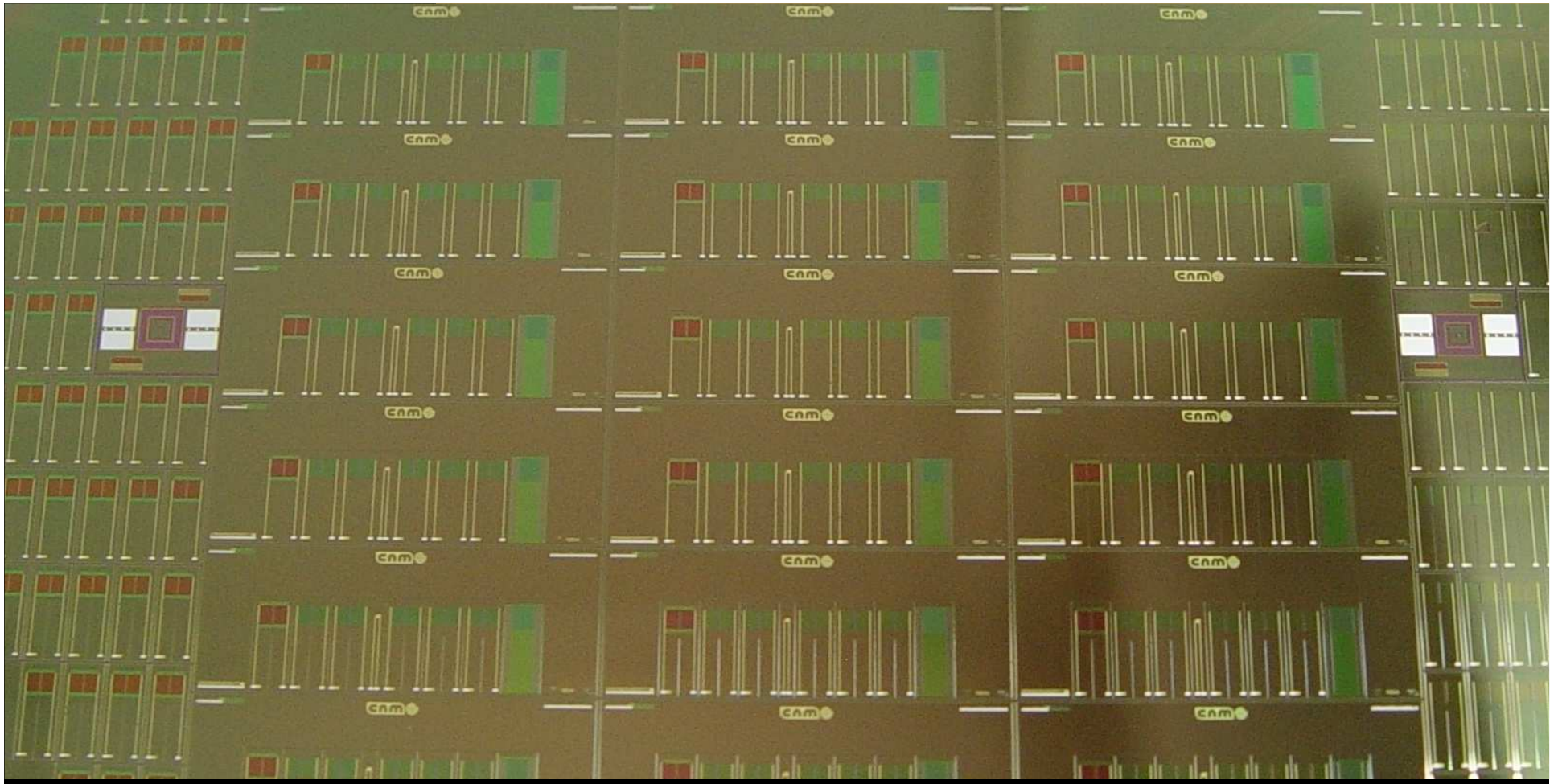


# Sistemes multisensors aplicats al control de qualitat dels vins

Cecilia Jiménez
Institut de Microelectrònica de Barcelona (IMB-CNM) CSIC

gtq silicon technologies for sensing

TECNIO Be tech. Be competitive

CNM Centre Nacional de Microelectrònica IMB

CSIC Consejo Superior de Investigaciones Científicas

# Barcelona Institute of Microelectronics (IMB-CNM), CSIC

SPANISH COUNCIL FOR SCIENTIFIC RESEARCH (CSIC)

CSIC

D+T Microelectrónica, A.I.E.

NATIONAL CENTER OF MICROELECTRONICS (CNM)

BARCELONA INSTITUTE OF MICROELECTRONICS (IMB)

LARGE SCALE FACILITY (Integrated Clean Room)

MADRID INSTITUTE OF MICROELECTRONICS (IMM)

SEVILLA INSTITUTE OF MICROELECTRONICS (IMSE)

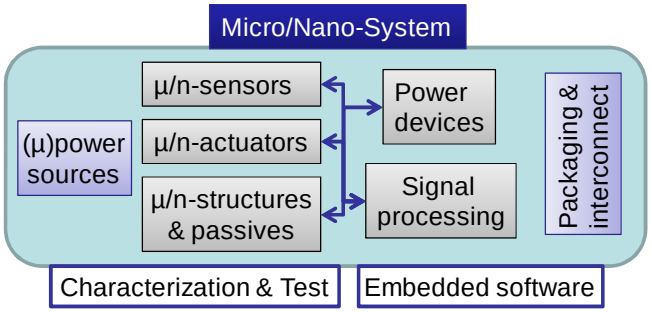
2011 IMB Budget: 11.5 M€
External funding: 50 %

| IMB STAFF (2012) | |
|---|---|
| • Researchers | 66 |
| • Ph.D. Students | 57 |
| • Clean room | 43 |
| • Support services | 28 |
| • Admin. & general serv. | 20 |
| • Visitors | 5 |
| **TOTAL:** | **219** |

# Research at IMB:

- Micro – Nanotechnologies
- Nanofabrication and functional properties of nanostructures
- **Transducers for chemical and biochemical sensing**
- Micro-Nano-Bio systems
- Integrated circuits and systems
- Power devices and systems


## Technology focus : MICRO & NANO INTEGRATED SYSTEMS

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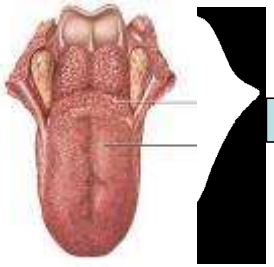
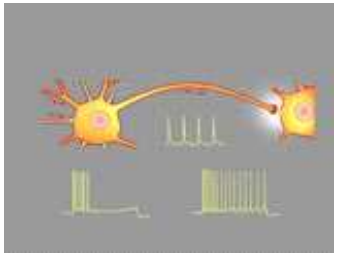
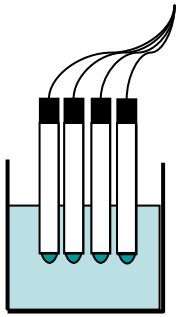
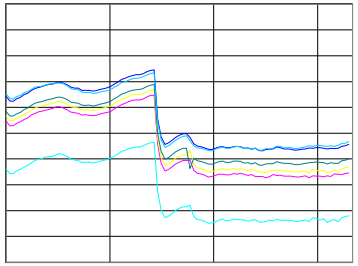
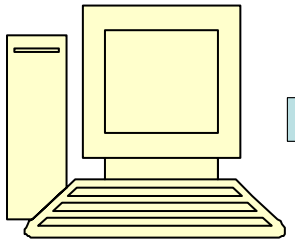
# Electronic Tongue: analogy to gustative organ

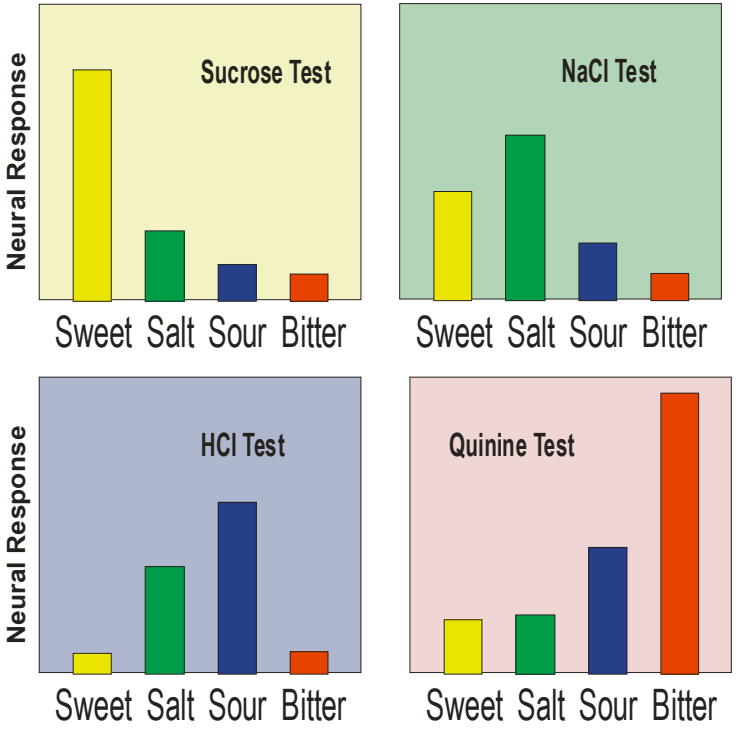
| Recognition Element | Obtained Data | Treatment | Results |
|---|---|---|---|
|  Nerve endings of the tongue |  Transmission of nerve pulse |  Brain | **Taste sense**<br>• sweet<br>• salty<br>• bitter<br>• sour<br>• umami |
|  Array of sensors (crosselectivity) |  Signals (electrochemical, absorbance, …) |  Chemometric processing tools (PCA, NNs, PLS) | **Qualitative Analysis**<br>**Classification**<br>**Quantitative Analysis** |

