

La percezione degli odori da parte dell'uomo è di fondamentale importanza nella valutazione della qualità dei prodotti alimentari. Numerosi sforzi sono stati fatti in questi ultimi anni per introdurre sul mercato strumenti che operino con principi simili a quelli olfattivi umani: il “*naso elettronico*” è uno strumento che unisce alla sensibilità discriminante del naso umano l'oggettività della risposta strumentale fornendo risultati comparabili in tempi brevi.

## DEFINIZIONE

Il “*naso elettronico*” è uno strumento che comprende una serie di sensori chimici non specifici e un sistema di pattern recognition in grado di riconoscere odori semplici e complessi (Gardner and Bartlett, 1994. Sensors and Actuators B, 18, 221,).



# IL NASO



## COME E' COSTITUITO IL NASO ELETTRONICO?

Similmente al sistema olfattivo umano, è costituito da:

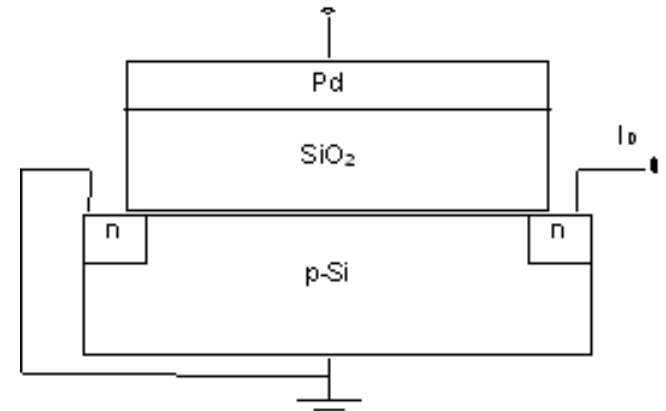
- **Sensori chimici (10 MOSFET and 5 MOS)** simili ai recettori olfattivi umani
- **Un software di pattern recognition (NST Senstool)** simile al cervello umano

# SENSORI MOSFET

## Transistor di ossidi di metallo ad effetto di campo

Sono costituiti da tre strati:

- Silicio semiconduttore
- Isolante ad ossido di silicio
- Metallo catalitico (Pt, Pd, etc.)



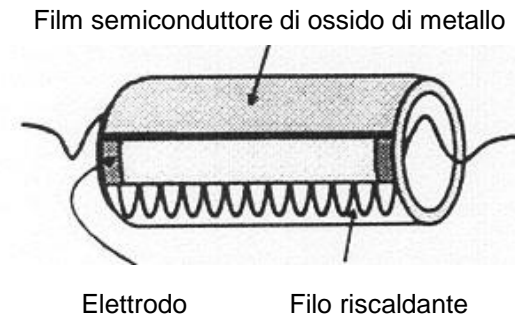
**Operano come un transistor a cui viene applicato un potenziale. Sono sensibili a composti contenenti idrogeno (ammine, aldeidi, esteri, chetoni, aromatici ed alcoli) e lavorano alla temperatura di 140-170°C. Quando una molecola polare interagisce con il metallo, il campo elettrico viene modificato, ciò provoca una variazione di corrente. Lo strumento registra il cambiamento di voltaggio necessario per riportare la corrente al valore iniziale.**

# SENSORI MOS

## Semiconduttori ad ossidi di metallo

Sono costituiti da tre strati:

- Substrato di ceramica
- Filo riscaldante
- Film semiconduttore di ossidi di metallo (Zn, Co, etc.)



**Si basano su cambi di conducibilità indotti da reazioni superficiali dovute all'adsorbimento del gas. Sono sensibili a molti gas di combustione (idrocarburi saturi, NO, CO). Operano alla temperatura di 300-400°C. Il meccanismo di reazione si basa su uno scambio di ossigeno tra le molecole volatili ed il film metallico, che provoca un cambio di resistenza registrato e correlato ai composti adsorbiti.**

# NST SENSTOOL

**Analizza i dati utilizzando tre metodi di pattern recognition:**

- **PCA:** Principal Component Analysis
- **PLS:** Partial Least Square Regression
- **ANN:** Artificial Neural Network

