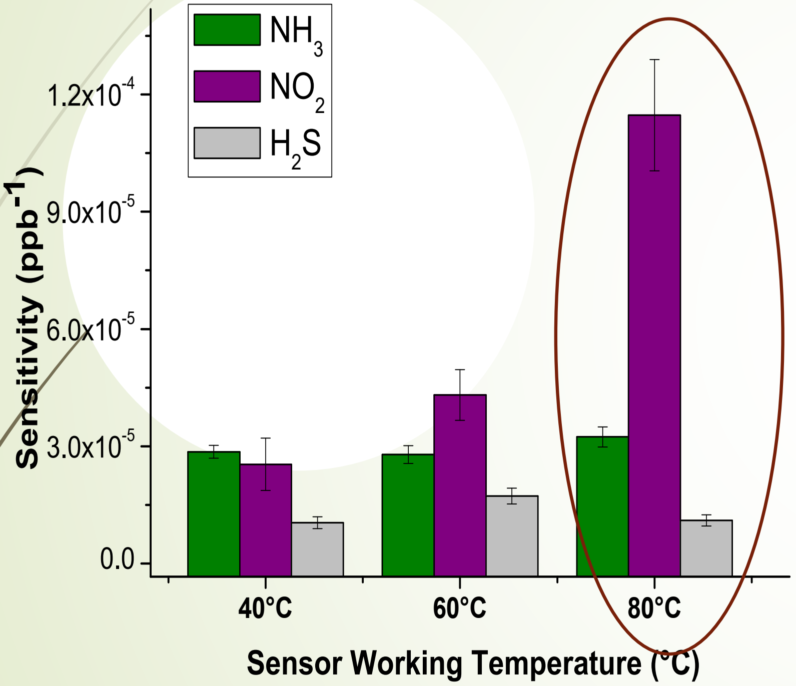


LOD: a few ppb

Avossa et al., Front. Chem, 2018, 6, 432

SENSOR SELECTIVE TO NO2 (T=80°C)

PHB+PS+G



SENSOR SELECTIVE TO NO_2

T=80°C Sensitivity 4 times higher than at 40°C.

The increase in sensitivity could be due to:
redistribution and orientation of graphene within polymer fibers due to the heating, allowing the gas adsorption onto a larger number of exposed binding sites, despite of the unfavorable energies involved in the phenomena of ad-adsorption.

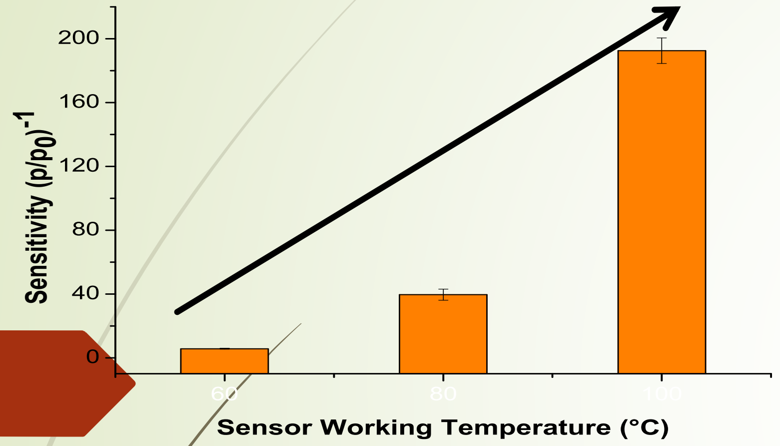
The $LOD_{80°C}$ (defined as 3 * standard deviation of the blank) has been calculated to be ~**2 ppb.**