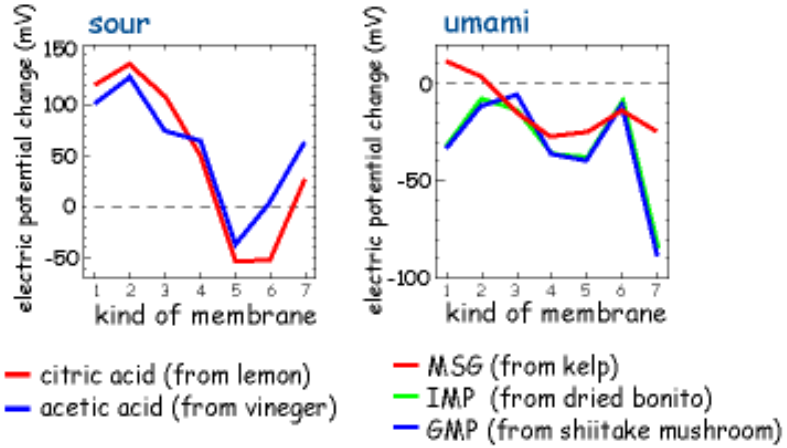
# Electronic Tongue: analogy to gustative organ

**Sabor: Sensación debida a conjunto de substancias**
**Categorías**:

- **Salado**: NaCl
- **Dulce**: glucosa, fructosa
- **Amargo**: quinina, cafeína
- **Acido**: HCl, ácido acético
- "**Umami**": glutamato monosódico (MSG)

**Respuesta de sistema gustativo a distintos compuestos**




Toko, K., *Taste sensor.* Sensors and Actuators B-Chemical, 2000. **64**(1-3): p. 205-215.

**Respuesta de conjunto de sensores a distintos compuestos**

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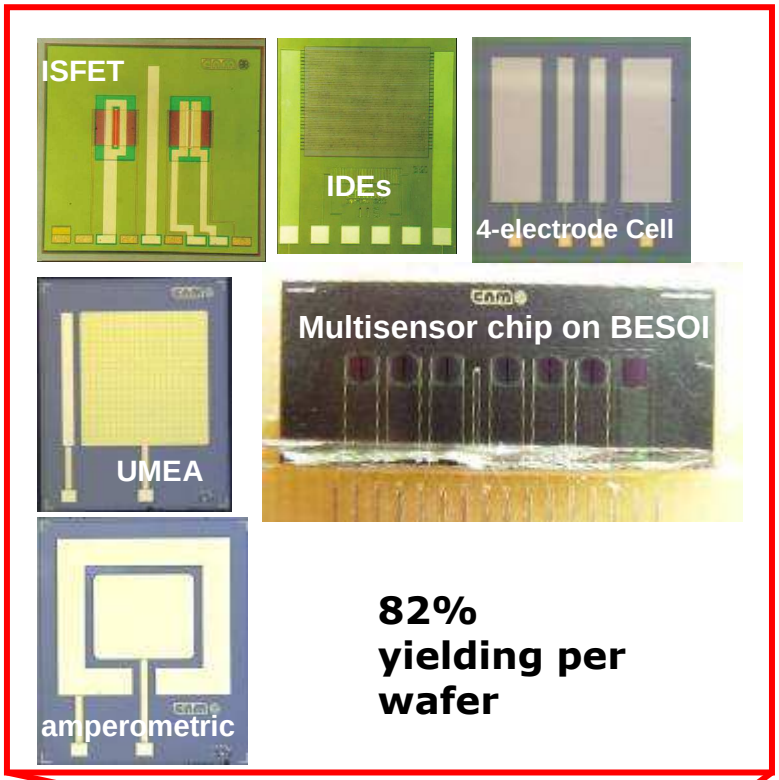
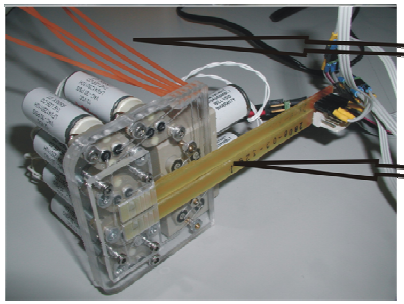
# Microelectrodes used

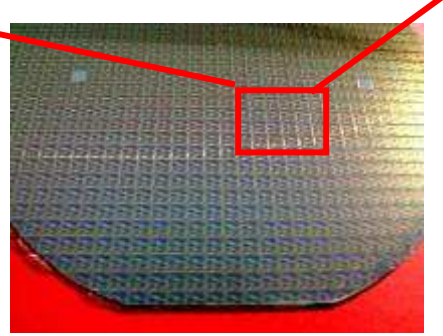
## Fabricated with microelectronic technology

Advantages
- Low cost (mass produced)
- Low energy consumption
- Reproducible
- Miniaturization (μTAS or LOC)
- Circuit integration

**Type of transducers:**
- **ISFET based sensors**: pH, ions Na, K, Ca, Cl, NO3, etc
- **Microelectrodes and UMEAs** (Voltamperometry): $Cl_2$ and COD, heavy metals, molecules
- **Interdigitated electrodes (IDEs):** conductivity, dielectric properties.
- **Multisensor chips** (compatibilization of fabrication technologies)



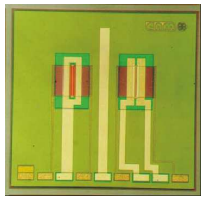



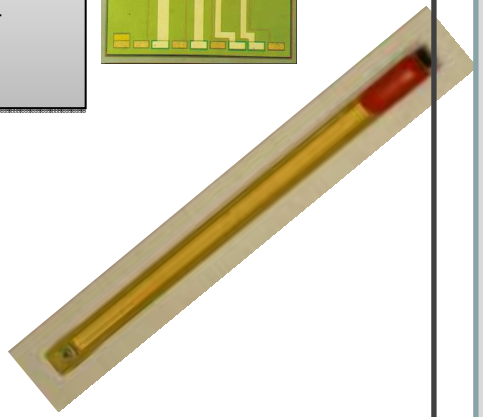


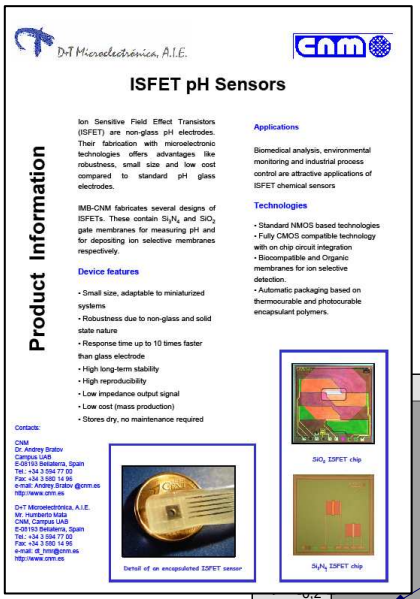
# ISFET and CHEMFETs

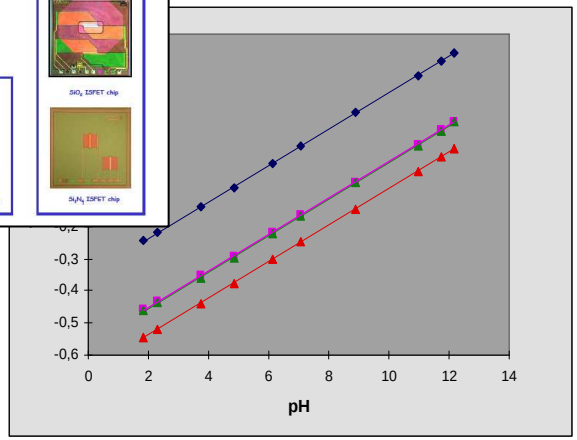
**Detection of:**

- pH
- Cations $Ca^{2+}$, $K^{+}$, $Na^{+}$
- Anions: $Cl^{-}$, $CO_3^{2-}$





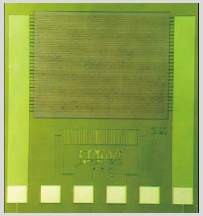


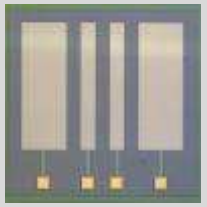

# Pt/Au Microelectrodes

- Conductivity/impedance
- Redox Potential (ORP)
- Dissolved Oxygen ($O_2$)
- Cloride ($Cl_2$)
- Heavy Metals
- Electrochemical oxygen demand (EOD)

