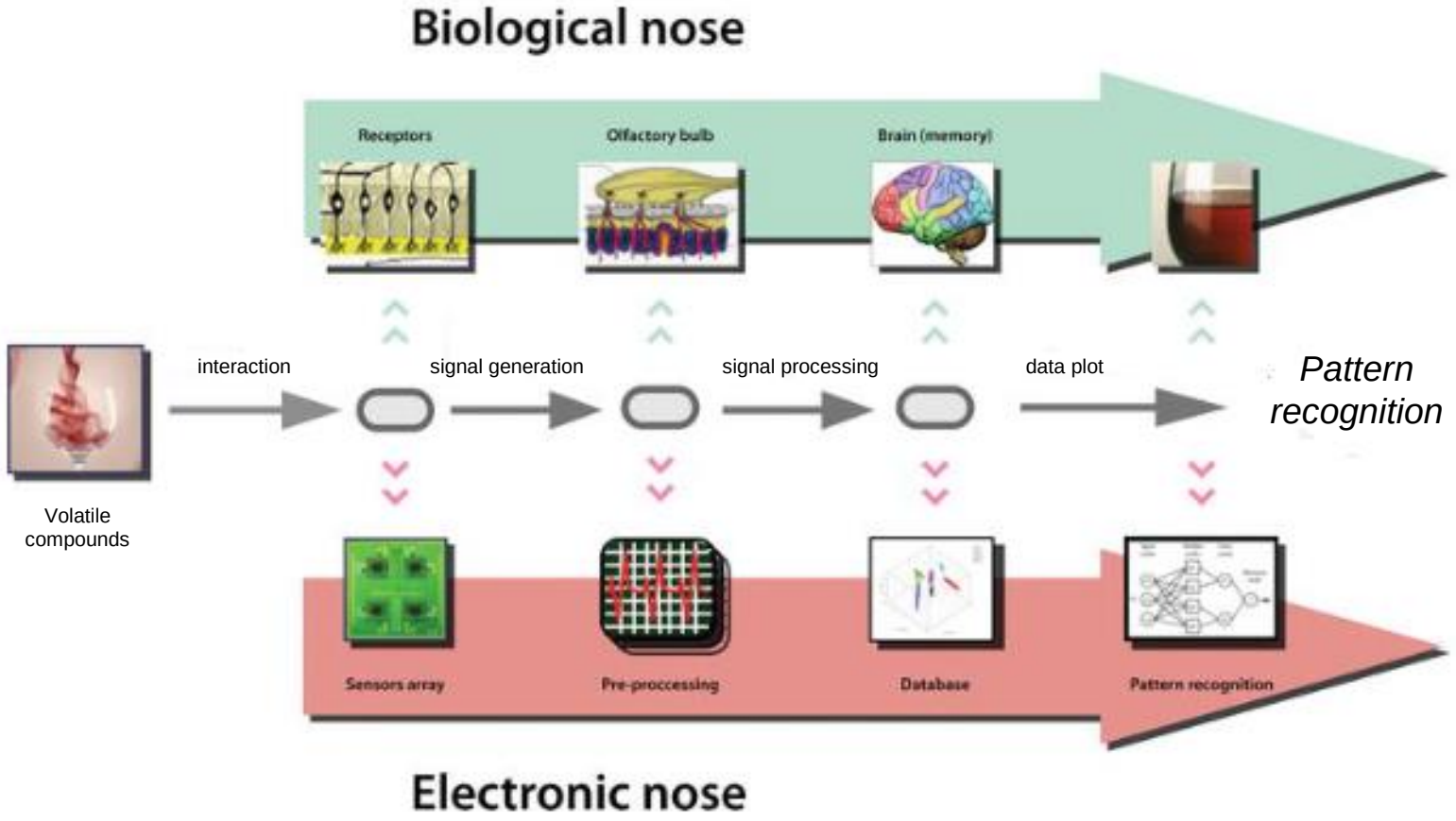
Electronic noses

- *environmental monitoring for air quality control*

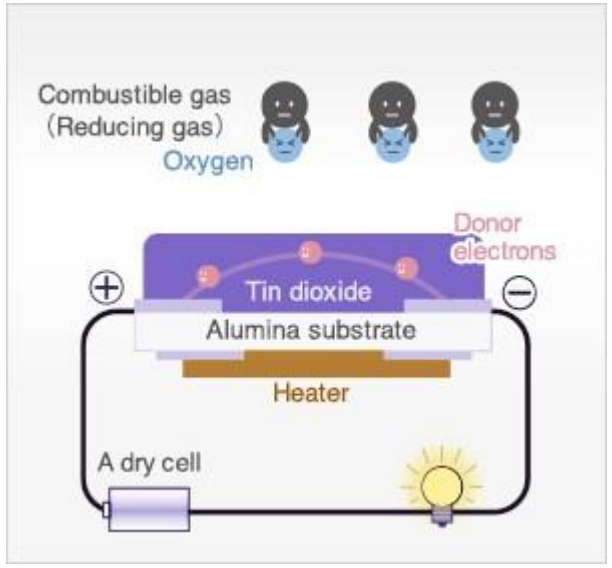
- *food quality and safety control*

- *cosmetic industry control*



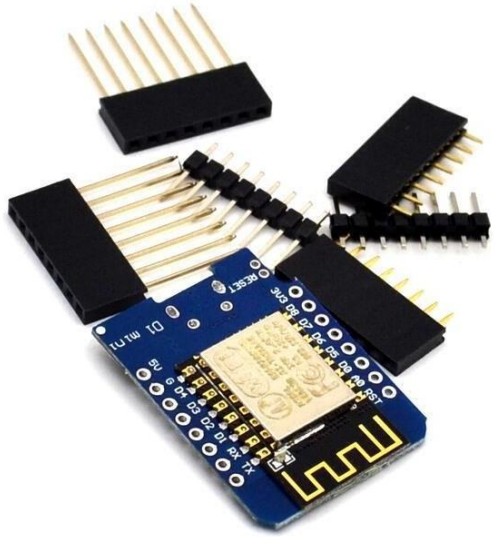
'An electronic nose is an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognizing simple or complex odors' *[1]*

[1] Gardner, Julian W., and Philip N. Bartlett. "A brief history of electronic noses." *Sensors and Actuators B: Chemical* 18.1-3 (1994): 210-211.



MOS SENSORS

Metal oxide semiconductors



Constituted by three main parts:

- Ceramic substrate
- Heating wire or thermistor
- Semiconducting metal oxides film (Zn, Co, etc.)

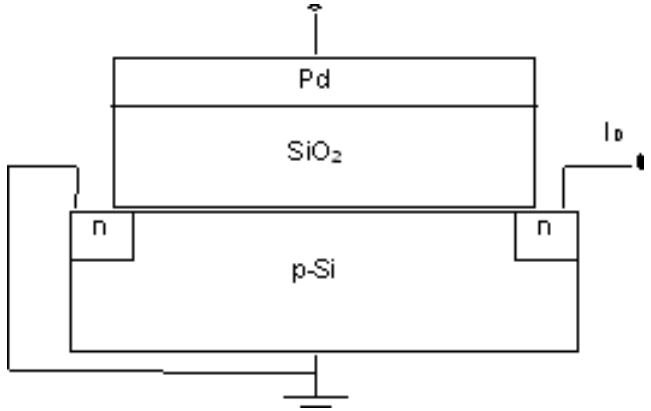
They measure conductivity changes onto the surface of the sensors induced by gases. Sensitive to combustion gases (hydrocarbons, NO, CO). Work at 300-400°C. An exchange between the gas and the oxygen on the film causes a change in resistance dedendent on the adsorbed gas.

MOSFET SENSORS

Field effect metal oxides transistors

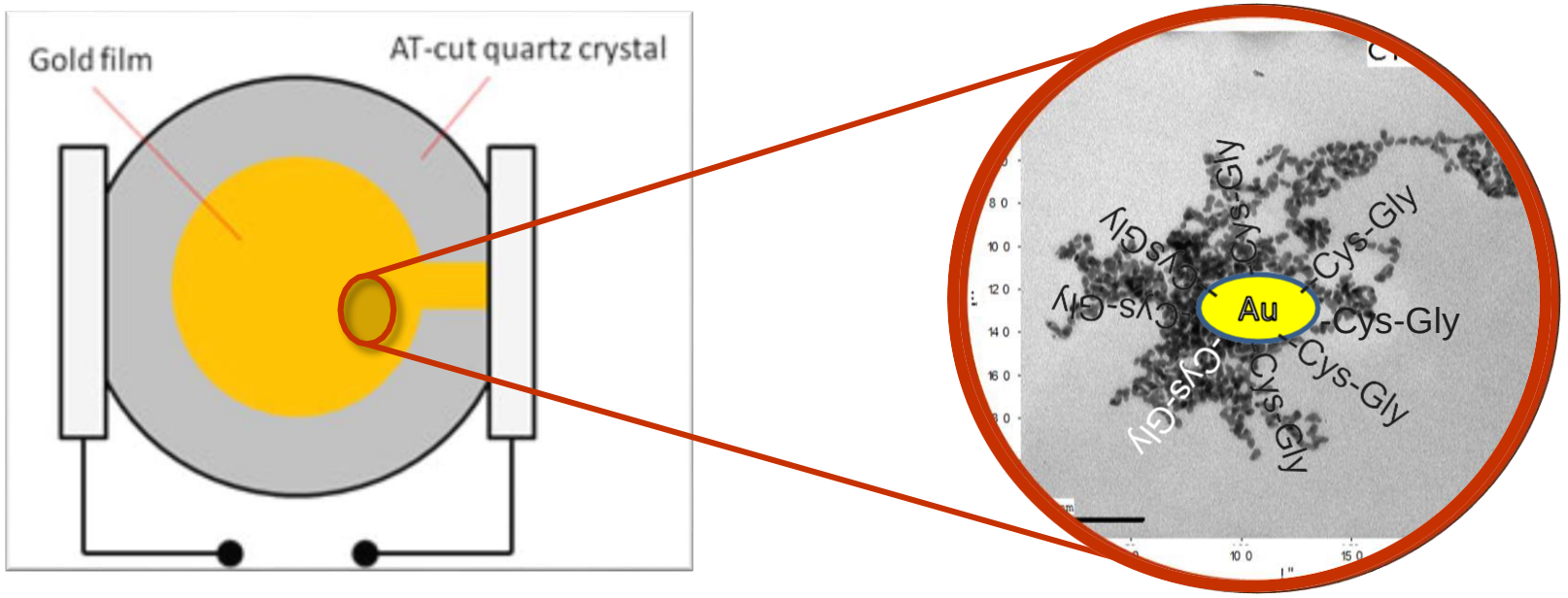
Made by 3 parts:

- Semiconducting Silicon
- Insulating silica layer
- Catalytic metal (Pt, Pd, etc.)



Work as a transistor at applied potential at 140-170°C. Sensitive to compounds containing hydrogen (amines, aldehydes, esters, chetons, aromatics ed alcohols). Whwn a polar molecules interacts with the metal the electric field is modified and a change in current occurs. The device output is the voltage necessary to have the current back at the initial value.