**Essi permettono di:**

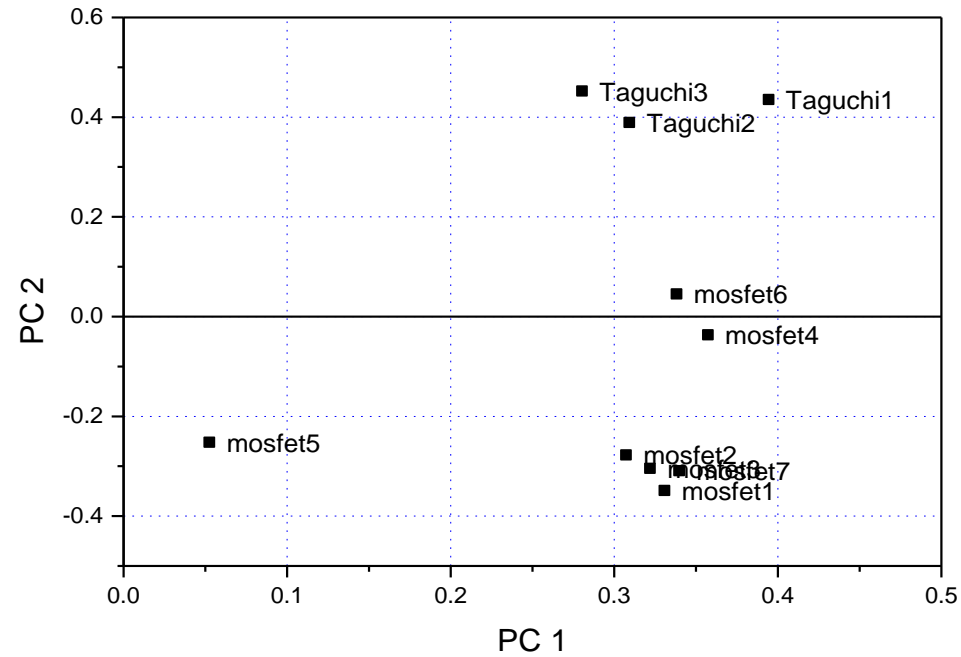
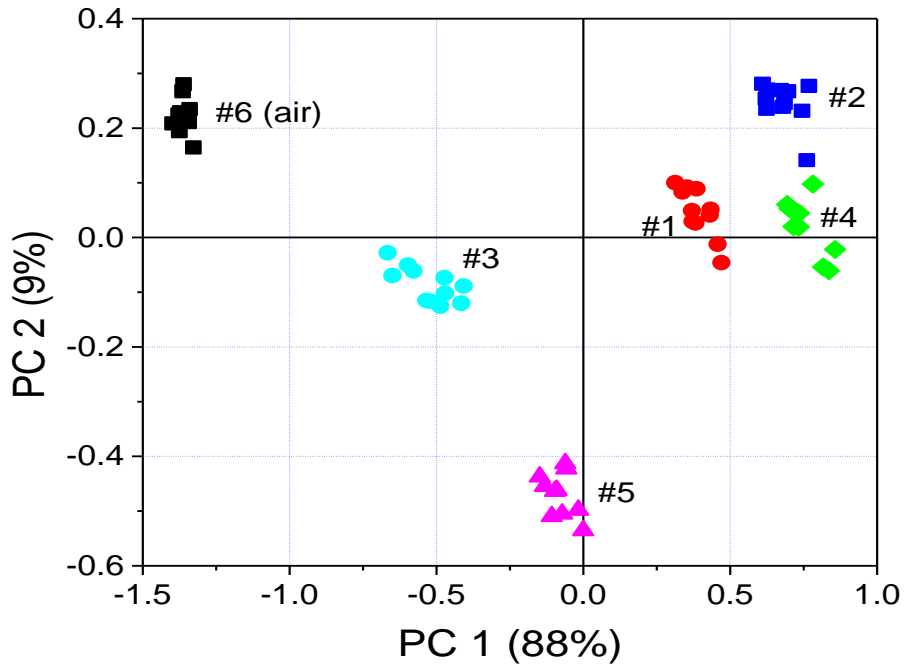
- studiare l'insieme dei dati (PCA e PLS)
- predire le proprietà dei campioni (PLS e ANN)



# RISULTATI PCA

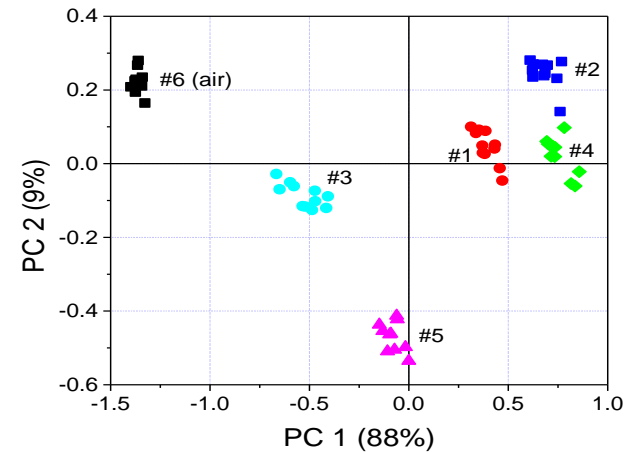
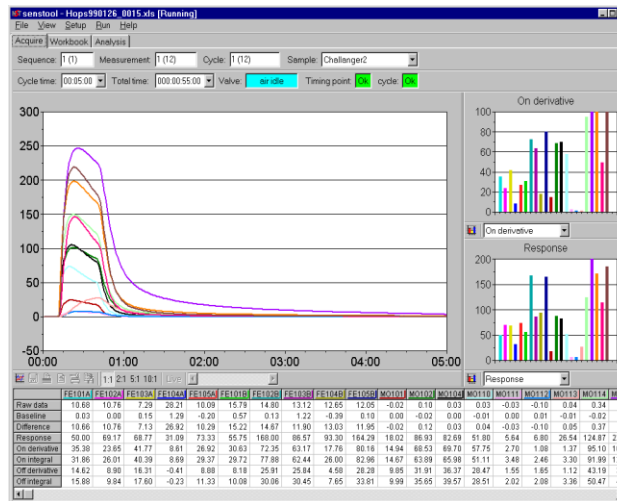
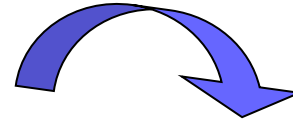
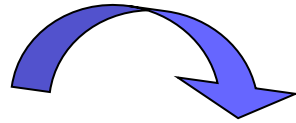
## Score plot

