SIAGRO Simpósio Nacional de Instrumentação Agropecuária - 2019

SENSORS FOR AGRO-FOOD

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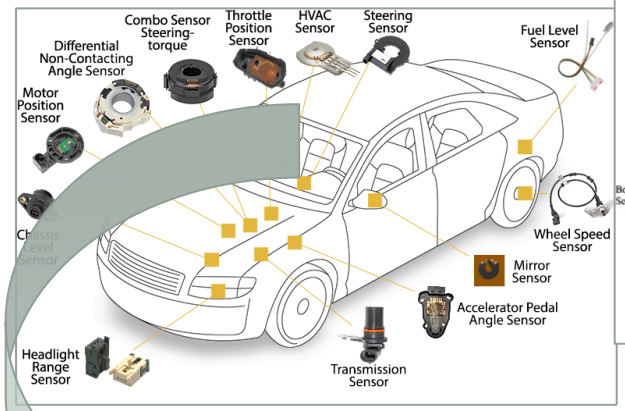
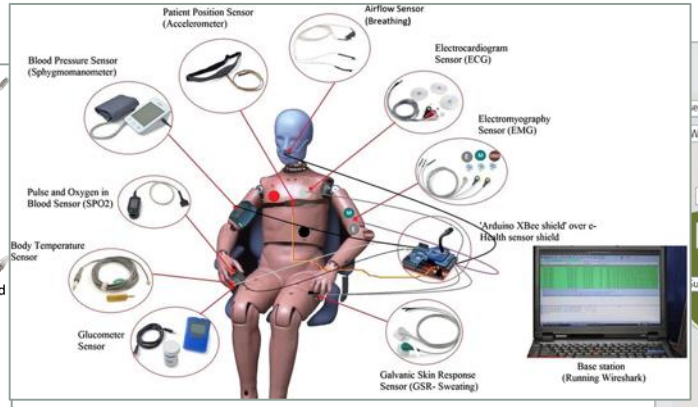
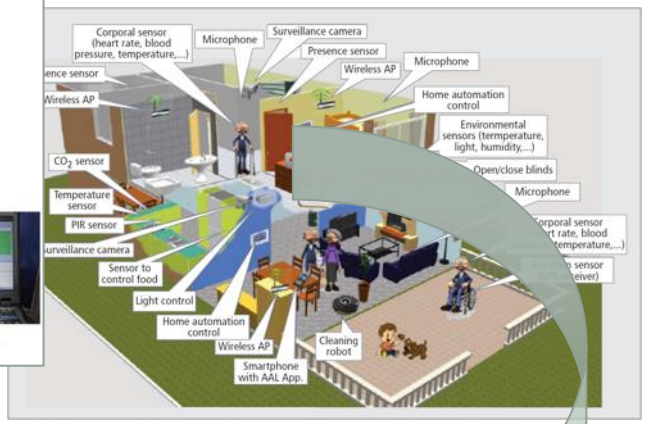
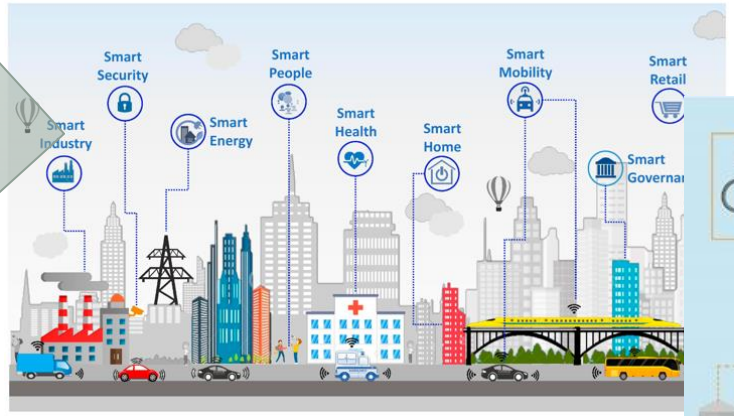
Pervasive electronics

- Microelectronics: expanded computing capabilities at reduced size and price
- Efficient communication infrastructures: Bluetooth, WiFi, 5G … Internet
- Sensors









Microsensors

- Integrated sensors
  - Silicon technology (microelectronics) enables the fabrication of integrated systems where both the sensitive element and the electronics are integrated in the same chip. MEMS (Micro Electro Mechanical Systems)

420 PROCEEDINGS OF THE IEEE, VOL. 70, NO. 5, MAY 1982

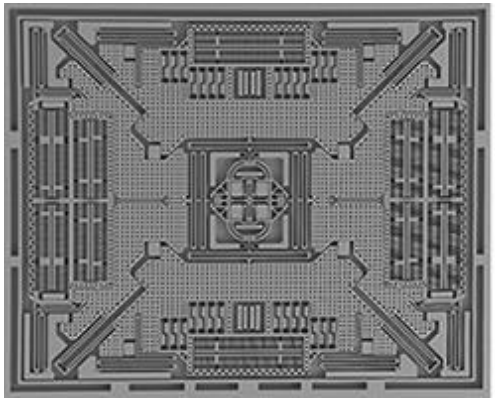
Silicon as a Mechanical Material

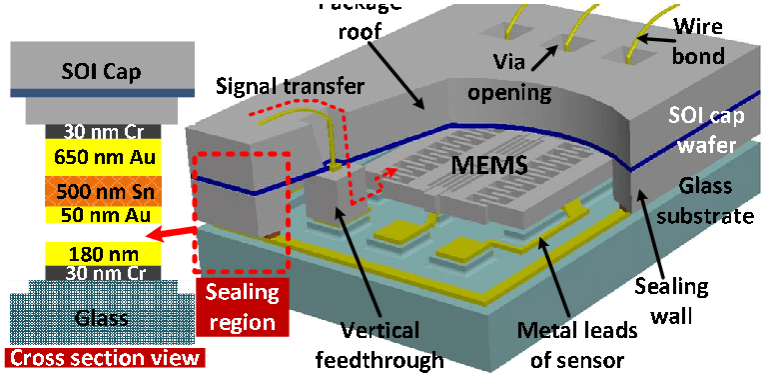
KURT E. PETERSEN, MEMBER, IEEE

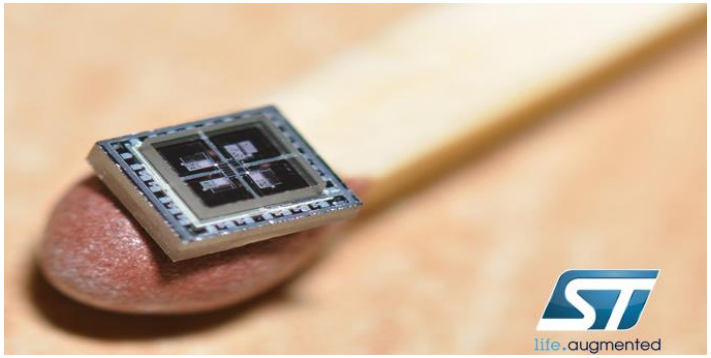
Abstract—Single-crystal silicon is being increasingly employed in a variety of new commercial products not because of its well-established electronic properties, but rather because of its excellent mechanical properties. In addition, recent trends in the engineering literature indicate a growing interest in the use of silicon as a mechanical material with the ultimate goal of developing a broad range of inexpensive, batch-fabricated, high-performance sensors and transducers which are easily interfaced with the rapidly proliferating microprocessor. This review describes the advantages of employing silicon as a mechanical material, the relevant mechanical characteristics of silicon, and the processing techniques which are specific to micromechanical structures. Finally, the potentials of this new technology are illustrated by numerous detailed examples from the literature. It is clear that silicon will continue to be aggressively exploited in a wide variety of mechanical applications complementary to its traditional role as an electronic material. Furthermore, these multidisciplinary uses of silicon will significantly alter the way we think about all types of miniature mechanical devices and components.

miniaturized mechanical devices and components must be integrated or interfaced with electronics such as the examples given above.

