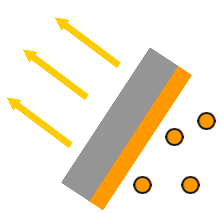
What are sensors and biosensors?

"…a biosensor is a self-contained integrated device, which is capable of providing specific quantitative or semiquantitative analytical information using a biological recognition element (biochemical receptor) which is retained in direct spatial contact with a transduction element."

Technical report " Reccomended definition and classification" IUPAC (Physical Chemistry and Analytical Chemistry Divisions) 2001

A *sensor* is a device able to transform a physical or chemical info (e.g. concentration of one or more compounds in a solution), into an analytical useful signal

Useful signal



analita

Molecular binding system

Chemical sensing

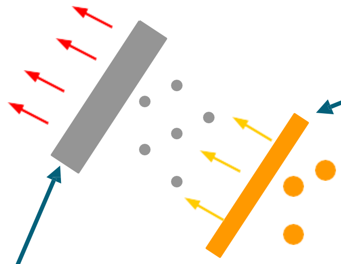
Biological interaction

Biosensors are chemical sensors nwhich the binding element is a biological molecule

Self-testing

Numbers:
- 85% of the global market for biosensors
- 70 million tests per day worldwide
- 15 billion $ in 2015
- 30 billion $ in 2024 (exp.)

The biological element translates the info of the biochemical domain (e.g. concentration) into a chemical or physical signal with a certain selectivity



Biological binding system

- selectivity
- sensitivity

Transducing element

Tranducers
- electrochemical
- optical
- piezoelectric
- thermal

- potentiometric
- amperometric
- voltammetric
- conduttimetric, impedimetric

Classification of biosensors on the basis of the biological element

Catalytic biosensors

catalysis of a chemical reaction

ex: enzymes, cells, tissues

Affinity biosensors

formation of a stable complex with the ligand

ex: antibodies, DNA strands, proteic receptors

Biomimetic biosensors

affinity biosensors using a synthethic receptor

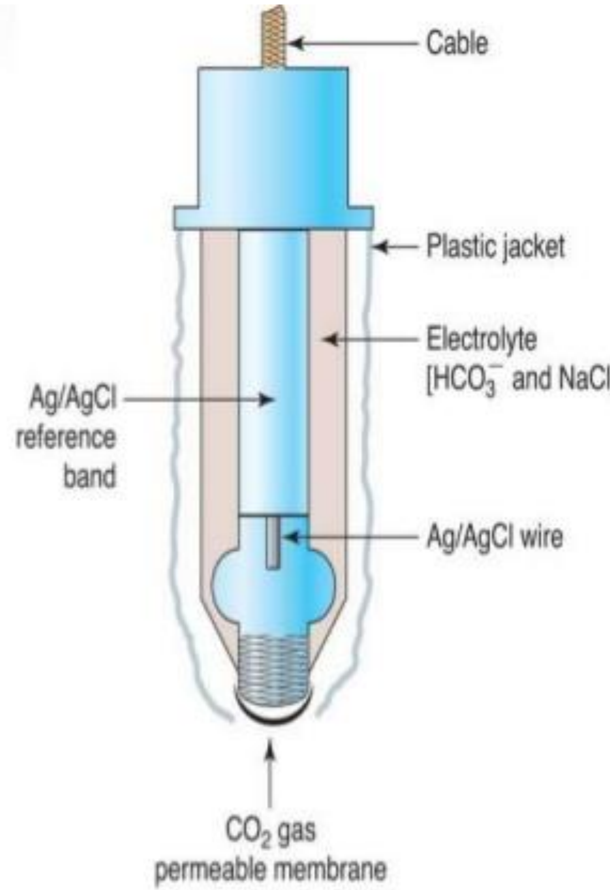
es: peptides, aptamers, molularly imprinted polymers

Ion selective electrodes for biosensors

The most used ISEs for the development of biosensors have been CO_2 and NH_3 probes.
This potentiometric gas-sensors are realised using a pH glass electrode and a reference behind a gas permeable membrane (polytetrafluoroethilene, polypropylene, etc.). A very thin film of a suitable electrolyte is present between the gas permeable membrane and the surface of the pH electrode. Hydrolysis of NH_3 or CO_2 (diffused from the sample) in the electrolyte causes a change in H^+ that is measured at the electrode.
This is related to the partial pressure of the gas in the sample solution. Immobilisation of a suitable enzyme onto the surface leads to the detection of metabolites in the 10^{-5} – 10^{-2} mol/L range.

PCO_2 ELECTRODE

- Measurement of PCO_2 in routine blood gases
- A modified pH electrode with a CO_2 permeable membrane covering the glass membrane surface
- A bicarbonate buffer separates the membranes
- Change in pH is proportional to the concentration of dissolved CO_2 in the blood



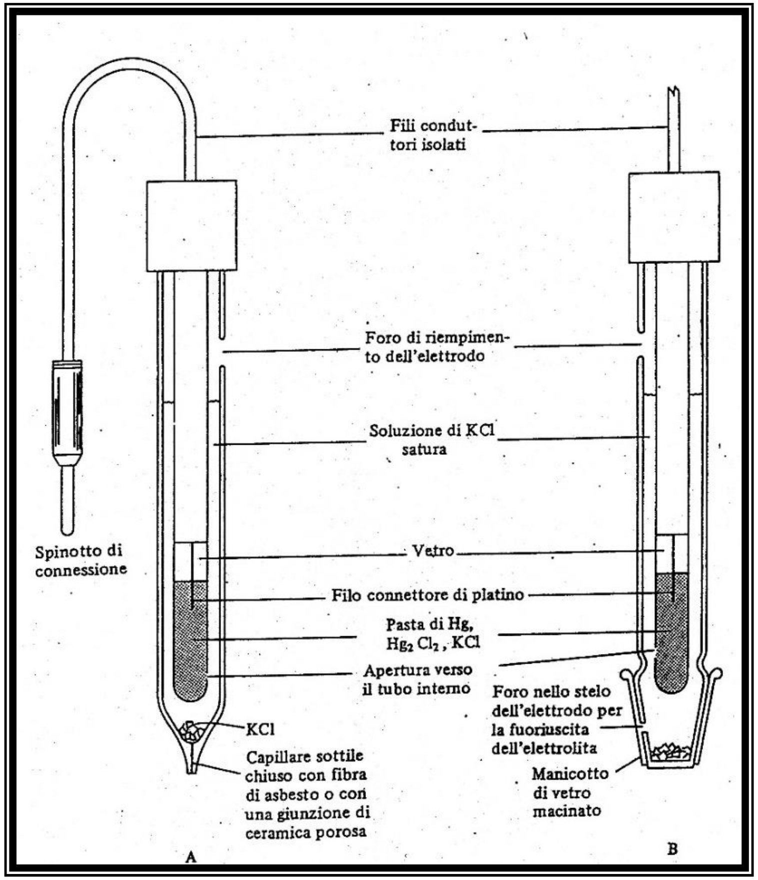
Reaction occuring in the electrolyte solution:

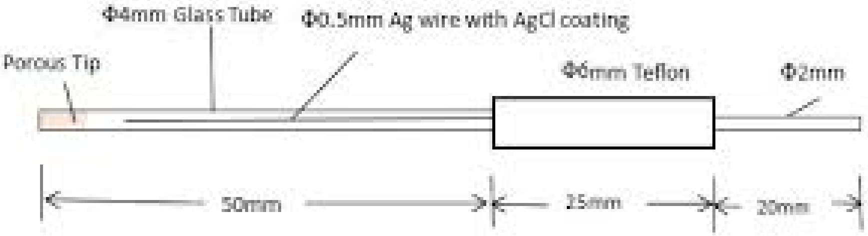
$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Reference electrodes

Ag/AgCl

calomel





CS901 Ag/AgCl Reference Electrode

Amperometric sensors monitor the current flow when a selected fixed potential is applied at a working electrode with respect to a reference electrode. The current generated by the oxidation (or reduction) of a compound is dependent by:

- **heterogeneous rate constant k**
- **diffusion (mass transfer) of the electroactive specie at the electrode surface**
- **preceding or following chemical reactions**
- **surface reactions (adsorption)**

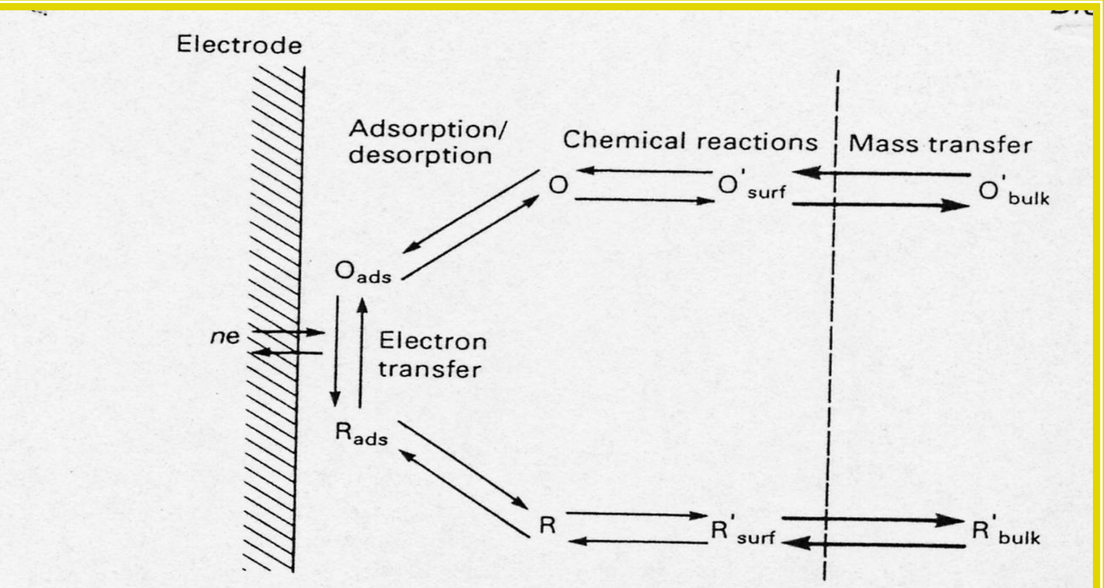
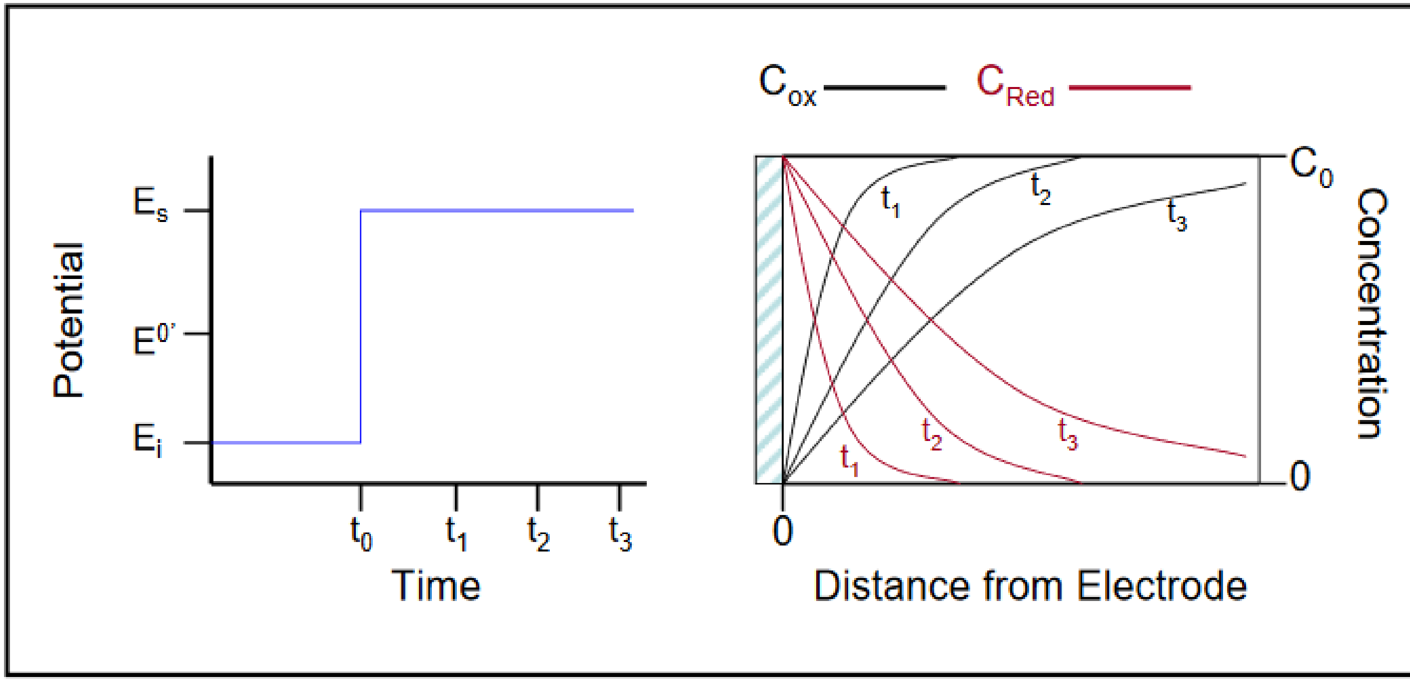


Fig. 5.4 Pathway of surface processes involved in a general electrode reaction.



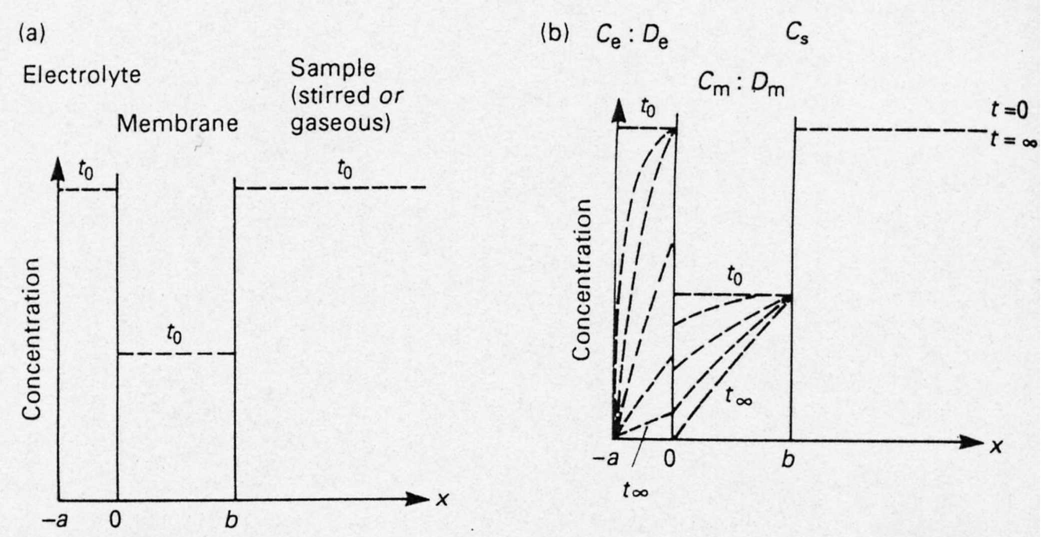
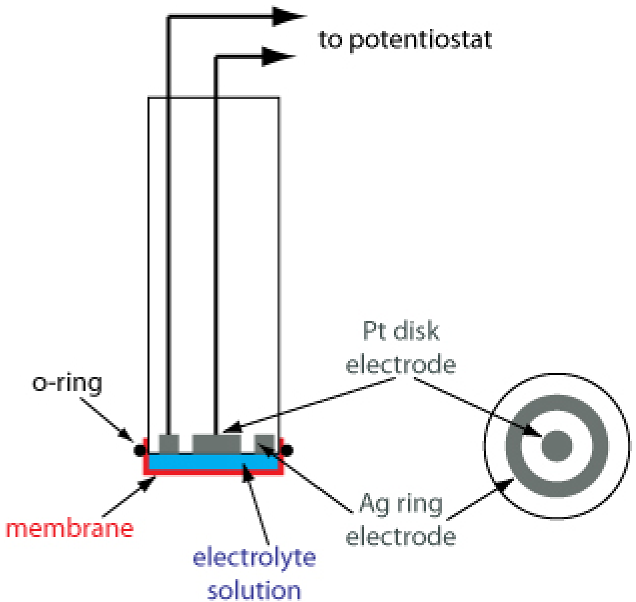
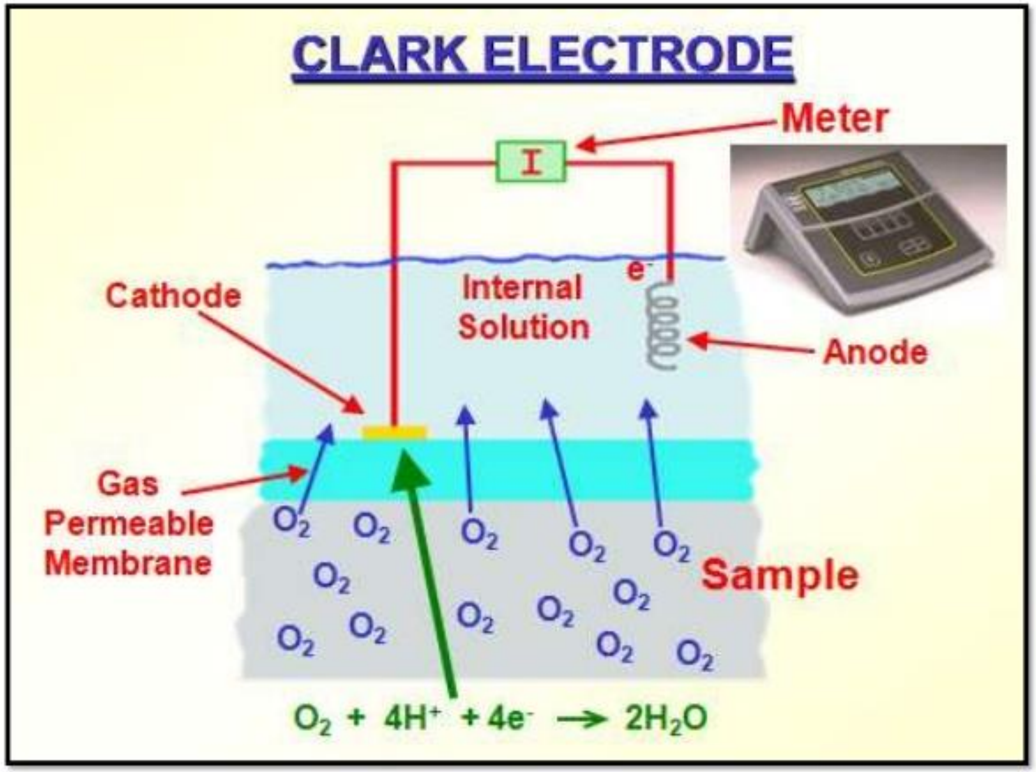


Fig. 5.8 Concentration profiles for a membrane-covered electrode. (a) The initial profile; (b) the development of concentration gradients through the different phases during attainment of steady state.