## Loading plot



# PROCESSO ANALITICO

## Come lavora il naso elettronico?

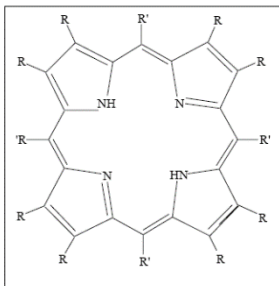
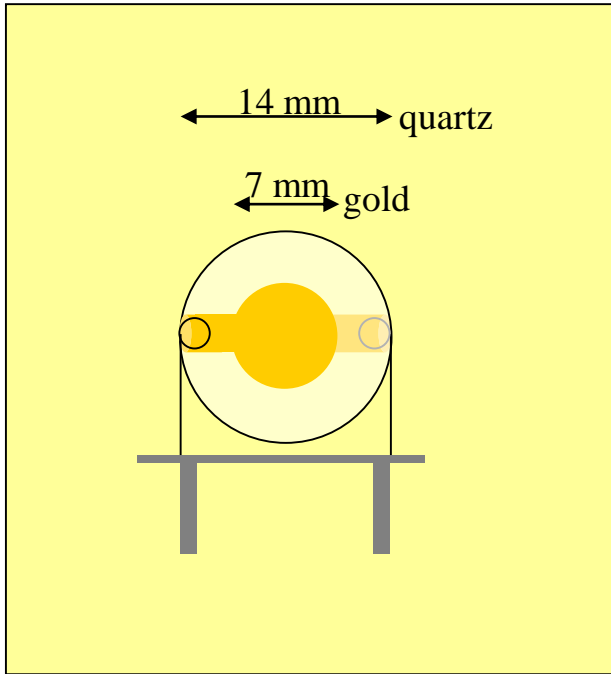


Lo spazio di testa del campione è aspirato e trasferito sulla superficie dei sensori

La risposta dei sensori è convertito in un segnale elettrico monitorabile dal computer

La risposta dei sensori viene elaborata usando metodi di analisi multivariata

# Piezoelectric System Electronic nose



Butyloxy Tetra Phenyl Porphyrin



Cu  
Co  
Zn  
Mn  
Fe  
Sn  
Ru  
Cr





An electronic nose can now diagnose cancerous tumors. A new research have designed an electronic nose to help diagnose malignant mesothelioma early on. This nose can detect the presence of the tumor with a breath test. Malignant mesothelioma is an uncommon, usually fatal, cancerous tumour of the lining of the lung and chest cavity or lining of the abdomen (peritoneum) caused by long-term asbestos exposure. The device was designed to distinguish between benign and malignant disease and to detect the disease early. “If you catch it earlier, your chances of actually giving people the right treatment to stop it spreading are actually better,” said team leader, Deborah Yates. “We tried to exclude the other asbestos diseases because it’s very important from a patient’s point of view that you don’t pick up something that is a benign asbestos disease, so that you don’t diagnose them with something that’s not actually a problem,” added Yates.

<https://www.thehealthsite.com/news/electronic-nose-helps-locate-deadly-tumour/>

# Applicazioni del naso elettronico nel settore alimentare

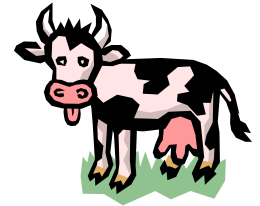
## Birra e bevande

- Controllo materie prime
- Shelf-life
- Monitoraggio (on line) fermentazione



## Carne e derivati

- Rancidità
- Shelf-life
- Odori estranei



## Latte e derivati

- Odori estranei nel latte
- Rancidità nel latte e formaggi
- Conservazione dei formaggi



## Vegetali

- Freschezza
- Additivi
- Shelf-life



## Prodotti della pesca

- Shelf-life
- Freschezza



## Succhi di frutta

- Odori estranei
- Purezza
- Origine
- Ossidazione

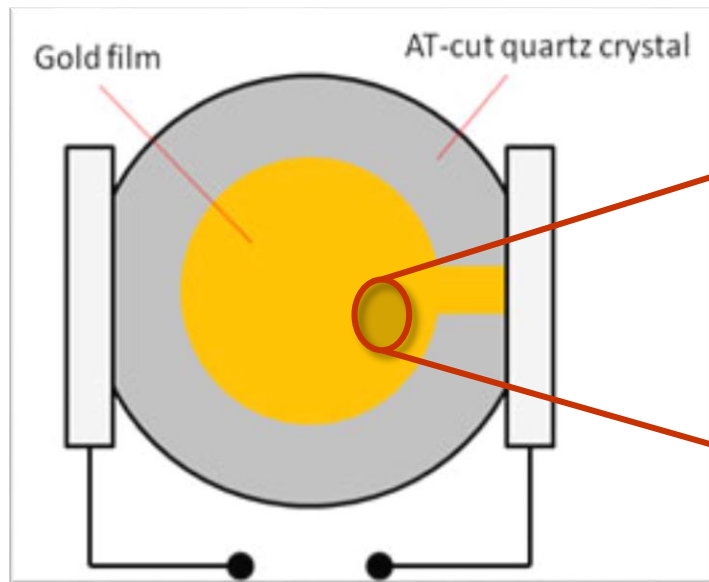


## Grani

- Classificazione
- Umidità

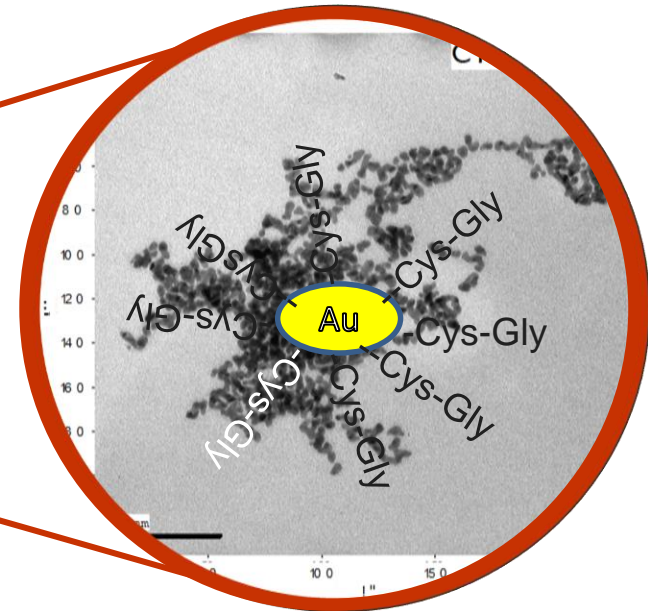


# Quartz crystal micro-balance



14 mm AT quartz

7 mm gold



Resonant frequency 20  
MHz

## Chocolate

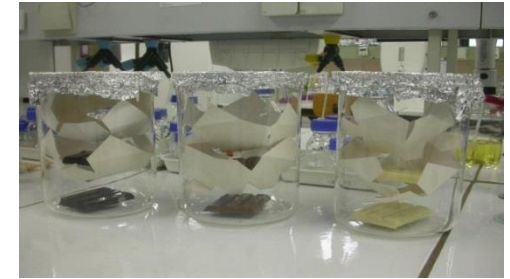
- ✓ **Temperature: 40°C**
- ✓ **Equilibration time: 10 min**
- ✓ **15g in 100 mL lab bottle grated and melted**
- ✓ **4 L/h**