## Standard technology $Si/SiO_2$/metal

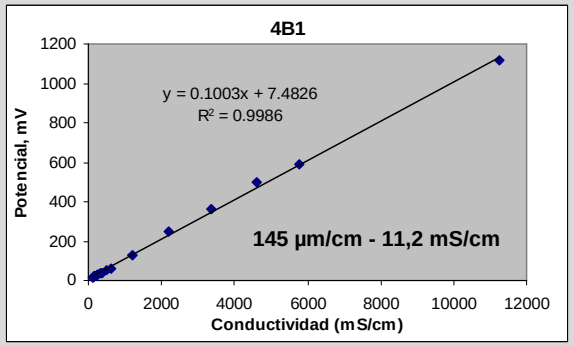


IDS



4 bars

Au/Pt microelectrodes



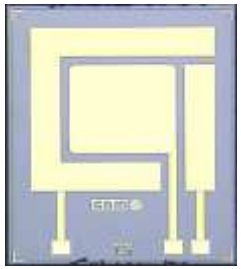

Conductivity calibration curve

TECNIO Be tech. Be competitive

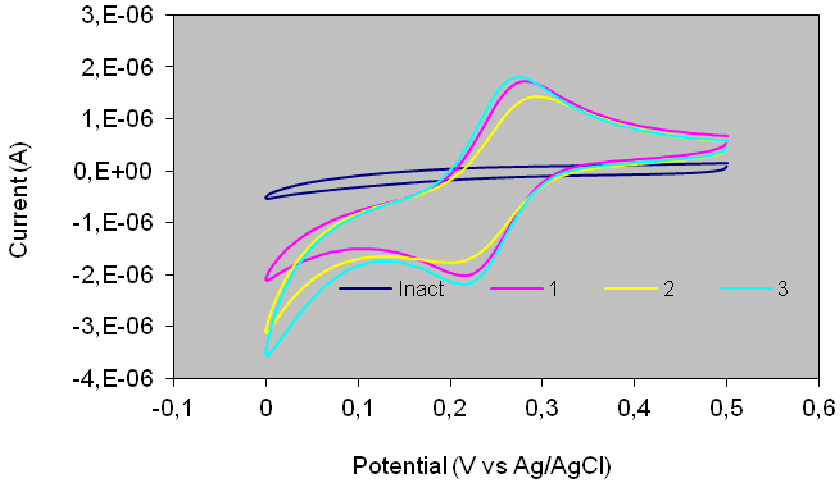
Centre Nacional de Microelectrónica IMB

CSIC Consejo Superior de Investigaciones Científicas

# Amperometric Microelectrodes



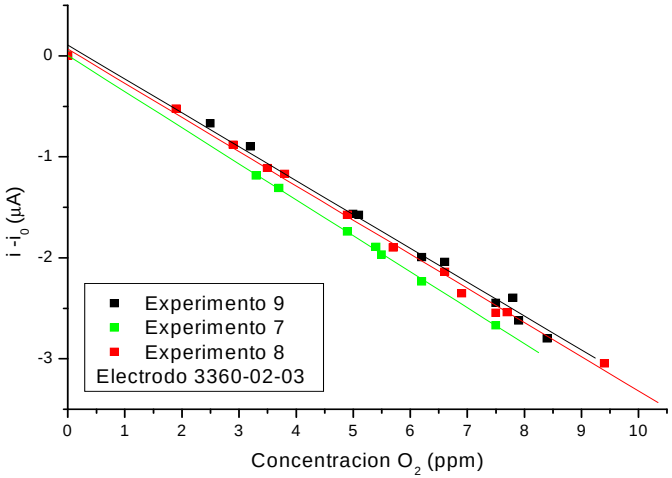
3-cell Au/Pt microelectrodes



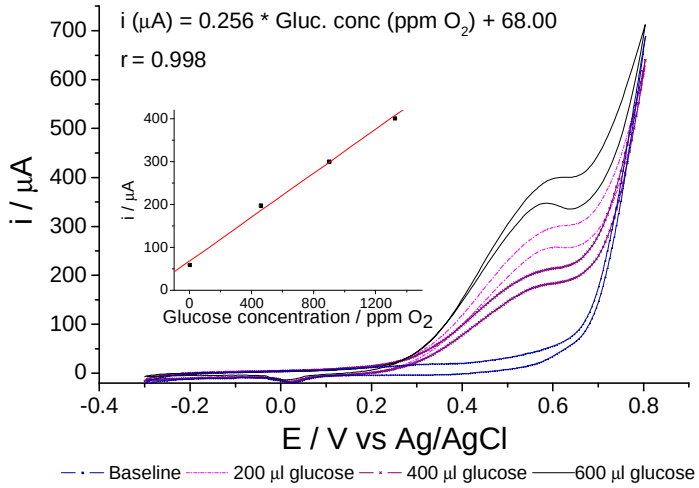

Oxidation- Reduction reactions: $Fe^{2+}$

Eq. Randles $I_p = K \times C$

## Disolved $O_2$ sensor



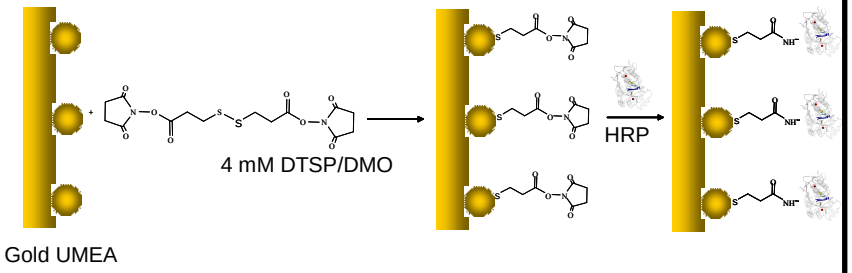

## Glucose sensor

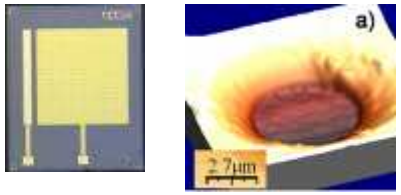


# Biosensors based on nanomaterials

## UMEA modified with Au nanoparticles

**Peroxidase Biosensors**

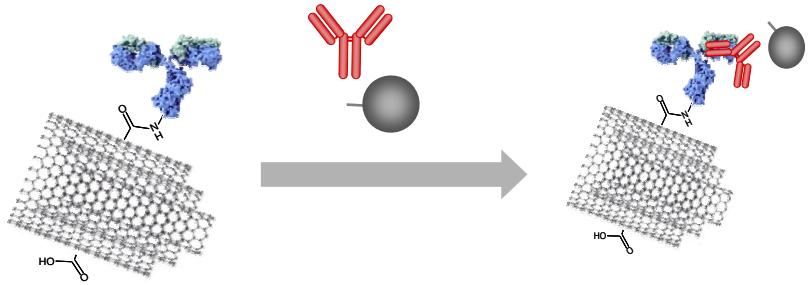



10 times higher sensitivity/ Au microelectrode

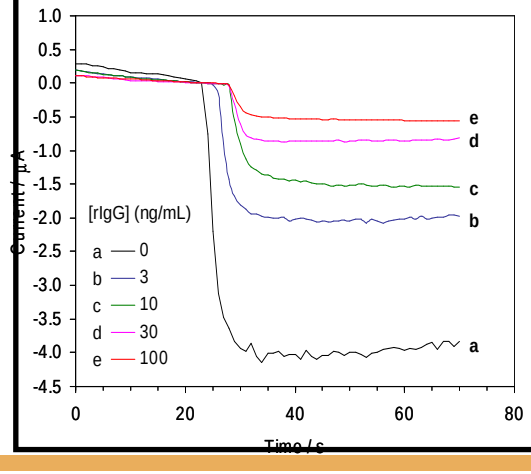
## Carbon nanotube-polystyrene composite electrodes

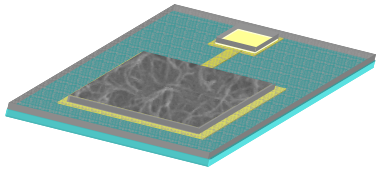
**Immunosensor approach for the detection of rabbit IgG**



*Covalent immobilization of rabbit IgG*

*Biological recogntion event using anti-rabbit IgG peroxidase conjugate*



Calibration:

- I/µA = 0.44*log[rIgG] - 2.47
  r= 0.99; n= 4

Linear range:

- 3-100 ng/mL IgG rabbit

Limit of detection:

- 3 ng/mL

# Multisensor chips

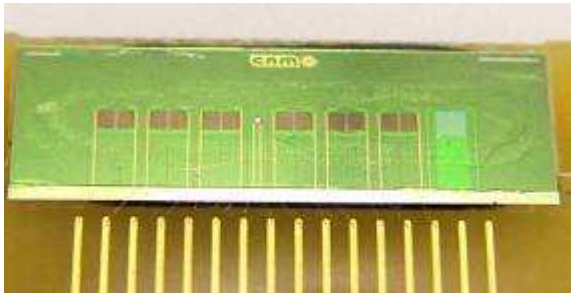
**Monolithic Integration on BESOI substrate**

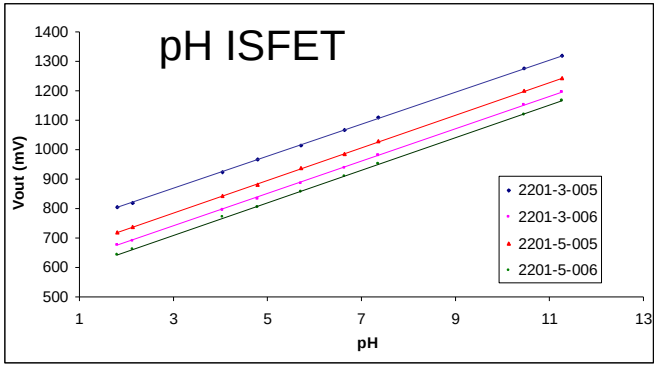
**6 NMOS ISFET**

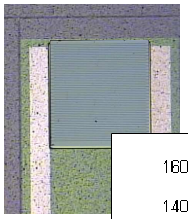
**1 IDEs**

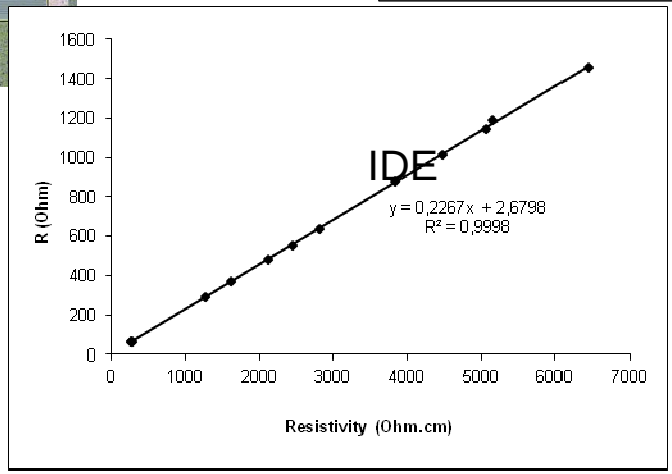
**1 Temperature Diode**

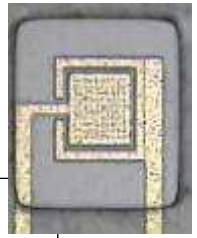
**Electrically Isolated by Trench (SOI Substrate)**