Applied potential
-0.7 V vs. Ag/AgCl

Dissolved Oxygen Electrode /Sensor
Industrial Type Model : MS DO 714

OXYGEN PROBE

The cathode should possess: high catalytic activity for the reduction of O_2 , (large exchange current) , sufficient electrical conductivity (low adsorption of organic impurities or O_2),it should be inert , it should exhibit a large overvoltage for the decomposition of water (no hydrogen liberation), it should permit the required construction operation (e.g. sealing into glass)

Pt and Au are the most used materials

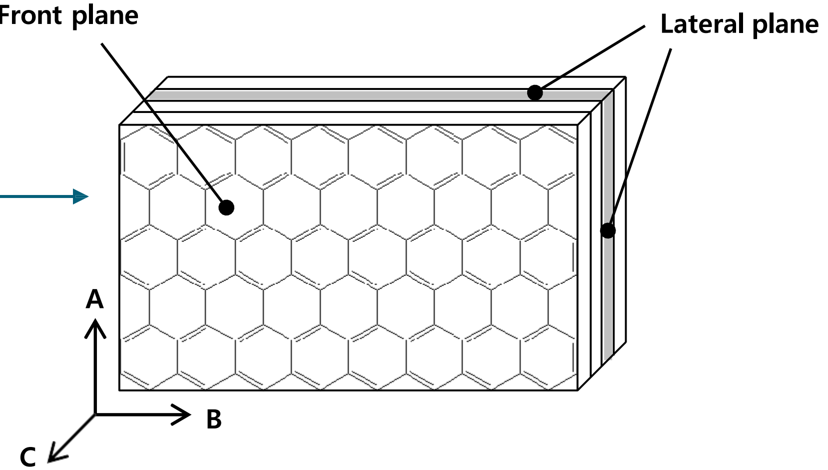
The gas permeable membrane protects the electrodes from contamination, provides for reproducible conditions of oxygen tranport and minimize undesirable changes in electrolyte composition. Ideally, it shoud be with low permeability and high diffusivity for oxygen.

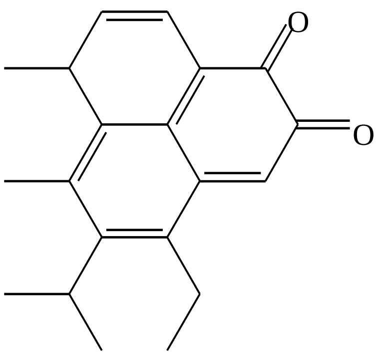
Non-hydratable polymers as polytetrafluoroethylene (PTFE), polypropylene (PP) and polyethylene (PE) are generally used. Alternatively elastic rubber or silicone are useful, even though less stable in alkaline medium.

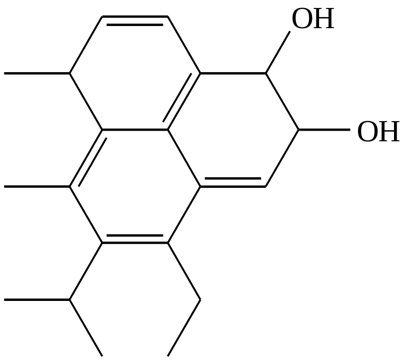
The anode is Ag/AgCl and a neutral or alkaline electrolyte is used in the final assembling.

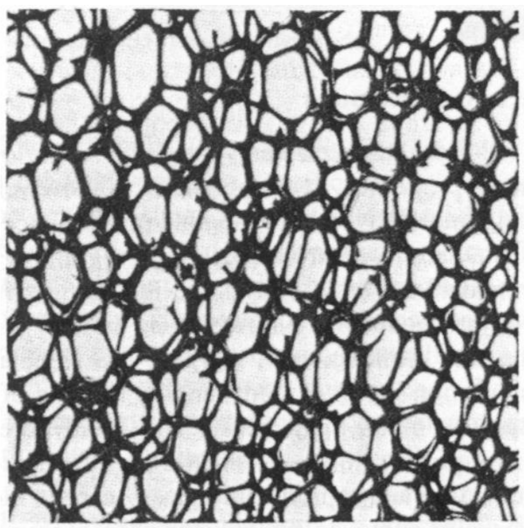
Conventional carbon based probes:

- graphite
- carbon paste
- pyrolitic graphite
- glassy carbon

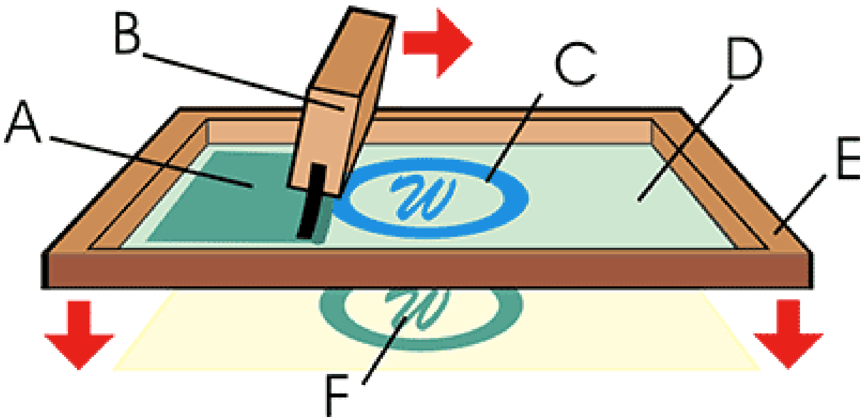








Printing electrodes: serigraphy

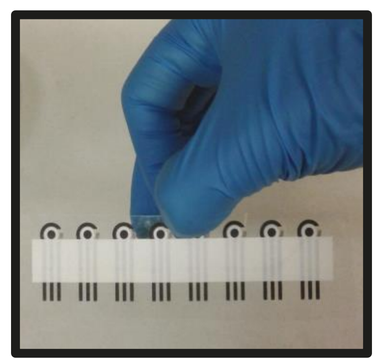


A. ink; B. squeege;

C. printing mask;

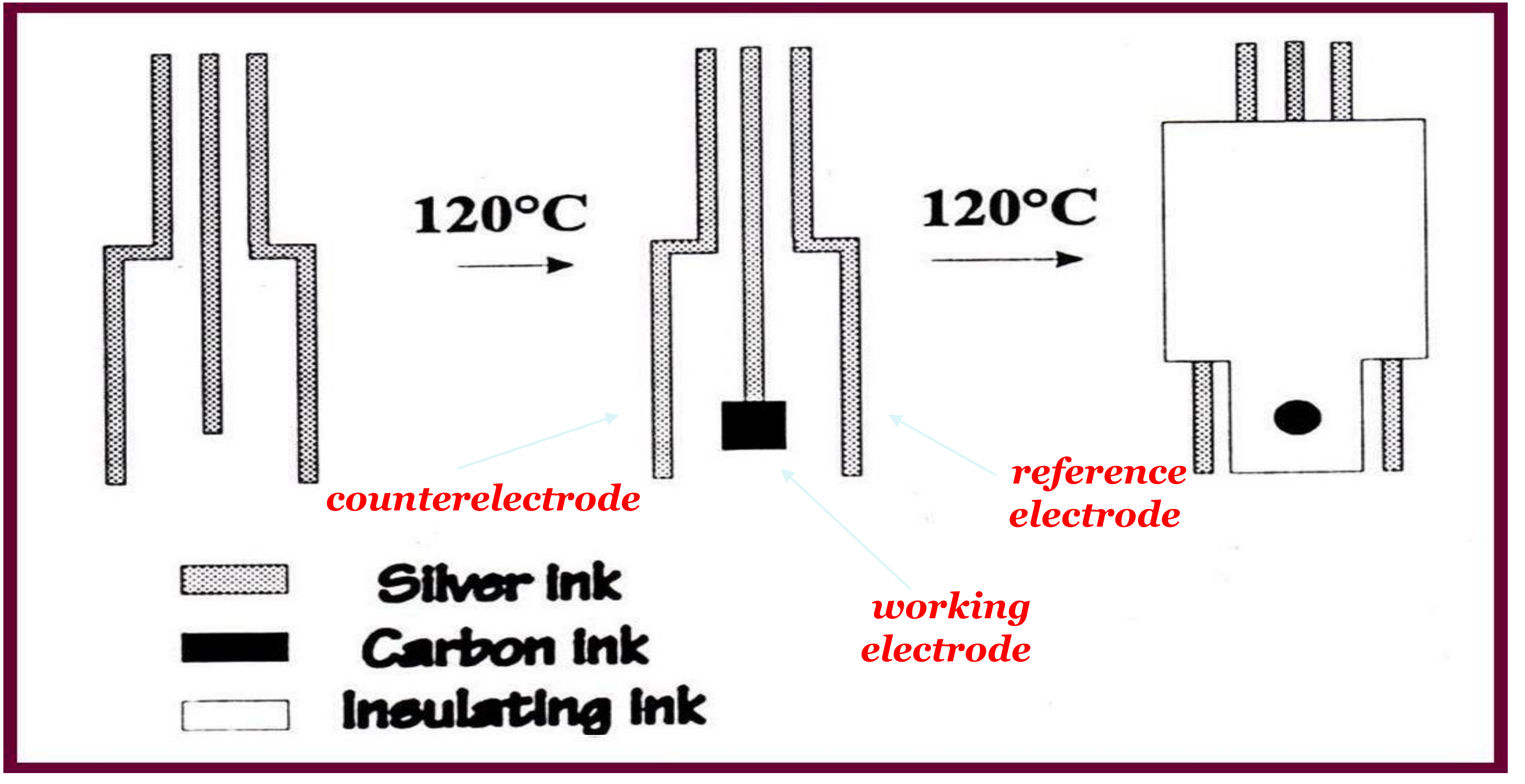
D. printing mesh;

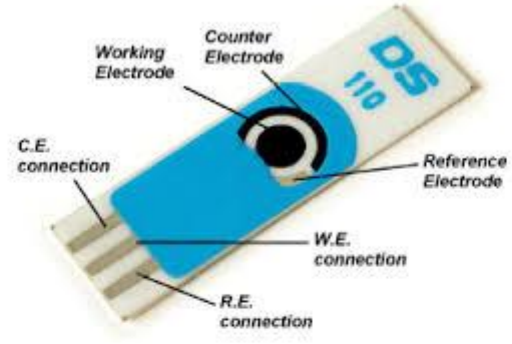
E. frame; F. printed ink



Advantages:
- Dimension
- Disposable
- Low-Cost

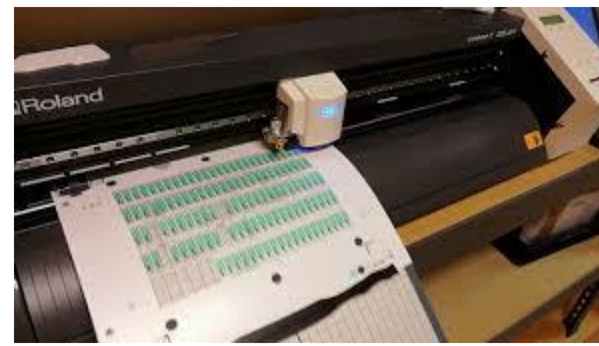
DISPOSABLE SCREEN-PRINTED CARBON ELECTRODES

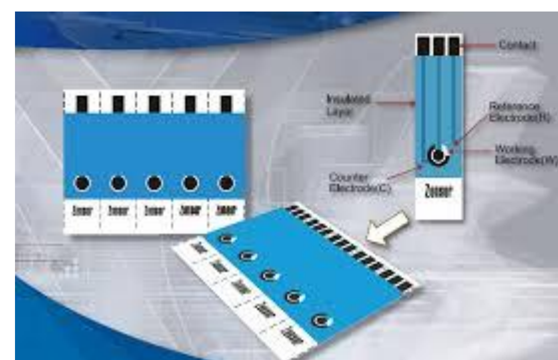


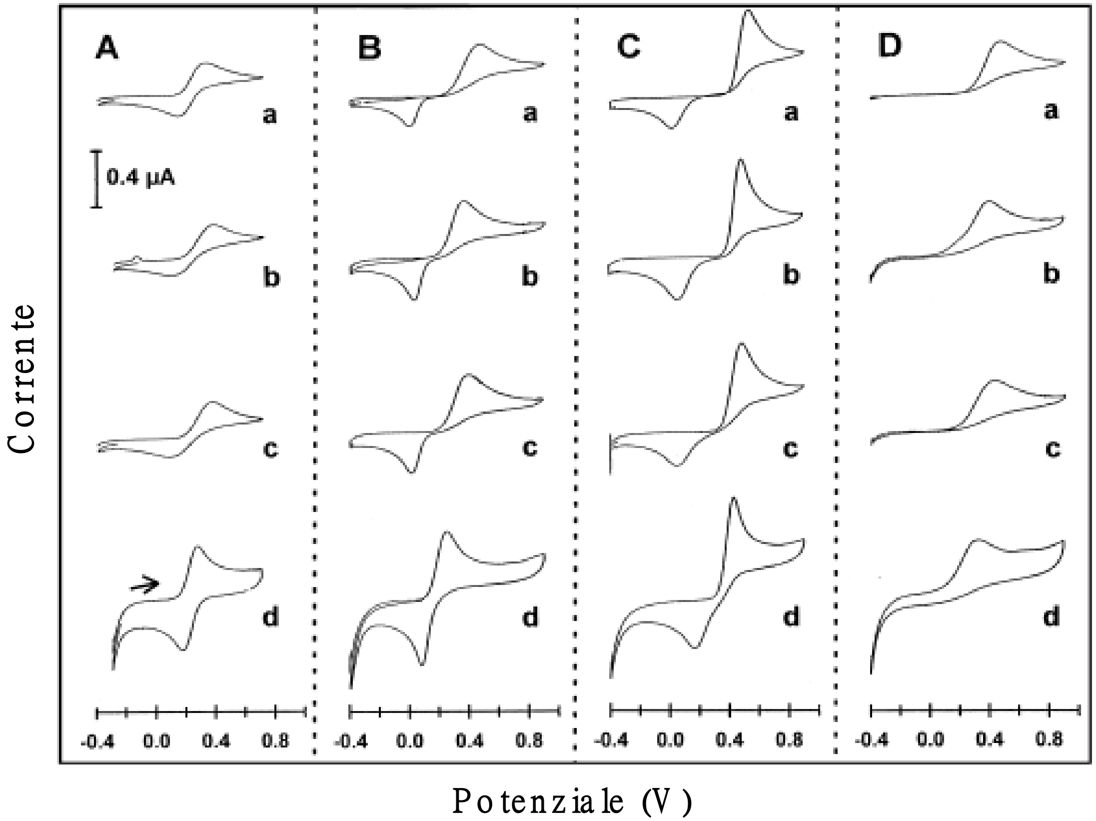

Working Electrode
Counter Electrode
DS
110
C.E. connection
Reference Electrode
W.E. connection
R.E. connection


DS
110
DS
550
DS
220BT
DS
220AT


Z&P

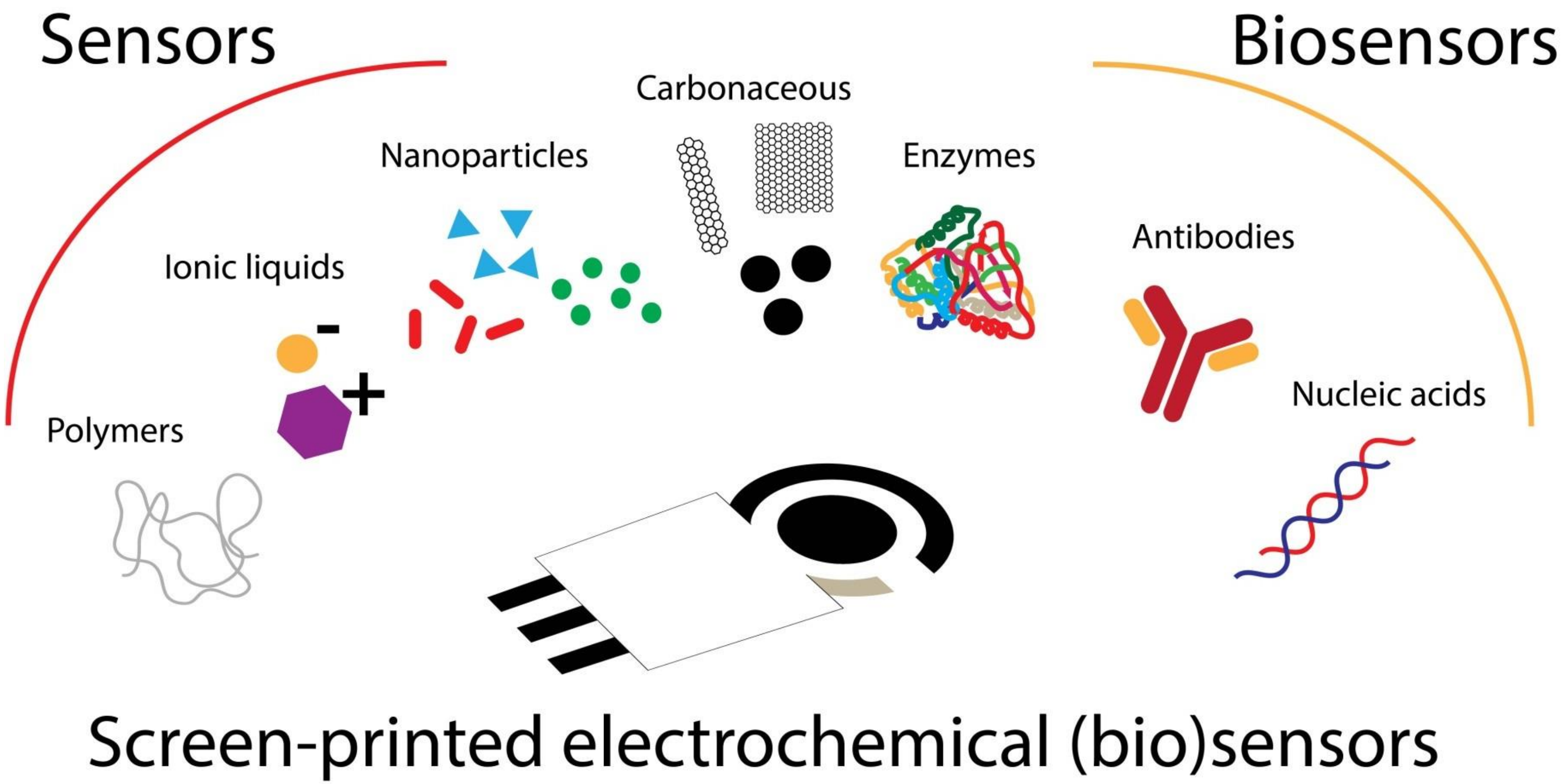

Roland


Contact
Insulated Layer
Reference Electrode(R)
Working Electrode(W)
Counter Electrode(C)