QUARTZ CRYSTAL MICRO-BALANCE



Resonant frequency 20 MHz

REAL SAMPLES

Chocolate

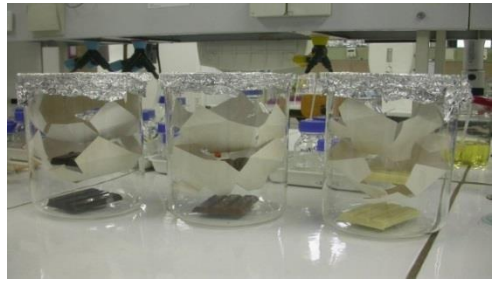
- **Temperature: 40°C**
- **Equilibration time: 10 min**
- **15g in 100 mL lab bottle grated and melted**
- **4 L/h**

Standard Samples

Off-flavoured samples

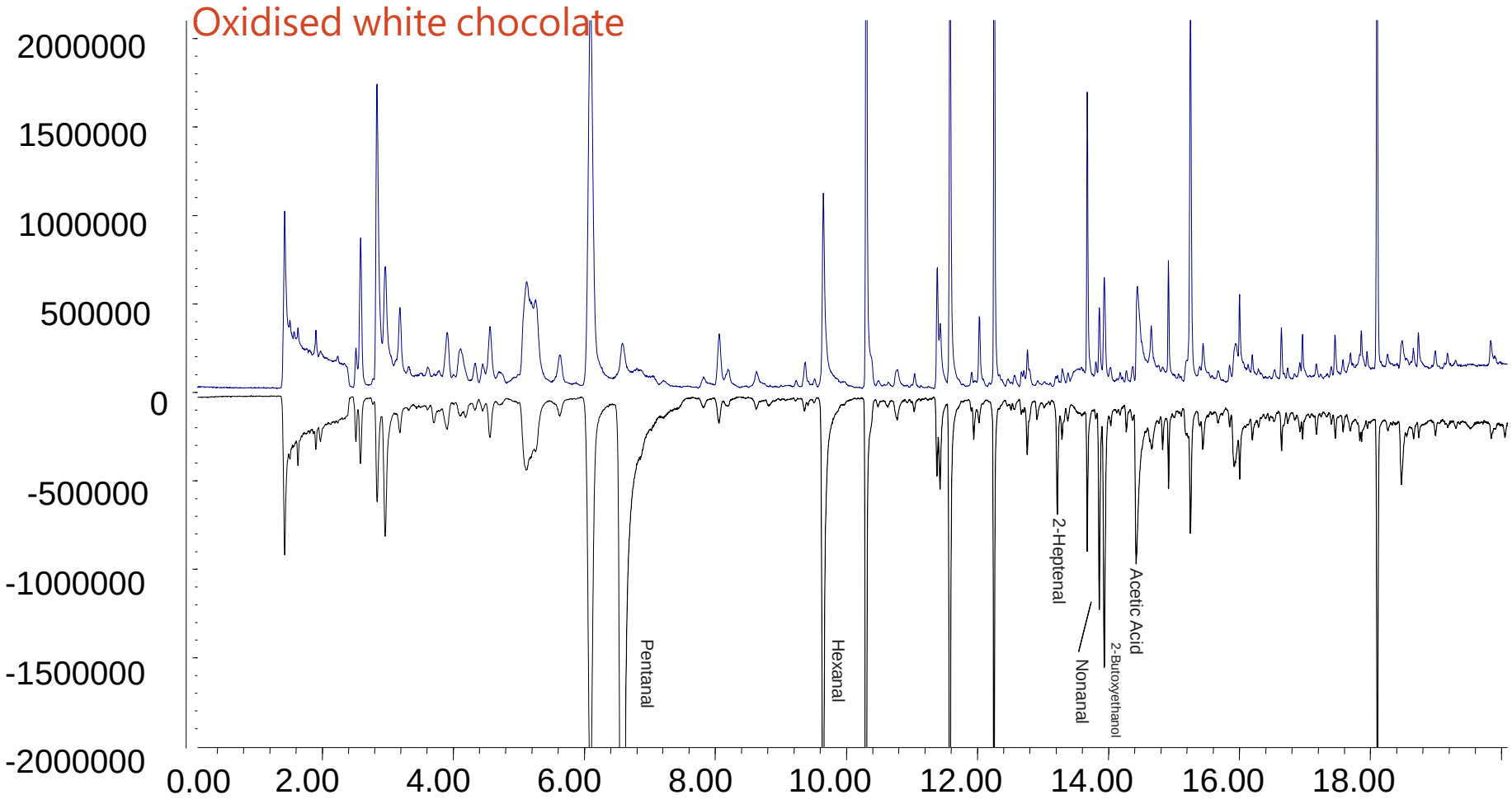
PLS-DA analysis

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



ELECTRONIC NOSE SENSOR ARRAYS

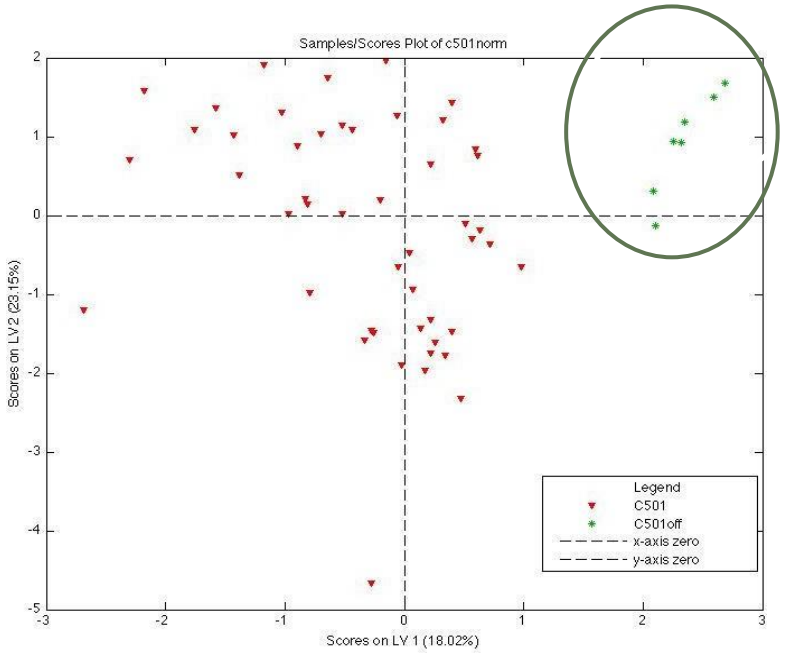
GNP-Peptide based

- **GNP-GLUTATHIONE**
- **GNP-CYS-GLY GNP-CYS**
- **GNP-THIOGLICOLIC ACID GNP-CYS-ARG-GLN-VAL-PHE GNP-CYS-ILE-HIS-ASN-PRO GNP-CYS-ILE-GLN-PRO-VAL GNP**

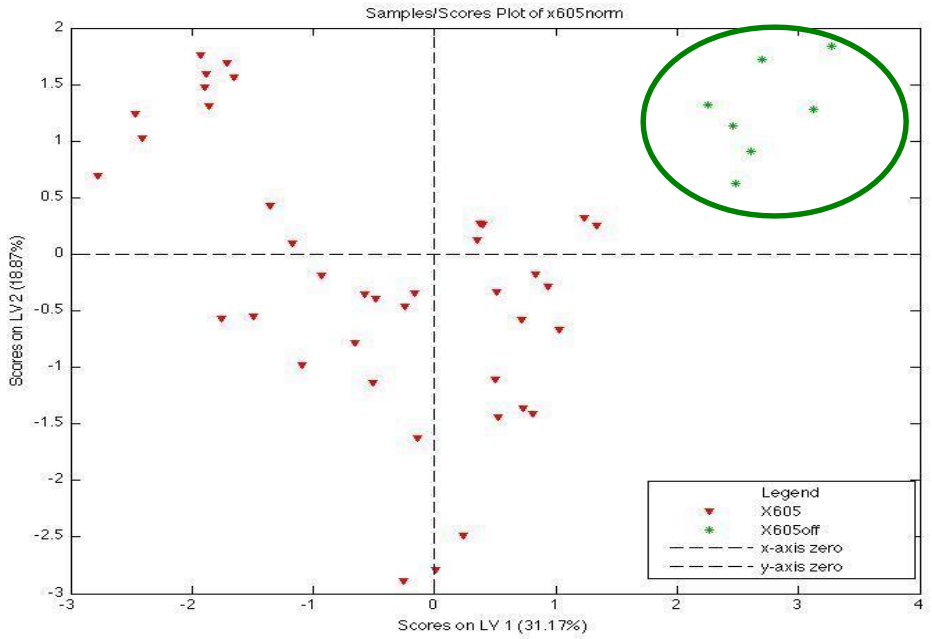
Porphyrin based

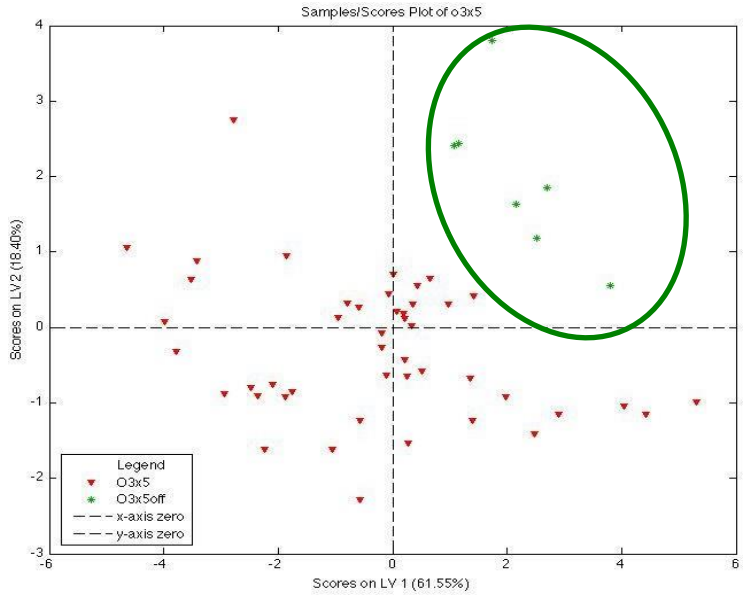
- **CU-BUTI-TPP**
- **CO-BUTI-TPP**
- **ZN-BUTI-TPP**
- **MN-BUTI-TPP**
- **FE-BUTI-TPP SN-BUTI-TPP H_2-BUTI-TPP**
- **MG-BUTI-TPP**

Dark Chocolate



White Chocolate





Milk Chocolate

UNITE

AuNP-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:

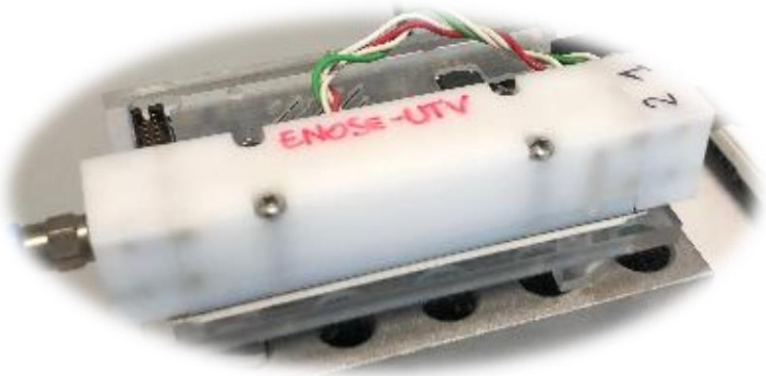
	Regular	Off Flavours	% Correct
Regular	13	1	92
Off flavours	4	8	67