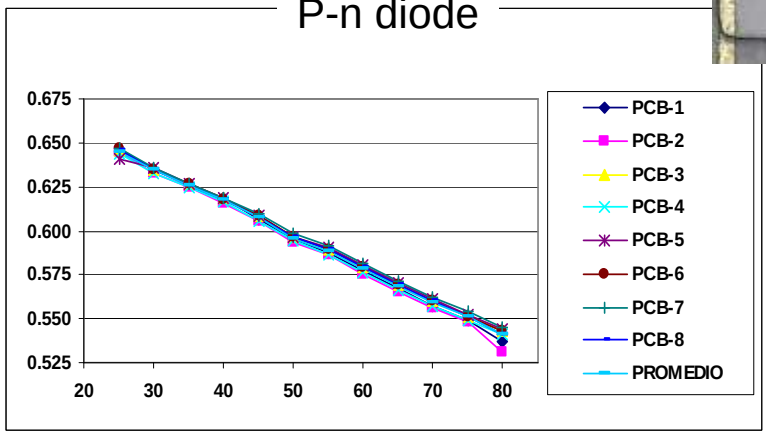




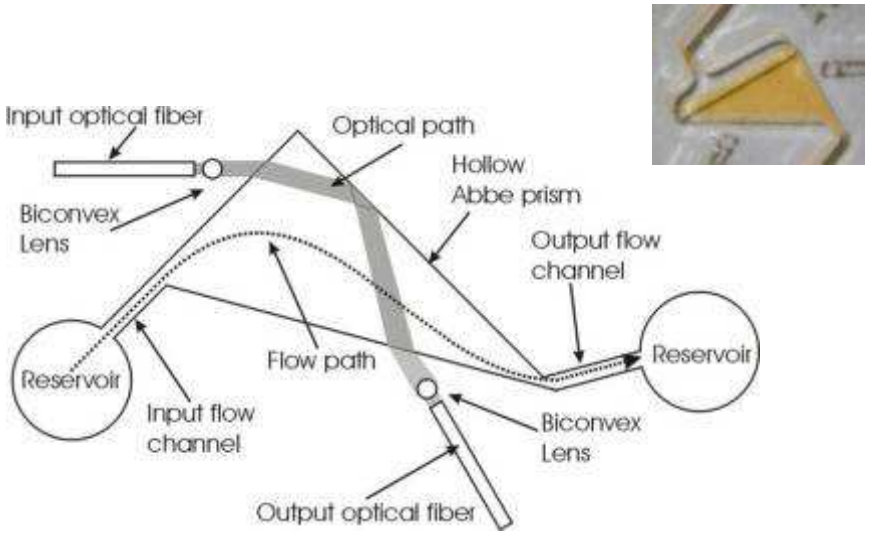





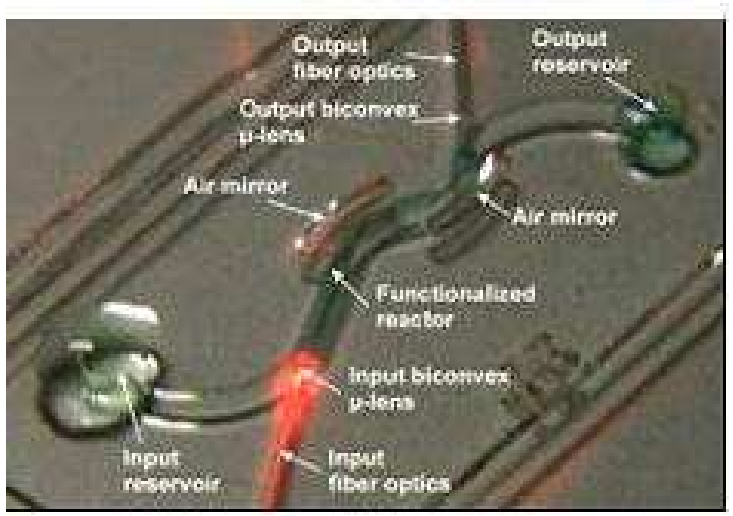


# Optical integrated systems

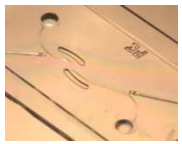


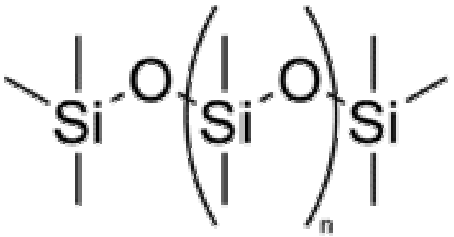



**Prism configuration**




**MIR configuration**






PDMS

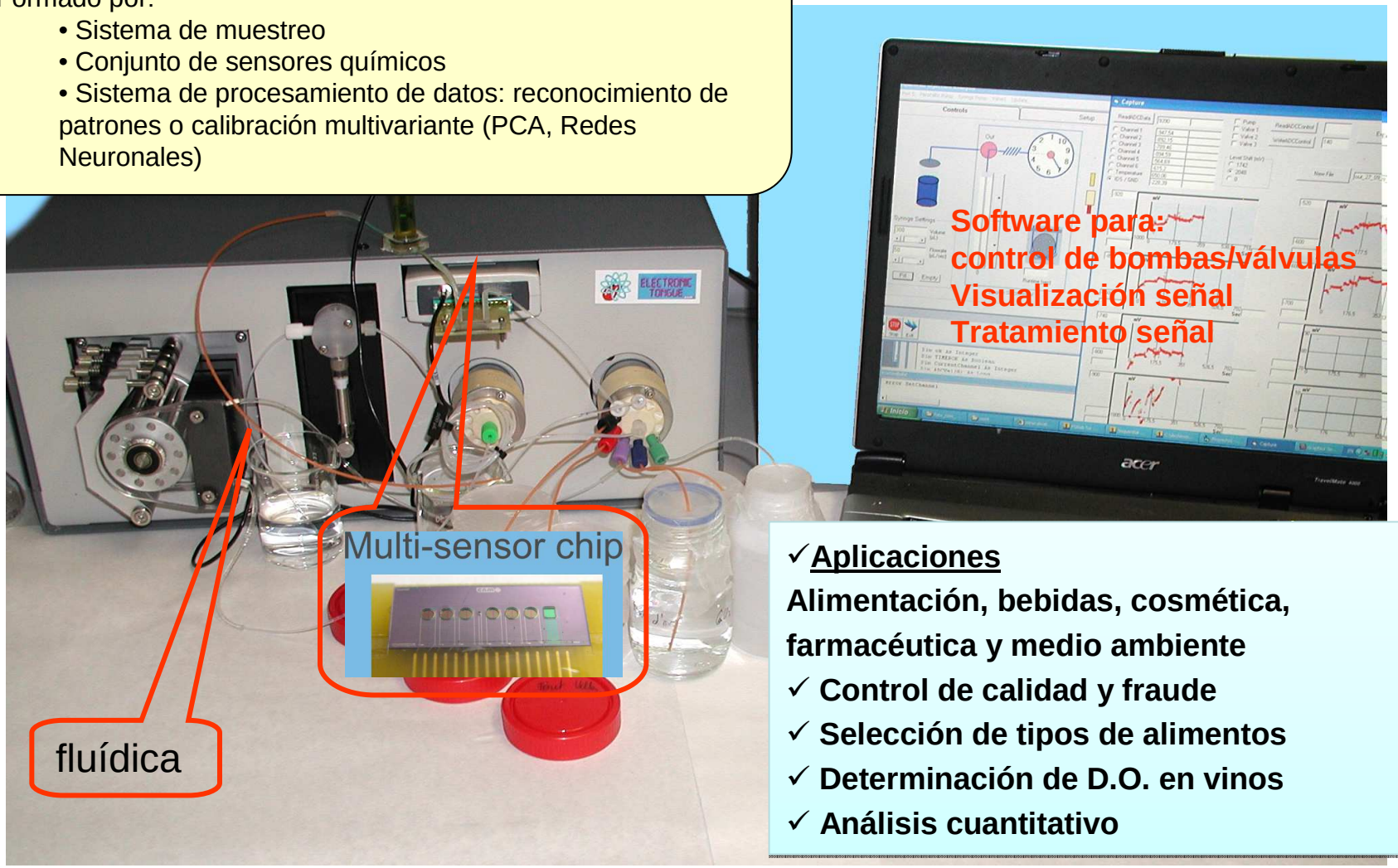
Polydimethylsiloxane

**Characteristics:**

- Method of fabrication is fast and easy.
- Monolithic integration (μTAS).
- Compatible with aqueous media.
- Biocompatible, chemically stable and non-toxic.
- Absorbance between 200 and 1000 nm