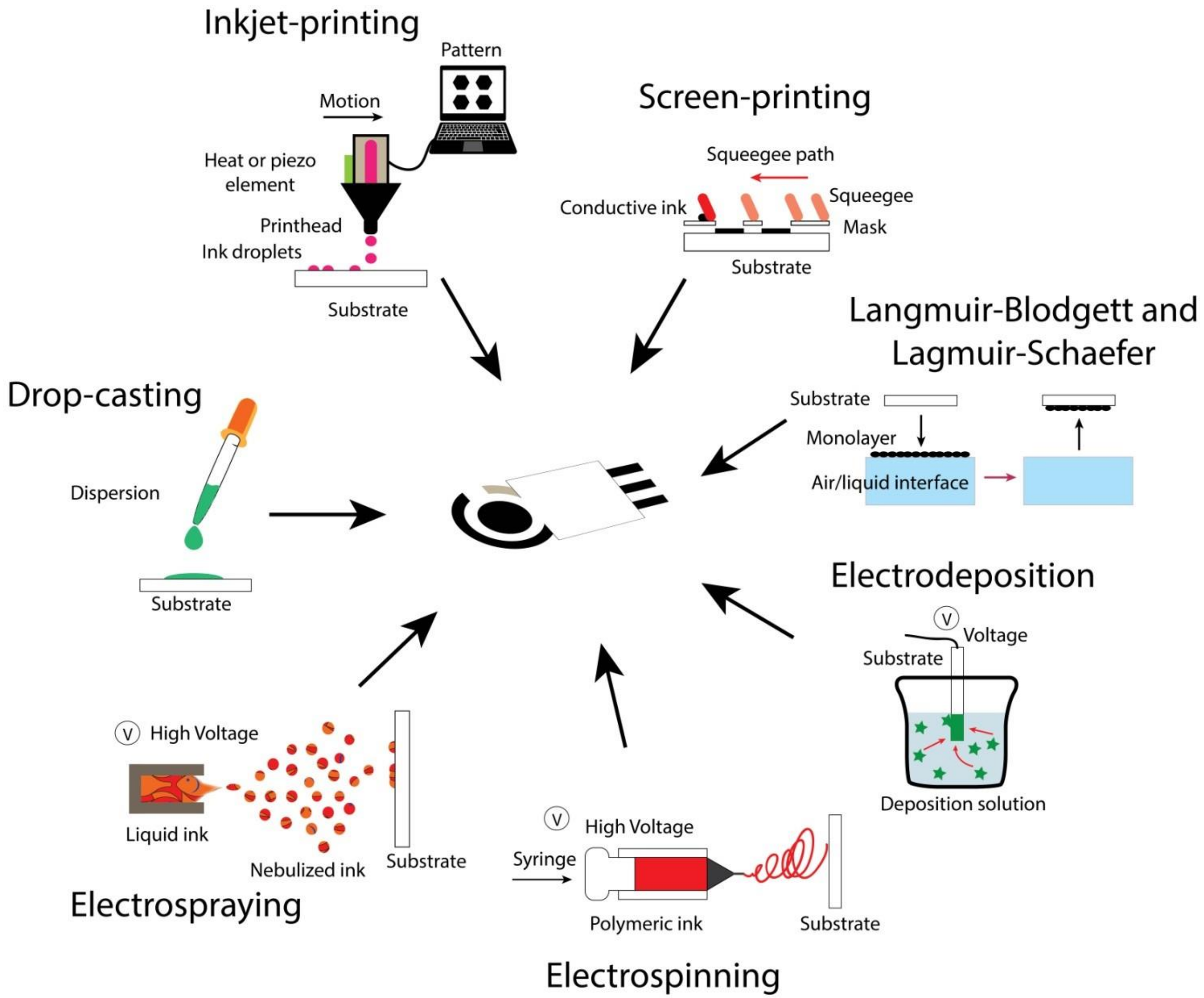


Cyclic voltammetries of ferricyanide (A), cathecol (B), acetamminophene (C), ascorbic acid (D) carried with dfferent screen-printed electrodes: Dupont (a), Ercon (b), Acheson (c) Gwent (d). Supporting electrolyte; KCl 0.1M (A), scan rate 20 mV/s.

Screen-Printed Electrodes



How do we tune them?



TISSUE BASED BIOSENSORS

bovine liver (rich in catalase)

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

banana (rich in polyphenol oxidase)

$$\text{dopamine} + O_2 \rightarrow \text{dopamine quinone}$$

CELL BASED BIOSENSORS

measurement of ethanol using *acetobacter xylinum* (O_2 electrode)

Determination of the BOD (biological oxygen demand).

The BOD values indicate the amount of biochemicallly degradable organic material (carbonaceous demand) and the oxygen used to oxidise sulphides and ferrous ion.

Conventional methods include BOD_5 and BOD_7 which need 5 and 7 days.

BOD biosensors have been developed using *Trichosporon cutaneum*, *Bacillus subtilis*, *Hansenula anomala*, *etc.*

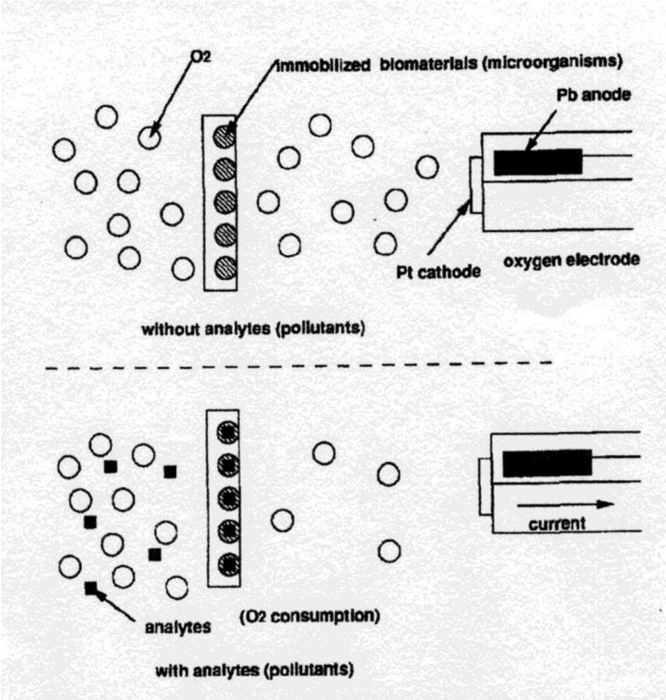
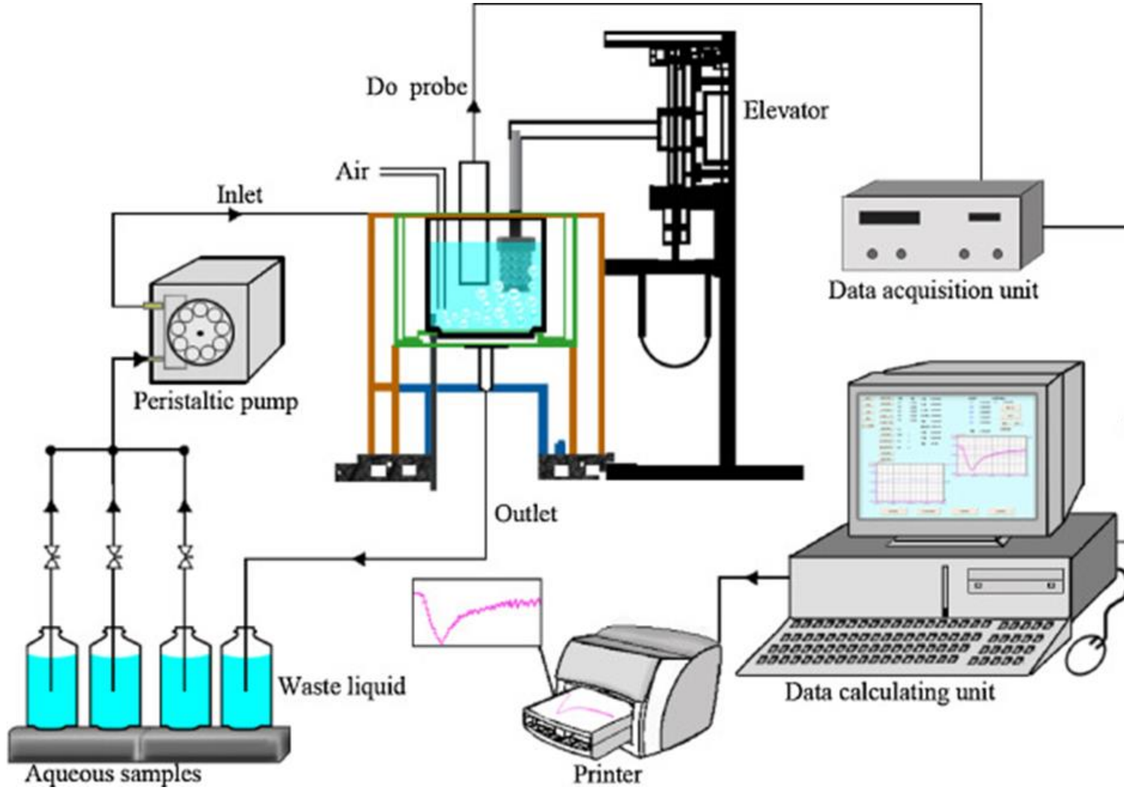
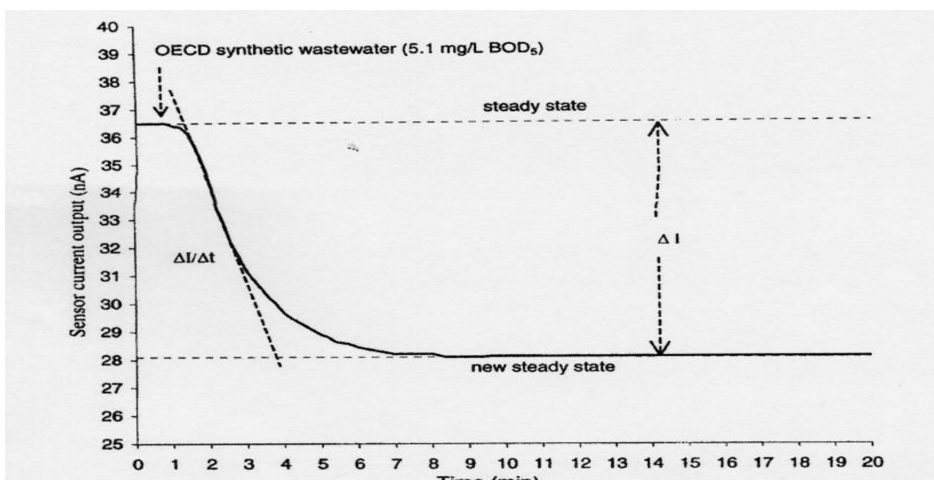


Fig. 1. Principle of biosensors. Microbial sensor of the respiration-activity measurement type.





Spectrophotometric enzymatic kits work as end-point reaction using enzymes in solution

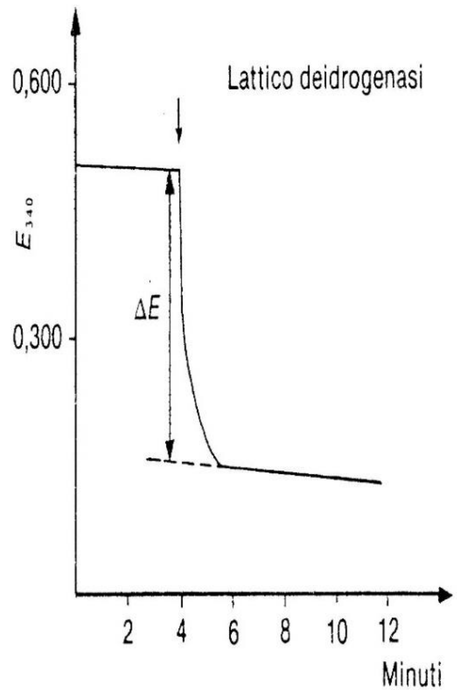


Figura 10.3 Dosaggio spettrofotometrico del piruvato con lattico deidrogenasi e NADH (dosaggio a termine con reazione semplice).

http://www.sigmaaldrich.com/life-science/metabolomics/enzymatic-kits.html

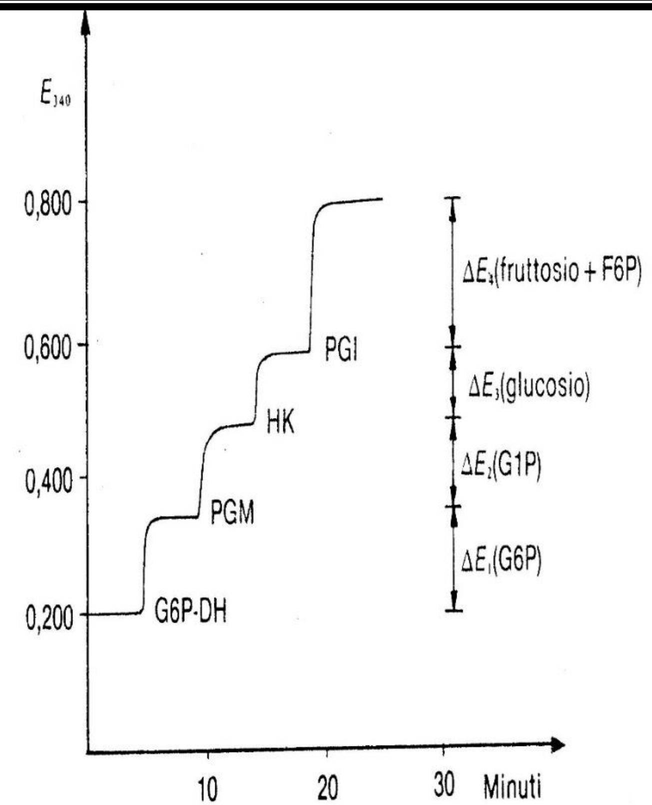
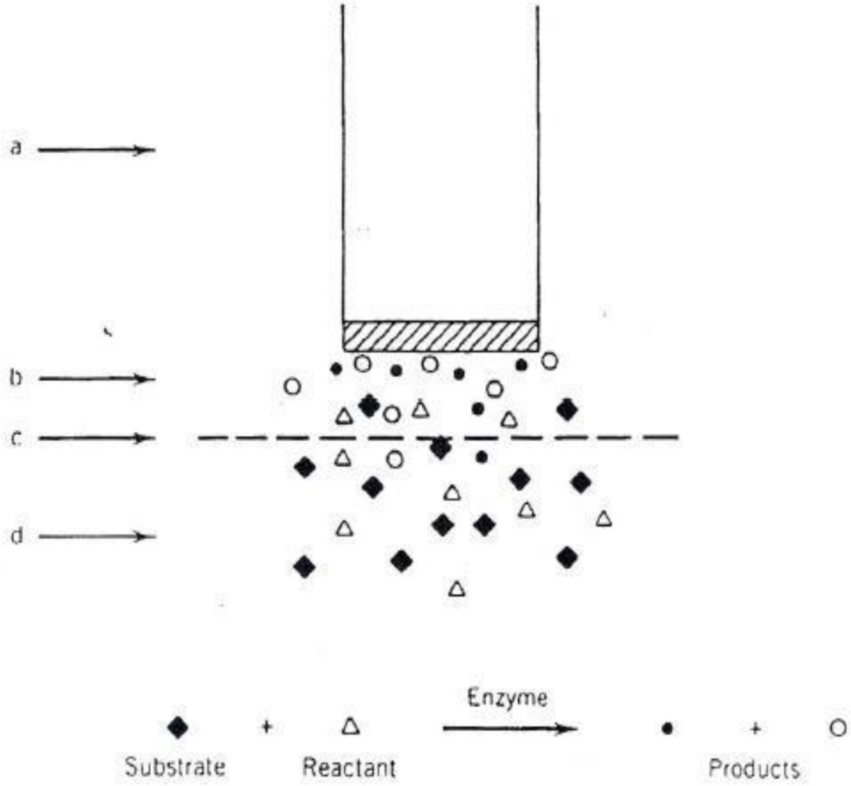


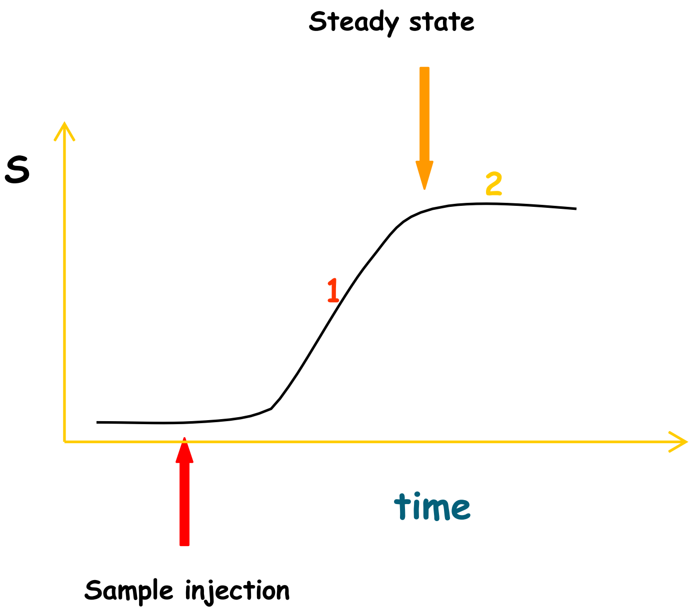
Figura 10.9 Dosaggio spettrofotometrico di G6P, G1P, glucosio, fruttosio + F6P in una singola cuvetta con G6P deidrogenasi (G6P-DH) e $NADP^+$; fosfoglucomutasi (PGM); esocinasi (HK) e ATP; G6P isomerasi (PGI) (dosaggio a termine con reazioni accoppiate).