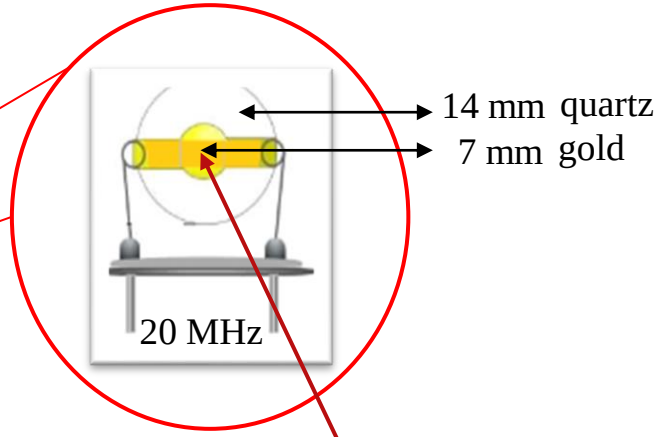
Tot. Correct:

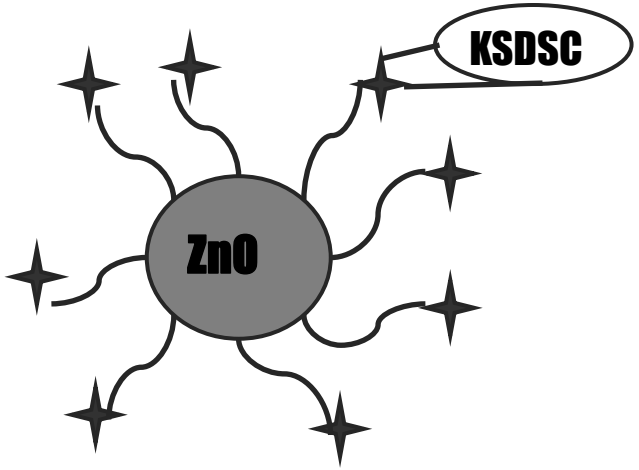
	Regular	Off Flavours	% Correct
Regular	15	1	94
Off flavours	4	8	67

Tot. Correct:

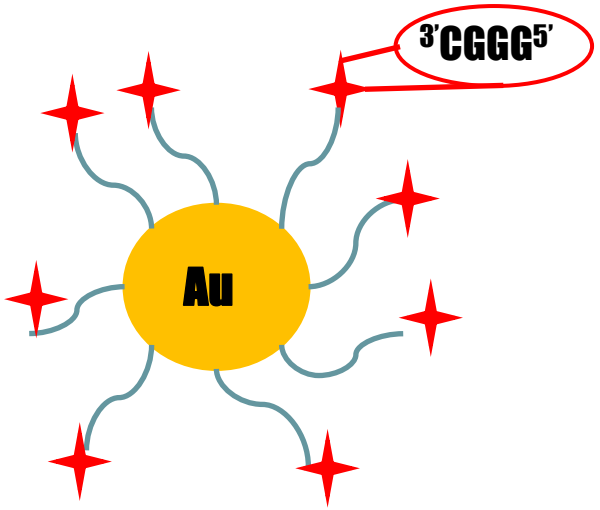
D. Compagnone, M. Faieta, D. Pizzoni, C. Di Natale, et al *Sensors and Actuator B*, 207, 1114, 2015.







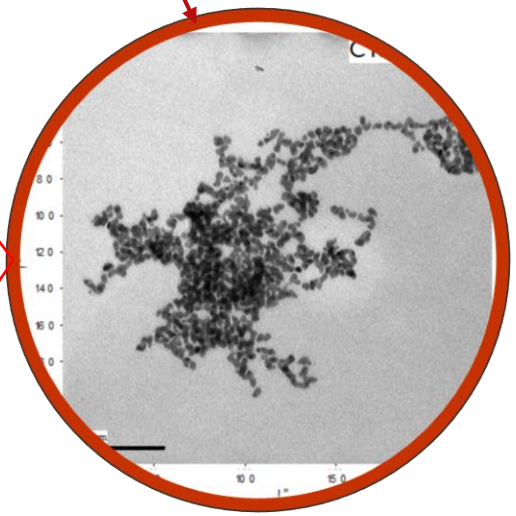
ZnONPs-Peptides



AuNPs-hpDNA

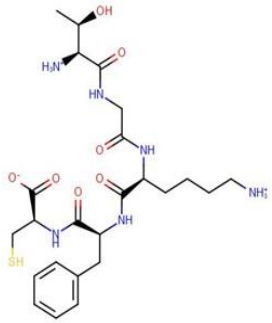
AuNPs-hpDNA

ZnONPs-Peptides

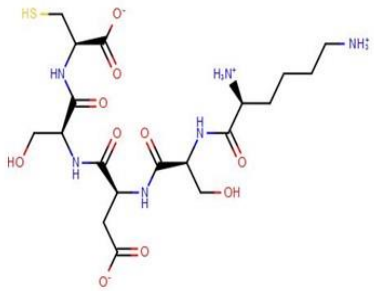


ELECTRONIC NOSE SEQUENCES…

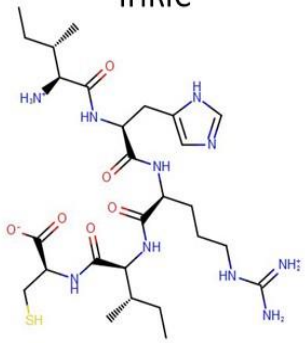
TGKFC



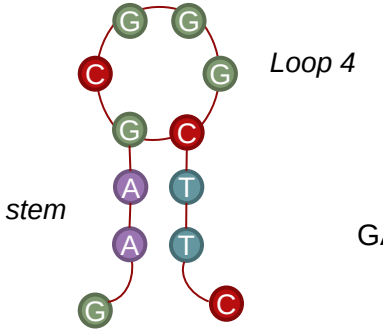
KSDSC



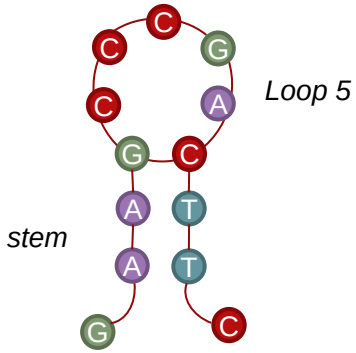
IHRIC



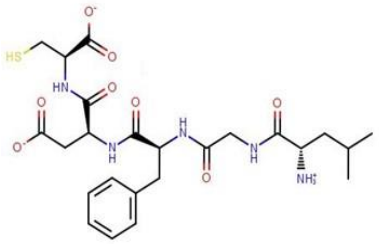
GAAGCGGGCTTC



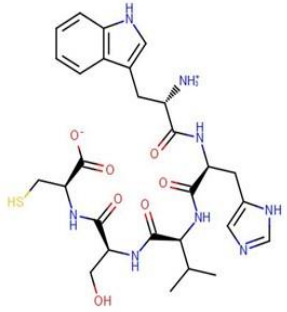
GAAGCCCGACTTC



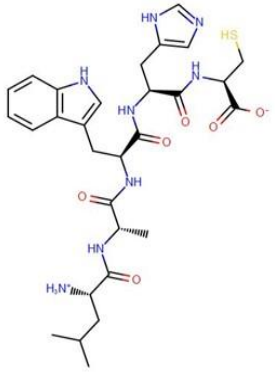
LGFDC



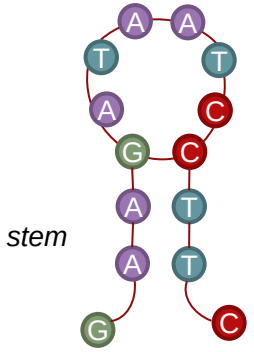
WHVSC



LAWHC



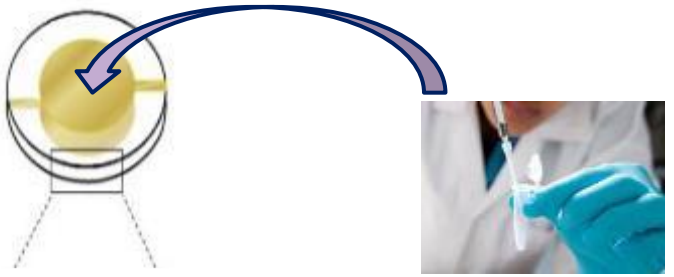
GAAGATAATCCTTC



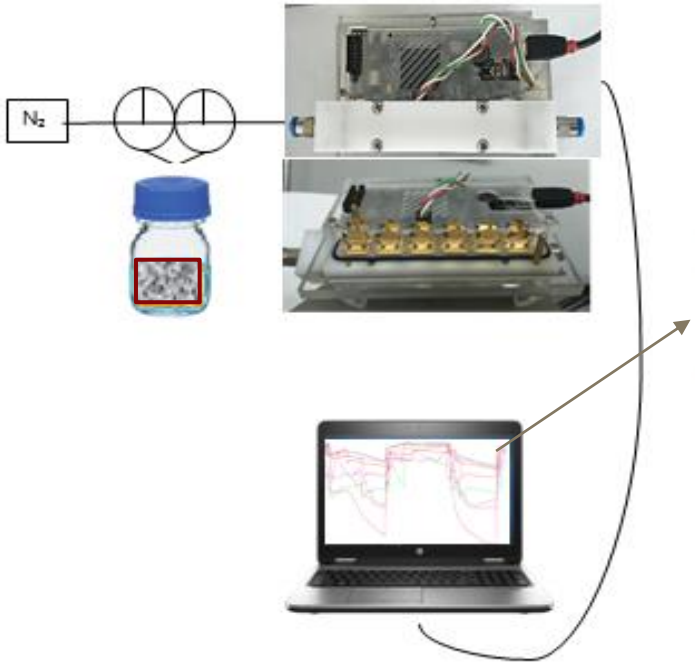
Materials and Methods

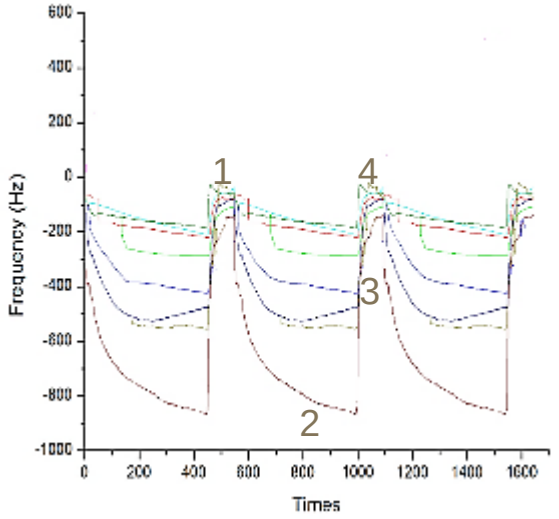
E-NOSE ANALYSIS:

5 µL of the AuNPs-hpDNA and ZnO-Peptide suspension on each side of the QCM



✓ **Aroma release in headspace of gas-tight bottle**





1.Start

2.Decrease

3.Equilibration

4.Baseline

Measurement of aroma compounds; the frequency shift was taken as analitical signal