# Sistema multisensor

- Instrumento analítico para control de calidad de alimentos
- Formado por:
  - Sistema de muestreo
  - Conjunto de sensores químicos
  - Sistema de procesamiento de datos: reconocimiento de patrones o calibración multivariante (PCA, Redes Neuronales)







✓**Aplicaciones**

**Alimentación, bebidas, cosmética, farmacéutica y medio ambiente**

- ✓ **Control de calidad y fraude**
- ✓ **Selección de tipos de alimentos**
- ✓ **Determinación de D.O. en vinos**
- ✓ **Análisis cuantitativo**

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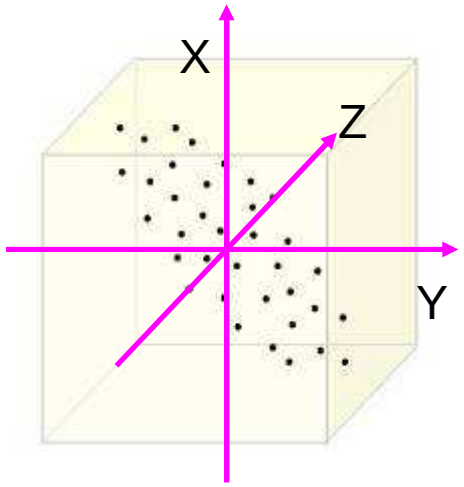
# Principal Component Analysis (PCA)

Original Data

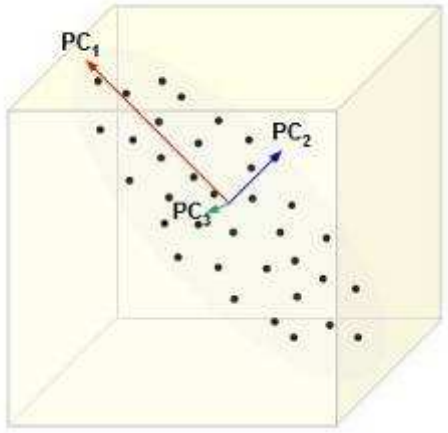



Method for pattern recognition

**PCA**

Change of the axes

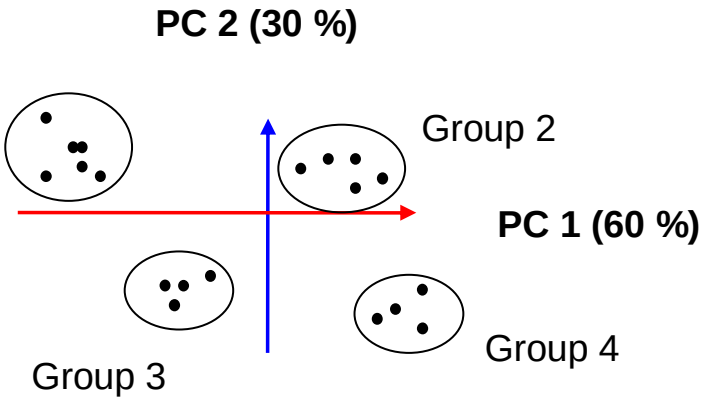
Directions of maximum variation, PCs




Reduction of variables

Representation in two dimensions

Graphic representation in the new axes



# Partial-Least Squares (PLS)

Standard Method in Chemometrics.

Method of multivariate calibration. Linear equation expressed generally like this:

$$y = b_0 + \sum_{k=1}^{k} b_k x_k$$

Reduction of variables

Components or factors ← Regression

Wine Samples

**Calibration set**: 2/3 of the total number of samples

**Prediction set**: the rest 1/3 of samples. At least, one sample of each variety

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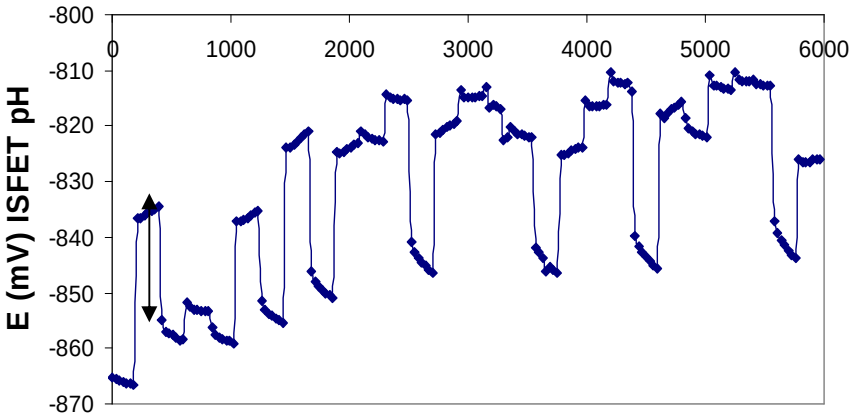
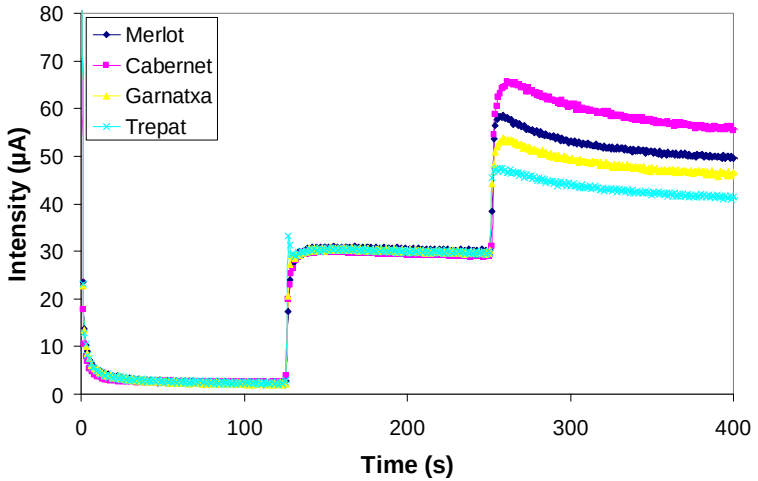
# Sensor signals: Electrochemical Microsensors

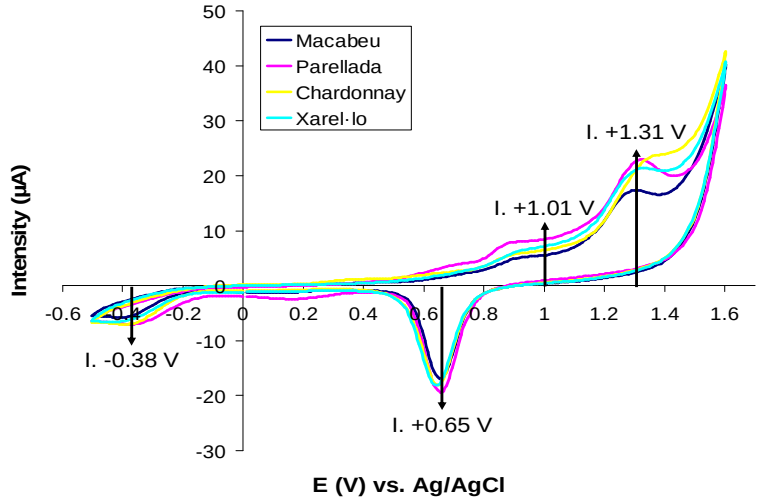



pH ISFET for the white wine set.

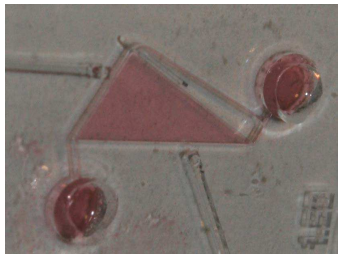
EOD sensor response from the red wine set.



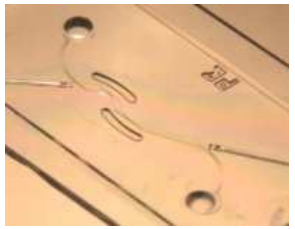

Amperometric measurements for the white wine set.