Food Industry
Beer and Spirits
Milk and Dairy Products
Fruits, Vegetables and Nuts
Meat, Poultry, Pork and Fish (Animal Protein)
Wine
Drinking Water

Molecular Target
Carbohydrates and Sugars
Inorganic Ions
Lipids (Fats)
Amino Acids and Proteins

Enzyme electrode





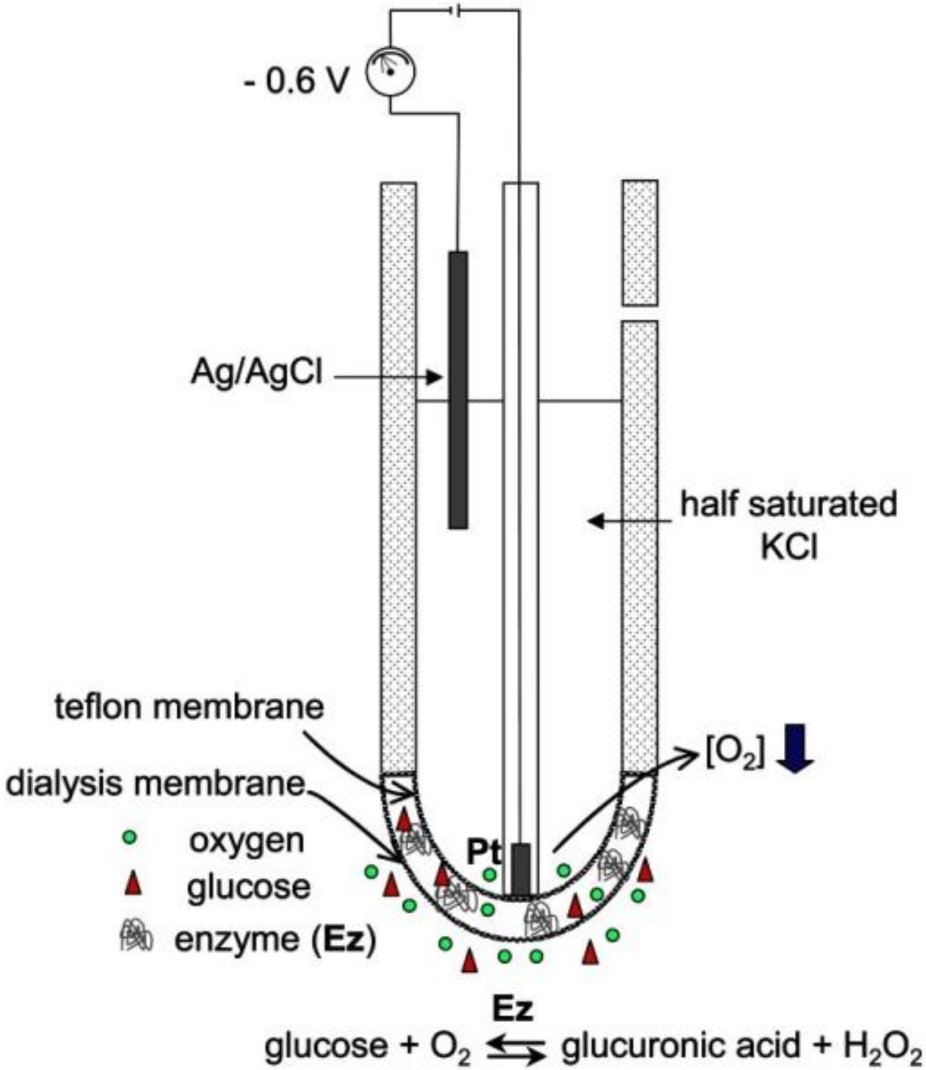
THE BIOLOGICAL ELEMENT SHOULD HAVE:

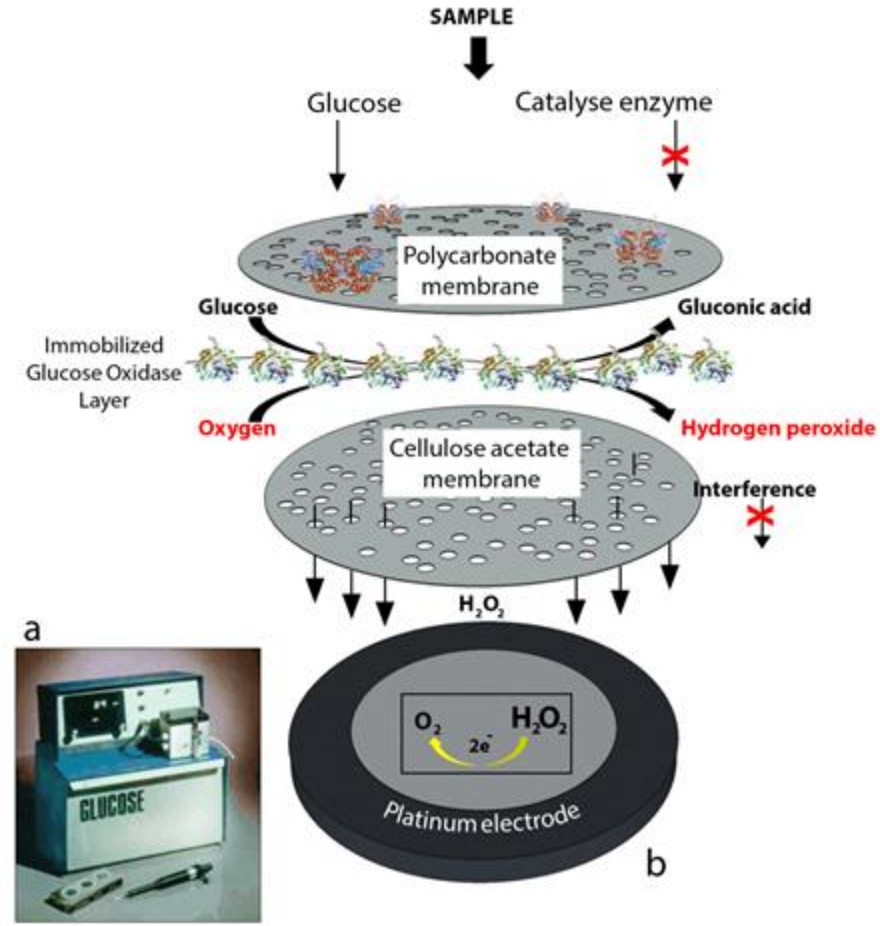
SPECIFICITY (HIGH SELECTIVITY) FOR THE ANALYTE(S)

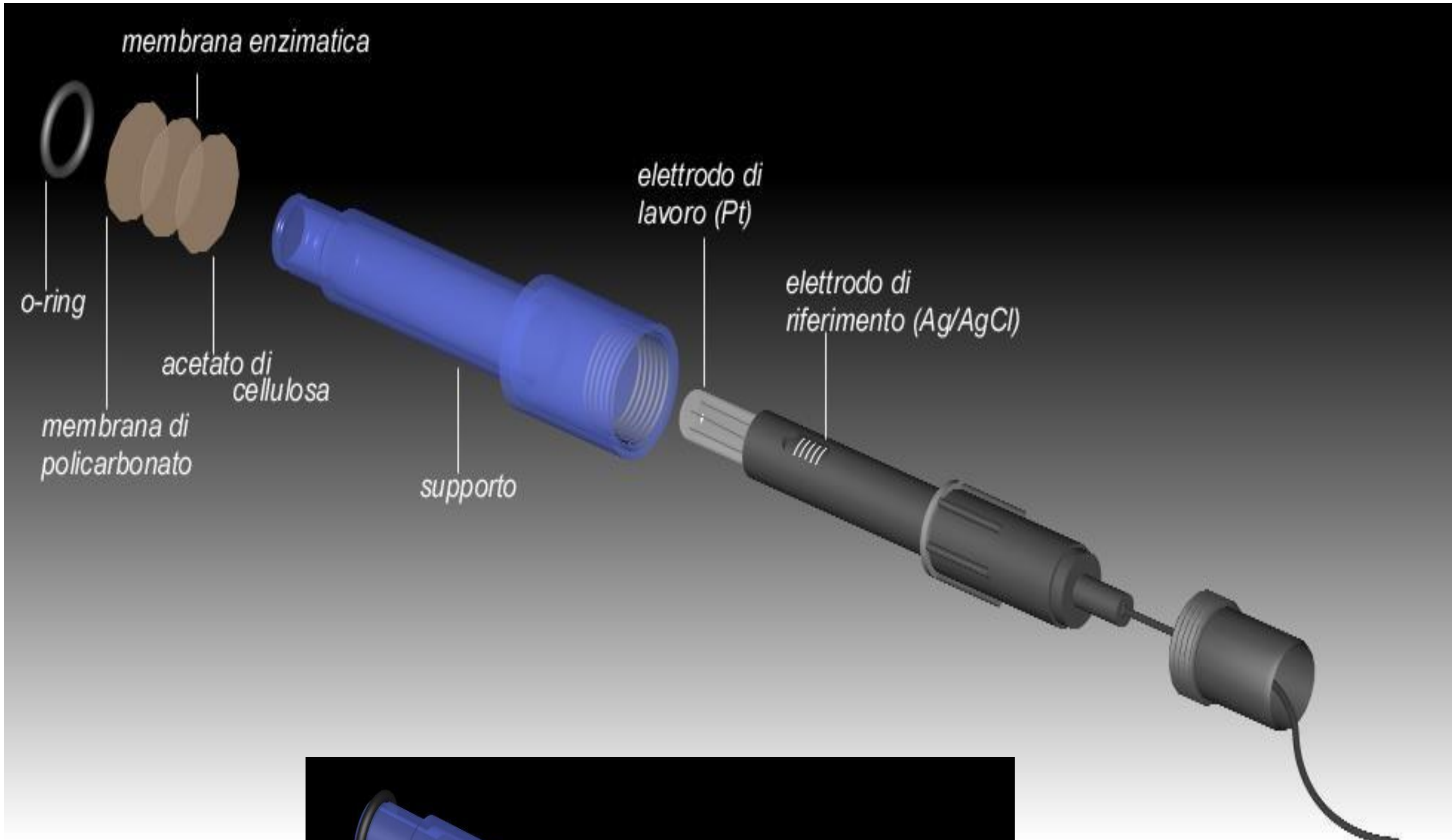
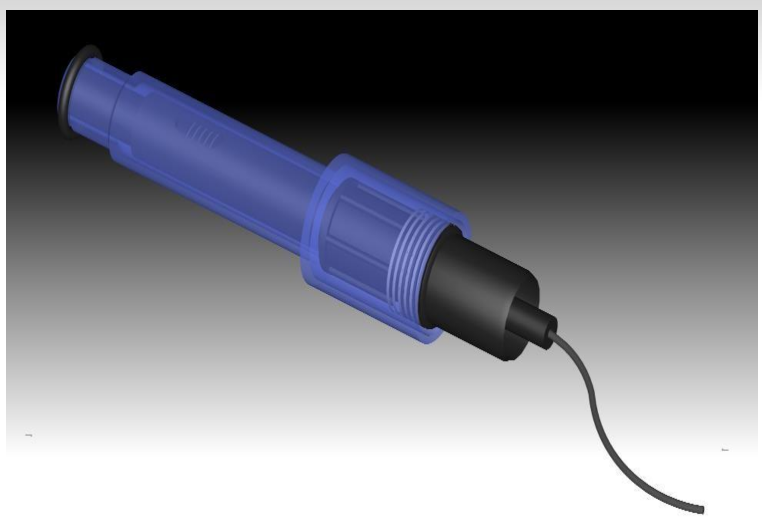
GOOD STABILITY IN OPERATING CONDITIONS (t, pH, μ)

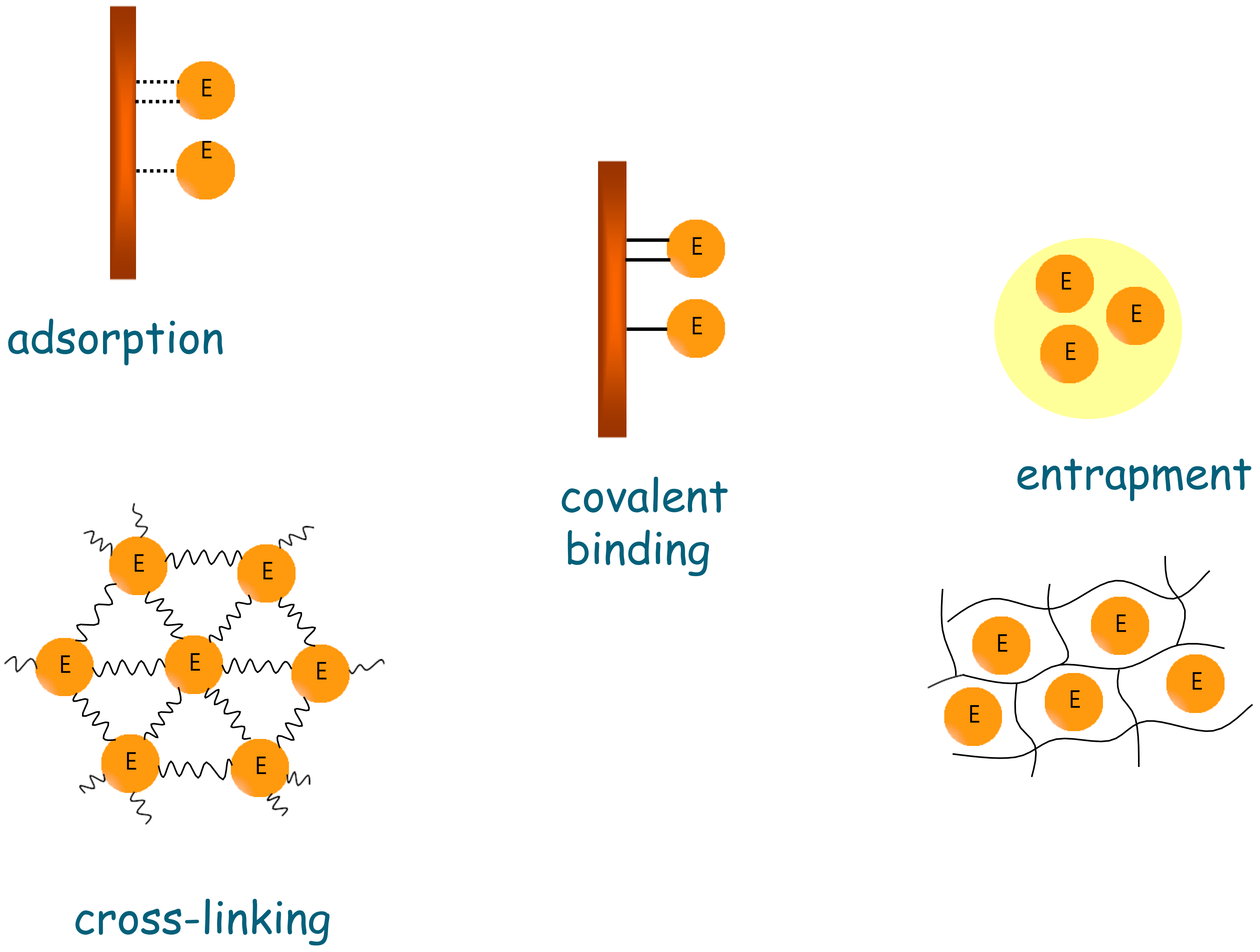
RETENTION OF SUFFICIENT BIOLOGICAL ACTIVITY WHEN IMMOBILISED

NO (VERY LOW) INHIBITION BY THE SAMPLE

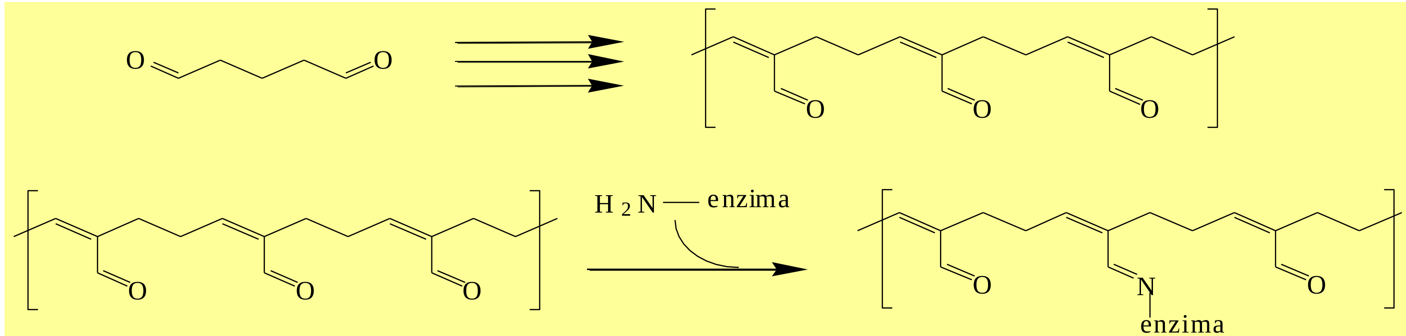

- 0.6 V
Ag/AgCl
half saturated
KCl
teflon membrane
dialysis membrane
[O2]
Pt
oxygen
glucose
enzyme (Ez)
Ez
glucose + O2 ⇄ glucuronic acid + H2O2