Avossa et al., Front. Chem, 2018, 6, 432

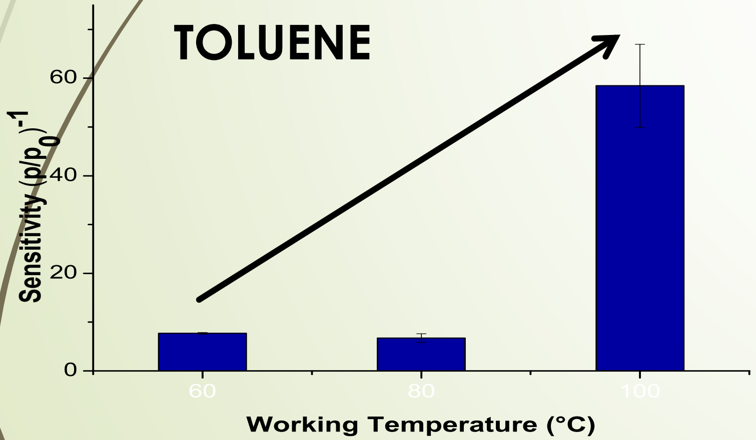
VOCs measurements COMPARISON

G+PP+Porf

ACETIC ACID

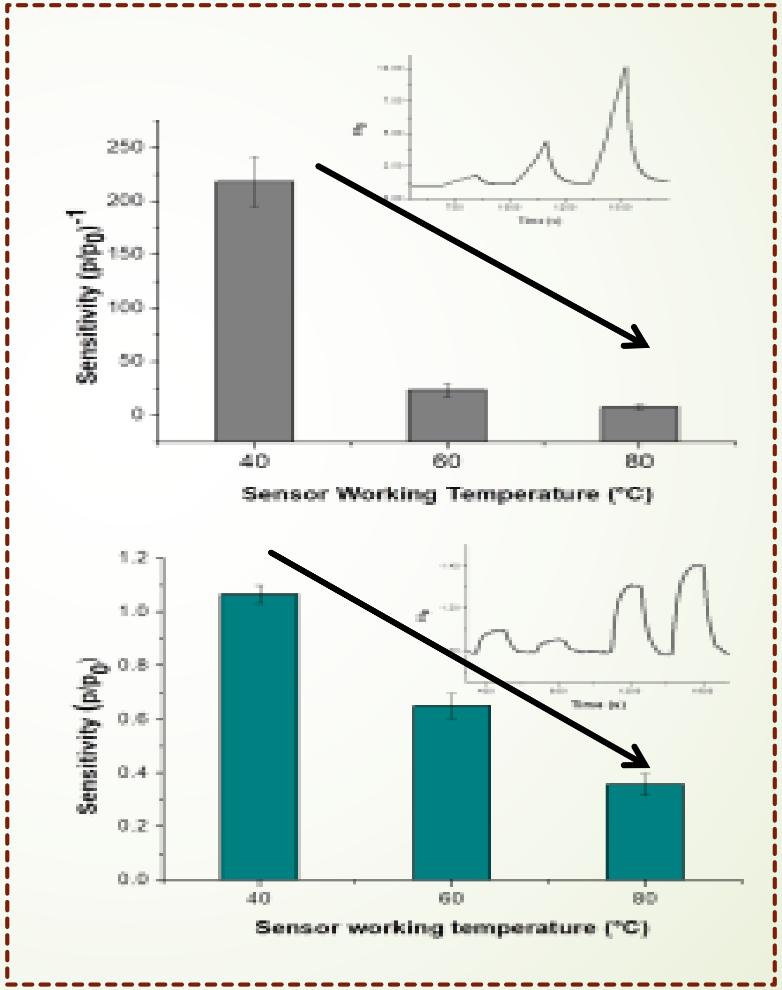


TOLUENE



LOD: 3 ppm

G+PP



Completely different effects of temperature to VOCs responses:

- ✓ Kinetics
- ✓ Sensitivity values

Temperature looks to favor VOCs interaction when porphyrin is inside fibres

...changing the Metal, Porphyrin selectivity and sensitivity change too

PRELIMINARY CONCLUSIONS for Conductive sensors Based on Polymers, Graphene and Porphyrins