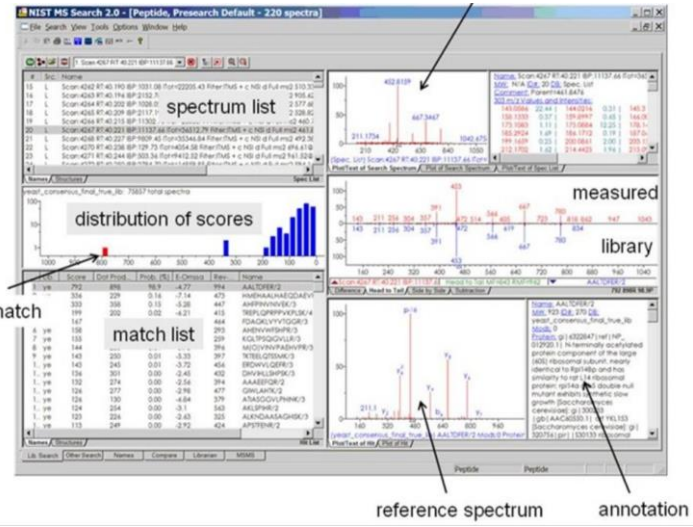
✓ **The samples was introduced in a gas-tight bottle (100 mL)**

Materials and Methods

SPME-GC/MS ANALYSIS

headspace analysis

Desorption



Confirmed by Retention index…

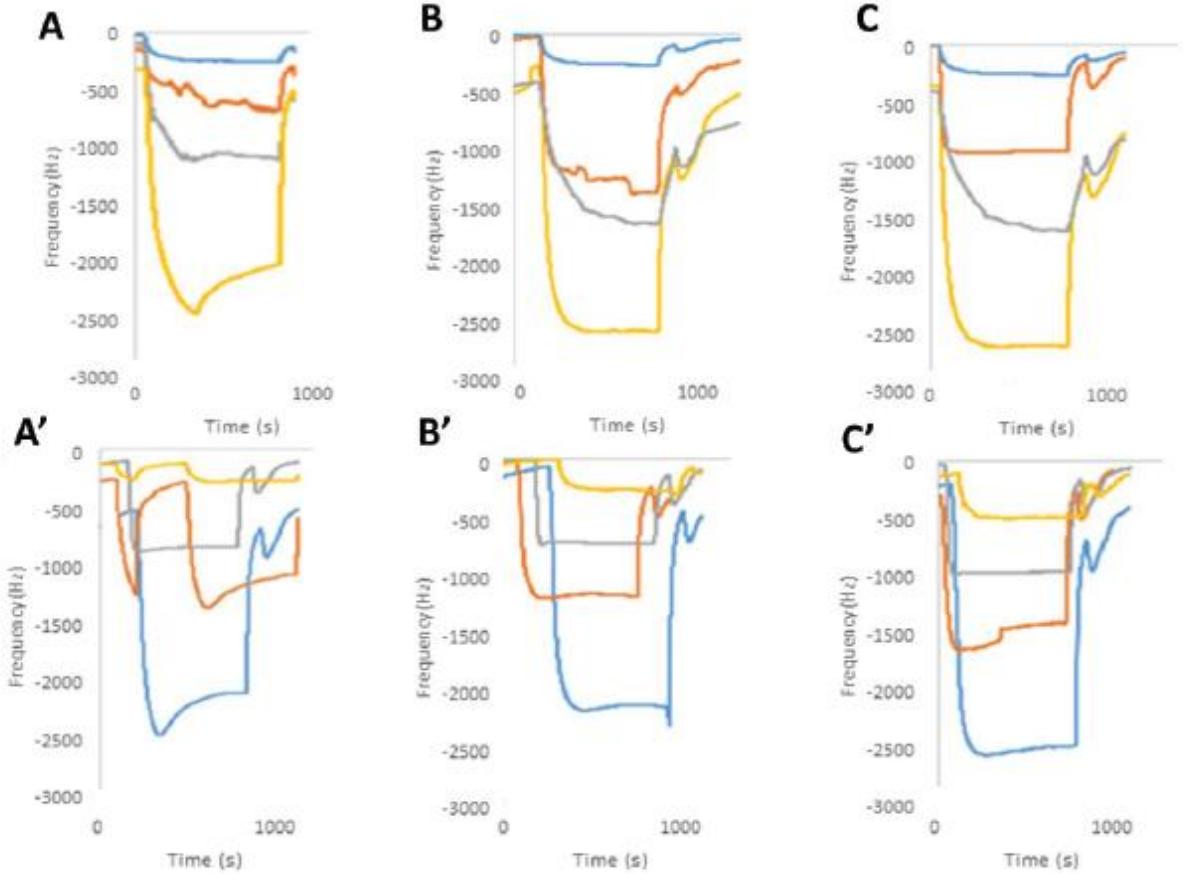
Example…

Peak no.	RT[a] (min)	RI_{lit}[b]	RI_{cal}[c]	Identification[d]	Metabolite	MF[e]	*m/z*[f]	Similarity (%)	Peak area (×10⁶ area units) ± RSD (%)					
									DVB/CAR/PDMS[g]	PDMS[g]	CAR/PDMS[g]	PDMS/DVB[g]	PEG[g]	PA
1	1.42	-	908	MS, RI	Isoprene	C_5H_8	32, 67, 53	96	0.1 ± 7.8	-	0.4 ± 1.2	0.7 ± 1.5	-	-
2	3.92	1007	1016	MS, RI, ST	α-Pinene	$C_{10}H_{16}$	93, 77, 121	93	0.7 ± 9.7	1.0 ± 2.8	0.6 ± 2.9	0.5 ± 2.5	0.1 ± 3.1	0.02 ± 8.2
3	4.77	1075	1057	MS, RI	Camphene	$C_{10}H_{16}$	93, 121, 41	94	0.04 ± 8.7	0.2 ± 9.5	0.1 ± 8.5	0.3 ± 3.2	0.01 ± 5.5	-
4	5.73	1116	1107	MS, RI, ST	β-Pinene	$C_{10}H_{16}$	93, 41, 69	91	2.4 ± 1.2	5.8 ± 3.9	3.0 ± 3.2	3.2 ± 8.0	0.5 ± 2.7	0.1 ± 1.3
5	8.79	1145	1135	MS, RI, ST	β-Myrcene	$C_{10}H_{16}$	93, 69, 41	97	153.3 ± 1.1	191.1 ± 1.7	159.3 ± 1.9	126.7 ± 1.9	27.7 ± 2.5	7.6 ± 5.0
6	9.53	1180	1172	MS, RI, ST	Limonene	$C_{10}H_{16}$	68, 93, 79	93	1.3 ± 1.3	1.1 ± 5.0	1.2 ± 5.0	1.7 ± 7.6	0.3 ± 2.9	0.1 ± 2.1
7	10.01	1185	1182	MS, RI	β-Phellandrene	$C_{10}H_{16}$	93, 77, 136	95	1.1 ± 2.6	0.2 ± 6.8	0.9 ± 5.1	1.1 ± 1.0	-	-
8	11.64	1242	1246	MS, RI	*trans*-β-Ocimene	$C_{10}H_{16}$	93, 79, 41	89	0.1 ± 1.2	0.1 ± 7.4	0.1 ± 1.1	0.1 ± 2.4	0.01 ± 4.2	-
9	11.79	1262	1267	MS, RI, ST	α-Terpinene	$C_{10}H_{16}$	93, 136, 77	91	0.1 ± 1.4	0.1 ± 3.3	0.1 ± 2.6	0.1 ± 2.7	0.01 ± 3.5	-
10	12.48	1274	1279	MS, RI	*cis*-β-Ocimene	$C_{10}H_{16}$	93, 76, 41	92	2.1 ± 1.3	2.6 ± 3.2	2.2 ± 2.5	1.5 ± 2.5	0.2 ± 1.0	0.03 ± 1.3
11	13.15	-	1290	MS, RI, ST	o-Cymene	$C_{10}H_{14}$	119, 32, 134	95	0.1 ± 1.9	0.1 ± 2.7	0.1 ± 1.3	0.04 ± 1.3	0.01 ± 1.2	-
12	13.75	1284	1280	MS, RI	α-Terpinolene	$C_{10}H_{16}$	93, 121, 136	97	0.1 ± 3.4	0.1 ± 3.6	0.1 ± 1.0	0.1 ± 2.8	0.01 ± 1.1	-
13	22.88	1295	1305	MS, RI	Perillene	$C_{10}H_{14}O$	69, 81, 150	96	0.2 ± 1.5	0.2 ± 8.6	0.2 ± 2.9	0.2 ± 2.5	0.03 ± 2.3	-
14	26.07	1476	1481	MS, RI	Ylangene	$C_{15}H_{24}$	105, 119, 161	95	0.4 ± 2.0	0.2 ± 5.8	0.3 ± 2.0	0.2 ± 3.2	-	-
15	26,64	1480	1491	MS, RI	α-Cubebene	$C_{15}H_{24}$	161, 119, 105	91	1.2 ± 2.0	0.8 ± 1.7	0.8 ± 1.6	0.7 ± 3.5	0.1 ± 2.2	0.3 ± 1.6
16	33.62	1663	1621	MS, RI, ST	α-Humulene	$C_{15}H_{24}$	133, 93, 69	96	48.1 ± 7.5	52.8 ± 2.0	41.4 ± 1.5	36.8 ± 3.7	10.9 ± 2.6	3.1 ± 8.0
17	38.63	1657	1665	MS, RI, ST	β-Caryophyllene	$C_{15}H_{24}$	93, 80, 121	93	42.4 ± 4.1	21.3 ± 2.3	16.8 ± 1.9	15.4 ± 3.6	3.6 ± 2.5	1.0 ± 2.2
18	39.90	1681	1687	MS, RI	γ-Muurolene	$C_{15}H_{24}$	161, 105, 119	88	1.7 ± 2.7	1.3 ± 2.8	0.9 ± 1.8	0.8 ± 1.4	0.6 ± 3.3	0.1 ± 1.9
19	41.40	1566	1554	MS, RI	Methyl geranate	$C_{11}H_{18}O_2$	69, 41, 114	90	3.7 ± 1.1	3.1 ± 4.2	1.3 ± 3.1	2.3 ± 2.0	0.4 ± 2.8	0.1 ± 3.2
20	41.89	1724	1713	MS, RI, ST	α-Selinene	$C_{15}H_{24}$	189, 161, 93	92	0.8 ± 9.8	0.2 ± 2.3	0.2 ± 6.8	0.4 ± 4.1	0.2 ± 3.0	0.04 ± 2.3
21	42.50	-	1744	MS, RI	α-Muurolene	$C_{15}H_{24}$	105, 161, 93	89	0.3 ± 2.5	0.3 ± 1.8	0.2 ± 1.6	0.2 ± 4.1	0.1 ± 3.6	0.02 ± 1.4
22	44.59	1749	1740	MS, RI, ST	(+)-δ-Cadinene	$C_{15}H_{24}$	161, 134, 119	89	1.9 ± 2.2	1.6 ± 1.8	1.0 ±1.5	1.0 ± 4.2	0.4 ± 2.6	0.1 ± 1.0
23	45.88	-	1755	MS, RI, ST	Cubenene	$C_{15}H_{24}$	119, 105, 161	93	0.3 ± 5.4	0.2 ± 5.7	0.1 ± 1.2	0.2 ± 4.4	0.1 ± 3.8	0.01 ± 7.1
24	46.60	-	1769	MS, RI	Naphthalene H4,7DM 1R[h]	$C_{15}H_{24}$	105, 161, 91	96	0.2 ± 2.5	0.1 ± 2.1	0.1 ± 2.0	0.1 ± 4.7	0.1 ± 6.3	0.01 ± 9.8
25	48.27	-	1780	MS, RI	β-Fenchene	$C_{10}H_{16}$	79, 32, 67	95	0.1 ± 3.0	0.1 ± 4.6	0.02 ± 2.7	0.04 ± 5.2	0.01 ± 1.1	0.01 ± 1.0
26	49.30	1800	1789	MS, RI, ST	3-Carene	$C_{10}H_{16}$	69, 93, 41	98	0.9 ± 2.5	0.4 ± 1.1	0.3 ± 2.3	0.4 ± 5.0	0.3 ± 1.2	0.04 ± 8.0
27	51.68	1825	1835	MS, RI, ST	*cis*-Geraniol	$C_{10}H_{18}O$	69, 41, 93	92	0.2 ± 2.0	0.1 ± 3.9	0.1 ± 3.2	0.1 ± 2.0	0.1 ± 1.0	-
					Total peak area (×10⁶)				**263.7**	**285.0**	**231.8**	**194.4**	**45.6**	**12.4**
					Average RSD (%)				**3.4**	**3.9**	**2.7**	**3.4**	**2.8**	**3.9**
					No. metabolite by fiber				**27**	**26**	**27**	**27**	**24**	**17**

a) Retention time (min).
b) Kovat's retention index reported in the literature for BP-20 capillary column or equivalents [53].
c) Kovat's retention index relative n-alkanes(C_8–C_{20}) on a BP-20 capillary column.