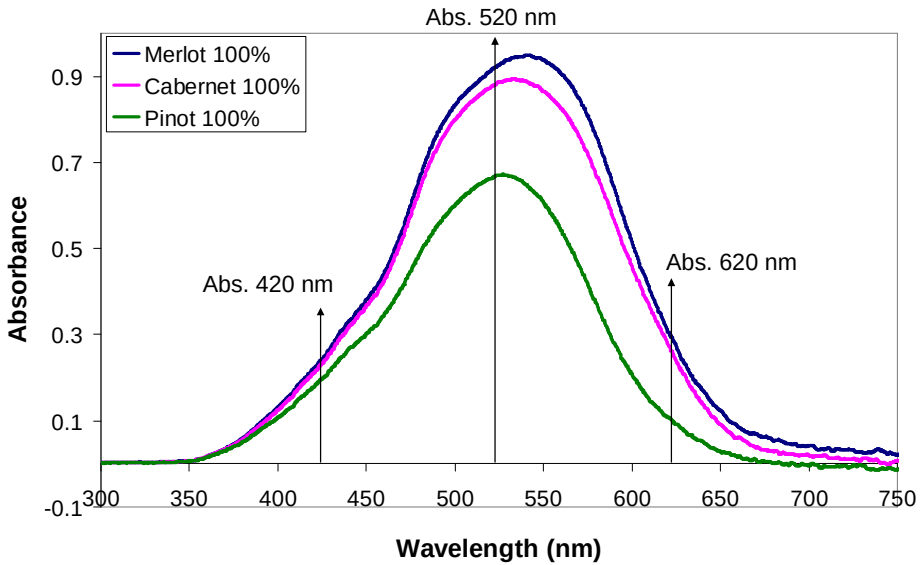
# Sensor Signals: Optical sensors



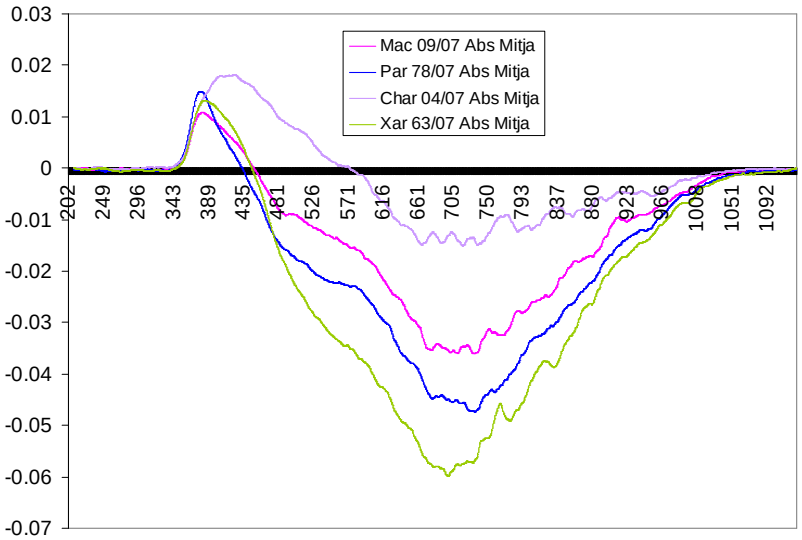
Absorbance spectra obtained with the optical sensor using DI water as reference



## Red wines




## White wines



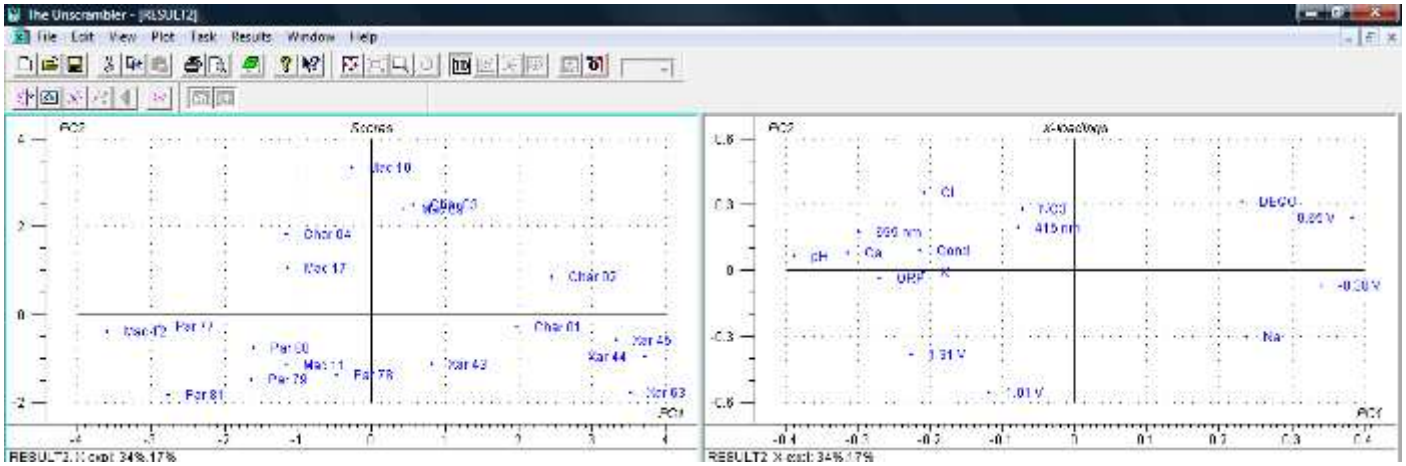
# PCA analysis

The Unscrambler - [ConCupatges]

File Edit View Plot Modify Task Results Window Help

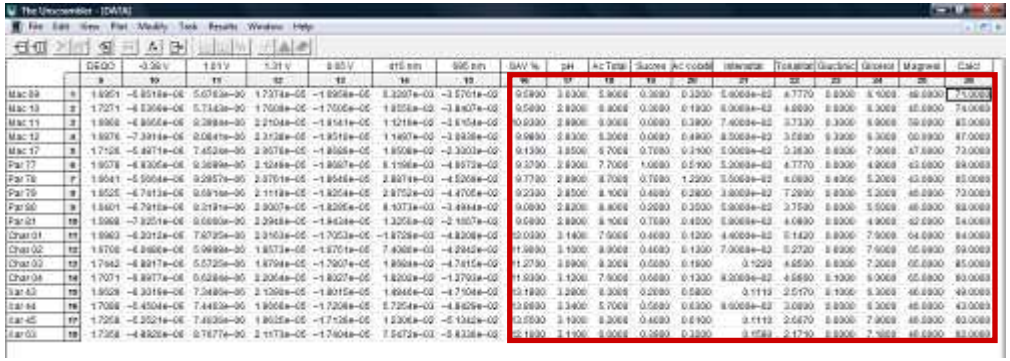
| | | pH | Na | K | Ca | Cl | NO3 | Cond | ORP | DEQO | -0.38 V | 1.01 V | 1.31 V | 0.65 V | 415 nm | 695 nm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Par 78 | 7 | 30.3700 | −8.9800 | 13.8800 | −2.1400 | 19.0600 | 7.3200 | 1.4400 | 226.8900 | 1.6641 | −5.5664e−06 | 9.2957e−06 | 2.0761e−05 | −1.8646e−05 | 2.8874e−03 | −4.5269e−02 |
| Par 79 | 8 | 29.9100 | −4.7300 | 17.2500 | 1.6800 | 19.3700 | 9.6100 | 1.4700 | 215.2100 | 1.6525 | −6.7413e−06 | 8.6914e−06 | 2.1118e−05 | −1.9254e−05 | 2.8752e−03 | −4.4705e−02 |
| Par 80 | 9 | 34.3400 | −8.5500 | 17.5500 | −0.9200 | 6.1000 | 7.1800 | 1.5000 | 217.8900 | 1.6401 | −6.7810e−06 | 8.3191e−06 | 2.0007e−05 | −1.8295e−05 | 9.1073e−03 | −3.4944e−02 |
| Par 81 | 10 | 31.8900 | −8.2200 | 14.9600 | −1.5200 | 9.8000 | 7.4800 | 1.4100 | 221.5100 | 1.5988 | −7.0251e−06 | 8.6060e−06 | 2.2946e−05 | −1.9434e−05 | 1.3250e−02 | −2.1667e−02 |
| Char 01 | 11 | 24.1100 | −7.4400 | 13.2700 | −2.7400 | 20.0600 | 6.2500 | 1.3900 | 165.6100 | 1.6983 | −6.2012e−06 | 7.8705e−06 | 2.0163e−05 | −1.7053e−05 | −1.8728e−03 | −4.8208e−02 |
| Char 02 | 12 | 22.7400 | −6.7800 | 11.6000 | −3.8200 | 20.3200 | 1.9800 | 1.4500 | 173.6100 | 1.6700 | −6.0486e−06 | 5.9998e−06 | 1.8573e−05 | −1.6751e−05 | 7.4086e−03 | −4.2942e−02 |
| Char 03 | 13 | 24.4200 | −6.9100 | 8.7000 | −0.4600 | 22.7800 | 10.5300 | 1.7100 | 202.9000 | 1.7442 | −6.8817e−06 | 5.5725e−06 | 1.9794e−05 | −1.7807e−05 | 1.9684e−02 | −4.7415e−02 |
| Char 04 | 14 | 28.2300 | −12.5000 | 12.6700 | −1.9800 | 23.0400 | 6.5600 | 1.4100 | 177.5700 | 1.7071 | −6.9977e−06 | 6.6284e−06 | 2.2064e−05 | −1.9027e−05 | 1.8202e−02 | −1.2793e−02 |
| Xar 43 | 15 | 23.6500 | −7.1700 | 11.9000 | −0.4600 | 8.9200 | 0.9200 | 1.1800 | 219.8300 | 1.6629 | −6.3019e−06 | 7.3486e−06 | 2.1390e−05 | −1.8015e−05 | 1.4846e−02 | −4.7104e−02 |
| Xar 44 | 16 | 23.6500 | −7.5900 | 10.8400 | −5.0300 | −3.0500 | 3.9700 | 1.1400 | 170.7100 | 1.7088 | −5.4504e−06 | 7.4463e−06 | 1.9666e−05 | −1.7209e−05 | 5.7254e−03 | −4.8429e−02 |
| Xar 45 | 17 | 24.4200 | −5.3000 | 9.0000 | −4.4200 | −2.9800 | 8.8500 | 1.1600 | 230.6500 | 1.7258 | −5.2521e−06 | 7.4036e−06 | 1.9635e−05 | −1.7136e−05 | 1.2306e−02 | −5.1342e−02 |
| Cupatge 1 | 18 | 34.1800 | −10.1900 | 12.2100 | 0.0000 | 13.5200 | 4.8900 | 1.3300 | 228.4900 | 1.6618 | −6.2653e−06 | 8.1879e−06 | 2.0975e−05 | −1.8225e−05 | 3.4651e−03 | −3.7414e−02 |
| Cupatge 2 | 19 | 29.4500 | −11.6700 | 15.1100 | −2.6300 | 20.5000 | −0.9200 | 1.3600 | 197.3700 | 1.7125 | −5.8380e−06 | 6.8481e−06 | 1.8295e−05 | −1.6385e−05 | −1.4966e−03 | −5.1209e−02 |
| Cupatge 3 | 20 | 31.8900 | −10.4500 | 15.7200 | 0.3100 | 18.7500 | 14.9600 | 1.4500 | 236.9400 | 1.6412 | −7.5623e−06 | 9.0546e−06 | 2.3459e−05 | −2.0163e−05 | 7.1376e−03 | −3.1644e−02 |
| Cupatge 4 | 21 | 25.3300 | −6.4700 | 9.3100 | −1.3700 | 11.0300 | −5.6500 | 1.2100 | 207.6800 | 1.6945 | −5.8685e−06 | 6.7413e−06 | 1.9055e−05 | −1.7532e−05 | 1.2880e−02 | −4.9674e−02 |
| Cupatge 5 | 22 | 30.5200 | −8.9800 | 11.9000 | −1.8300 | 13.4100 | 7.9300 | 1.3200 | 210.9000 | 1.6959 | −6.1157e−06 | 8.7555e−06 | 2.0508e−05 | −1.8152e−05 | 1.1742e−02 | −3.8200e−02 |
| Cupatge 6 | 23 | 30.6700 | −9.8400 | 16.3200 | −1.5200 | 19.0900 | 13.7300 | 1.4100 | 248.2500 | 1.7147 | −6.7963e−06 | 6.8420e−06 | 1.9296e−05 | −1.8567e−05 | 9.2301e−03 | −3.9665e−02 |
| Cupatge 7 | 24 | 32.2000 | −2.2900 | 13.4300 | −2.7400 | 16.0900 | 13.5800 | 1.2800 | 228.4600 | 1.7841 | −6.1096e−06 | 7.1808e−06 | 2.0825e−05 | −1.8555e−05 | 9.5100e−03 | −5.1037e−02 |
| Grasevina | 25 | 5.1900 | −4.8900 | 1.5300 | −17.7000 | 25.5400 | −7.7800 | 1.9100 | 4.7000 | 1.6728 | −4.8492e−06 | 1.0101e−05 | 2.3621e−05 | −1.8158e−05 | 1.2607e−02 | −5.3398e−02 |
| Zelenac | 26 | 3.9700 | −2.7500 | 4.5800 | −3.6600 | 27.8700 | −3.5100 | 1.5600 | 134.6600 | 2.0923 | −5.6610e−06 | 7.9956e−06 | 2.2562e−05 | −1.8048e−05 | 2.5051e−02 | −4.4232e−02 |
| Xar 63 | 27 | 17.8500 | −3.0500 | 12.8100 | −1.3700 | 9.2100 | 4.1200 | 1.3600 | 176.6400 | 1.7358 | −4.8920e−06 | 8.7677e−06 | 2.1173e−05 | −1.7404e−05 | 7.5472e−03 | −5.9336e−02 |