The continuing development of silicon micromechanical applications is only one aspect of the current technical drive toward miniaturization which is being pursued over a wide front in many diverse engineering disciplines. Certainly silicon microelectronics continues to be the most obvious success in the ongoing pursuit of miniaturization. Four factors have played crucial roles in this phenomenal success story: 1) the active material, silicon, is abundant, inexpensive, and can now be produced and processed controllably to unparalleled standards of purity and perfection; 2) silicon processing itself is based on very thin deposited films which are highly amenable to miniaturization; 3) definition and reproduction of the

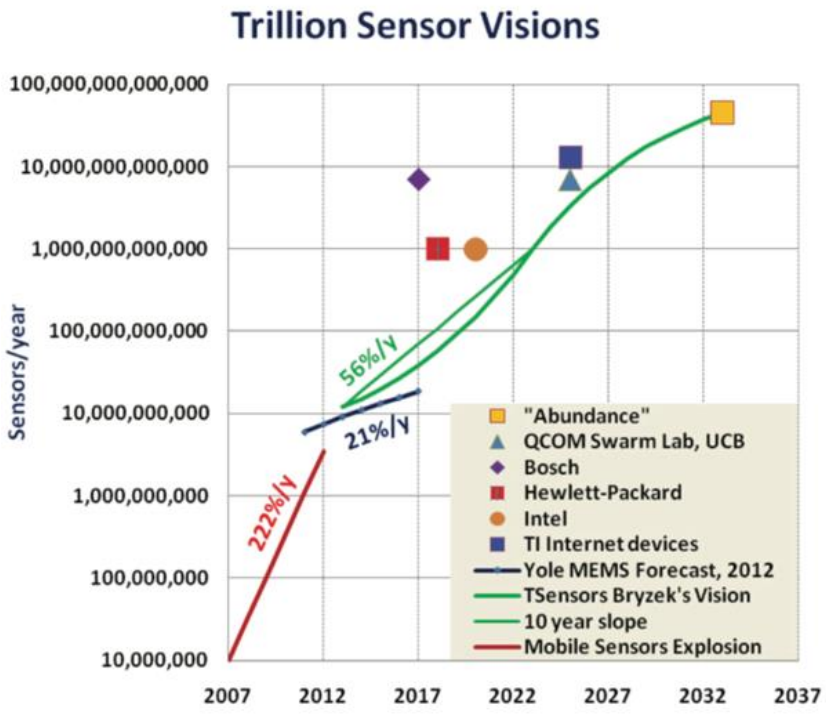






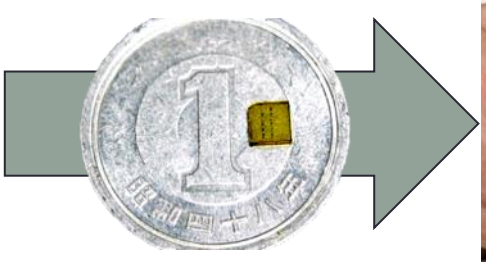
Ubiquitous sensing

- Sensors data available to anyone and anywhere: Internet of Things
- 10^{12} connected sensors
- Big Data

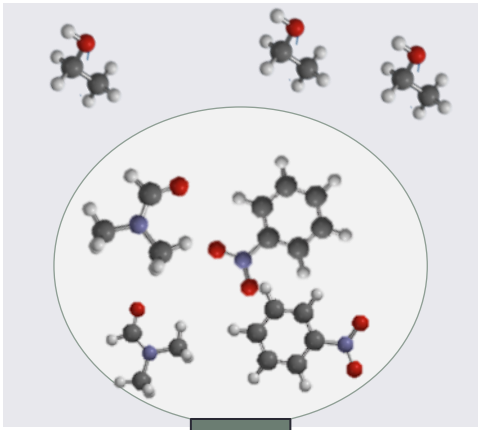


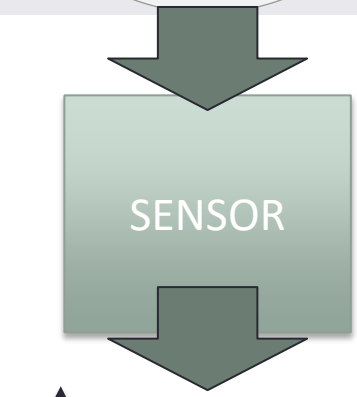
- 2 Microphones
- 2 image sensors
- 3D accelerometer
- 3D gyroscope
- Pressure sensor
- 3D compass
- Ambient light sensor
- Proximity sensor
- **Chemical Sensors ?**

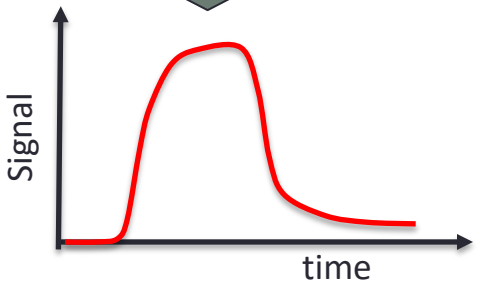
Analytical Chemistry ➔ Chemical Sensors

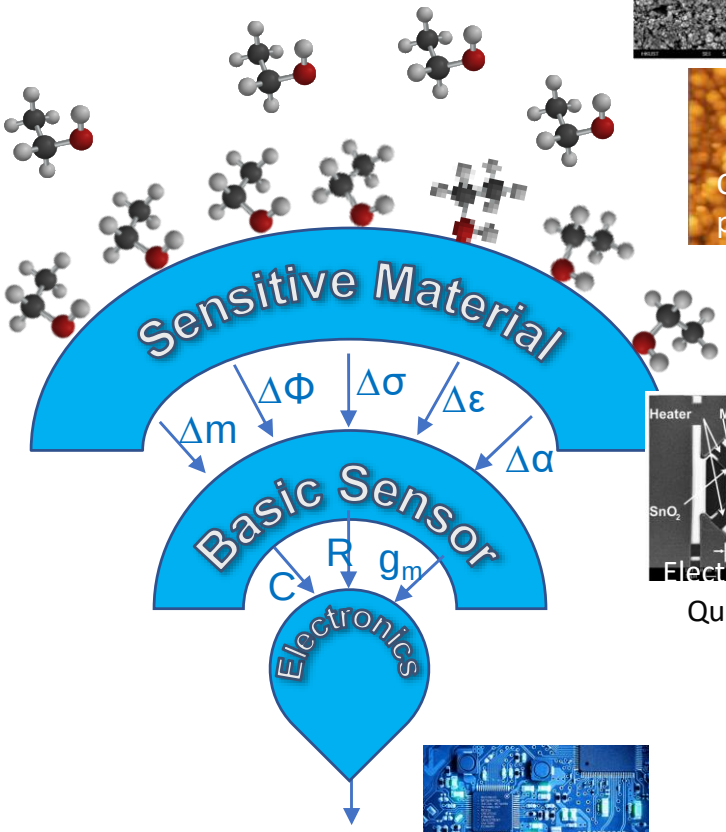


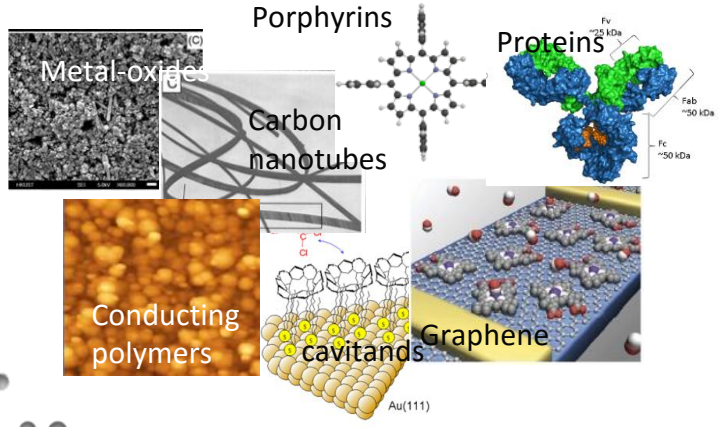
Chemical Sensors

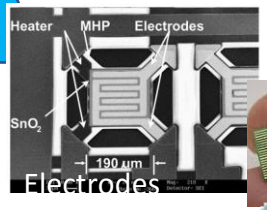


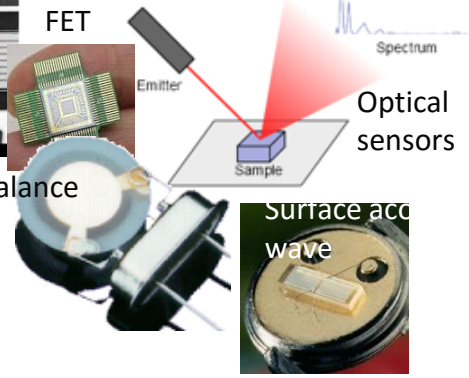


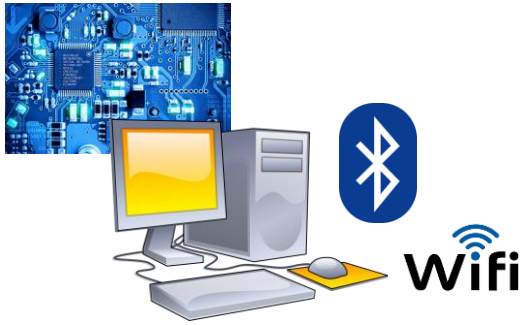






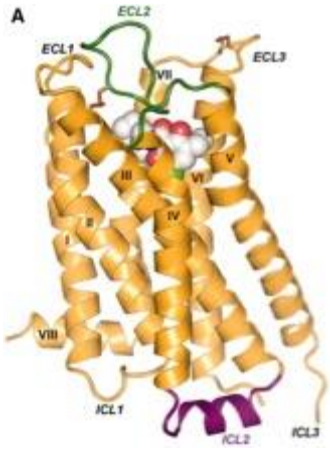




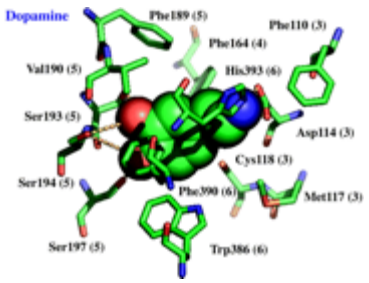


Nature: a paradigm for sensors development

- In living beings there are two main approaches to chemical sensing
  - *specific receptors for few selected molecules*
- receptors
- antibodies
- Pheromones
  - *Technological analogue: Biosensors*