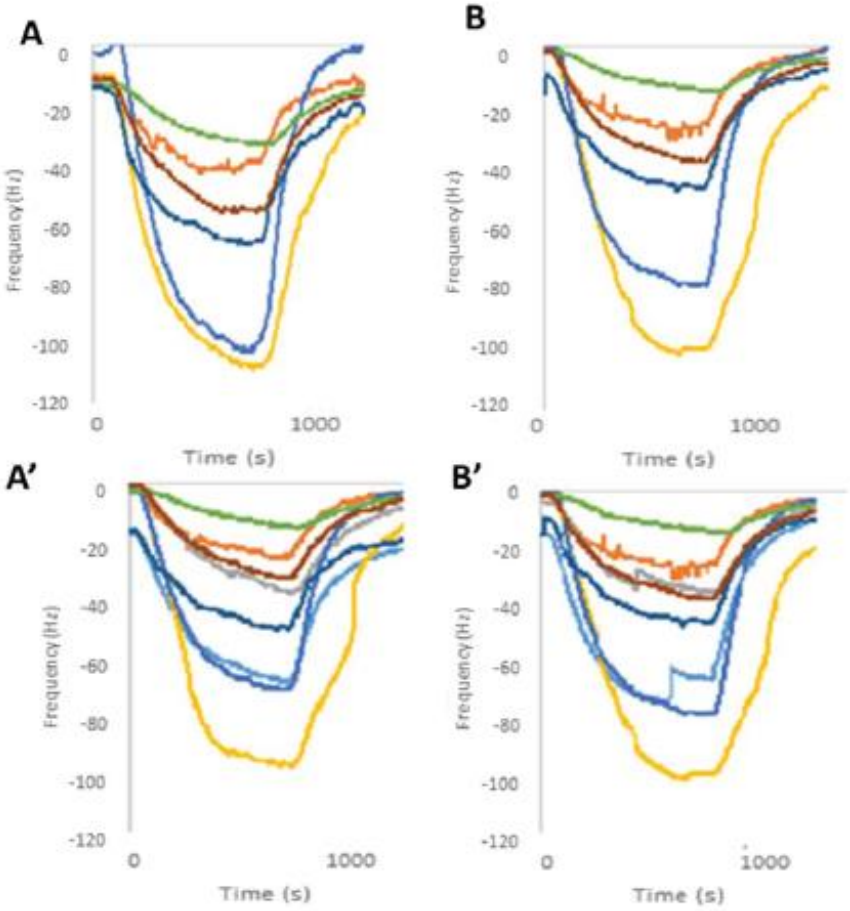
[4] Gallily, R., Yekhtin, Z. and Hanuš, L.O., 2018. The Anti-Inflammatory Properties of Terpenoids from Cannabis. Cannabis and cannabinoid research, 3(1), pp.282-290.

AuNPs-peptide

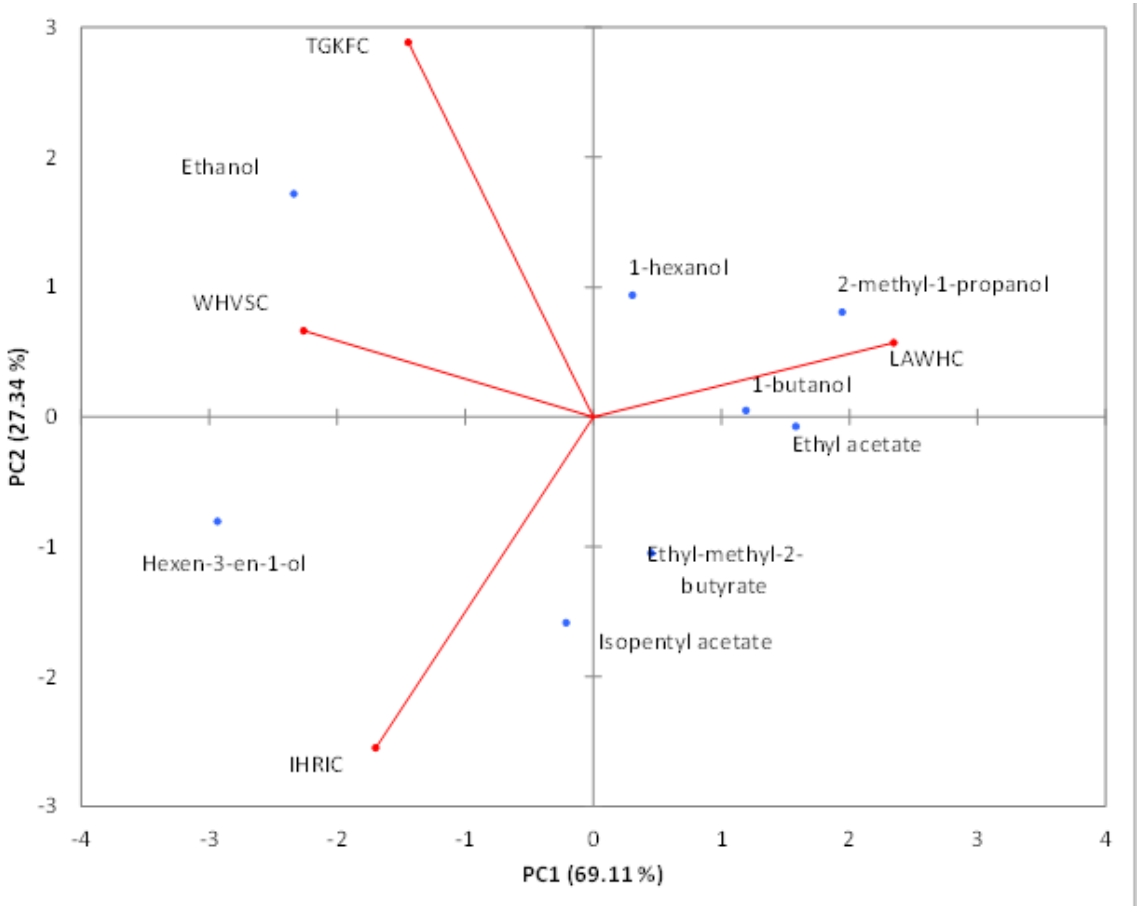


Example of frequency shift of four sequences and 1:9 v/v and 2:8 v/v water/solvent mixtures. A, A' =water/acetonitrile; B,B'=water/methanol; C,C'=water/acetone (yellow = glutathione, grey=TGKF, orange=IHRI, light blue=LGFD .

ZnO-peptide

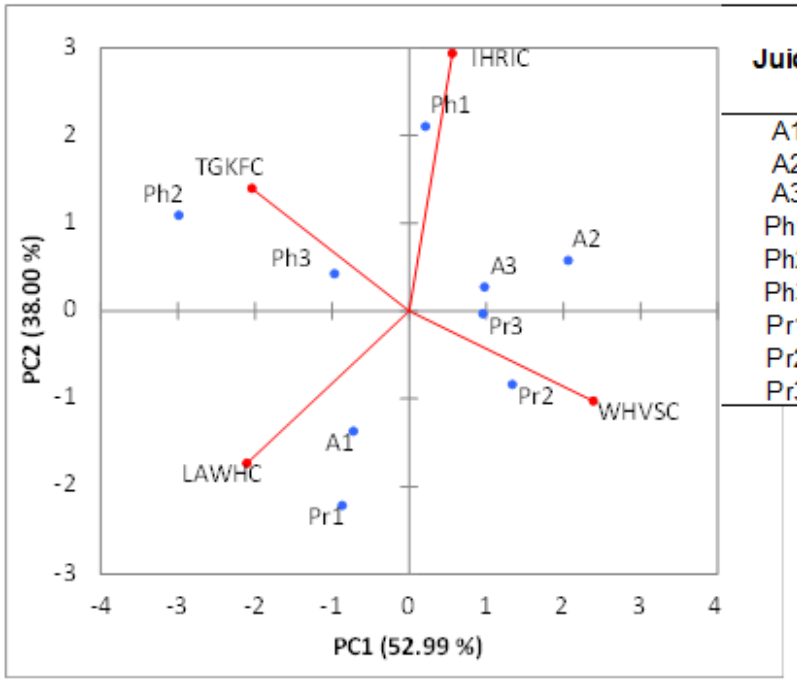


Example of frequency shift of the ZnONPs sensor array with 1:9 v/v and 3:7 v/v water/solvent mixtures. A, A' =water/acetonitrile; B, B'=water/methanol. (Yellow=TGKFC, Light blue=IHRIC, blue=LGFDC, brown=KSDSC; orange=glutathione; green=WHVS; grey=ZnONPs).



PCA of the piezoelectric response. The biplot (Score and loading) of the first two principal components showed 94.45% of the cumulative variance. Rows normalization were applied to the gas sensors array dataset. Data were auto scaled before PCA.

A



B

Juice	Fruit quantity (%)	Sugar (g)
A1	90	14.5
A2	50	13.1
A3	50	13
Ph1	40	14.3
Ph2	40	14
Ph3	40	9.7
Pr1	50	13.3
Pr2	50	14.1
Pr3	50	14.2

(A) The biplot values (sores and loadings) for fruit juices analysis along with the percentage (B) of fruit quantity and sugar concentration in the different fruit juices.