SAMPLE
Glucose
Catalyse enzyme
Polycarbonate
membrane
Glucose
Gluconic acid
Immobilized
Glucose Oxidase
Layer
Oxygen
Hydrogen peroxide
Cellulose acetate
membrane
Interference
H2O2
a
GLUCOSE
O2
2e-
H2O2
Platinum electrode
b


membrana enzimatica
o-ring
acetato di
cellulosa
membrana di
policarbonato
supporto
elettrodo di
lavoro (Pt)
elettrodo di
riferimento (Ag/AgCl)


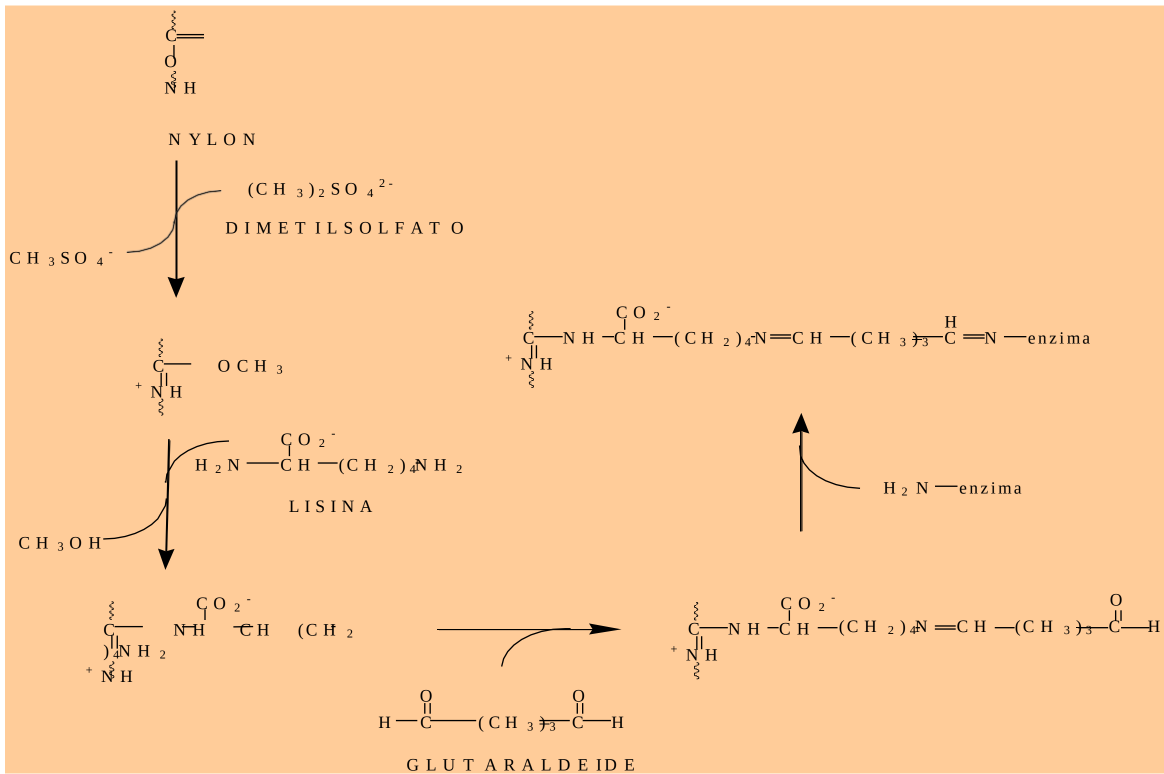


E
E
adsorption
E
E
covalent binding
E
E
E
entrapment
E
E
E
E
E
E
E
cross-linking
E
E
E
E
E

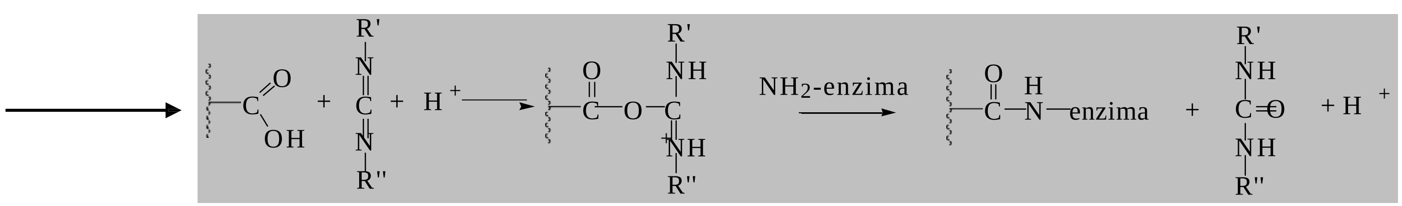


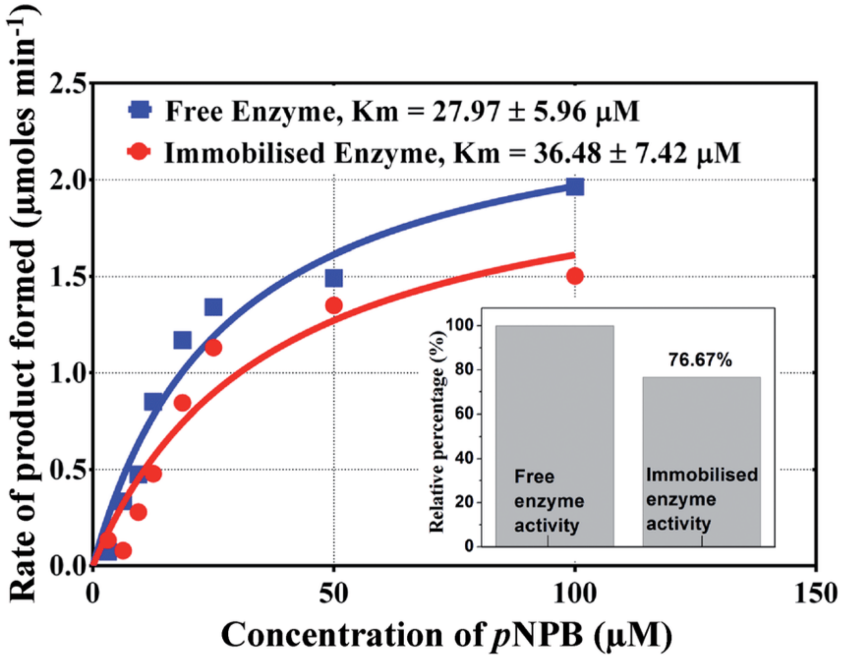
glutaraldehyde reactions: polimerization and lysine amino group

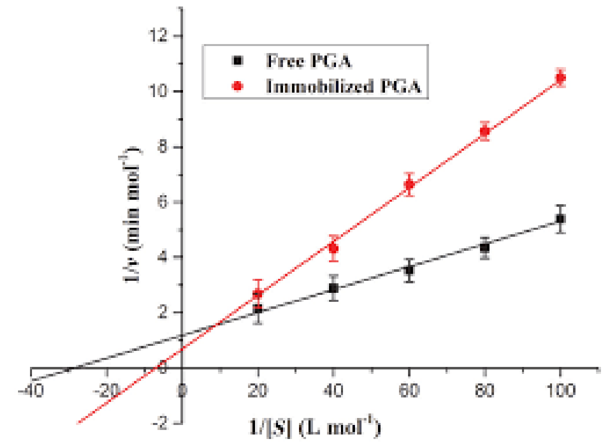
CHO
|
$(CH_2)_3$
|
CHO

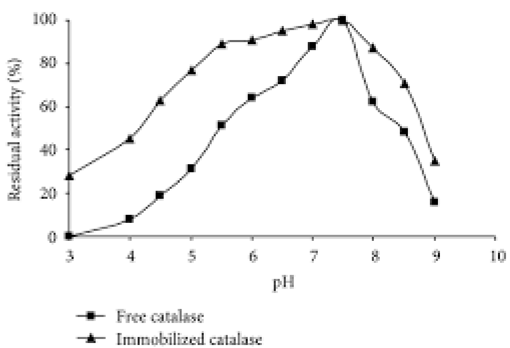


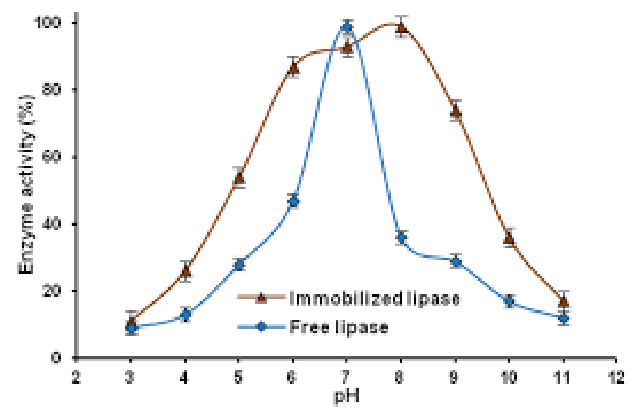
Immobilisation via carbodiimide











The immobilised enzyme has always a higher (apparent) K_m ,a shifted and larger optimum pH and lower enzymatic activity compared to the enzyme in solution

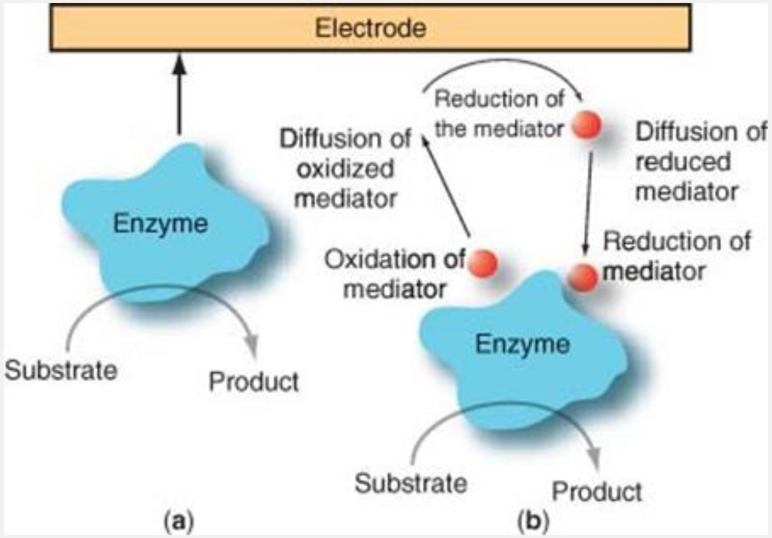
Enzyme electrodes are generally classified according to the mechanism of the electron transfer:

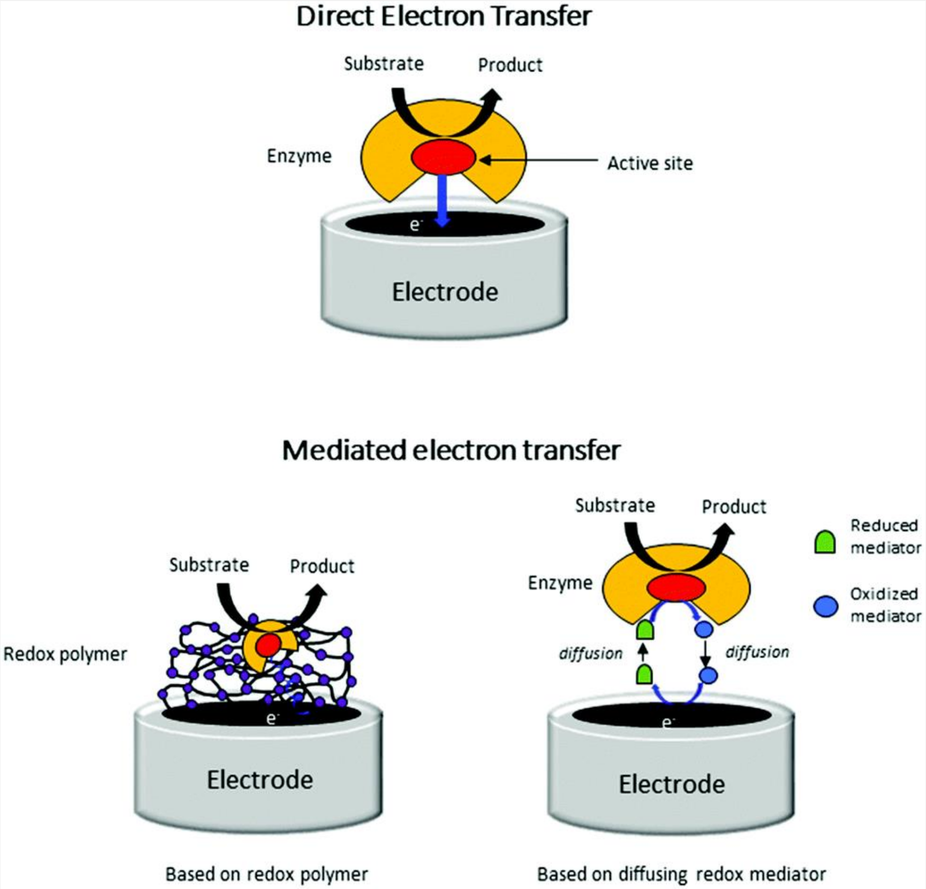
1. First generation: the enzyme is immobilised using a membrane that is in contact with the electrode surface. Usually there are other membranes to protect and regulate diffusion. Response time at the stady state is on the order of minutes

2. Second generation: electron transfer occurs via an electrochemical mediator in solution. The mediator shuttles electrons between the enzyme and the electrode. Faster response times.

3. Third generation: direct exchange of electrons between the electrode and the enzyme. Very fast response time.

Second and third generation





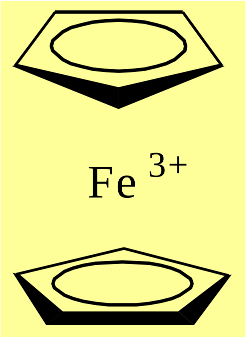
A good electrochemical mediator characteristics :

- rapid reaction with the enzyme
- rapid and reversible electron trasfer rate
- low overpotial for the redox reaction
- pH independent
- stability in the reaction medium in both redox forms
- Should not react with the dissolved oxygen in solution
- no toxicity

$Fe^{3+} + e^- \;\; Fe^{2+}$ $E° = +0,53\ V$

Ferrycianide $E° = +0,45\ V$

Ferrocene $E° = +\mathbf{0,165}\ V$

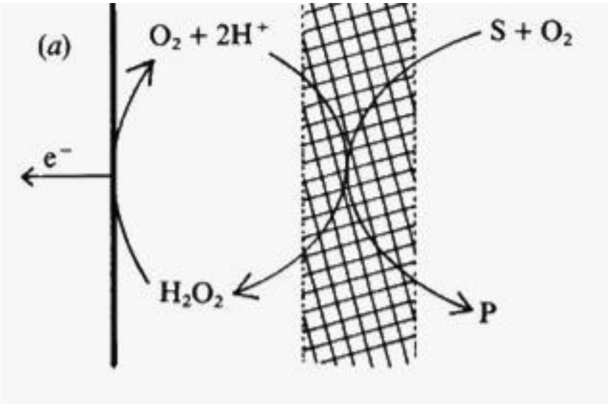


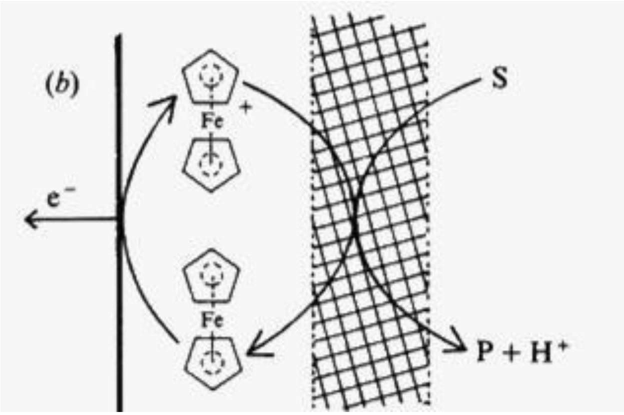
ferrocene is an excellent mediator for the oxidation of glucose catalysed by glucose oxidase

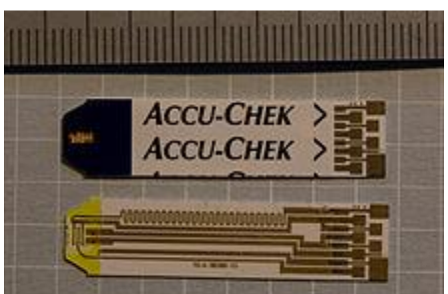
$$\text{glucose} + GOD_{ox} \rightarrow \text{gluconolactone (gluconic acid)} + GOD_{rid} + 2H^+$$