-able to work alone or in array (ENose),
-no-expensive,
-with fast responses,
-easy to be produced in large-scale,

-ultrasensitive to acetic acid and NO_2

-able to create ultrasensitive sensors with a good selectivity to be applied for multifaceted environments of artworks

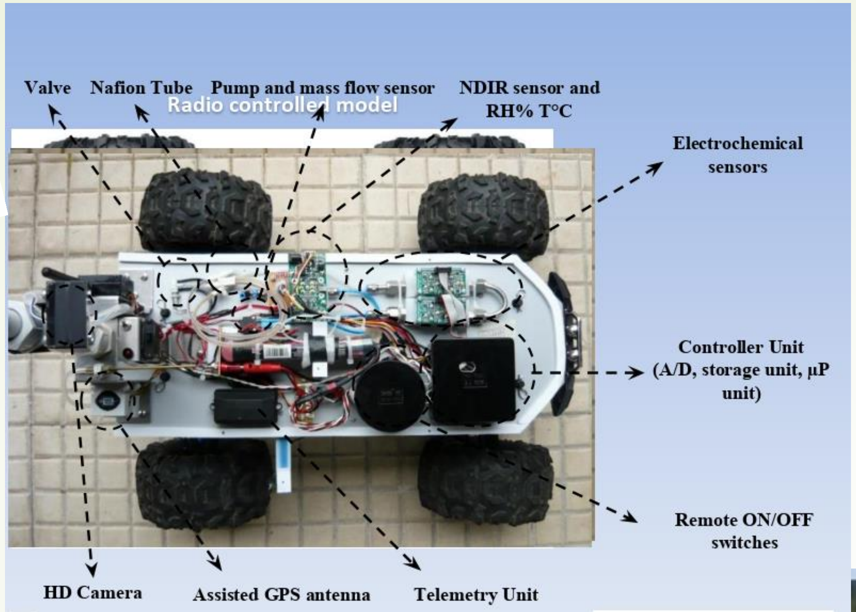
CNR-IIA

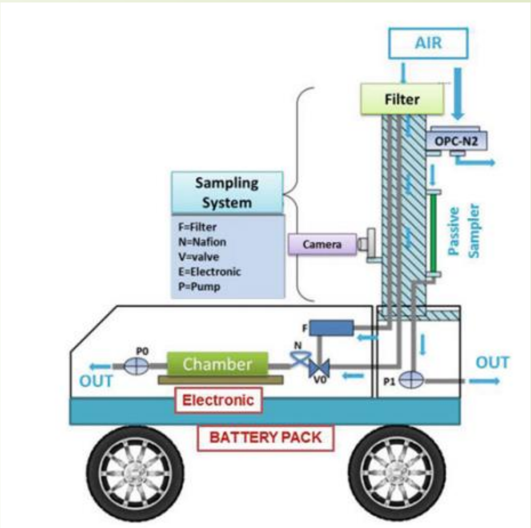
ENOSE outdoor monitoring and mapping

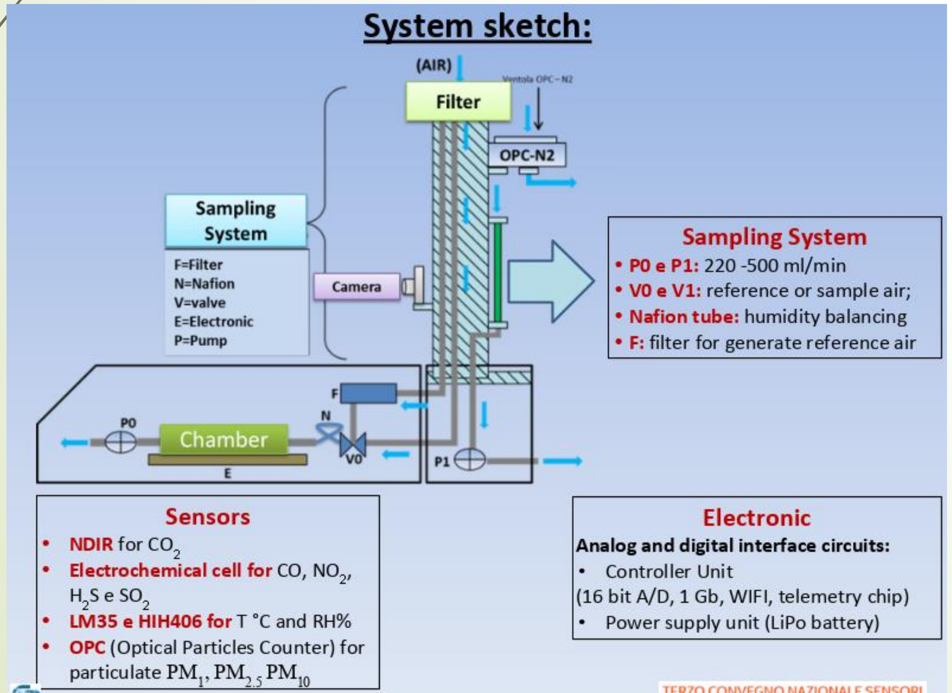
Remotely Controlled Terrestrial Vehicle Integrated Sensory System for Environmental Monitoring

Emiliano Zampetti(✉), Paolo Papa, Francesco Di Flaviano, Lucia Paciucci, Francesco Petracchini, Nicola Pirrone, Andrea Bearzotti, and Antonella Macagnano

B. Andò et al. (eds.), Sensors, Lecture Notes in Electrical Engineering 431,
DOI 10.1007/978-3-319-55077-0_43







CNR-IIA

CONCLUSIONS and PERSPECTIVES

- Air monitoring is the first step to prevent damages
- Electronic noses or hybrid devices sound as good choices to check the chemicals where cultural heritages have been exposed
- A modular system provides a good versatility to the sensing device improving the application scenarios (indoor, outdoor, microclimate, etc.)
- Further step: measurements in field

THANKS TO:

Natural painting composed of protein aggregates on nanofibres (optical micrograph)

Prof. GiuseppeScarascia Mugnozza
Dr. Fabrizio De Cesare
University of Tuscia, Viterbo

Prof. Eyal Zussman
Technion, Israel

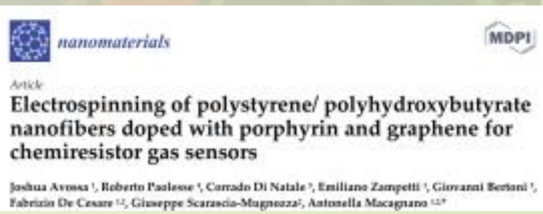
Eng. Emiliano Zampetti
Dr. Laura Ragazzi
Dr. Joshua Avossa
Dr. Andrea Bearzotti
Dr. Paolo Papa
Mr. Alessandro Capocecera
IIA-CNR, Rome

Prof. Corrado Di Natale
Prof. Roberto Paolesse
University of Tor Vergata, Rome

Work co-funded by a 2-Year National Project, BRIC ID.12 2016 - National Institute for Insurance against Accidents at Work (INAIL), titled: "Design and development of a sensory system for the measurement of volatile compounds and the identification of job-related microorganisms (2017-2019)

frontiers in Chemistry

Thermally Driven Selective Nanocomposite PS-PHB/MGC Nanofibrous Conductive Sensor for Air Pollutant Detection



nanomaterials

MDPI

Article

Electrospinning of polystyrene/ polyhydroxybutyrate nanofibers doped with porphyrin and graphene for chemiresistor gas sensors

Joshua Avossa, Roberto Paolesse, Corrado Di Natale, Emiliano Zampetti, Giovanni Bertoni, Fabrizio De Cesare, Giuseppe Scarascia-Mugnozza, Antonella Macagnano

Natural painting composed of protein aggregates on nanofibres (optical micrograph)

THANK YOU