Pasta

- Drying is the most important unit operation in pasta;

- the high-temperature (HT) drying technology has been widely applied by pasta manufacturers;

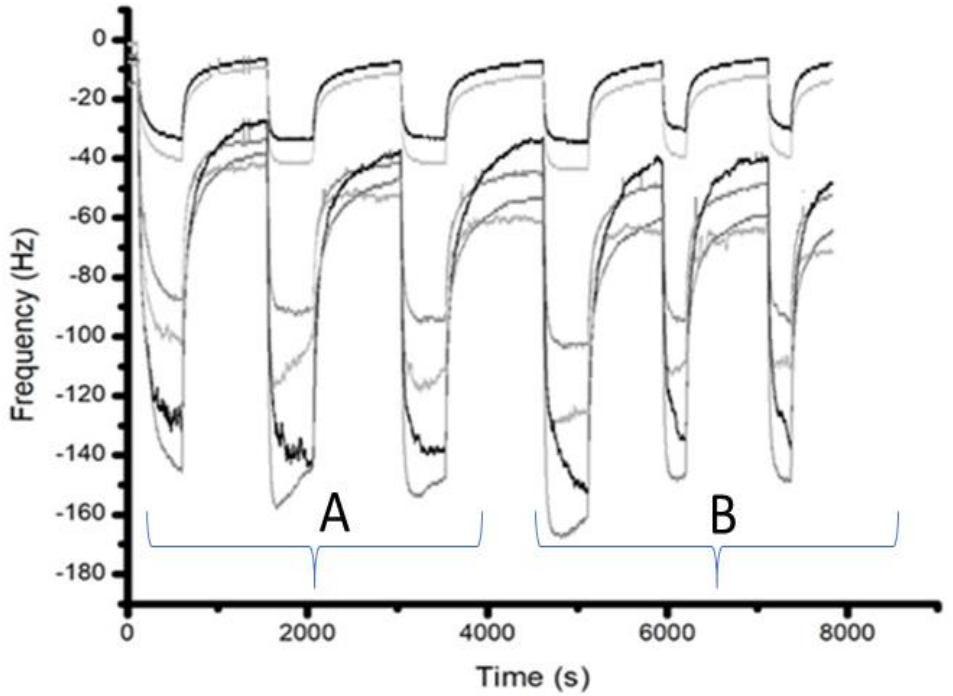
- HT drying has a positive influence on the mechanical properties of pasta;

- To avoid Maillard's reaction as much as possible, it is necessary to monitor volatile compounds, which may be markers of the quality of the finished product.

Volatile compounds																		
	A	A	A	B	B	B	C	C	C	D	D	D	E	E	E	F	F	F
3-methyl-furan	-	-	-	-	-	-	-	-	1±1.15	-	-	-	-	-	-	-	-	-
pentanal	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
lattamide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,3-butanediol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-furanmethanol	-	-	-	-	-	-	-	-	-	1±0.58	-	-	-	7±0.6	-	-	-	-
furfuryl alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
hexanal	24±1.5	30±2.65	23±1.53	15±2.08	41±4.04	7±2.00	-	2±2.08	-	-	2±2.31	11±1.00	3±2.52	-	1±1.53	3±1.15	1±0.58	1±0.58
2-hexenal	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
benzaldehyde	1±1.15	3±1.00	-	2±2.08	7±2.00	2±1.52	-	-	-	-	-	-	-	-	-	-	-	-
4-methylbenzaldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-methylbenzaldehyde	-	-	-	-	-	-	-	-	-	3±1.00	-	-	-	10±1.52	6±1.00	4±0.57	5±1.15	6±1.00
2-pentylfuran	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
nonanal	6±1.00	3±1.52	13±1.53	15±4.50	10±1.00	5±4.00	2±1.52	2±1.15	4±2.00	4±1.52	1±1.15	5±2.00	4±1.52	-	-	-	-	-
2-nonenal	10±2.00	7±0.57	4±3.51	5±3.00	1±1.00	-	-	-	-	-	-	1±1.52	-	-	-	-	-	-
decanal	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7±4.5
3,7-dimethyl-1-octanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,2,4,4-tetramethyltetrahydrofuran	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1±1.53	1±2.08	1±1.33	15±3.51
2-isopropyl-5-methyl-1-heptanol	-	-	-	-	-	-	-	-	-	-	-	-	3±3.00	6±0.57	6±1.18	9±3.00	10±3.08	14±3.05
2-butyl-1-octanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,1-dodecanediol	-	1±0.59	-	1±1.53	2±3.05	-	-	-	-	-	-	1±1.15	-	-	-	-	-	-

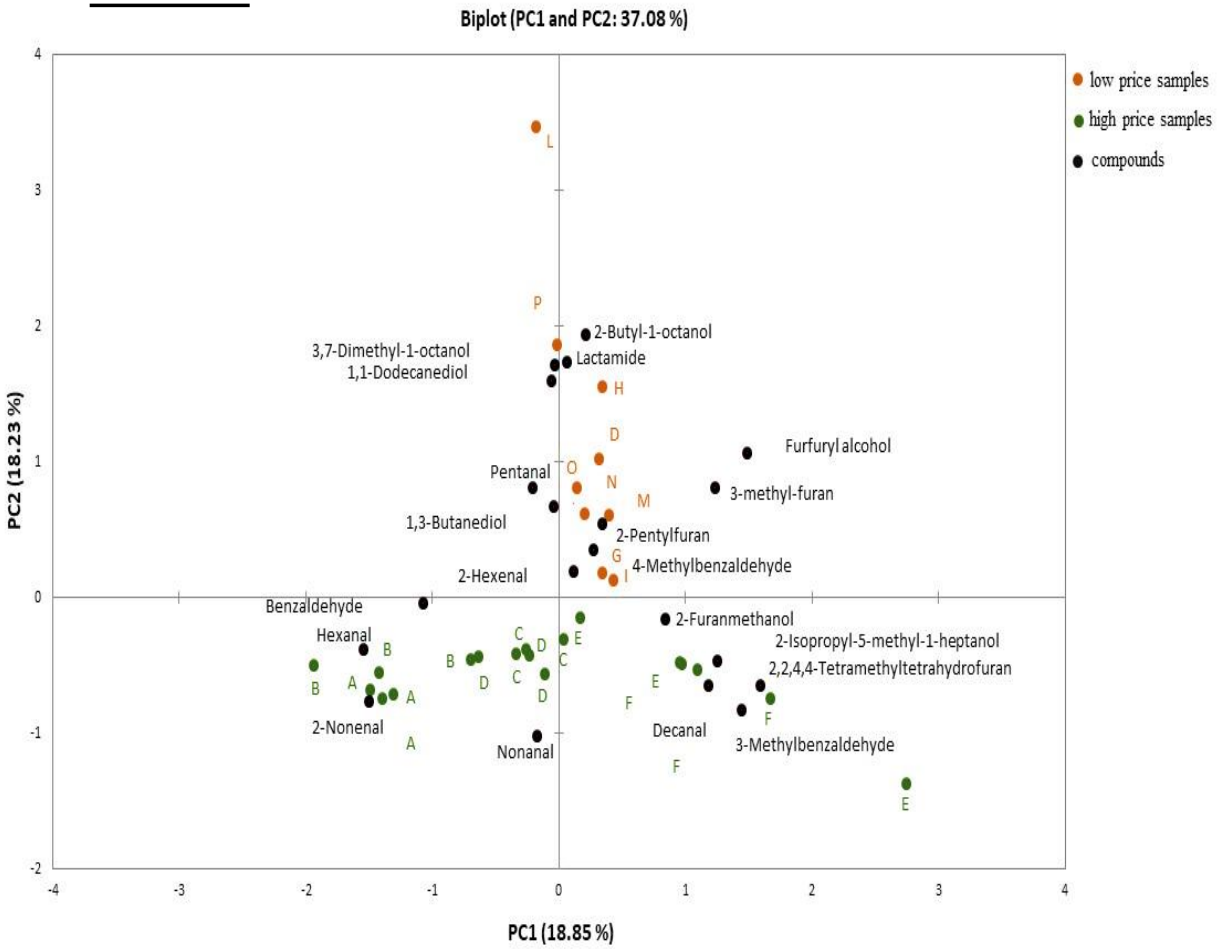
Volatile compounds of high-price pasta samples. Data were expressed as % of the total GC area.

Volatile Compounds		WHVSC	IHRIC	TGKFC	KSDSC	LAWHC	LGFDC
Furfuryl alcohol	Mean	10	11	17	21	20	10
	St.dev.	2	3	3	5	3	2
	RSD-	15	25	18	22	17	15
1,3-butanediol	Mean	9	17	21	20	16	10
	St.dev.	1	2	4	4	4	2
	RSD-	14	13	21	19	23	18
benzaldehyde	Mean	17	32	54	38	26	17
	St.dev.	2	3	4	9	6	2
	RSD-	12	8	8	24	21	9
2-pentylfuran	Mean	2	3	3	8	2	3
	St.dev.	1	1	1	2	1	0
	RSD-	37	39	41	29	35	0
pentanal	Mean	14	36	62	41	36	15
	St.dev.	0	1	3	3	2	1
	RSD-	3	3	5	7	6	4
3-methylbenzaldehyde	Mean	9	4	7	12	7	8
	St.dev.	1	1	6	2	1	1
	RSD-	8	35	81	18	20	9
decanal	Mean	6	14	12	16	16	5
	St.dev.	1	2	1	1	1	1
	RSD-	10	11	8	4	7	11
nonanal	Mean	8	20	14	24	23	8
	St.dev.	1	4	2	1	2	1
	RSD-	13	18	11	2	9	13
2-nonenal	Mean	10	32	20	32	35	11
	St.dev.	1	3	3	2	3	1
	RSD-	6	11	13	5	9	5
hexanal	Mean	15	52	36	53	55	16
	St.dev.	2	4	3	5	2	1
	RSD-	10	7	7	9	4	6



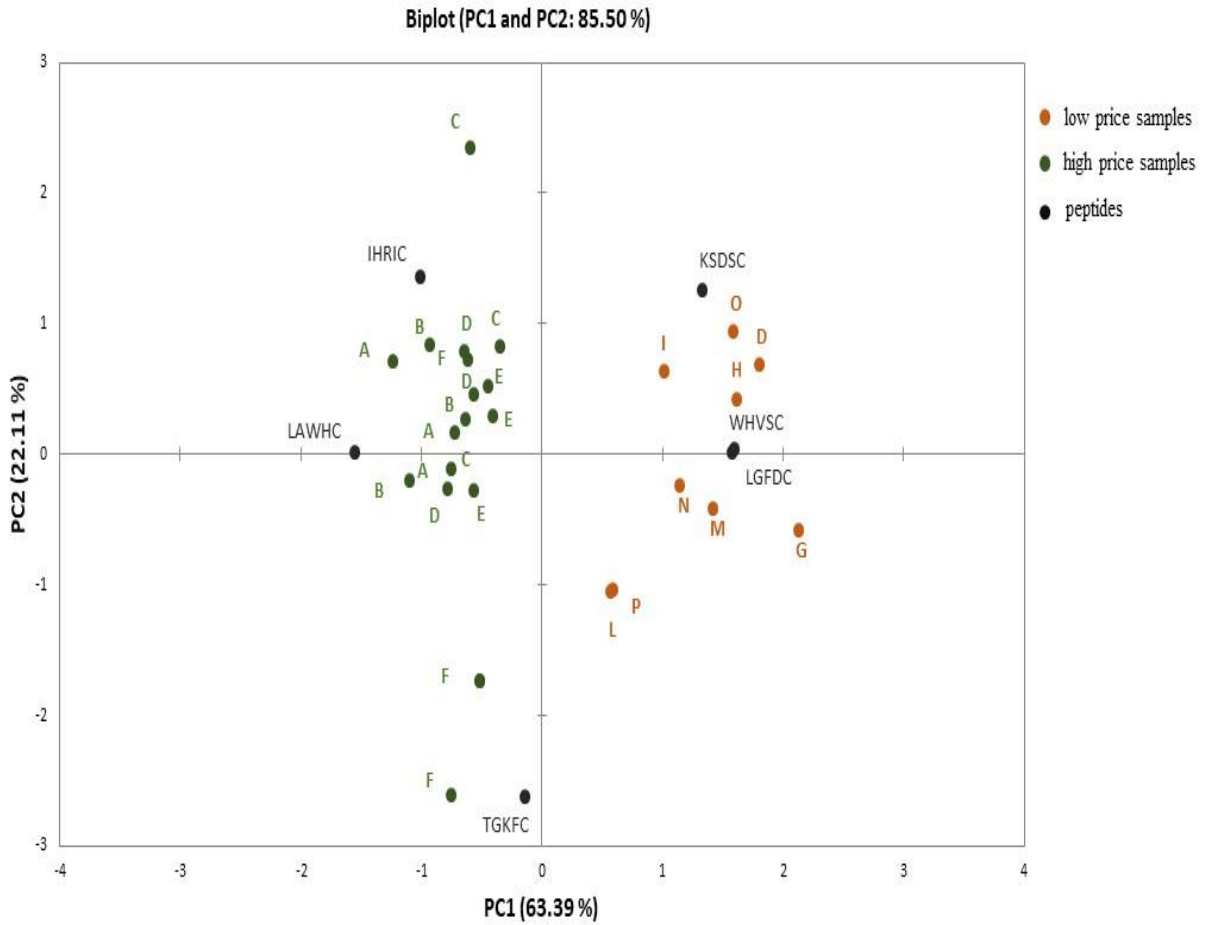
Typical replicate measurement of pasta sample with ZnO-peptides based E-nose. A and B were a single batch of different pasta samples at high price.