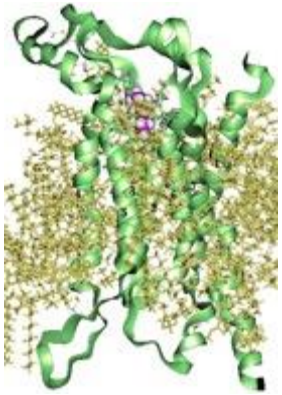


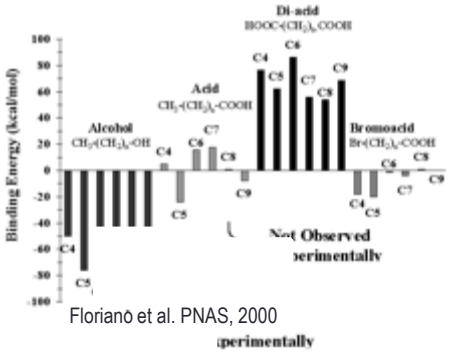
Chien et al. Science, 2010



Kalani et al. PNAS, 2004

- *non-specific receptors for unpredictable compounds*
- in liquid: gustatory receptors → tastes (clustered in five classes)
- in air: olfactory receptors → odors (millions)
  - *Technological analogue: Electronic Noses/Tongues*





Floriano et al. PNAS, 2000

Combinatorial selectivity and the Electronic Nose/Tongue principle

Arrays of olfactory neurons:

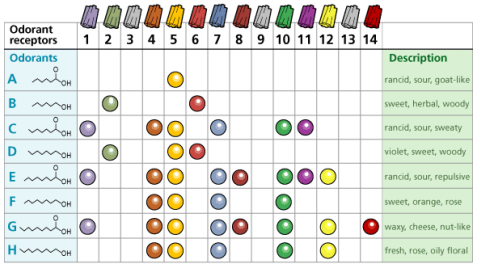
- Many ORNs each with a different pattern of sensitivity
- Protein chemistry offer a biologically efficient method to build different ORNs with the same building blocks

Array of sensors:

- Many sensors each with a different pattern of sensitivity
- Synthesis of organic and inorganic materials may provide the basis for the development of suitable sensors.

Combinatorial selectivity of OSN

Mammals

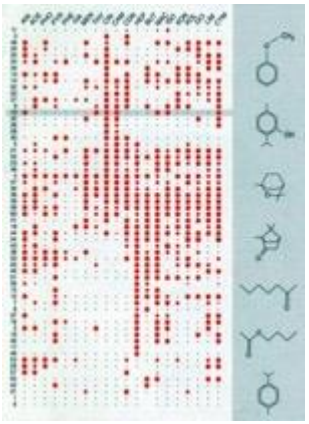


Malnic et al, Cell, 1999

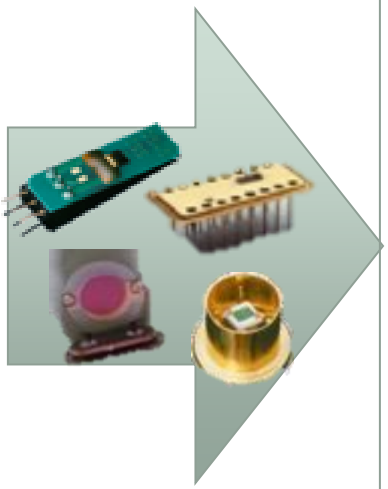
insects

Hallem et al. Cell, 2004

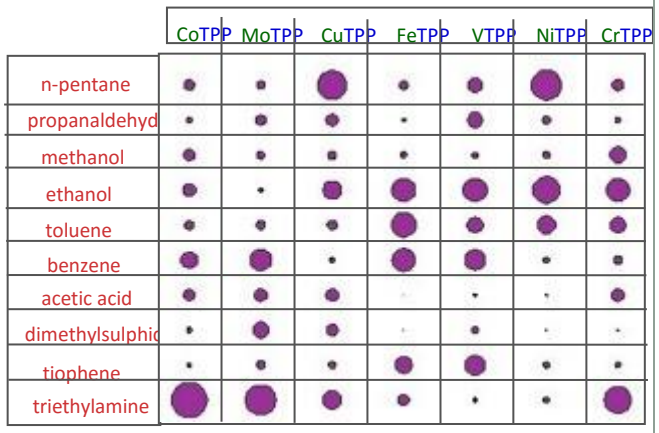
Amphibians



Sicard and Holley Brain Res., 1984



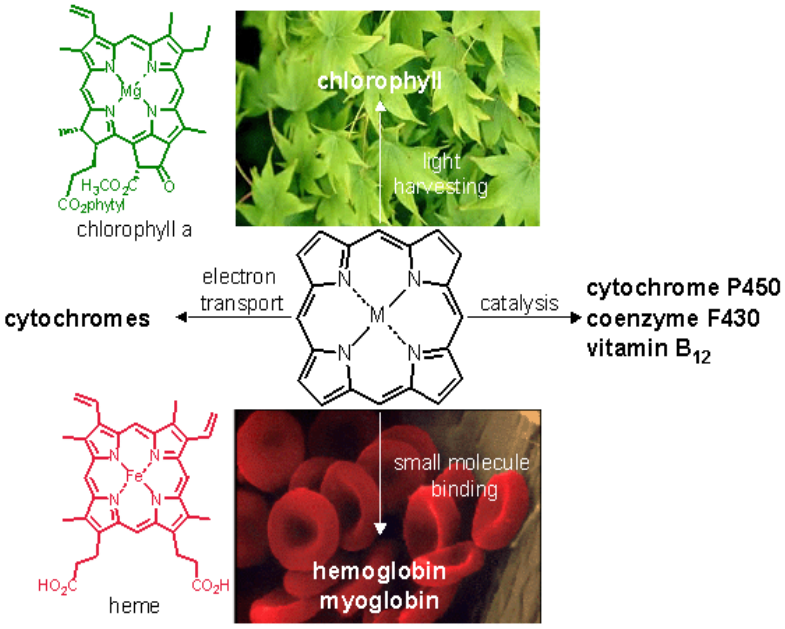
Sensor Array

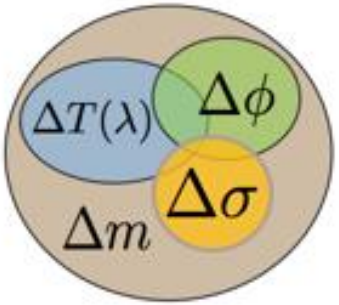


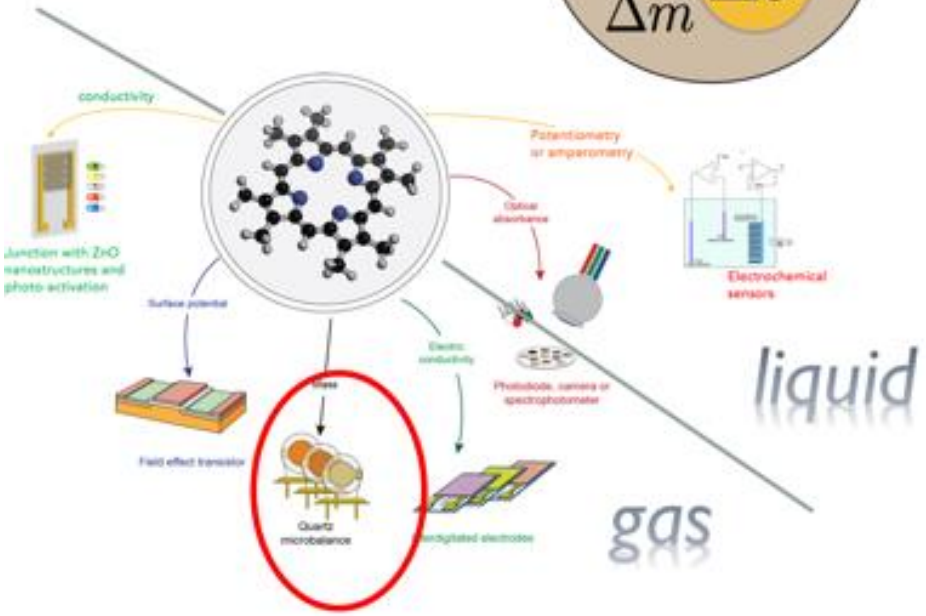
C. Di Natale et al. Sens. Act. B 2007

Porphyrins as receptors for sensor arrays

- Porphyrins may host a number of simultaneous interaction sites harboring different mechanisms
- They can be used to bind, either chemically or physically, a great diversity of guest molecules.
- The molecular structure can be modified by functional groups.