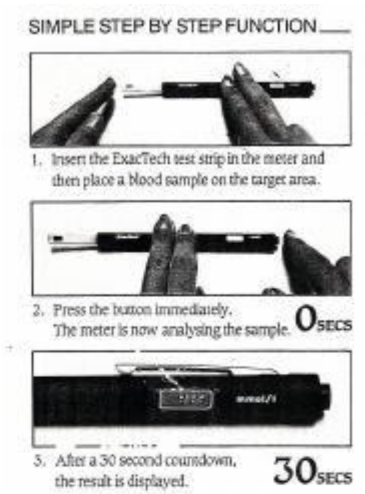
$$GOD_{rid} + 2Fe^+ \rightarrow GOD_{ox} + 2Fe$$

$$2\ Fe - 2\ e^- \rightarrow 2\ Fe^+$$









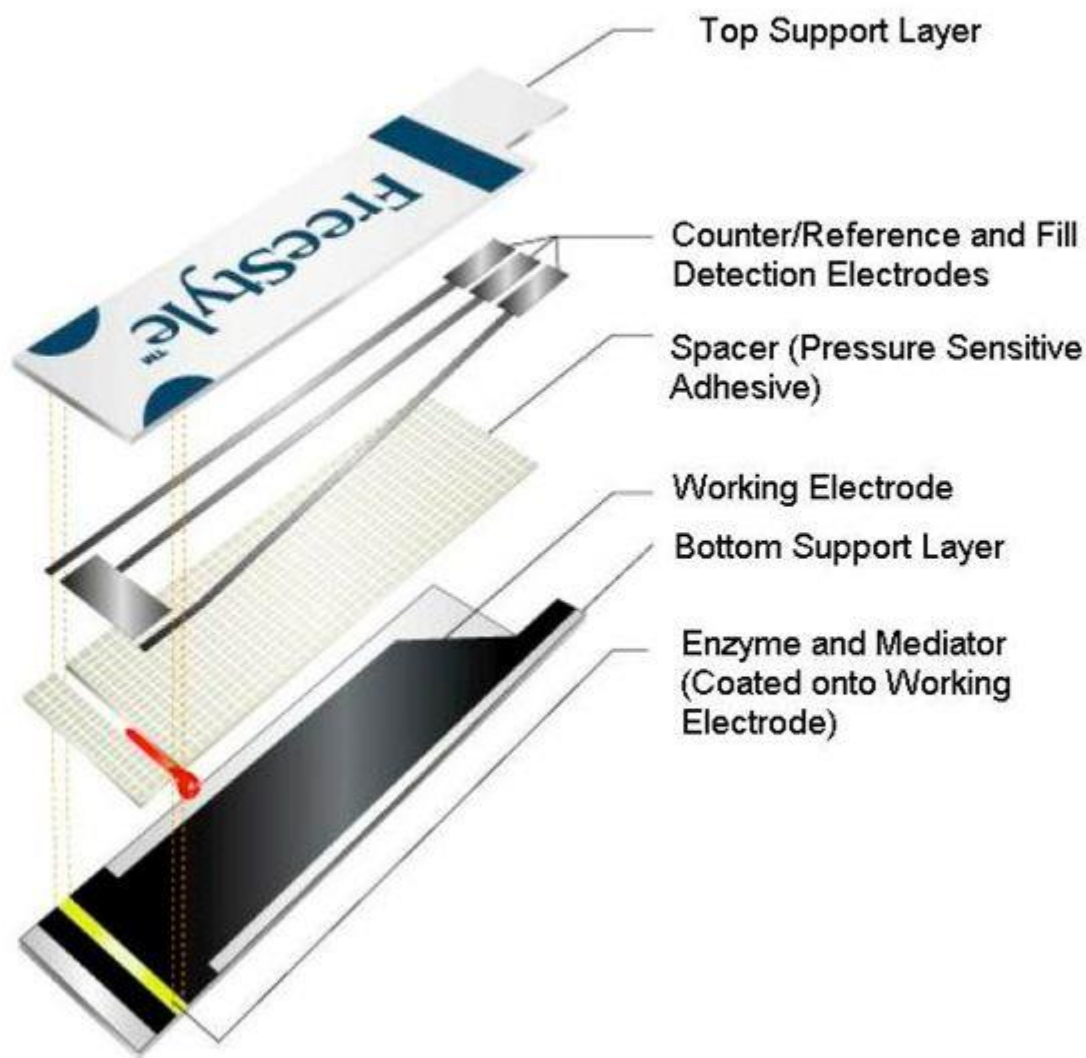
The ExacTech Blood Glucose Meter is shown Actual Size

Test Strips

- When blood added, glucose is oxidized by enzyme coated on working electrode

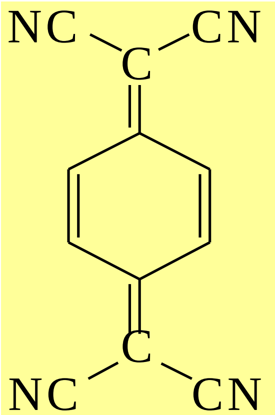
- Voltage applied between working and reference electrode

- Measure current between working and reference electrode



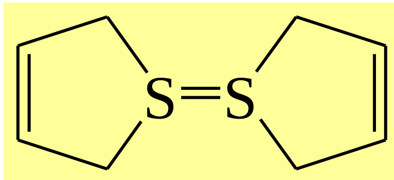
NATURAL	E(V) vs. SHC	SYNTHETIC	E (V) vs. SHC
Cytochrome a_3	+0,29	Esacyanoferrate(III)	+0,45
Cytochrome c_3	+0,24	2,6-dichlorophenol	+0,24
Ubiquinone	+0,10	Indophenolo	+0,24
Cytochrome b	+0,08	Ferrocene	+0,17
Vitamin K_2	-0,03	N-metilfenazium sulphate	+0,07
Rubredoxin	-0,05	Metilene blue	+0,4
Flavoproteins	da -0,4 a +0,2	Ftalocyanin	-0,02
$FAD/FADH_2$	-0,23	Fenosafranin	-0,23
$FMN/FMNH_2$	-0,23	Benzyl viologen	-0,36
$NAD^+/NADH$	-0,32	Methyl viologen	-0,46
$NADP^+/NADPH$	-0,32		
ferredossina	-0,43		

Third generation



Tetracyanochinodimethane
(TCNQ)

Conduting salts



Tetra tiafulvalene(TTF)

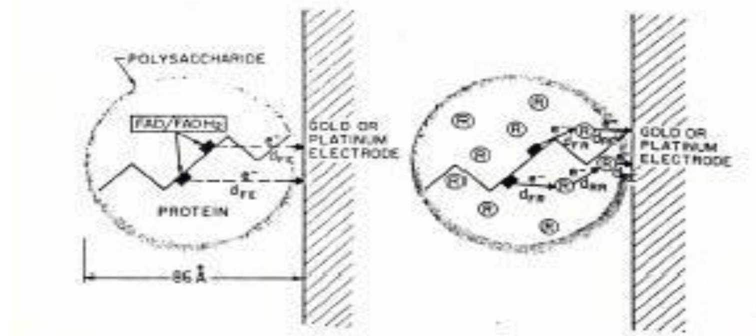
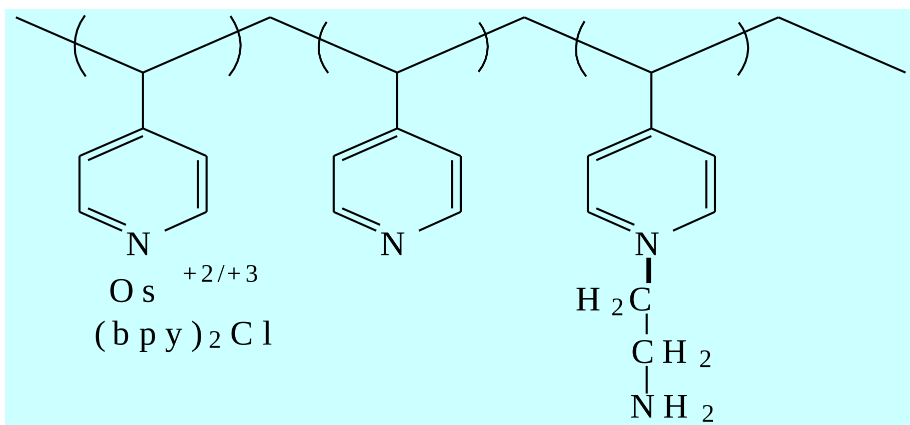


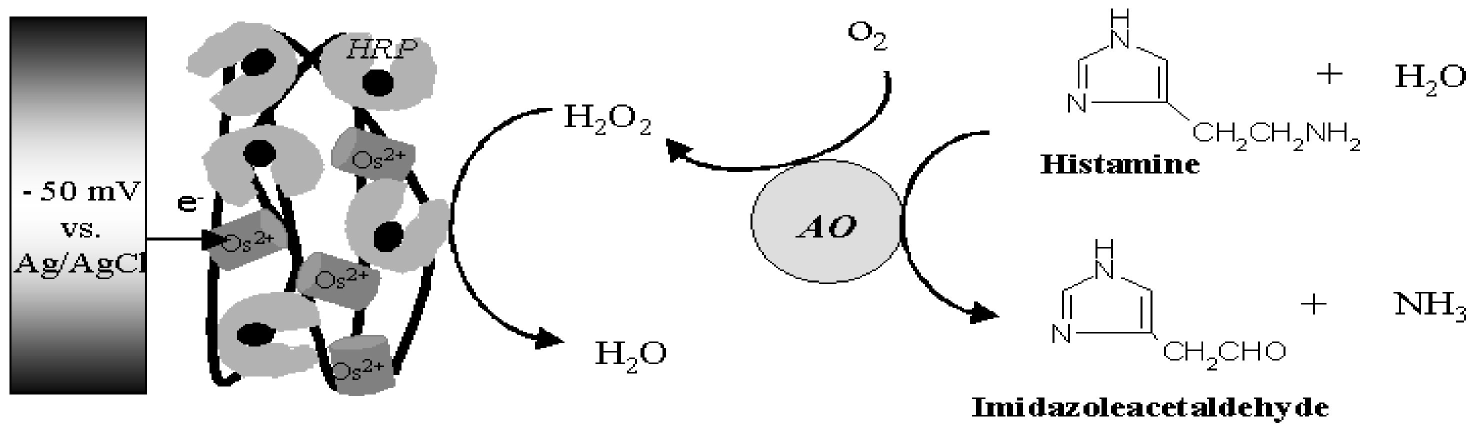
Figure 1. Schematic drawing of the glucose oxidase molecule, showing the electron-transfer distances involved in the various steps of moving an electron from its two FAD/FADH$_2$ centers to a metal electrode. Left: the enzyme before modification. Right: the modified enzyme, after chemical attachment of an array of electron-transfer relays.

Redox gel

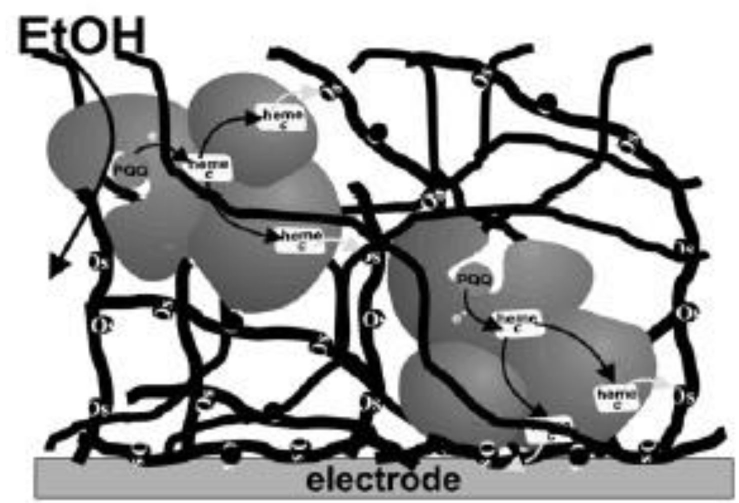


Struttura dell' l'osmio bipiridile legato a polivinilpiridina

Hystamine Biosensor



PQQ Alcohol Dehydrogenase entrapped in a Os hydrogel



NAD(P)H electrodes

The largest class of redox enzymes known is dehydrogenases which use the NAD(P)H / $NAD(P)^+$ couple as cofactor.

Oxidation of NADH at carbon and metal solid electrodes proceeds at high overvoltages (+400/ +700 mV vs. Ag/AgCl) via formation of the radical cation $NADH^{\cdot +}$. This can give side reactions (dimerisation) and adsorb onto the electrode (carbon).

A soluble mediator can be used to lower the overpotential and increase the electron transfer rate

$$NADH + Med_{ox} \Leftrightarrow NAD^{+} + Med_{red}$$

at the electrode surface polarised at the appropriate E :

$$Med_{red} \rightarrow Med_{ox} + ne$$

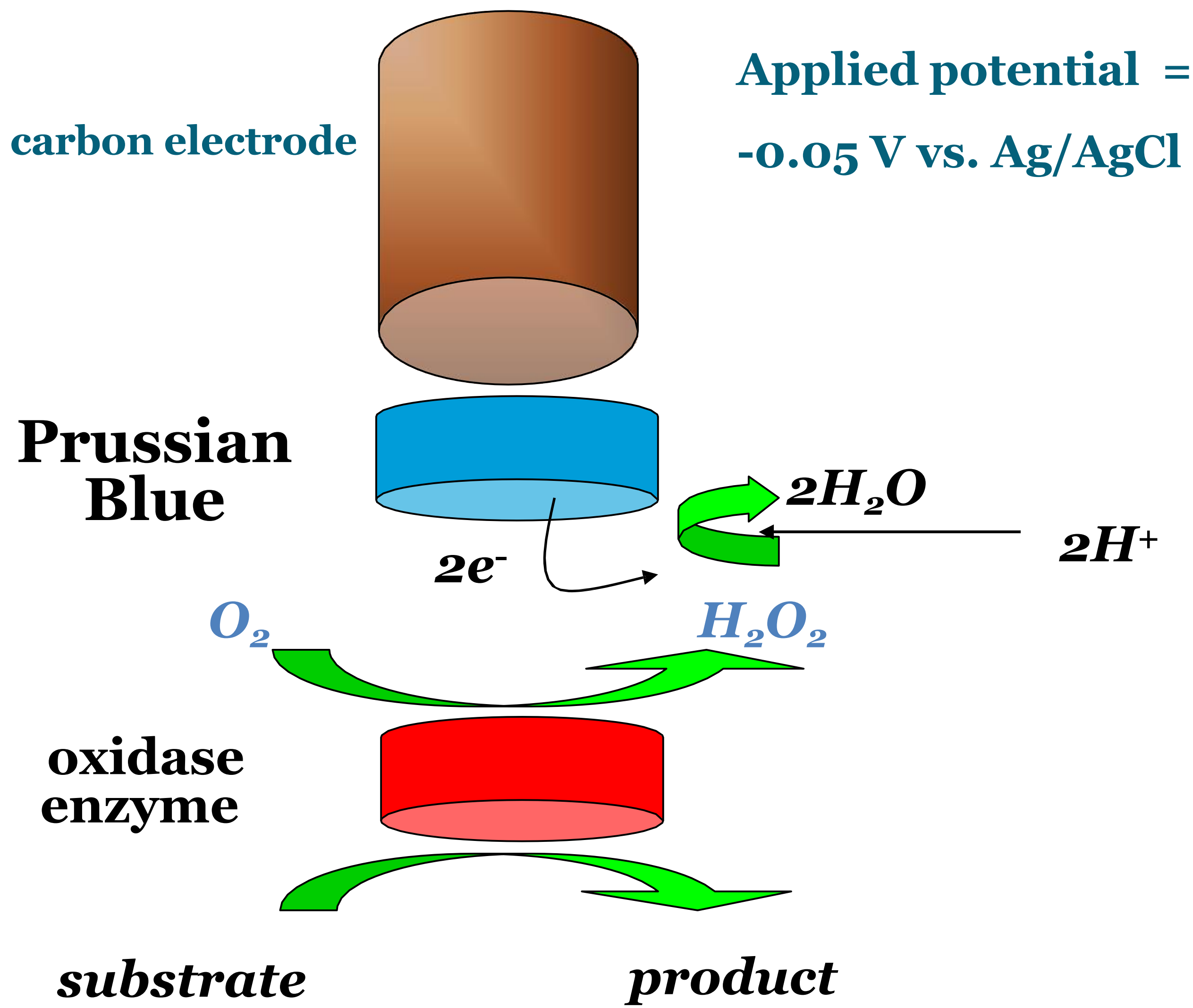
ortho- and para-quinones , quinone imines have been used and incorporated into larger molecules as indophenols, phenazines and phenoxazines

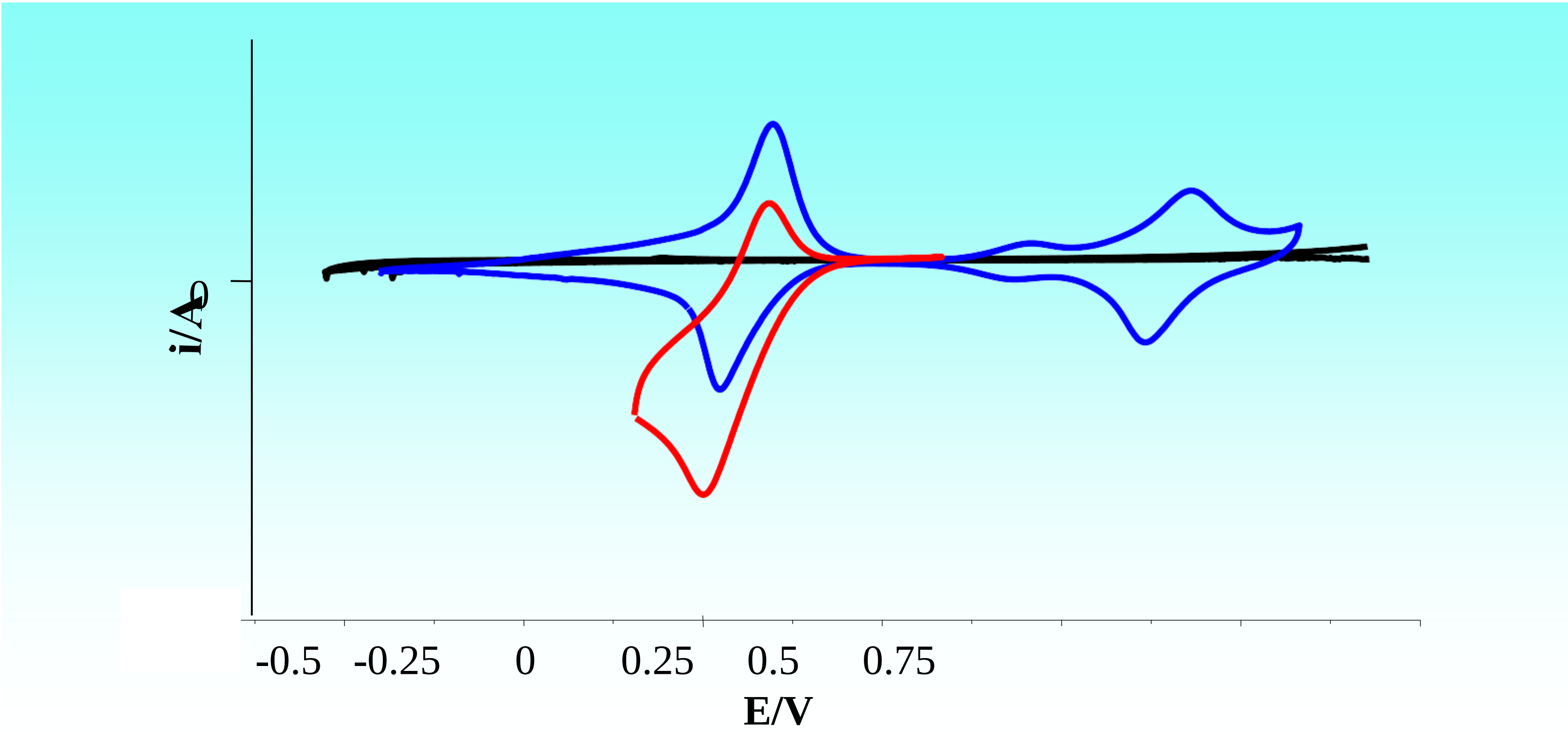
The mediator can be also immobilized at the electrode surface giving a chemically modified electrode for NADH