GC-MS



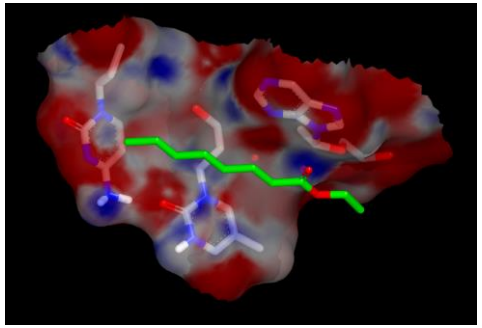
PCA of the GC-MS response for low price samples (orange) and high price samples (green). The biplot (Score and loading) of the first two principal components showed 37.08% of the cumulative variance. Data were expressed in (R.A. %) before PCA

E-nose



PCA biplot (score and loading) of the normalized piezoelectric response of the gas sensors.

Virtual screening method



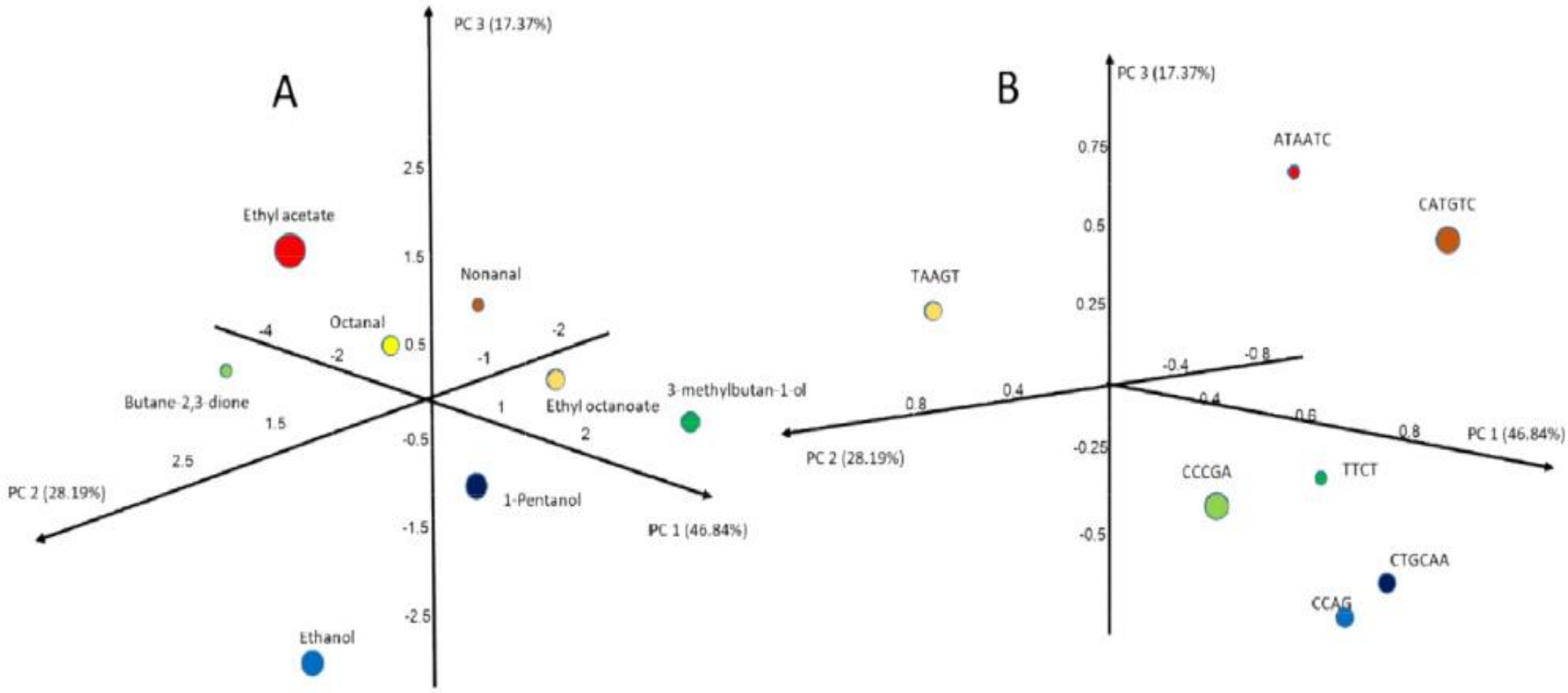
Electrostatic molecular surfaces of the ssDNA CTGCAA, with a planar interaction surface (binding score -2.26 Kcal/mol)

	CCAG	TTCT	CCCGA	TAAGT	ATAATC	CATGTC	CTGCAA
Ethanol	−2.72 ± 0.16	−2.41 ± 0.17	−2.77 ± 0.28	−2.28 ± 0.23	−3.21 ± 0.29	−3.09 ± 0.28	−3.24 ± 0.32
3-methylbutan-1-ol	−3.23 ± 0.29	−2.77 ± 0.17	−3.26 ± 0.20	−2.74 ± 0.19	−4.63 ± 0.23	−4.12 ± 0.29	−2.72 ± 0.19
1-pentanol	−3.30 ± 0.23	−3.22 ± 0.32	−3.53 ± 0.32	−2.48 ± 0.20	−5.14 ± 0.36	−4.21 ± 0.42	−2.82 ± 0.14
Alcohols	***−2.94 ± 0.15***	***−3.12 ± 0.16***	***−3.38 ± 0.30***	***−2.39 ± 0.12***	***−5.55 ± 0.28***	***−4.75 ± 0.38***	***−3.01 ± 0.21***
Octanal	−2.39 ± 0.19	−3.07 ± 0.15	−2.62 ± 0.16	−1.54 ± 0.08	−5.13 ± 0.26	−3.71 ± 0.22	−2.40 ± 0.22
Nonanal	−2.32 ± 0.16	−3.24 ± 0.26	−2.56 ± 0.26	−1.53 ± 0.09	−5.54 ± 0.44	−4.05 ± 0.36	−2.56 ± 0.26
Aldehydes	***−2.25 ± 0.18***	***−2.78 ± 0.28***	***−2.42 ± 0.22***	***−1.55 ± 0.14***	***−4.67 ± 0.23***	***−3.39 ± 0.17***	***−2.27 ± 0.14***
Ethyl acetate	−2.17 ± 0.15	−2.19 ± 0.15	−2.49 ± 0.22	−1.51 ± 0.14	−3.64 ± 0.18	−2.68 ± 0.16	−1.90 ± 0.17
Ethyl octanoate	−1.95 ± 0.14	−3.14 ± 0.16	−2.49 ± 0.17	−1.46 ± 0.07	−6.28 ± 0.57	−4.20 ± 0.38	−2.26 ± 0.11
Esters	−2.19 ± 0.20	−2.73 ± 0.22	−2.53 ± 0.23	−1.58 ± 0.16	−4.60 ± 0.23	−3.37 ± 0.24	−2.26 ± 0.14
Butane-2,3-dione	−2.02 ± 0.14	−2.51 ± 0.15	−1.88 ± 0.11	−1.44 ± 0.09	−3.13 ± 0.28	−2.17 ± 0.17	−1.95 ± 0.14
Ketones	−1.84 ± 0.15	−2.17 ± 0.11	−1.94 ± 0.16	−1.24 ± 0.12	−3.55 ± 0.18	−2.43 ± 0.15	−1.81 ± 0.16

Binding score average (Kcal/mol) of the tetramer, pentamer and hexamer DNA versus the VOCs tested in experimental part. In italic-bold, the binding score obtained by the simulations of the ssDNA versus the chemical classes (14 alcohols, 13 aldehydes, 18 esters and 5 ketones). The average and standard deviation was calculated over 10 conformers.

	CCAG	TTCT	CCCGA	TAAGT	ATAATC	CATGTC	CTGCAA
	Experimental K binding $\times 10^3$ ($Moles^{-1}$)						
Ethanol	4.3 ± 0.6	2.3 ± 0.1	7.4 ± 0.5	0.9 ± 0.1	6.5 ± 0.5	8.4 ± 0.8	18.4 ± 2.8
3-methylbutan-1-ol	6.7 ± 0.5	6.5 ± 0.6	23.6 ± 3.3	7.0 ± 0.6	91.2 ± 11.9	70.1 ± 3.5	21.7 ± 2.2
1-pentanol	3.3 ± 0.4	3.1 ± 0.3	60.3 ± 7.8	2.0 ± 0.1	530.6 ± 58.4	352.8 ± 17.6	10.3 ± 1.3
Octanal	2.6 ± 0.3	6.3 ± 0.6	4.7 ± 0.3	2.5 ± 0.1	582.2 ± 81.5	348.0 ± 41.8	3.8 ± 0.3
Nonanal	2.6 ± 0.2	7.9 ± 0.6	6.5 ± 0.8	1.9 ± 0.1	283.1 ± 14.2	97.9 ± 8.8	4.8 ± 0.4
Ethyl acetate	0.9 ± 0.1	2.4 ± 0.3	9.8 ± 1.5	3.1 ± 0.4	19.6 ± 1.2	17.8 ± 2.3	0.9 ± 0.0
Ethyl octanoate	8.8 ± 0.8	12.8 ± 0.6	43.1 ± 4.3	2.5 ± 0.2	519.2 ± 41.5	345.8 ± 17.3	6.9 ± 0.5
Butane−2,3-dione	1.4 ± 0.2	3.4 ± 0.3	2.9 ± 0.3	3.4 ± 0.4	9.2 ± 1.1	4.1 ± 0.3	2.5 ± 0.4
Correlation with Simulated results	0.16	0.63	0.65	0.37	0.83	0.67	0.80

HpDNA-AuNP sensors relative binding affinities vs the VOCs, estimated using piezoelectric response. The correlation coefficient between experimental and simulated binding is reported in the last row. The standard deviation was calculated using three measurements taken in three different days.