Standard Samples

Off-flavoured samples

PLS-DA analysis

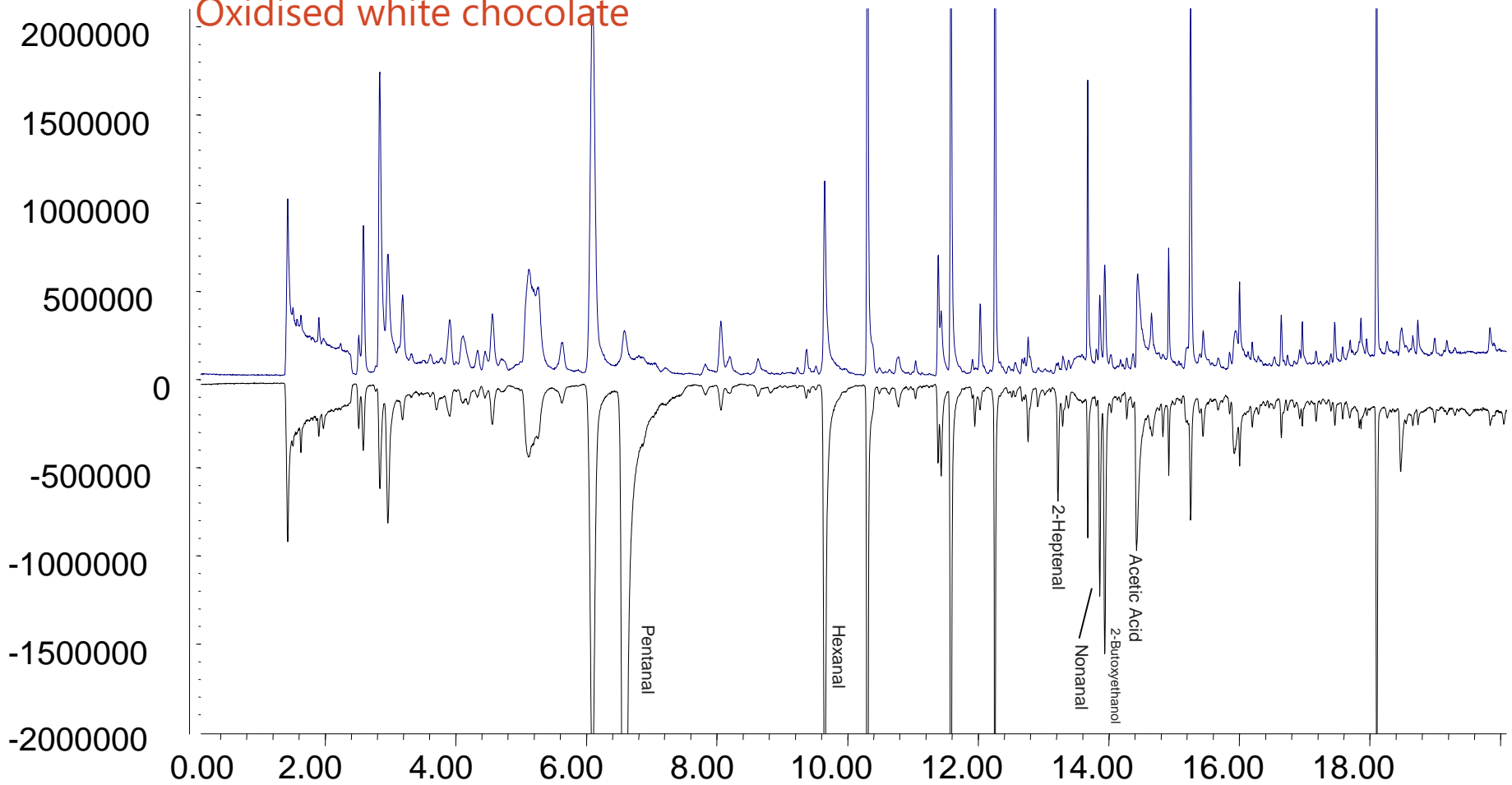
Off-Flavour	Process
3 methylbutanal	Fermentation volatiles
Phenylacetaldehyde	
Acetic Acid	Conching process
Tetramethylpyrazine	Roasting Process
2-acetylpyrrole	
2-nonenal	Fat related (oxidation)
2,4-decadienal (t,t)	



Off-flavours were preliminarily added in the cocoa butter to achieve the concentration of 125 ppm. One tea spoon of contaminated cocoa butter was then added to 400 g of chocolate to obtain an estimated final concentration in the sample of ~ 6ppm.