Sensitivity is excellent, major problems arise from selectivity and stability of the sensors

Reduced Prussian Blue is a selective catalyst for H_2O_2 reduction

$$K_2Fe^{II}[Fe^{II}(CN)_6] + H_2O_2 \rightleftharpoons KFe^{III}[Fe^{II}(CN)_6] + K^+ + OH^-$$



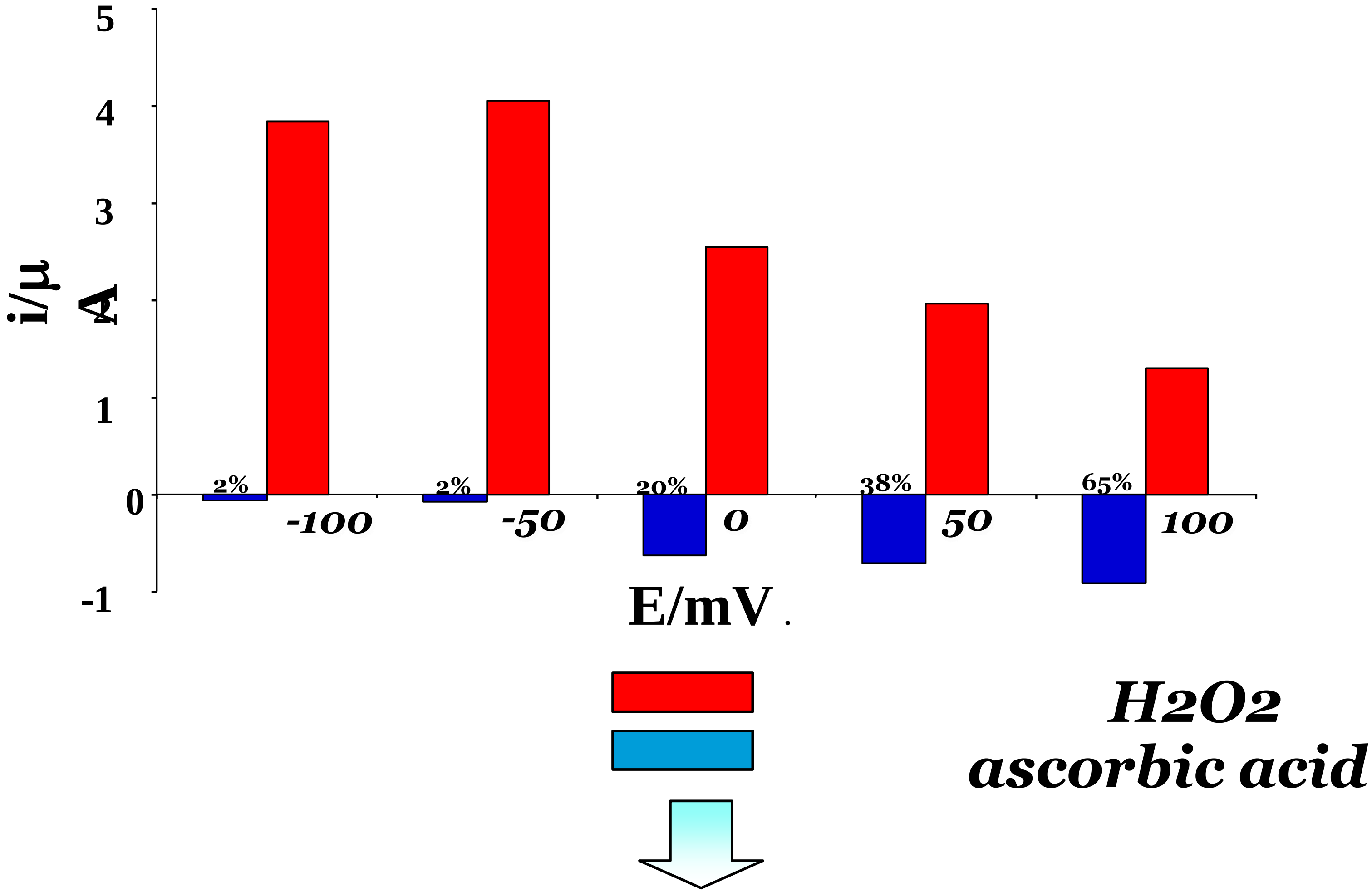


Bare electrode

Prussian Blue modified electrode

Prussian Blue modified electrode + H_2O_2

Selection of the applied potential



Potential selected - 50 mV vs. Ag/AgCl pseudo-ref.

Lysine biosensor, linear range and selectivity

L-lysine + O_2 + H_2O
$\rightarrow \alpha$-keto-$\mathcal{E}$-aminocaproate + NH_3 + H_2O_2

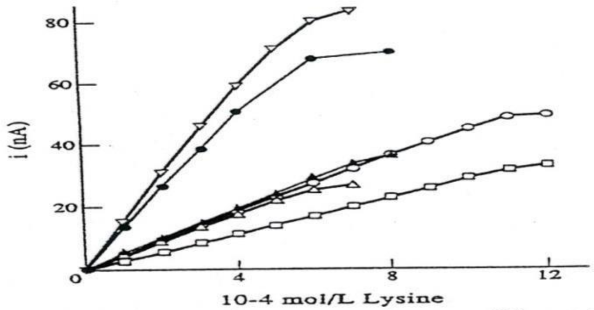


Fig. 1. Lysine calibration curves using two different immobilization procedures and protective polycarbonate membranes with different porosity. ▽ BSA/glutaraldehyde on Immobilon and 0.8-μm polycarbonate; ● Immobilon only and 0.8-μm polycarbonate; ○ BSA/glutaraldehyde on Immobilon and 0.03-μm polycarbonate; ▲ BSA/glutaraldehyde on Immobilon and 0.05-μm polycarbonate; △ Immobilon only and 0.05-μm polycarbonate; □ Immobilon only and 0.03-μm polycarbonate. Buffer phosphate 0.1M pH 7.0 $T = 25°$.

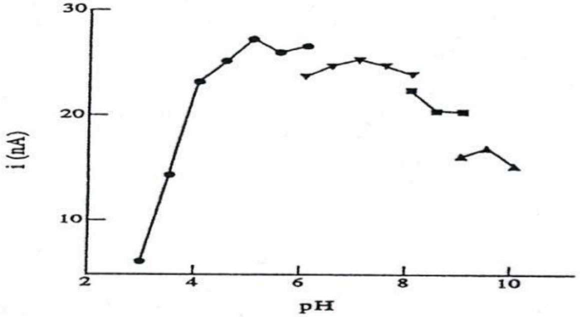


Fig. 2. Effect of pH on lysine oxidase activity. The enzyme activity was measured in the following buffers: ● citrate; ▼ phosphate; ■ tris; ▲ borax. $T = 25°$.

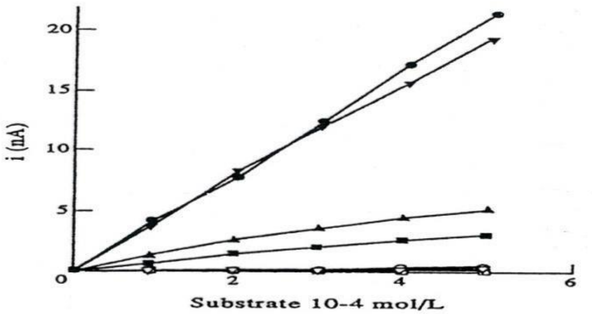
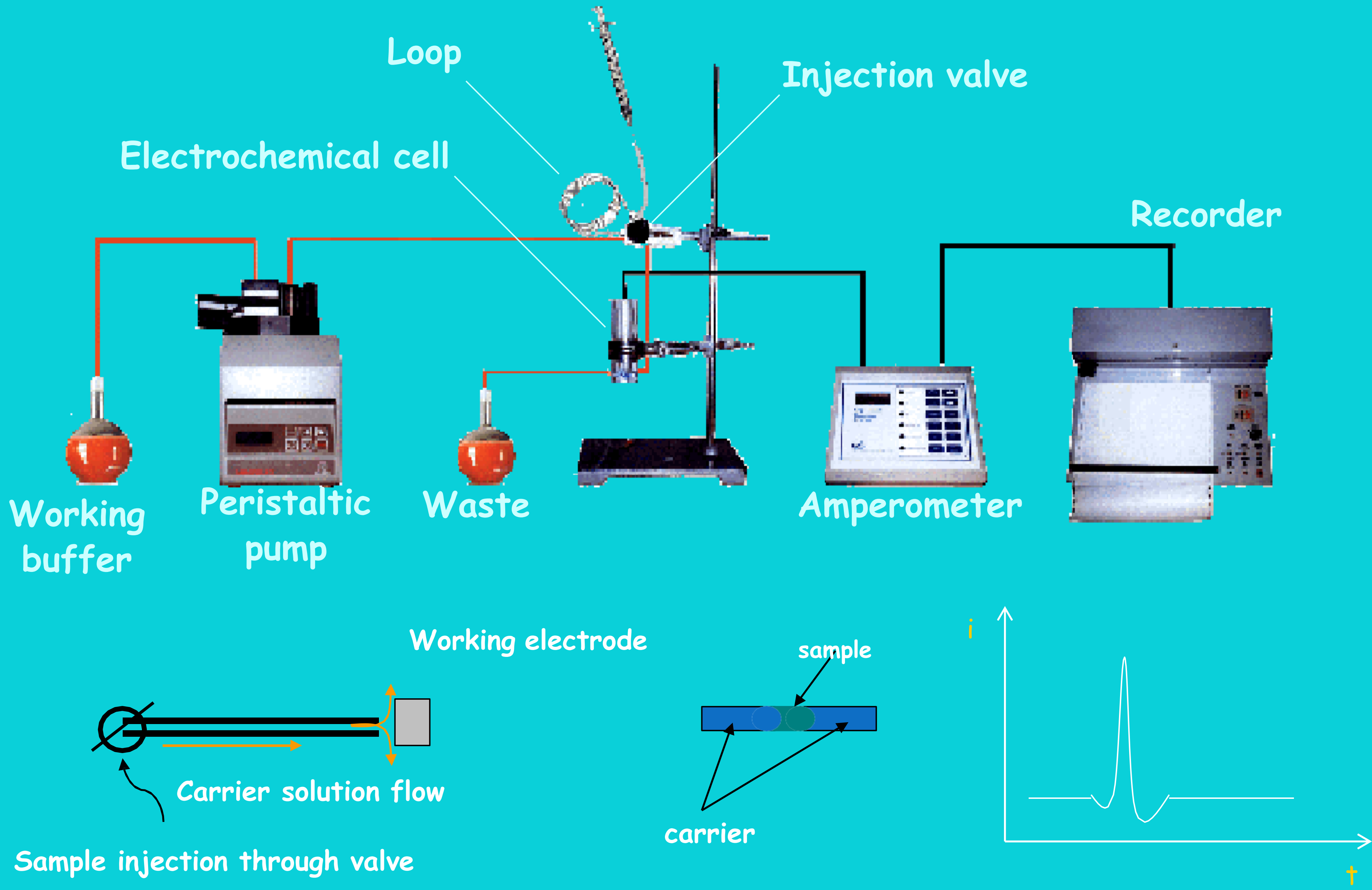
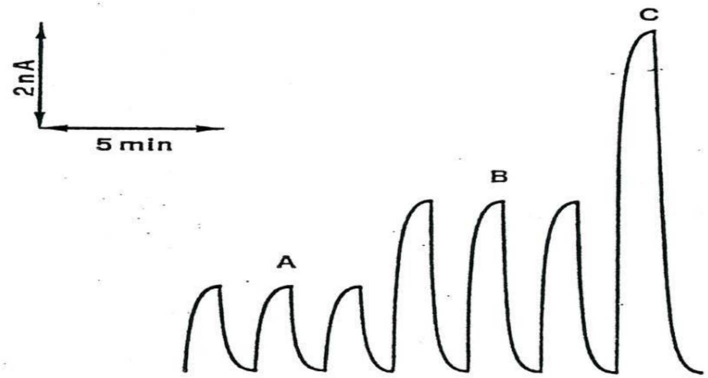


Fig. 4. Relative lysine oxidase activity toward some substrates pH 7.0 phosphate buffer $T = 25°$. ● lysine; ▼ lysine after the analysis of other aminoacids. ▲ ornithine; ■ arginine; ○ tyrosine; □ phenylalanine; ▽ histidine.


Loop
Injection valve
Electrochemical cell
Recorder
Working buffer
Peristaltic pump
Waste
Amperometer
Working electrode
Carrier solution flow
Sample injection through valve
sample
carrier
i
t

a



b

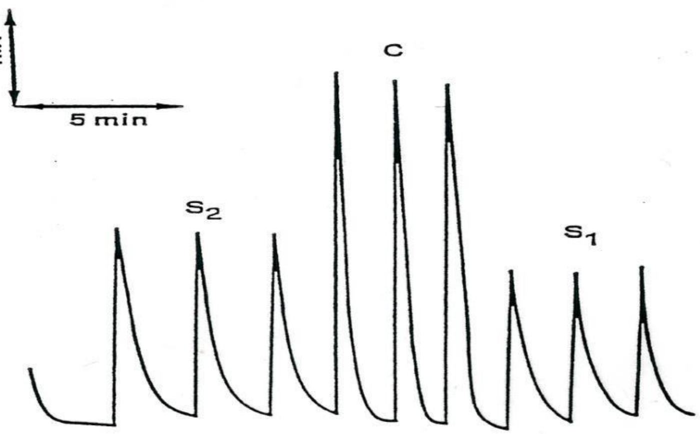


Figure 7 Reproducibility and response time of the bioprobe in flow through analysis and FIA.
a = flow through: Lysine concentration in standard solution.
A = $5 \cdot 10^{-5}$ mol/L; B = 10^{-4} mol/L; C = $2 \cdot 10^{-4}$ mol/L.
b = FIA; S_1 and S_2 foodstaff samples; C = Lysine standard $5 \cdot 10^{-4}$ mol/L.

Relative activity of 3 different purified lysine oxidase

compound	Yamasa	SIGMA	Univ. of Athens
Lysine	100	100	100
Phenylalanine	14	42	6
Arginine	2	17	0
Ornithine	3	14	0
Histidine	0	15	0
Furosine	0	0	0
Piridosine	0	0	0
Norleucine	3	17	3
AGPA*	0	0	0

Microwave hydrolysis + biosensor , analysis time 30 min

Sample	**Amino-acid analysis (mM)**	**L-lysine biosensor (mM)**	**Recovery (%)**
Milk	1.684	1.493 ± 0.014	88.66
pasta	0.299	0.308 ± 0.012	103.01

Lactic acid monitoring during mozzarella cheese manufacturing

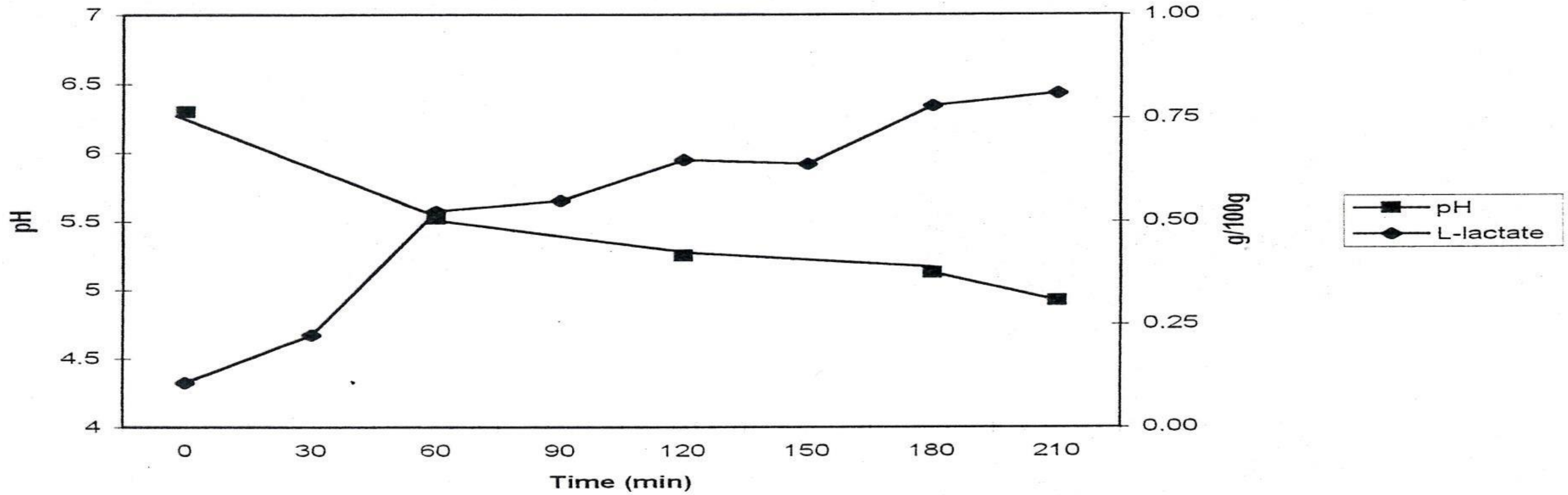
In mozzarella cheese manufacture L-Lactic acid is the main product of lactose fermentation generated by selected cultures of lactic acid bacteria. A progressive acidification of the curd md the whey occurs and had to be carefully controlled.