PCA of the piezoelectric responses of hpDNA-AuNP sensors obtained using 900 µmoles of each VOC. The plot of Scores (A) and the plot of loading (B) of the first three principal components showed 92.40% of the cumulative variance. Data were autoscaled before PCA.

- Monitoring and control of vegetable ripening are important parameters in the food industry, since the maturation state during harvest, storage and distribution on the market defines the quality of the finished product;

- To prevent enzymatic reactions during processing, storage and thawing, the packaged carrots were blanched at 95 °C for 8 min in a water bath

- 3 g of blanched carrots were placed in 20 ml gas-tight vials and hermetically sealed with a gas-tight septum. A total of 24 vials were prepared for each temperature tested (-18 °C, 4 °C, 25 °C, 40 °C), in order to have three replicates (three different vials) for each day of measurement (1, 4, 8, 12, 19, 26 days). Thus, a total of 140 vials for E-nose and GC-MS have been analyzed. Each vial was used only once for either the GC-MS or E-nose measurement and the relative sample was discarded.

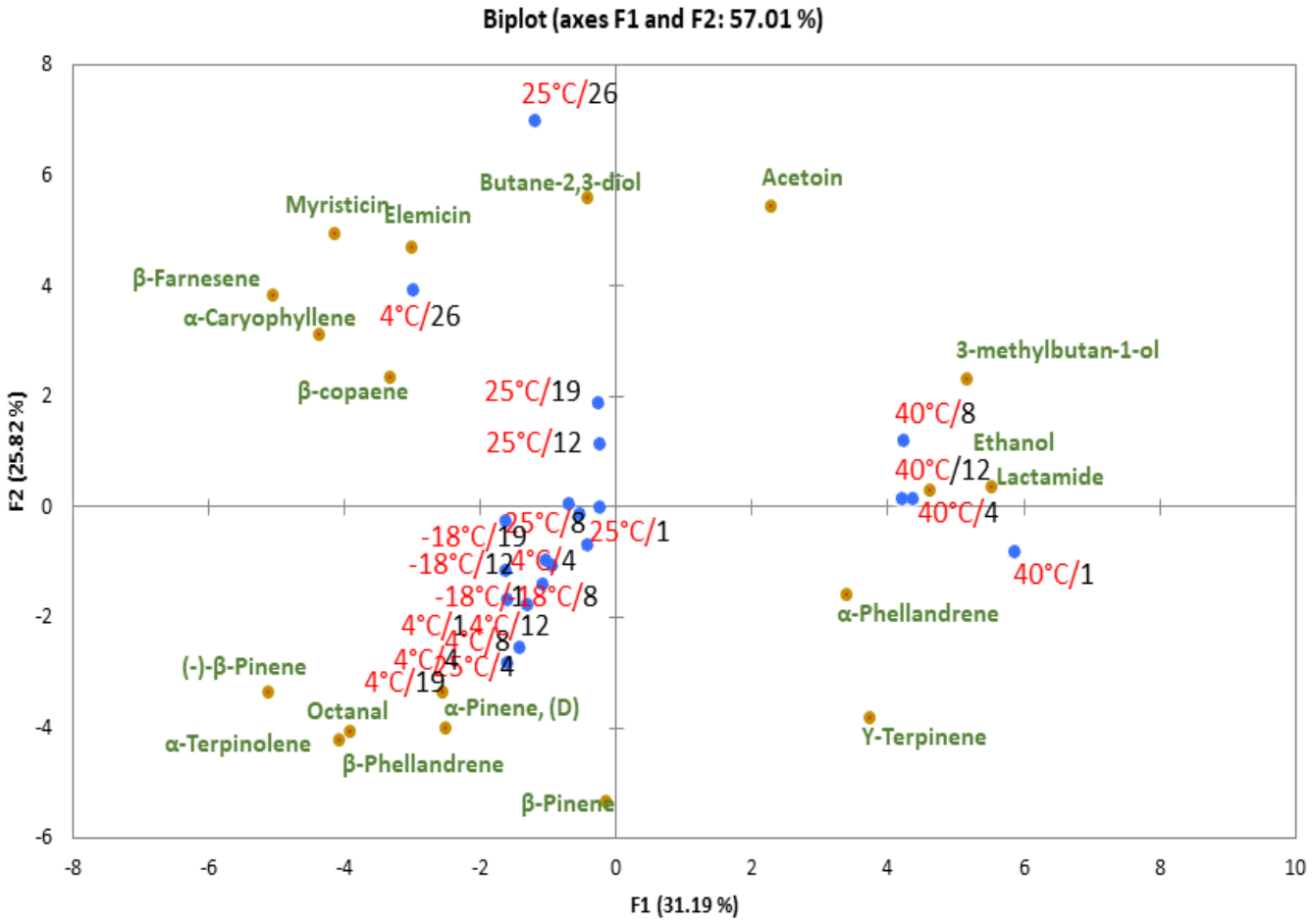
	GC area (%)																			
	Storage time (days)																			
	-18 °C					4°C						25 °C						40 °C			
Volatile compounds	1	4	8	12	19	1	4	8	12	19	26	1	4	8	12	19	26	1	4	8	12
α-phellandrene	n.d	n.d	n.d	n.d	n.d	1	1	1	1	1	n.d	n.d**	1	n.d	n.d	1	n.d	7	1	n.d	n.d
β-phellandrene	2	1	2	1	1	3	3	2	1	4	1	n.d	3	1	1	2	n.d	n.d	n.d	n.d	n.d
terpinolene	n.d	n.d	1	1	0	1	1	1	n.d	1	n.d	n.d	1	n.d	n.d	1	n.d	n.d	n.d	n.d	n.d
α-pinene	14	9	12	12	10	14	12	14	14	18	8	12	7	12	11	15	2	n.d	10	15	5
(-) -β-pinene	3	2	3	3	3	3	3	3	3	3	2	2	3	2	2	3	1	n.d	n.d	n.d	2
β-pinene	3	2	3	2	6	5	6	3	3	5	1	2	6	1	1	4	n.d	5	3	3	2
Octanal	1	1	n.d	n.d	n.d	1	1	1	1	n.d	n.d	1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
γ-terpinene	7	8	9	10	7	8	9	7	8	4	1	12	7	6	5	7	n.d	21	9	9	5
β-farnesene	1	1	1	1	1	1	1	1	1	n.d	1	1	1	1	1	1	2	n.d	n.d	n.d	n.d
α-caryophyllene	1	1	1	1	2	2	1	1	1	1	5	1	2	1	2	1	2	n.d	n.d	n.d	n.d
β-copaene	2	2	2	n.d	4	2	2	3	n.d	n.d	n.d	2	1	2	2	2	5	n.d	n.d	n.d	n.d
myristicin	1	1	1	1	2	1	1	1	1	1	5	2	1	2	n.d	1	4	n.d	n.d	n.d	n.d
elemicin	n.d	1	n.d	n.d	n.d	n.d	n.d	1	n.d	n.d	4	1	n.d	1	1	n.d	2	n.d	n.d	n.d	n.d
butane-2,3-diol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2	2	5	13	n.d	n.d	n.d	3
acetoin	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	9	3	6	15	5	3	5	6
ethanol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	5	n.d	n.d	6
lactamide	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	4	11	16	7
3-methylbutan-1-ol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1	2	1	3	3	3

*(mean value of n=3 repetitions); **n.d.: not detected.

Results of the gas-chromatographic (GC) analysis of the headspace of carrots samples. Data are expressed as % of the total GC area*.

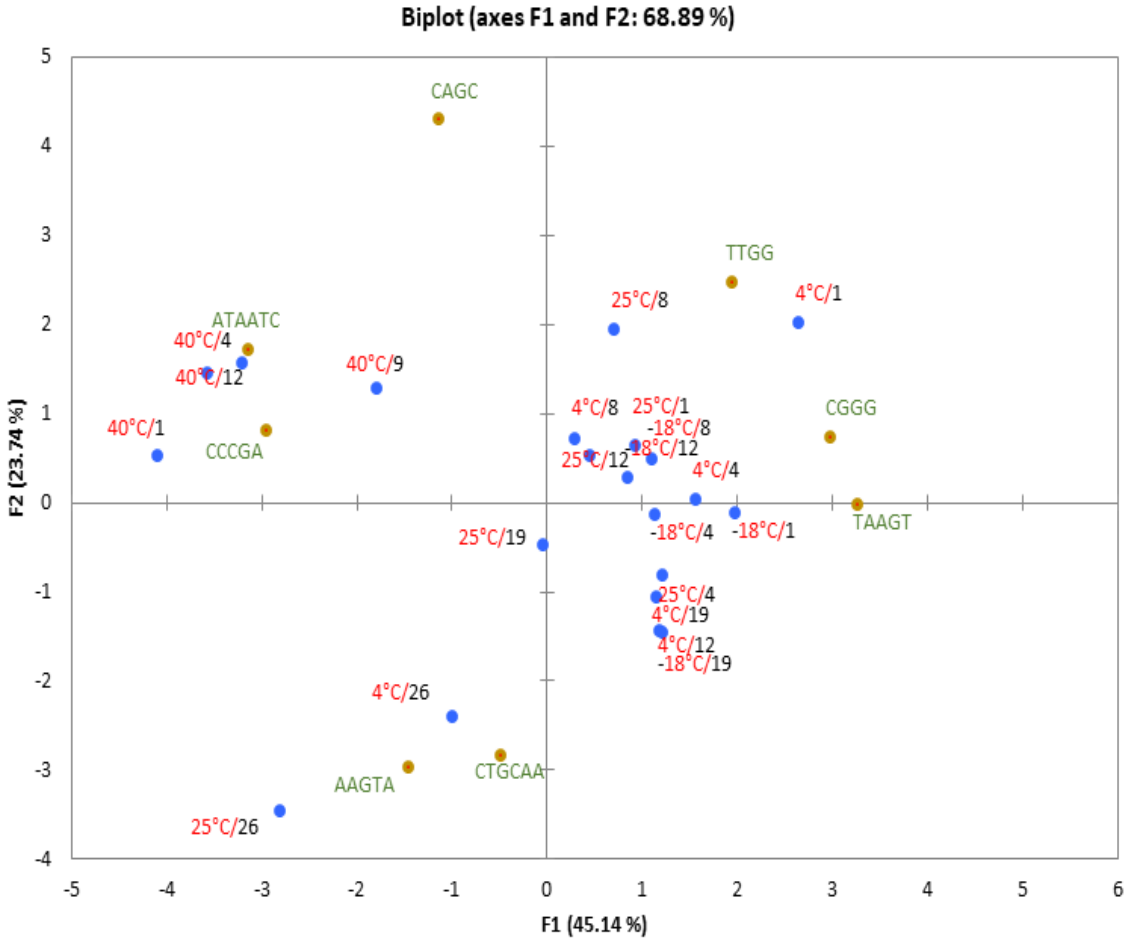
Frequency signal recorded with AuNPs-hpDNA testing carrots samples in triplicate

GC-MS



PCA of the GC-MS/SPME response of carrot samples stored for different time at various temperature. Data are expressed in (Relative Abundance %) before PCA

E-nose



PCA biplot (scores and loadings) of the E-nose response to carrots samples. Data were normalized before PCA