CHEMICAL REVIEWS

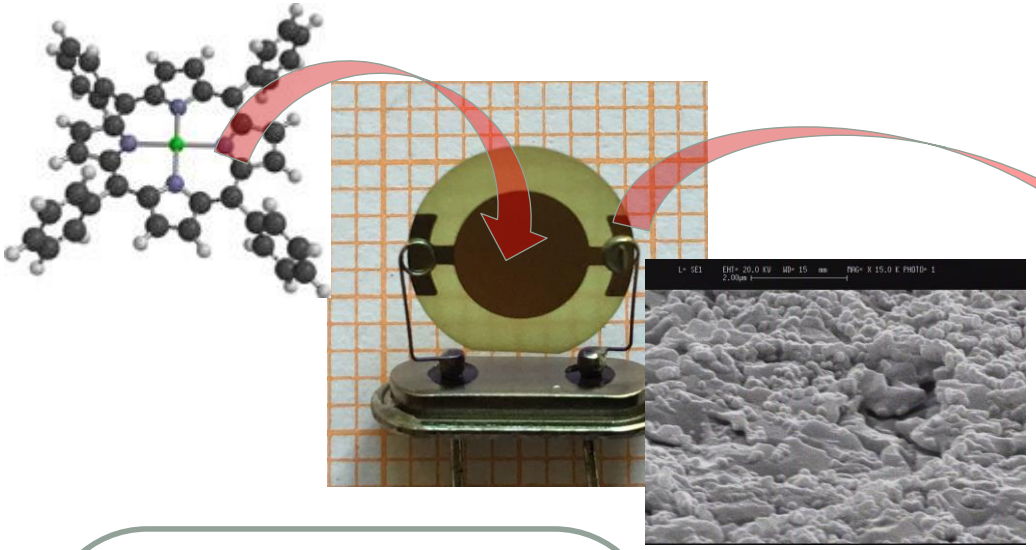
Review

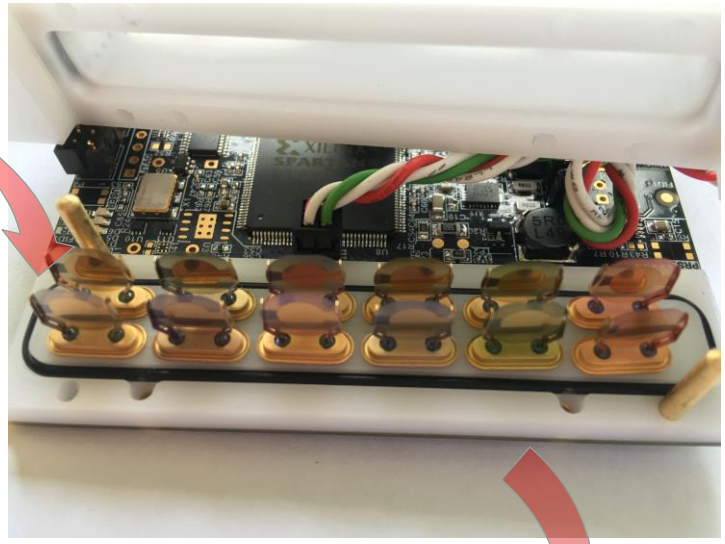
pubs.acs.org/CR

Porphyrinoids for Chemical Sensor Applications

Roberto Paolesse,*[†] Sara Nardis,[†] Donato Monti,[†] Manuela Stefanelli,[†] and Corrado Di Natale*[‡]

Porphyrins based electronic noses





International Space Station

QMB electronic nose applications

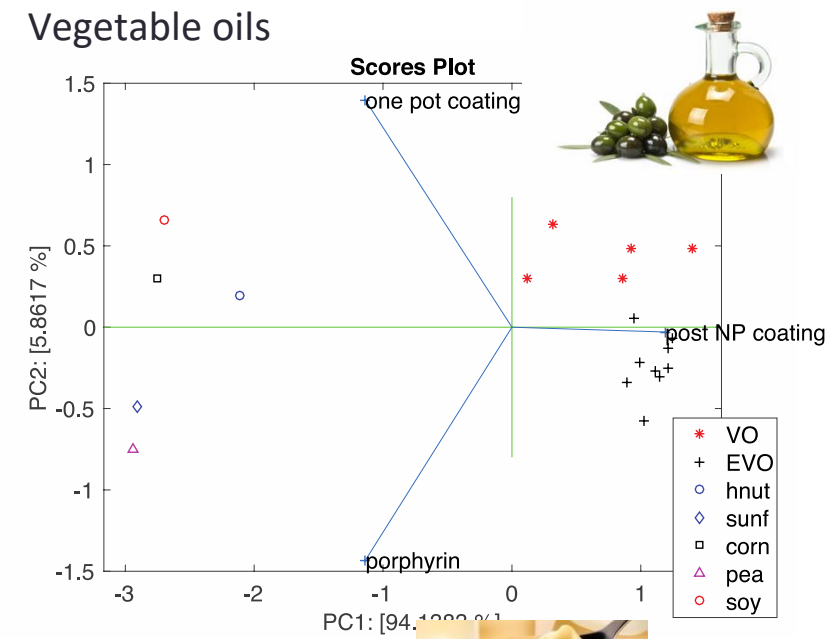
Food Quality and Control
Compagnone et al. Sens Actuators B 2015
Pizzoni et al. J Food Eng. 2015
Eifler et al. PLoS ONE, 2012
Santonico et al. Food Chem, 2010
Santonico et al. Sens Act. B 2008
Olafdsottir et al. Trends Food Sci Tech. 2004
Saevels et al. Posth. Sc. Techn. 2003
••••••

Medical Diagnosis
Capuano et al. Sci Reports 2019
Capuano et al. Sci Reports 2018
Murdocca et al. Oncotarget 2016
Capuano et al. Sci Reports 2015
Santonico et al. Lung Cancer 2012
D'Amico et al. Skin Res. Techn. 2007
D'Amico et al. Lung cancer, 2010
Montuschi et al. Chest, 2010
Di Natale et al. Bios. Bioelec. 2003
••••••

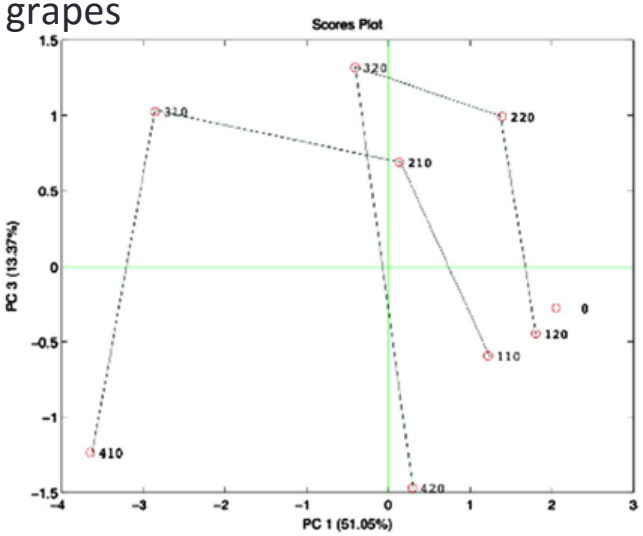
Spacecraft air quality control
Martinelli et al. Microgravity Sci Techn. 2008
Fortezza et al. Acta Astronautica, 2006
••••••

Examples of food applications

Vegetable oils



dehydrated grapes



flavoured custards

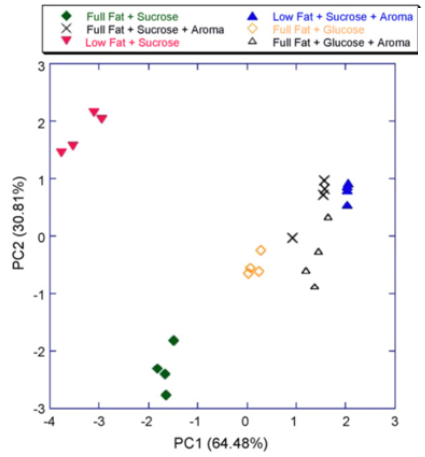


Fig. 1. Plot of the first two principal components of the PCA model built with electronic nose data related to flavoured and non-flavoured custards based on three different compositions (milk fat content and type of sugar).