# Real samples

Oxidised white chocolate



# Electronic nose sensor arrays

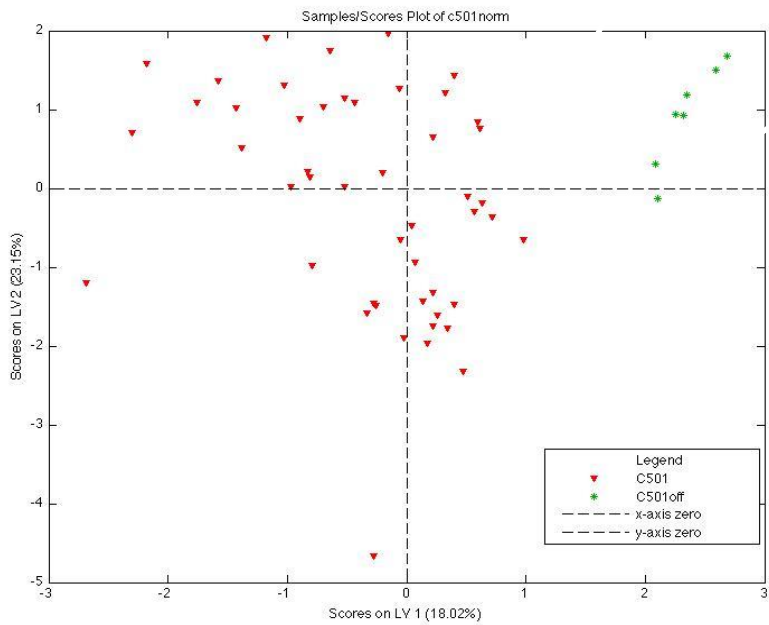
## GNP-Peptide based

- ✓ **GNP-Glutathione**
- ✓ **GNP-Cys-Gly**
- ✓ **GNP-Cys**
- ✓ **GNP-Thioglycolic Acid**
- ✓ **GNP-Cys-Arg-Gln-Val-Phe**
- ✓ **GNP-Cys-Ile-His-Asn-Pro**
- ✓ **GNP-Cys-Ile-Gln-Pro-Val**
- ✓ **GNP**

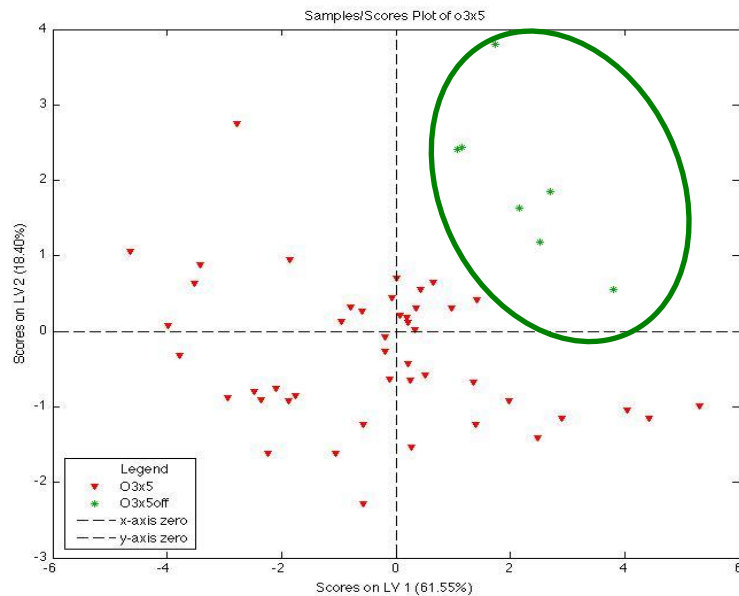
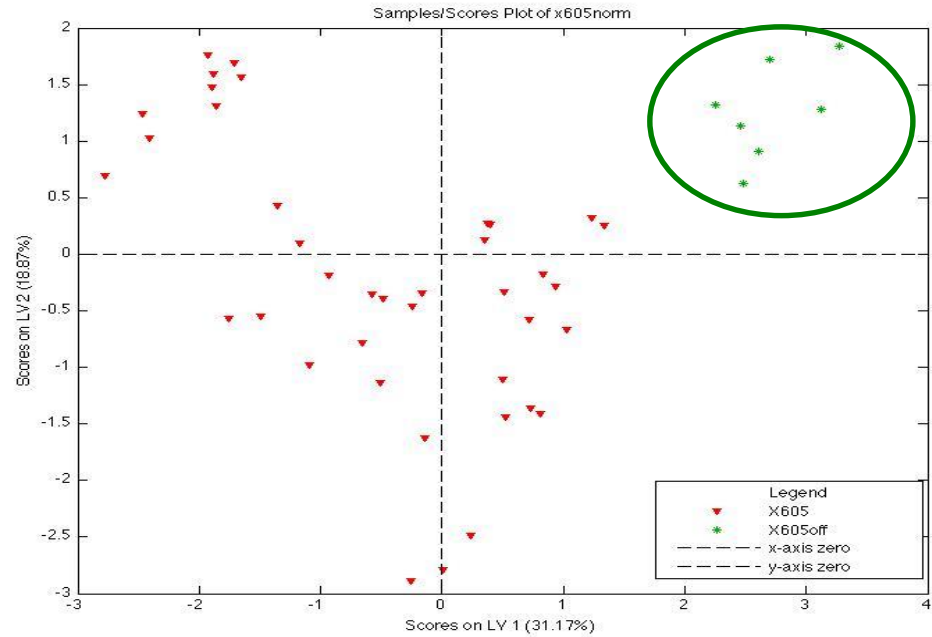
## Porphyrin based

- ✓ **Cu-Buti-TPP**
- ✓ **Co-Buti-TPP**
- ✓ **Zn-Buti-TPP**
- ✓ **Mn-Buti-TPP**
- ✓ **Fe-Buti-TPP**
- ✓ **Sn-Buti-TPP**
- ✓ **H<sub>2</sub>-Buti-TPP**
- ✓ **Mg-Buti-TPP**

# Dark Chocolate



# White Chocolate



# Milk Chocolate



# GNP-Peptide vs. Porphyrin

## GNP-Peptide based

	Regular	Off Flavours	% Correct
Regular	48	0	100
Off flavours	0	7	100

Tot. Correct:

	Regular	Off Flavours	% Correct
Regular	39	0	100
Off flavours	0	7	100

Tot. Correct:

	Regular	Off Flavours	% Correct
Regular	51	1	98
Off flavours	0	7	100

Tot. Correct:

## Porphyrin based

	Regular	Off Flavours	% Correct
Regular	14	1	93
Off flavours	1	9	90

Tot. Correct:

	Regular	Off Flavours	% Correct
Regular	13	1	92
Off flavours	4	8	67

Tot. Correct:

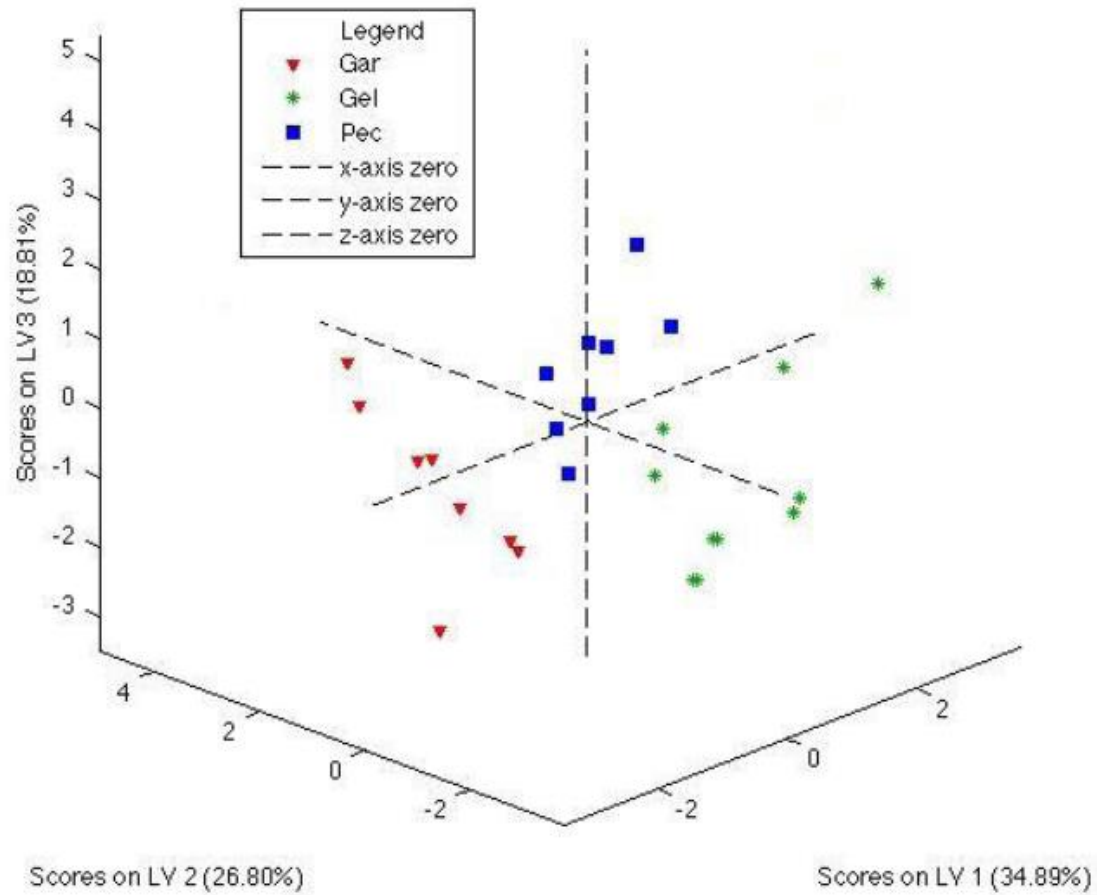
	Regular	Off Flavours	% Correct
Regular	15	1	94
Off flavours	4	8	67

Tot. Correct:

# Candies

- ✓ **3 structuring agents**
  - ✓ Gelatine [Gel]
  - ✓ Pectin [Pec]
  - ✓ Gum Arabic [G.Ar.]
- ✓ **2 aromas**
  - ✓ Natural [A]
  - ✓ Natural identic [B]
- ✓ **2 concentrations**
  - ✓ 0.15% [1]
  - ✓ 0.30% [2]