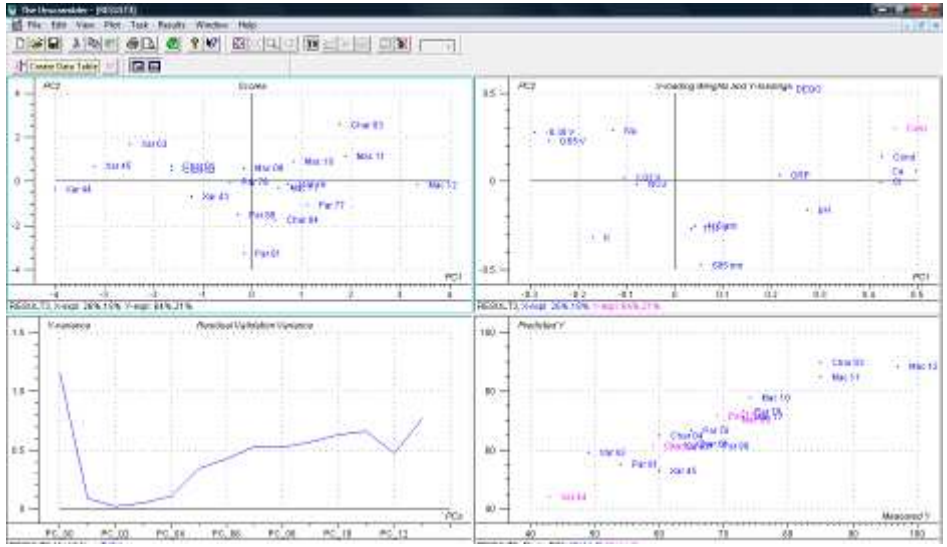
- Matrix of Data
- Variables vs samples
- We perform a PCA: all samples are used for the training
- Weight of samples: all are normalized to 1/sdv



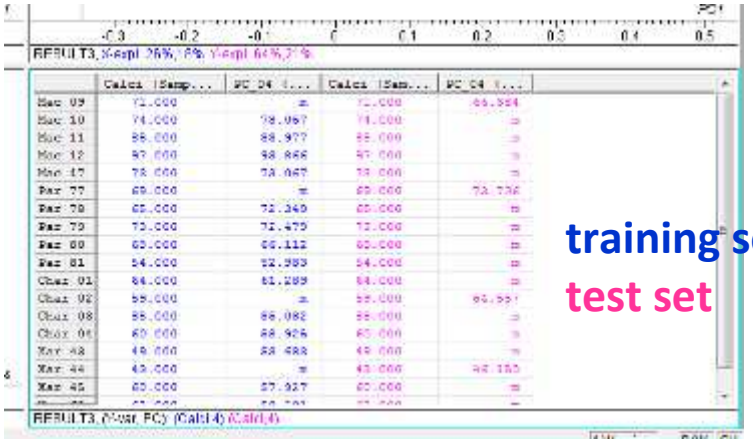

- Scores distribution of all the samples all through the 2 C
- Loadings distribution of the variables (weight of each variable)

## PLS analysis





- PLS 1. One model for each variable
- Comparison of our data with standard method



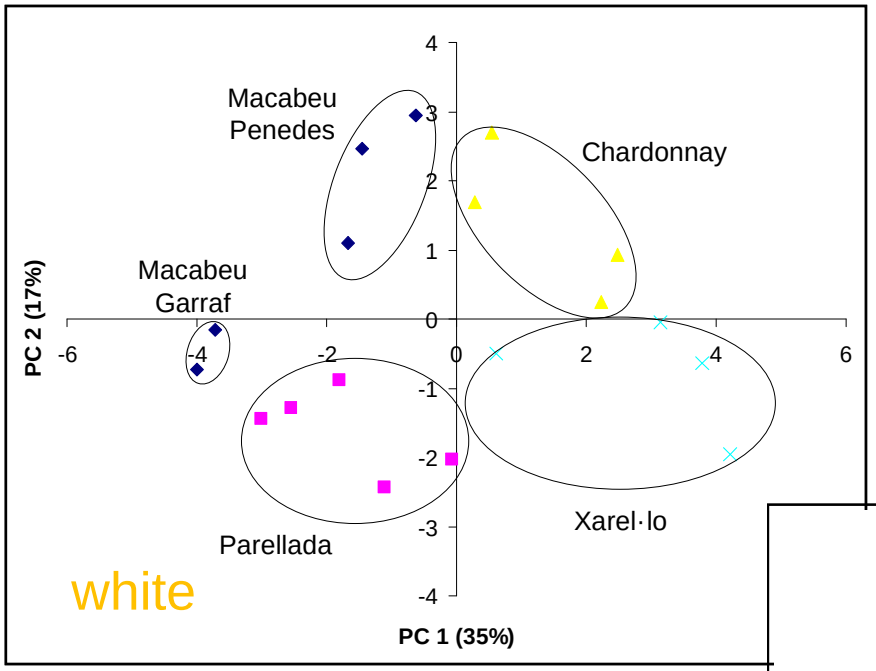
training set

test set

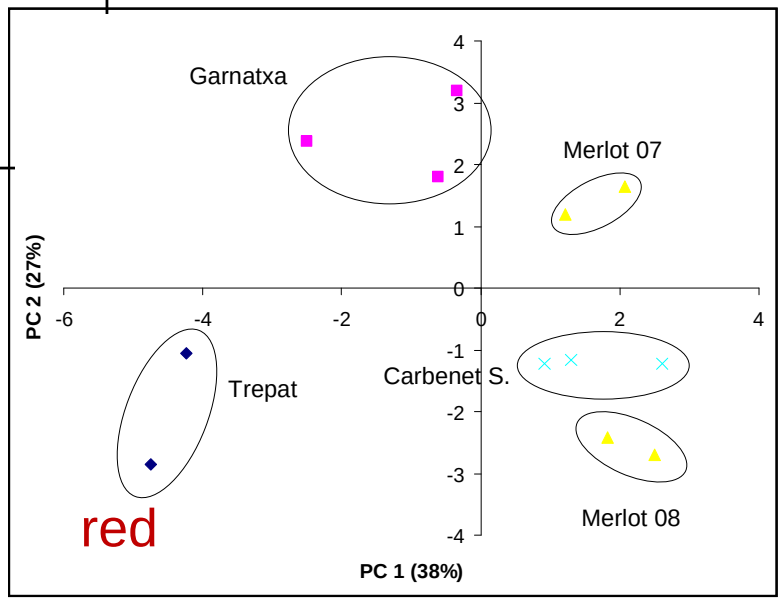
- One model for Ca detection
- Error ~ 0 for 2 PC
- Regression treatment