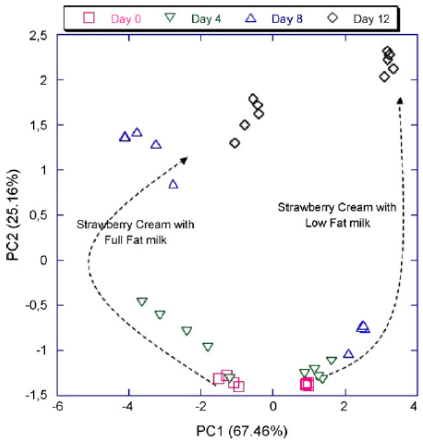
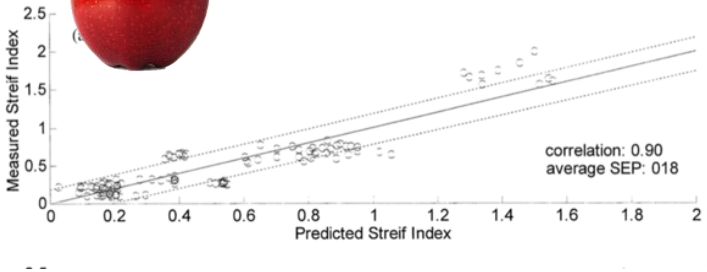


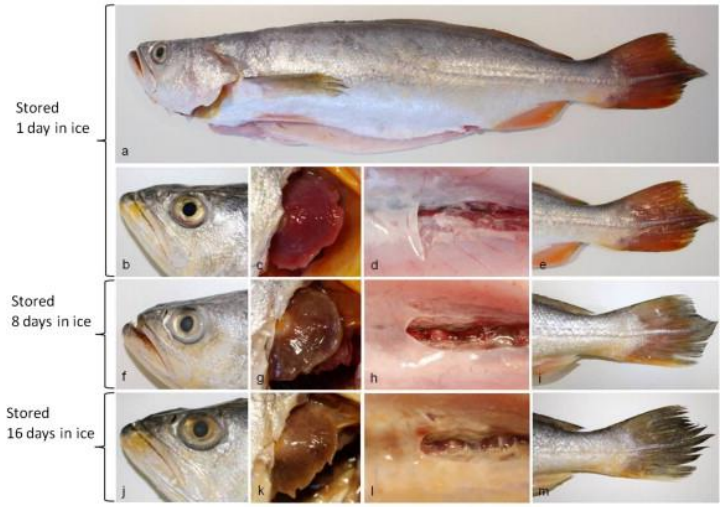
Fig. 5. Plot of the first two principal components of the PCA model built with the electronic nose data measuring the temporal evolution, from day 1 to day 12, of flavoured custards made with fat and skimmed milk.

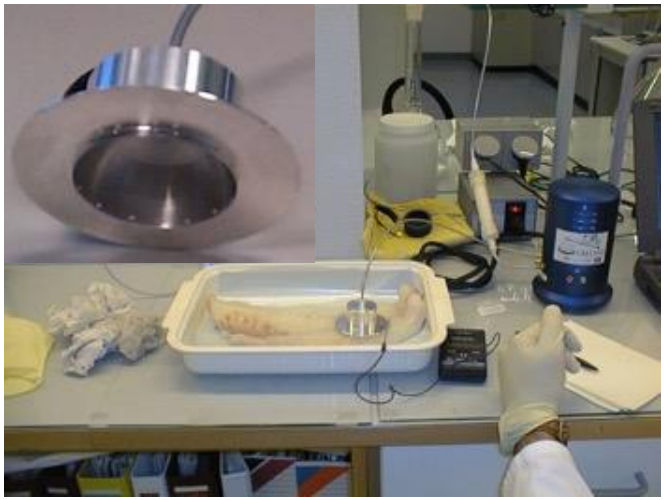
Optimal picking time of apples

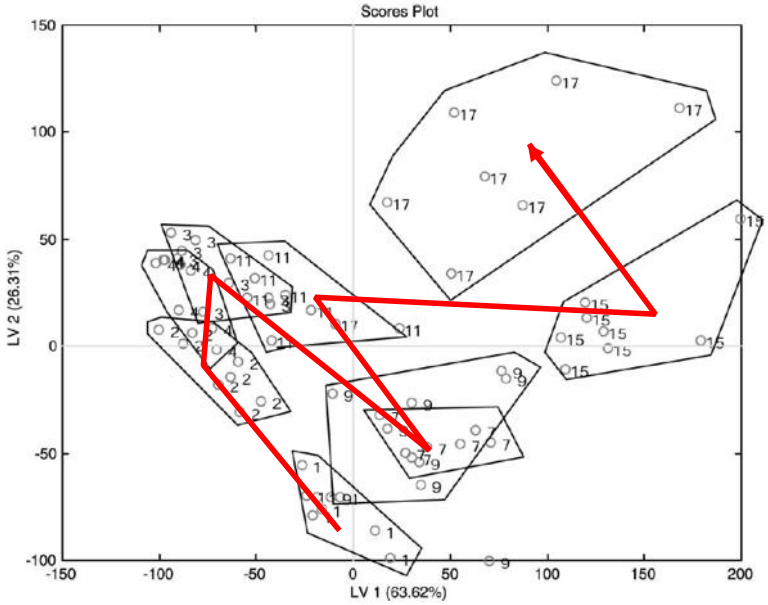
$$Streif\ Index = \frac{Firmness}{\%brix \cdot (starch\ transition\ stage)}$$

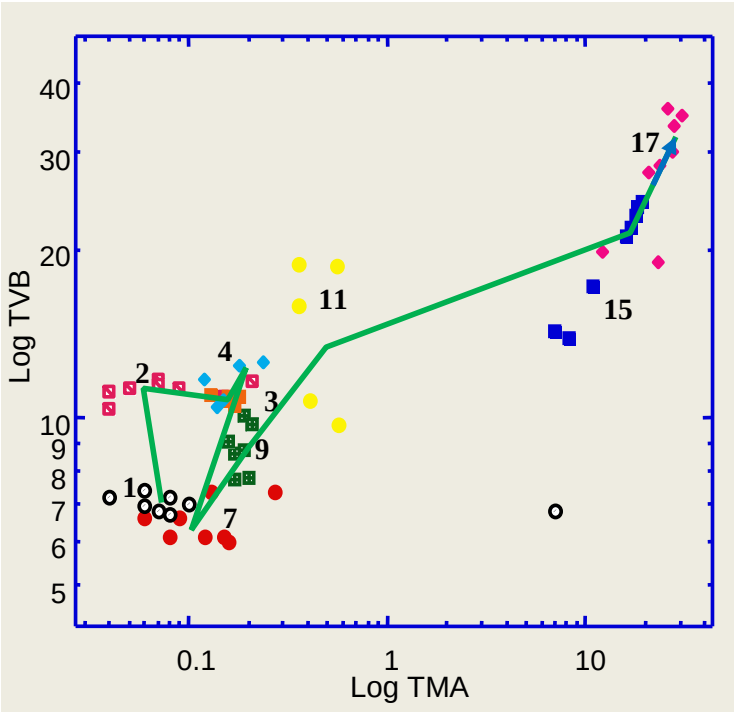


Fish freshness









Artificial Quality Index: cods

colorimeter

calibration

texture analyser

calibration

electronic nose

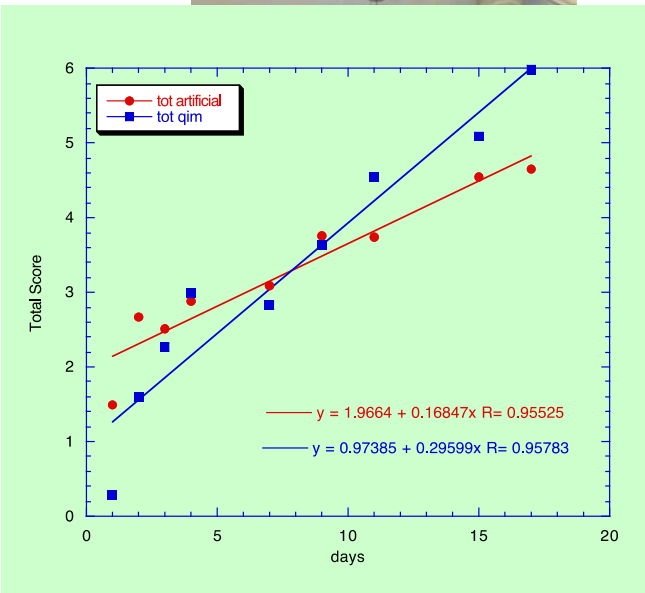
calibration

QIM Attributes

Appearance	Skin
	Firmness
Eyes	Cornea
	Form
	Colour of Pupil
Gills	Colour
	Smell
	Mucus

Σ

Artificial Quality Score



Trends in Food Science & Technology 15 (2004) 86–93

TRENDS IN FOOD SCIENCE & TECHNOLOGY

Review

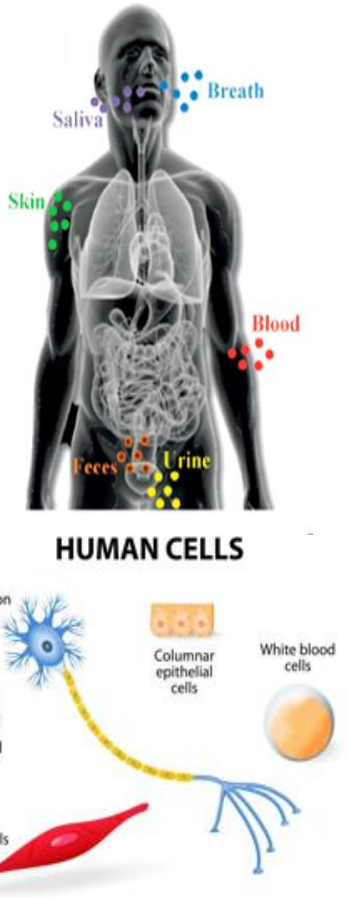
Multisensor for fish quality determination