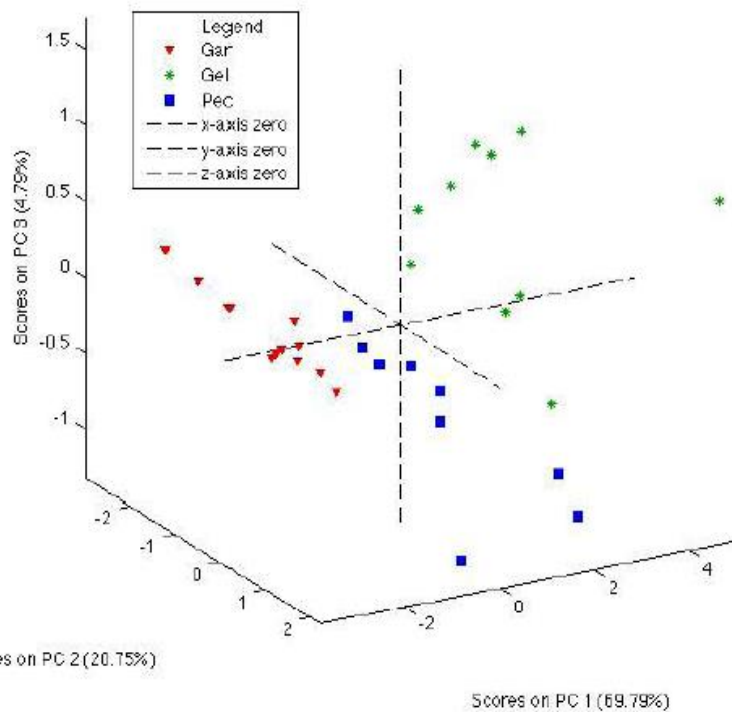


# Electronic nose

# Structuring

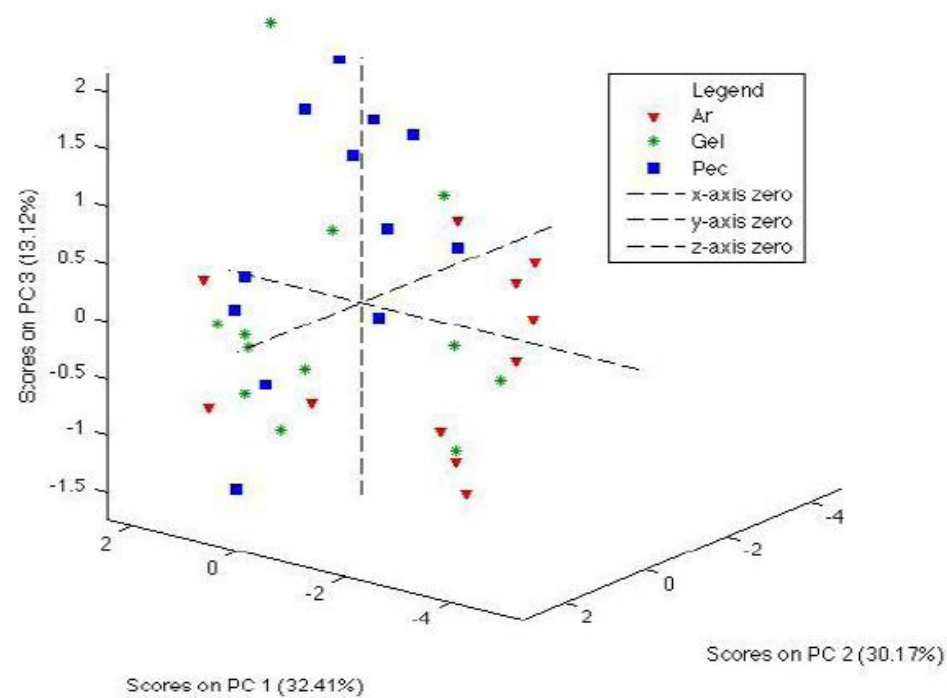
## GNP-Peptide based

Samples/Scores Plot of candy



## Porphyrin based

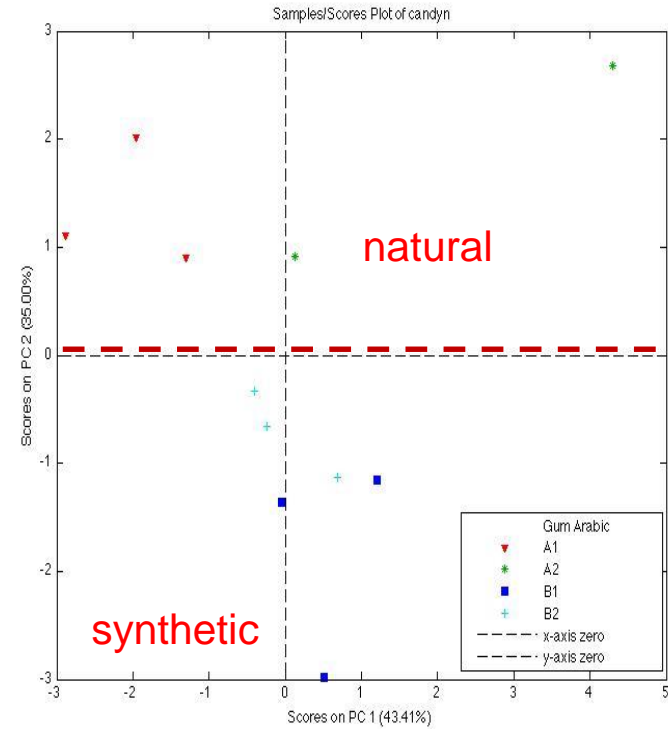
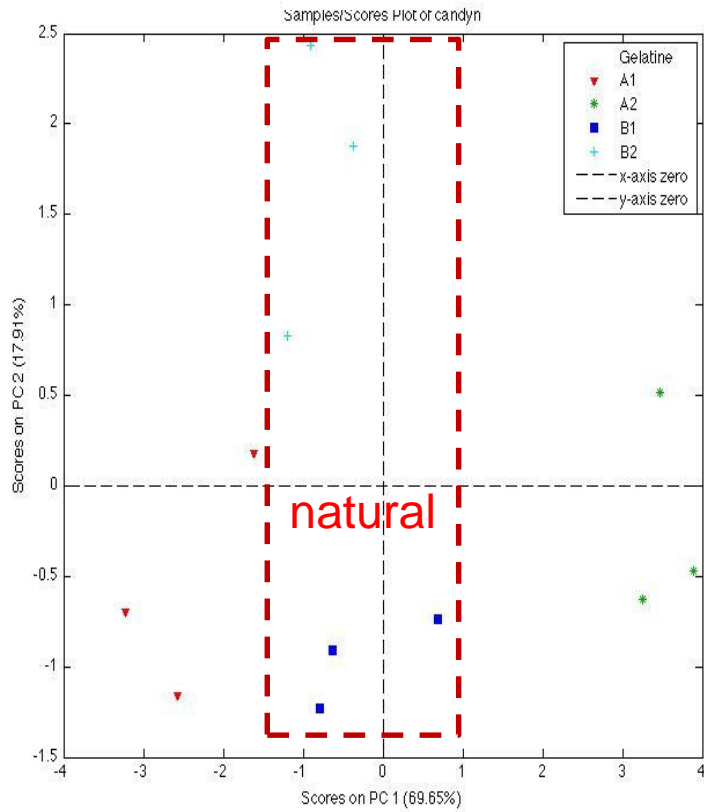
Samples/Scores Plot of data