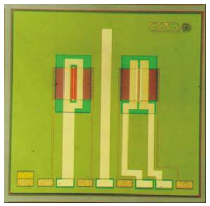
# Classification of wines

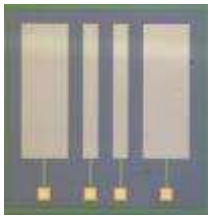
## PCA for monovarietal wines

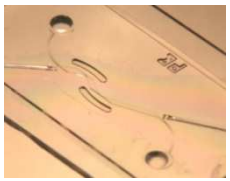



Classification according to:
- Grape variety
- vintage year
- geographical origin



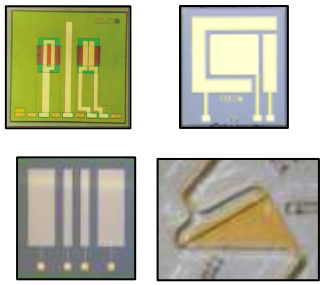




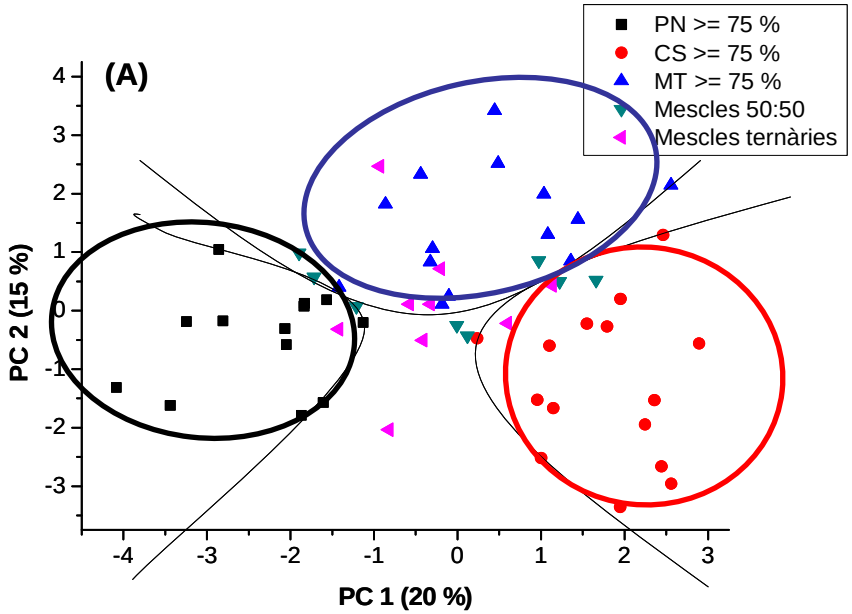
# Classification of wines

60 mixtures of

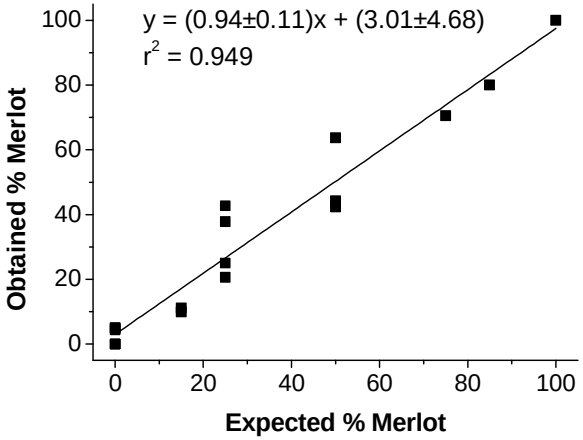
Cabernet Sauvignon, Pinot Noir and Merlot 0, 25, 50, 75, 85, 100%

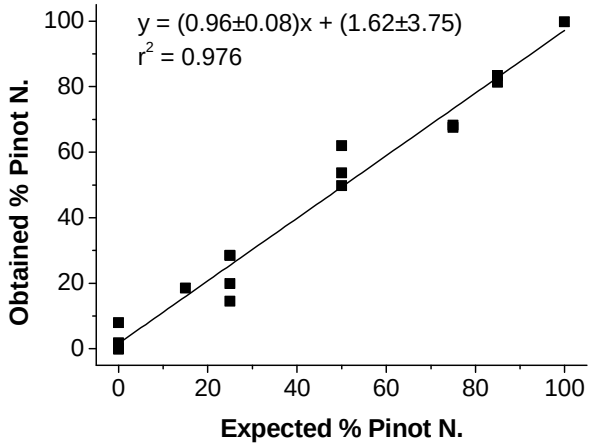


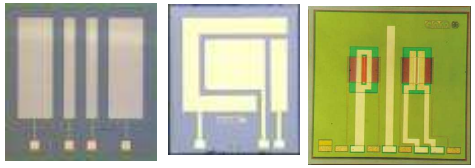
Wine classification according to the percentage of grape variety




Quantification of each variety





# PLS for Chemical Wine Parameters

Relative errors comparing with standard methods of analysis:

## White wine

| Sample | VAD | Total acidity | pH | $Ca^{2+}$ | $Mg^{2+}$ | Glycerol |
|---|---|---|---|---|---|---|
| **Macabeu 09/07** | 2.82 | −3.7 | −0.79 | −0.7 | −4.9 | 6.0 |
| **Parellada 77/07** | 0.07 | 9.5 | −3.55 | 5.1 | −0.1 | 2.0 |
| **Chardonnay 02/07** | 3.32 | −2.7 | 1.16 | 5.7 | −2.2 | −4.3 |
| **Xarel·lo 44/07** | −0.62 | 1.0 | −4.76 | 4.0 | −2.8 | 12.3 |

Error < 5 %

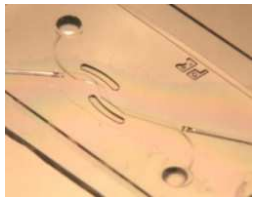
Error < 10 %

## Red wine

| Sample | VAD | Total acidity | pH | $Ca^{2+}$ | $K^{+}$ | Glycerol |
|---|---|---|---|---|---|---|
| **118/07 Trepat** | 4.45 | 0.6 | -2.20 | -5.1 | -4.0 | 8.8 |
| **95/07 Garnatxa** | -4.05 | -7.7 | 1.34 | -6.1 | 6.7 | 2.3 |
| **49/07 Merlot** | -2.31 | -2.6 | -0.91 | 3.9 | -0.7 | 3.8 |
| **45/08 Merlot** | -6.52 | 8.0 | 2.03 | -2.4 | -3.2 | -5.6 |
| **105/07 Cabernet** | 0.99 | -9.0 | -4.01 | 8.7 | -8.5 | -2.7 |

VAD: volatil alcoholic degree

# PLS for Optical Wine Paramenters



Relative errors comparing with standard methods of analysis:

## White wine

| Sample | Intensity of color | Tonality |
|---|---|---|
| **Macabeu 09/07** | 4.67 | 1.09 |
| **Parellada 77/07** | 4.56 | 3.66 |
| **Chardonnay 02/07** | 0.87 | 2.48 |
| **Xarel·lo 44/07** | 7.29 | −4.23 |

Error < 10 %

## Red wine

| Sample | Intensity of color | Tonality | CieLab a* |
|---|---|---|---|
| **118/07 Trepat** | -89.74 | 2.20 | -5.16 |
| **95/07 Garnatxa** | -44.57 | -3.14 | 7.90 |
| **49/07 Merlot** | -32.31 | 4.30 | 8.98 |
| **45/08 Merlot** | 17.43 | 3.17 | -7.16 |
| **105/07 Cabernet** | -10.22 | -5.65 | 3.41 |

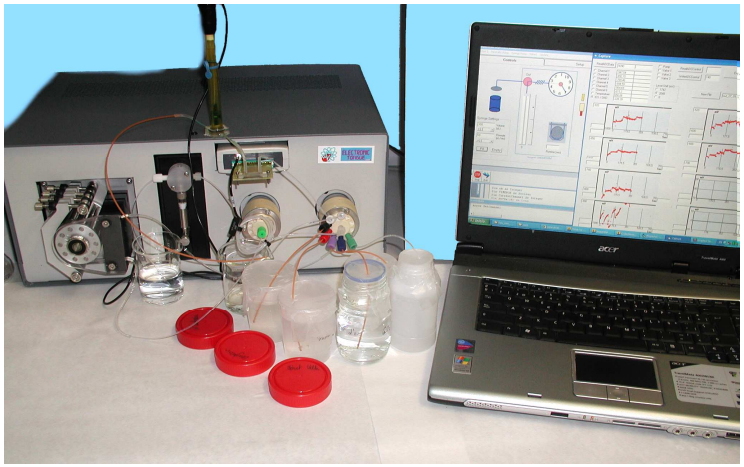
# Conclusions

• A multisensor system with different kind of sensors: potentiometric, voltamperometric, conductimetric, optical → **hybrid electronic tongue**

• The system is capable of discriminating wines samples not only according to the **grape variety,** but also to the origin and even the vintage.

• The system is able to quantify several parameters. The relative errors obtained are **below 10%.**

• The ET could be applied in the cellars as a system for **rapid detection**, **close to the** production and as an **alarm system**.



# Acknowledegements

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# Sistemes multisensors aplicats al control de qualitat dels vins

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gtq silicon technologies for sensing

TECNIO Be tech. Be competitive

CNM Centre Nacional de Microelectrònica IMB

CSIC Consejo Superior de Investigaciones Científicas