Gudrun Olafsdottir[a]*, Paul Nesvadba[b], Corrado Di Natale[c], Mercedes Careche[d], Jörg Oehlenschläger[e], Soffia V. Tryggvadóttir[a], Reinhard Schubring[e], Michael Kroeger[e], Karsten Heia[f], Margrethe Esaiassen[f], Antonella Macagnano[c], Bo M. Jørgensen[g]

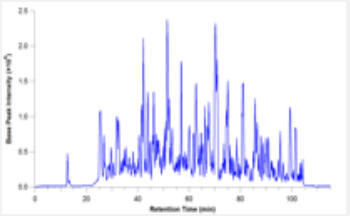
The European fish industry is still reluctant to implement methods other than sensory to monitor freshness and quality of fish products, although general concensus exists about the importance of various quality attributes and the need for methods to monitor quality. The objective of the project FAIR CT98-4076 (MUSTEC) was to evaluate several physico-chemical techniques and to integrate their outputs into a more robust estimate of the freshness quality of fish. The techniques used for this multisensor approach were based on visible light spectroscopy, electrical properties, image analysis, colour, electronic noses and texture. Combining the outputs of the instrumental techniques and calibrating them with sensory scores of Quality Index Method (QIM) for attributes like appearance, smell and texture, gives an Artificial Quality Index (AQI) that can be as accurate and precise as the QIM sensory score. The outcome provides a basis for the construction and industrial exploitation of multi-sensor-devices for defining the quality of fish.

Medical diagnosis

VOCs umani
- Alito: 1840
- Saliva: 359
- Sangue: 154
- Pelle: 532
- Urine: 279
- Feci: 381

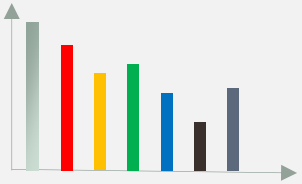


specific fingerprint
Analytical approach
GC-MS; SIFT-MS, PTR-MS....



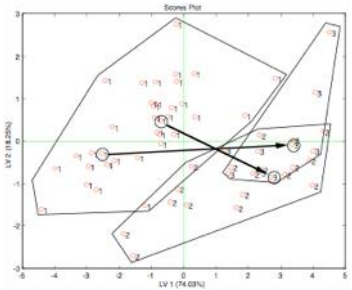
List and abundance of VOCs

non specific fingerprint
sensor arrays (electronic nose)



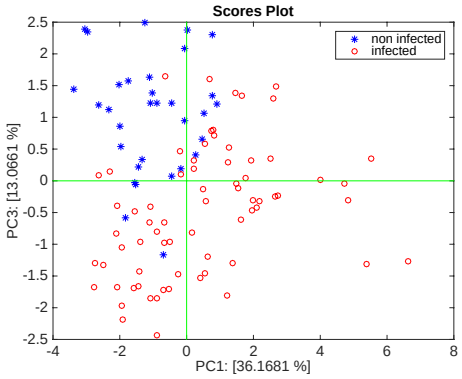
Sensors patterns
combination of VOCs abundance

Lung cancer



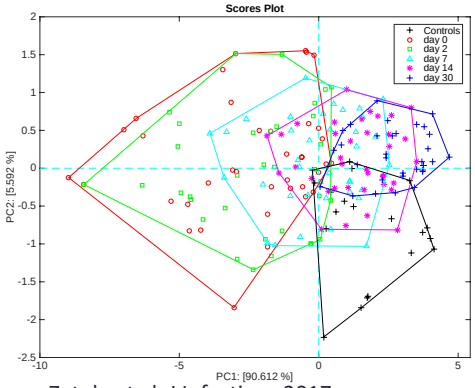
Di Natale et al. Bios. Bioelectronics 2003
Santonico et al. Lung Cancer 2012
Capuano et al. Scientific Reports 2015
Gasparri et al. J Breath Res 2016

Malaria in murine models



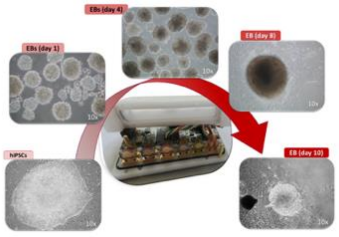
Capuano et al. Sens Actuators B 2017
Capuano et al Scientific Reports 2019

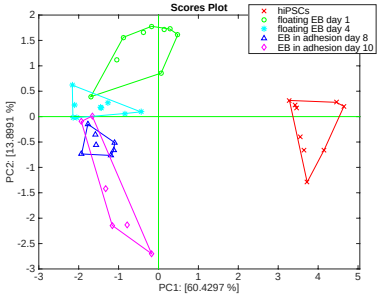
Therapy effects on tuberculosis



Zetola et al. J Infections 2017

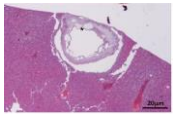
Stem cells differentiation in-vitro and in-vivo

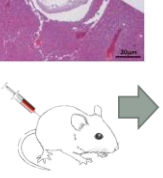


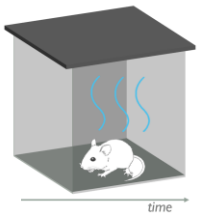


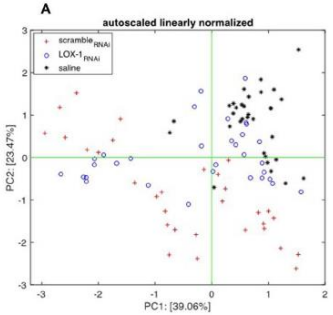
Capuano et al. Scientific Reports 2017
Capuano et al. Scientific Reports 2018

In-vitro and in-vivo Metastasis inhibition in colon cancer









Murdocca et al. Oncotarget 2016
Murdocca et al. Frontiers Oncolorgy 2019

Micro-organisms in cereals

Penicillium vs. Fusarium

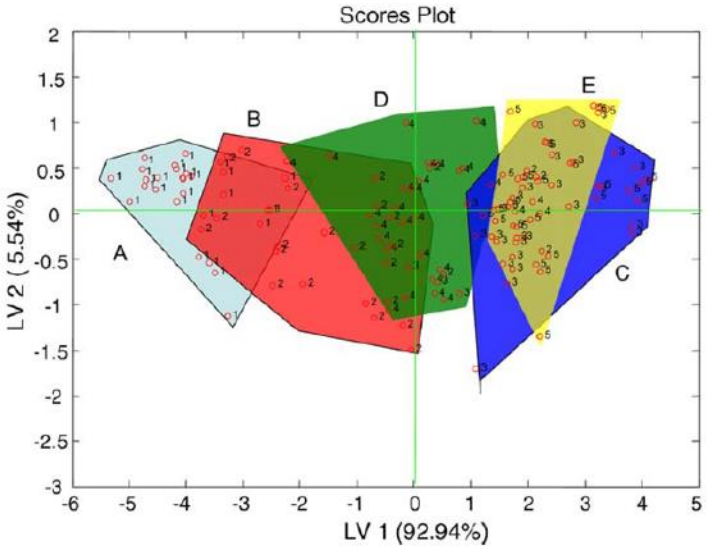


Fig. 3. Second experiment: the class (A) related to the blank (non-moistened); (B) related to blank samples with $a_w = 0.85$; (C) related to blank samples with $a_w = 0.95$; (D) related to samples with $a_w = 0.85$ inoculated with *P. chrysogenum*; (E) related to blank samples with $a_w = 0.95$ inoculated with *F. verticillioides*.

Table 3
Matrix concerning the third experiment

	1	2	3	4	5	6
1	12	0	0	0	0	0
2	0	8	1	2	0	0
3	0	1	8	1	1	0
4	0	0	2	8	1	0
5	0	0	1	0	10	0
6	0	0	0	0	0	12

(1) Non-moistened blank; (2) blank with $a_w = 0.85$; (3) blank with $a_w = 0.95$; (4) sample inoculated with *P. chrysogenum* and $a_w = 0.85$; (5) sample inoculated with *P. chrysogenum* and $a_w = 0.95$; (6) sample inoculated with *F. verticillioides* and $a_w = 0.95$.