# GNP-Peptide based (aroma)

## Arabic gum

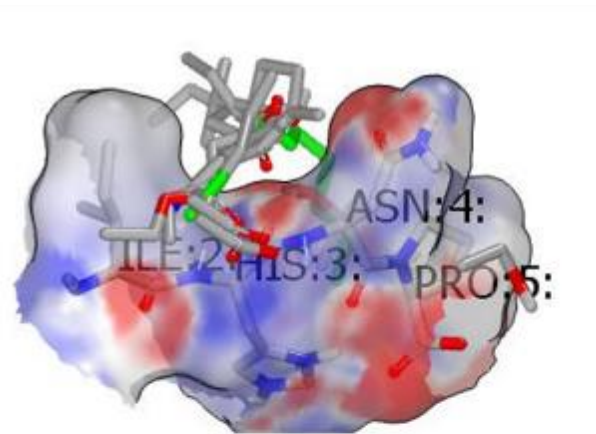
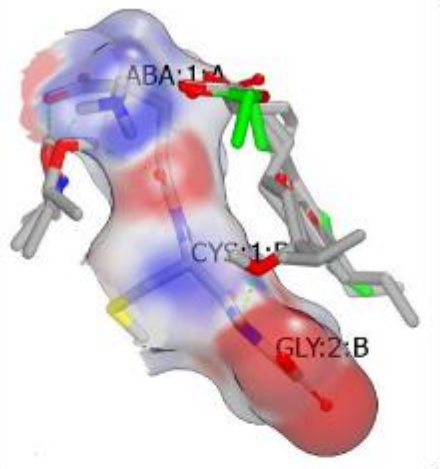
## Gelatin



# Peptide design

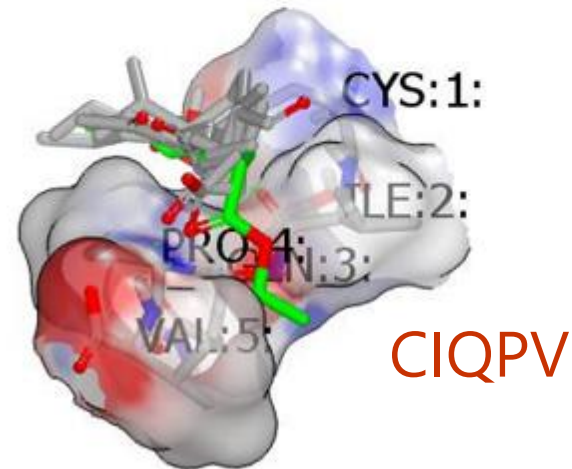
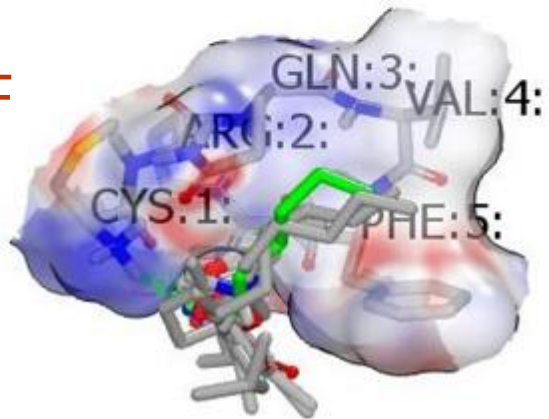
Virtual screening

Glutathione



CIHNP

CRQVF



CIQPV

# Peptide design

## Virtual VS Experimental data

- ✓ Binding scores compared with real samples  $\Delta F$  data (T-test), after normalization
- ✓ Data having  $p\text{-value} > 0.05$  were considered statistically equivalent as positive match (marked with "+")

	CG	Glutathione	CIHNP	CIQPV	CRQVF
2-Propanol	-	-	+	+	-
Acetone	-	+	-	+	+
Acetonitrile	-	+	+	+	+
Butane-2,3-dione	+	-	+	+	+
Ethanol	-	-	+	+	-
Ethyl acetate	+	+	+	+	+
Ethyl butanoate	+	+	+	+	+
Ethyl octanoate	-	+	-	-	+
Hex-3-en-1-ol	-	+	+	+	-
Hexane	+	+	+	+	+
Isopentyl acetate	-	+	+	+	-
Nonanal	-	+	+	+	+
Octanal	-	+	+	+	+
Terpinen-4-ol	-	-	+	+	+

78% good matching

# Peptide design

## Virtual VS Experimental data

	CG	Glutathione	CIHNP	CIQPV	CRQVF
2-Propanol	-	-	+	+	-
Acetone	-	+	-	+	+
Acetonitrile	-	+	+	+	+
Butane-2,3-dione	+	-	+	+	+
Ethanol	-	-	+	+	-
Ethyl acetate	+	+	+	+	+
Ethyl butanoate	+	+	+	+	+
Ethyl octanoate	-	+	-	-	+
Hex-3-en-1-ol	-	+	+	+	-
Hexane	+	+	+	+	+
Isopentyl acetate	-	+	+	+	-
Nonanal	-	+	+	+	+
Octanal	-	+	+	+	+
Terpinen-4-ol	-	-	+	+	+

- ✓ CG only 29% positive match
- ✓ Glut.: 71%. CRQVF: 71%  
CIHNP: 86% CIQPV: 93%
- ✓ Very bad matching with ethanol and 2-propanol
- ✓ Very good matching with Esters and Aldehydes
- ✓ Best matching with compounds with MW > 60g/mol