Paolesse et al. Sens Actuators B, 2006

fusarium species

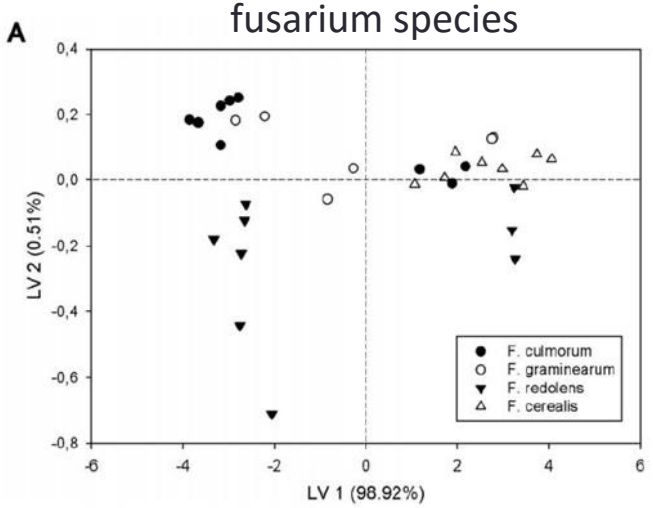


Table 1. Confusion matrix of true vs. estimated values of species classification.

True value	Estimated value			
	F. culmorum	*F. graminearum*	*F. redolens*	*F. cerealis*
F. culmorum	9	0	0	0
F. graminearum	0	5	0	1
F. redolens	0	0	8	1
F. cerealis	0	0	0	8

Table 2. Confusion matrix of true vs. estimated values of binary classification of infection levels.

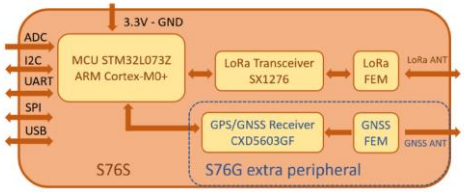
True values	Estimated values	
	Low	High
Low	20	1
High	2	9

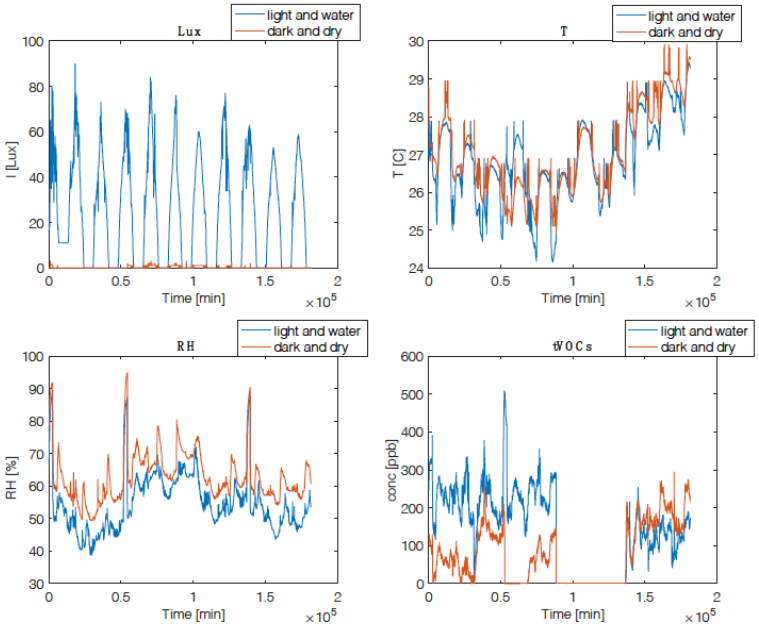
Samples with incubation times of 5 to 10 days were classified as low, samples with 15 days as high. Classification was done by PLS-DA.

Eifler et al. PLoS ONE, 2011

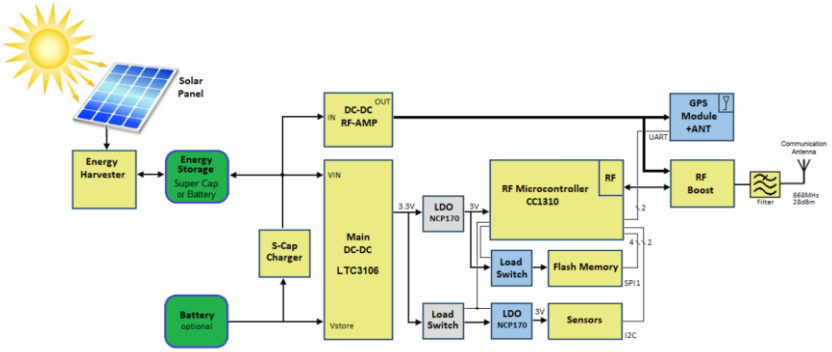
Wireless sensors nodes

Plant stress monitoring





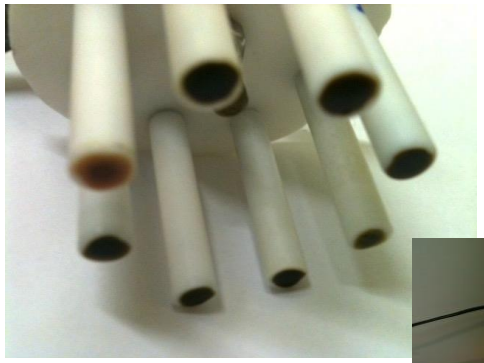
Wild animals tracking

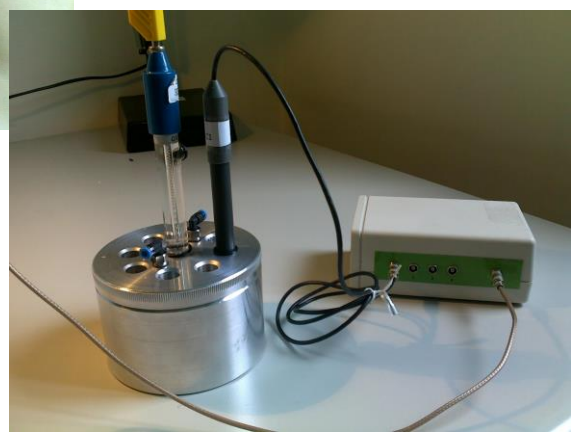


Catini et al. Sensors , 2019

Loreti et al. Sensors , 2019

Combinatorial selectivity in liquid: Potentiometric electronic tongue





Di Natale et al. Sens Actuators B 1996

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Vlasov et al. Pure Appl. Chem 2005

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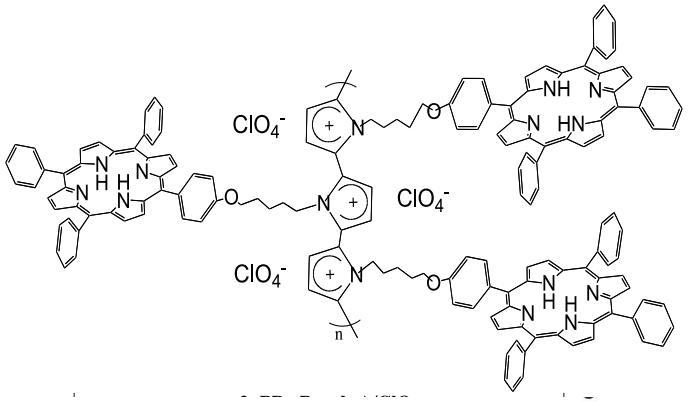
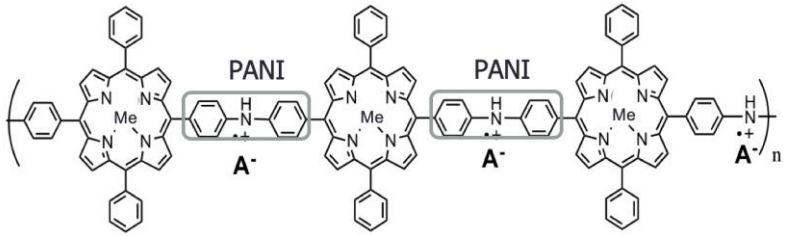
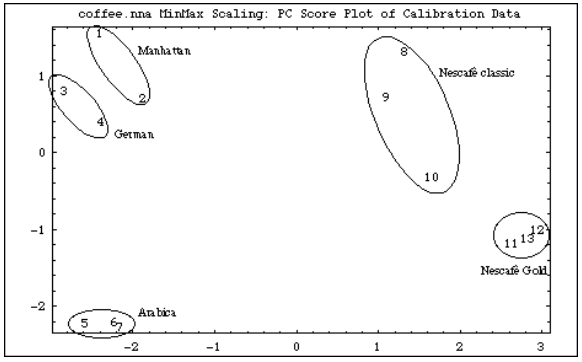
Lvova et al. Frontiers Chemistry 2018

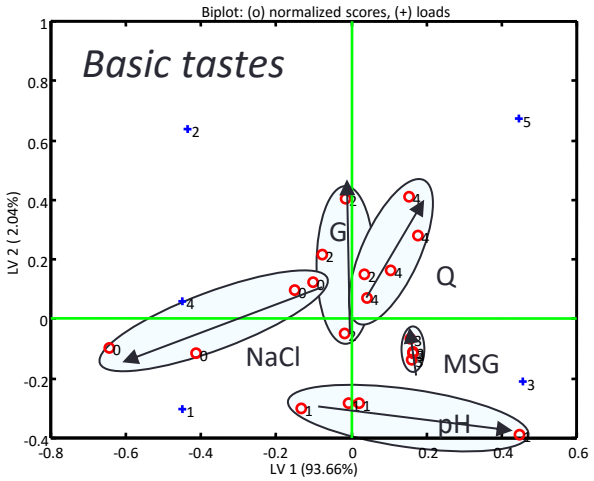




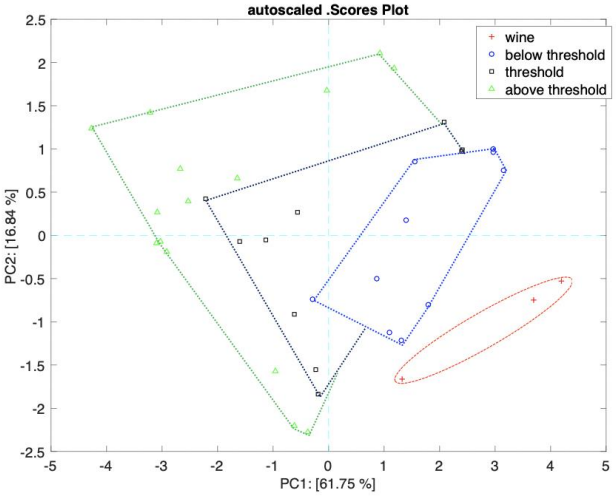
coffees



Legin et al. Sens Actuators B 1997

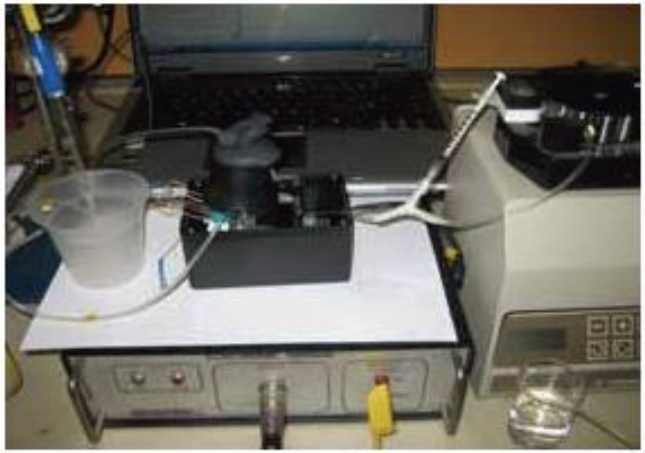


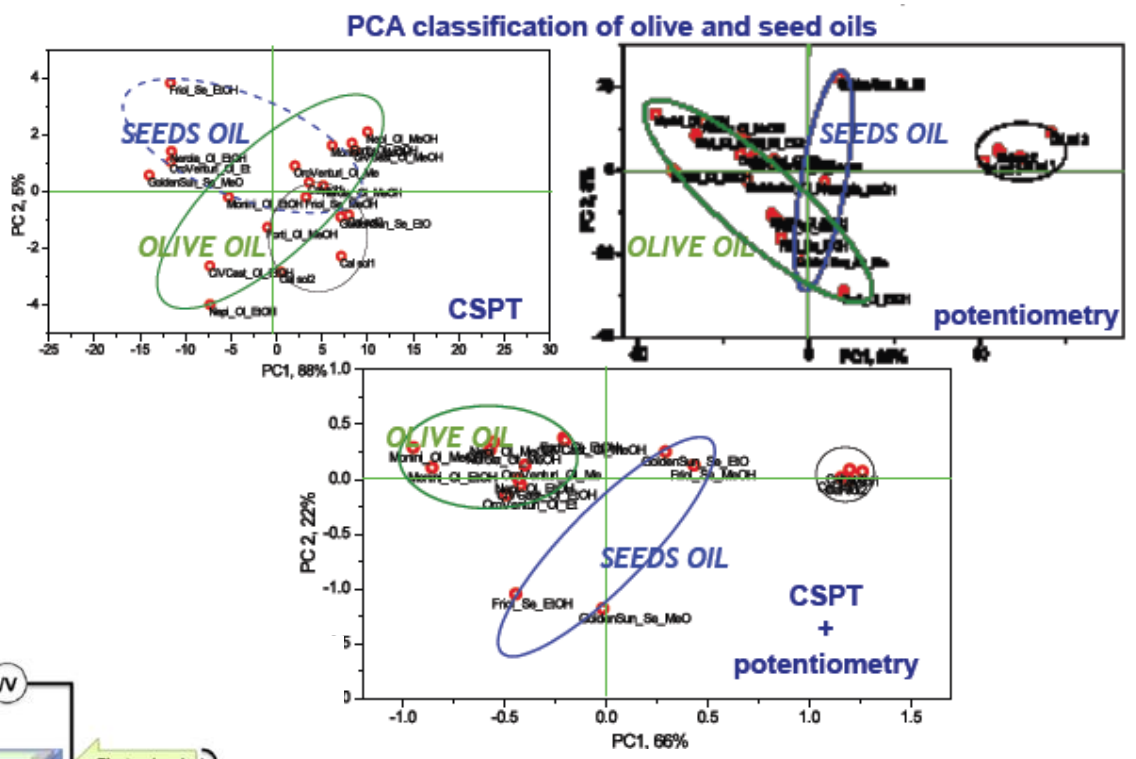
Defects in wine

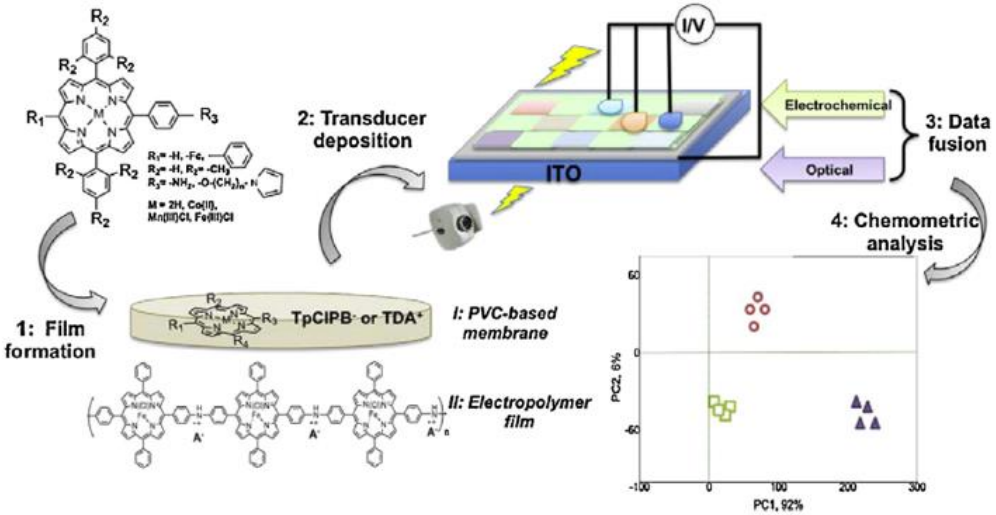


Multimodal Electronic tongue

Potentiometry and colorimetry





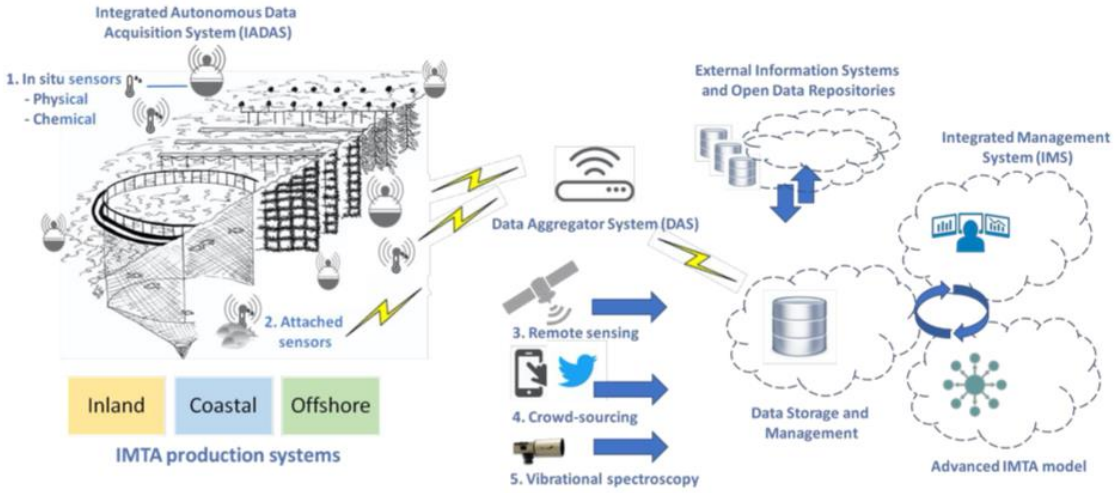


IMPAQT project
Integrated MultiTrophic Aquaculture

www.impaqtproject.eu

IMPAQT
Intelligent Management System for Integrated Multi-trophic Aquaculture

This project has received funding from the EU H2020 research and innovation programme under GA No 774109



Microfluidic systems for automatic optical and electrochemical measurements
Example: Nitrites sensor