Particularly, the pH of the "stretching point" is important in order to avoid loss of fats, a decrease in yield and low reproducibility of themanufacturing.

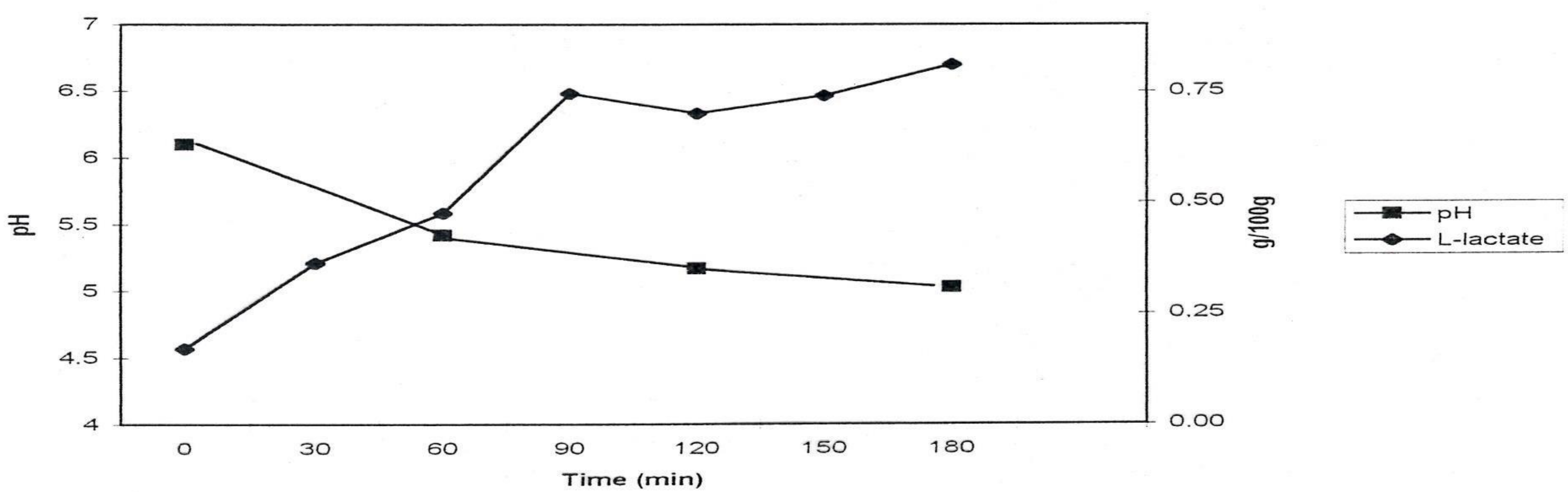
Optimum pH is 4.9 for water-buffalo milk and 5.1 for cow milk. At these pH values there is a great increase in the buffer capacity due to casein (isoelectric point pH ~ 5) and low molecular weight acids

A sensitive measurement of lactic acid in real time can be useful in the optimization of the mozzarella cheese manufacture

A

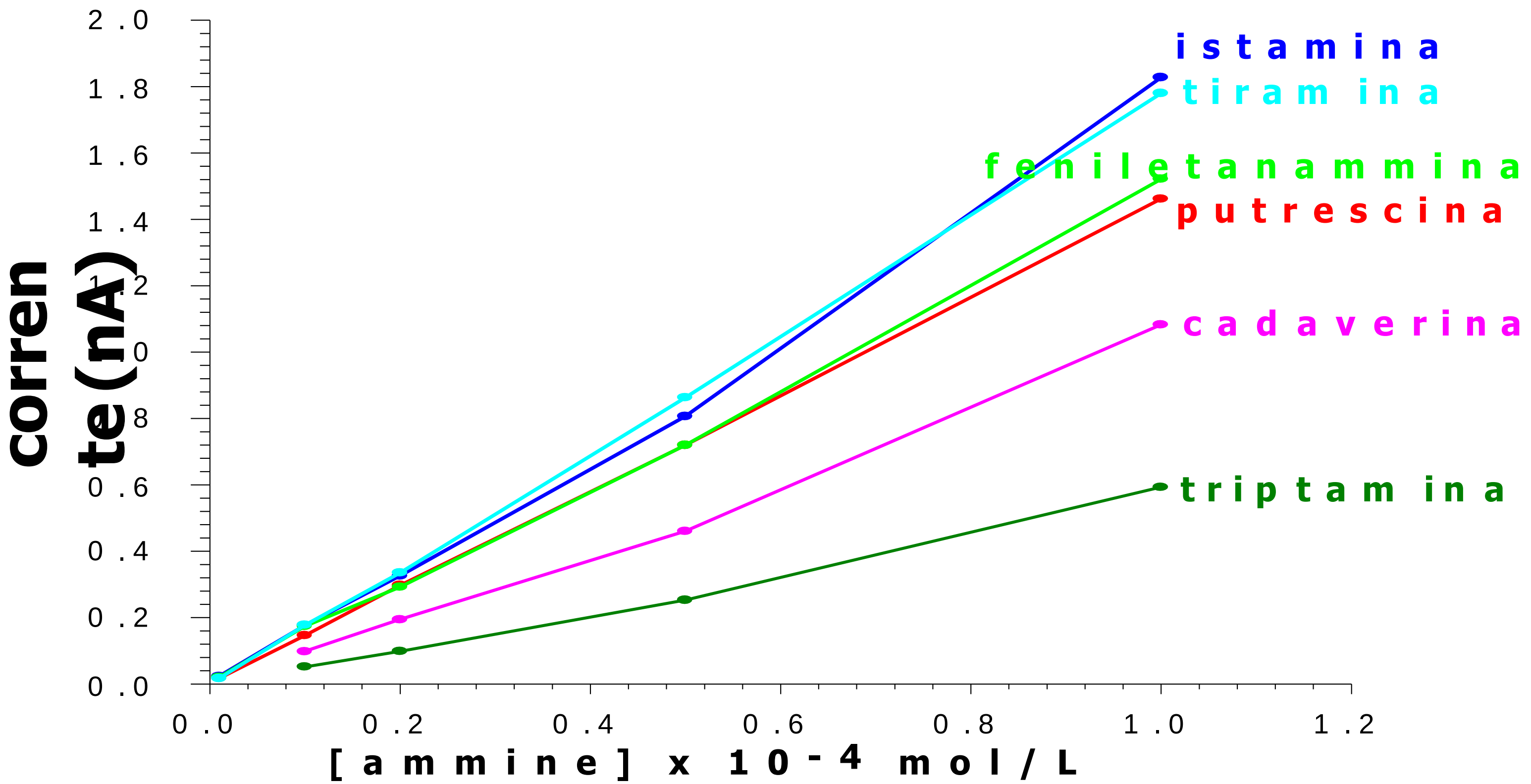

7
6.5
6
5.5
5
4.5
4
pH
1.00
0.75
0.50
0.25
0.00
g/100g
0
30
60
90
120
150
180
210
Time (min)
pH
L-lactate

B


7
6.5
6
5.5
5
4.5
4
pH
0.75
0.50
0.25
0.00
g/100g
0
30
60
90
120
150
180
Time (min)
pH
L-lactate

Biogenic amines

$$R\text{-}CH_2\text{-}NH_2 + O_2 + H_2O \longrightarrow R\text{-}CHO + NH_3 + H_2O_2$$



Total amines (mg/mL), expressed as equivalents of Put, measured in apricot samples using DAO biosensor[a].

		Storage time 20 days, temp. 0 ± 1°C		
variety	at harvest	LDPE	Super L	air
Pellecchiella				
ripening time I	5.6 ± 0.5	3.0 ± 0.2	2.9 ± 0.6	3.4 ± 0.6
ripening time II	5.5 ± 0.2	3.1 ± 0.4	3.0 ± 0.7	3.6 ± 0.0.2
Boccuccia				
ripening time I	5.2 ± 0.2	2.2 ± 0.1	3.7 ± 0.7	4.9 ± 0.2
ripening time II	5.1 ± 0.2	4.6 ± 0.8	4.6 ± 0.4	5.1 ± 0.1

$$alcohol + O_2 \xrightarrow{AOx} aldehyde + H_2O_2$$

Immobilization: PEI on Pall Immunodyne
Storage: 1% sucrose
Optimised operative conditions: 0.1 M phosphate buffer pH 7.0 + 0.02% Tween. Flow rate 1 mL/min; injection loop 500 μL.
Analitycal performances:
detection limit 10^{-6} mol/L
linearity 2 x 10^{-6} / 10^{-3} mol/L
stability: 20% decrease after 200 samples

$$glycerol + ATP(Mg^{2+}) \xrightarrow{GK} glycerol\text{-}3\text{-}P + ADP$$

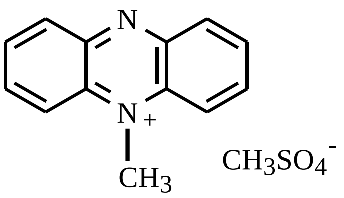
$$glycerol\text{-}3\text{-}P + O_2 + H_2O \xrightarrow{GPO} glycerone\text{-}3\text{-}P + H_2O_2$$

Immobilization: GK on aminopropyl glass beads (via glutaraldehyde), GPO on Immunodyne
Storage: DEAE-dextran/lactitol (1/5%)
Optimised operative conditions: 0.1 M borate buffer pH 8.5 + 3 mM ATP(Mg^{2+}) + 0.02% Tween. Flow rate 0.5 mL/min; injection loop 250 μL.
Analitycal performances:
detection limit 10^{-6} mol/L
linearity 2.5 x 10^{-6} / 5 x 10^{-4} mol/L
stability: 40% decrease after 200 samples

Fructose

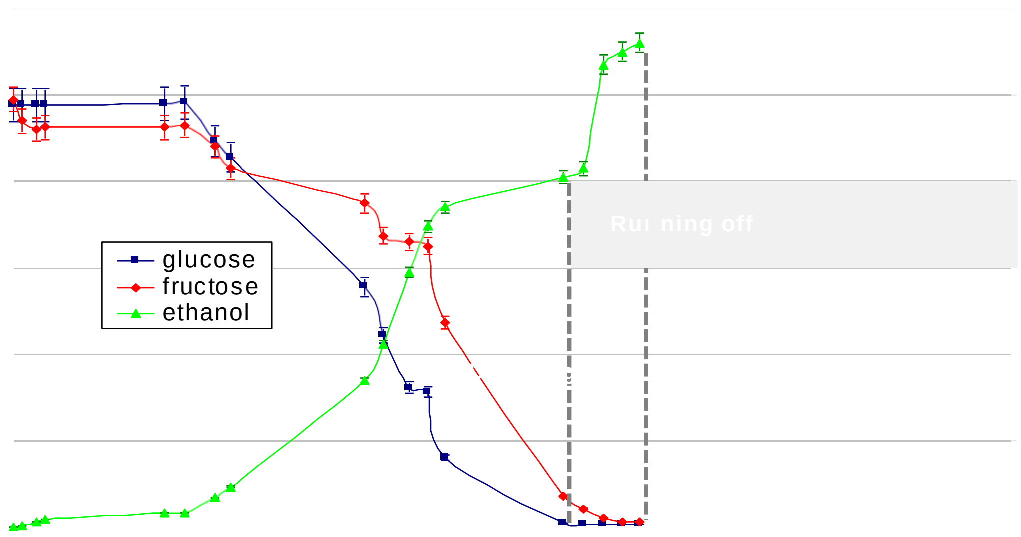
fructose + 2 PMS^+ —*FDH*→ ketofructose + 2 PMSH

PMSH —*+100 mV (Pt)*→ PMS^+ + e^-

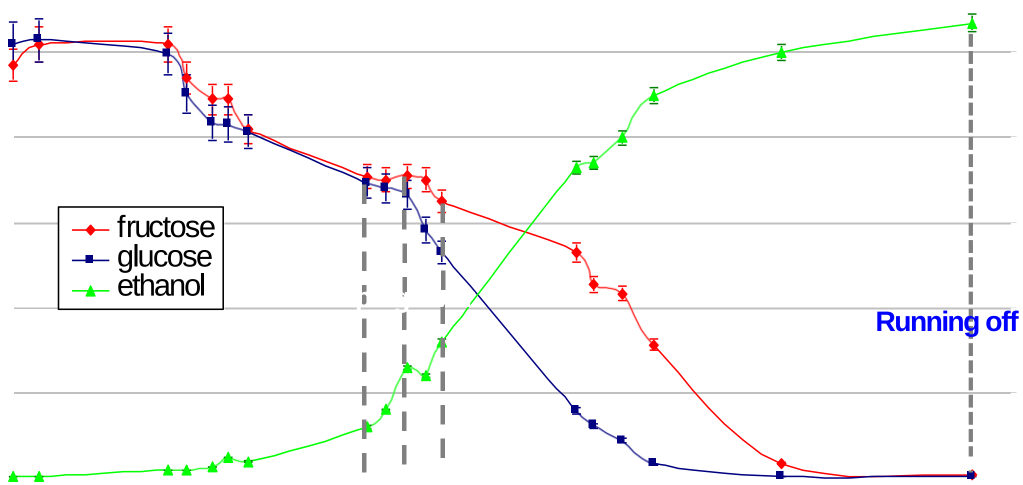


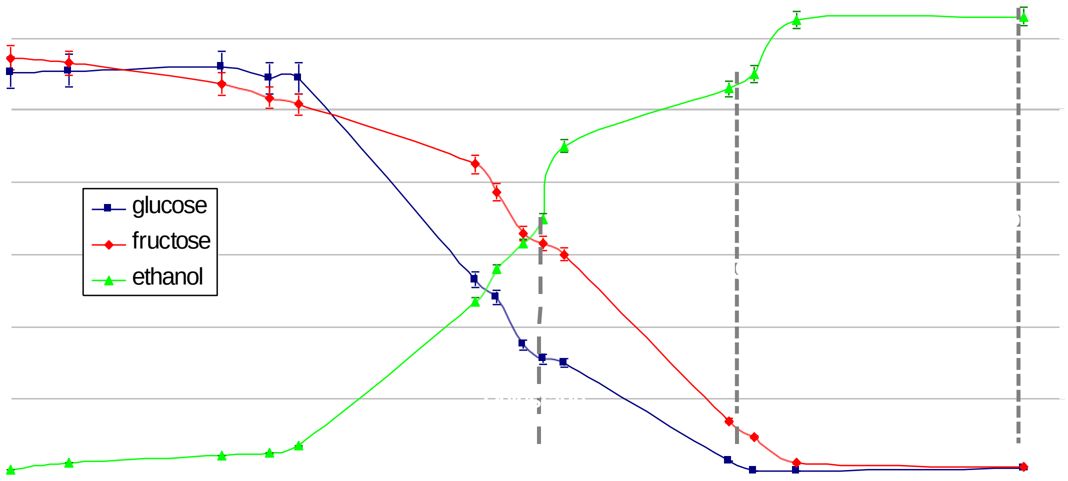
Immobilization: BSA-glutaraldehyde on Immobilon AV
Storage: DEAE-dextran/lactitol (1/5%)
Optimised operative conditions: 0.1 M citrate/phosphate buffer pH 4.5 + 0.02% Tween. Flow rate 0.5 mL/min; injection loop 100 µL.
Analitycal performances:
detection limit 5 x 10^{-7} mol/L
linearity 10^{-6} / 8 x10^{-4} mol/L
stability: 30% decrease after 200 samples

One delestage

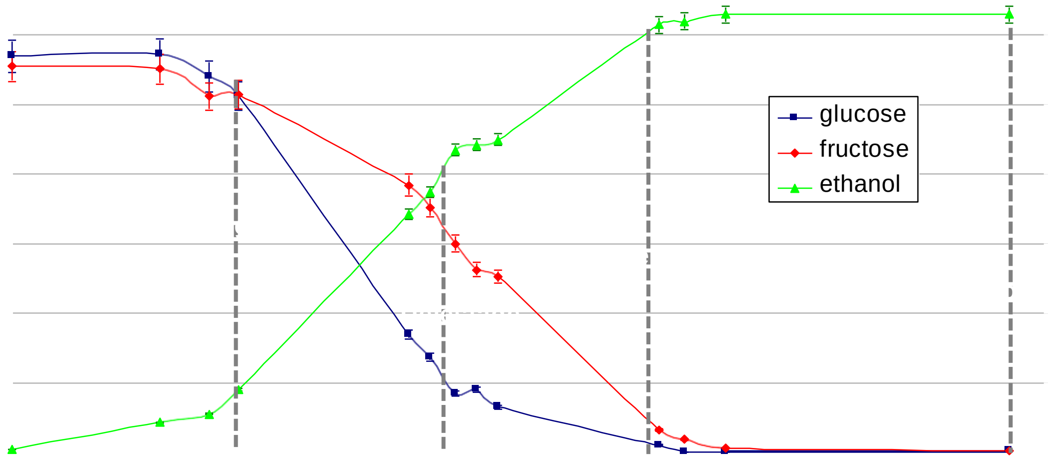


Pumping-over



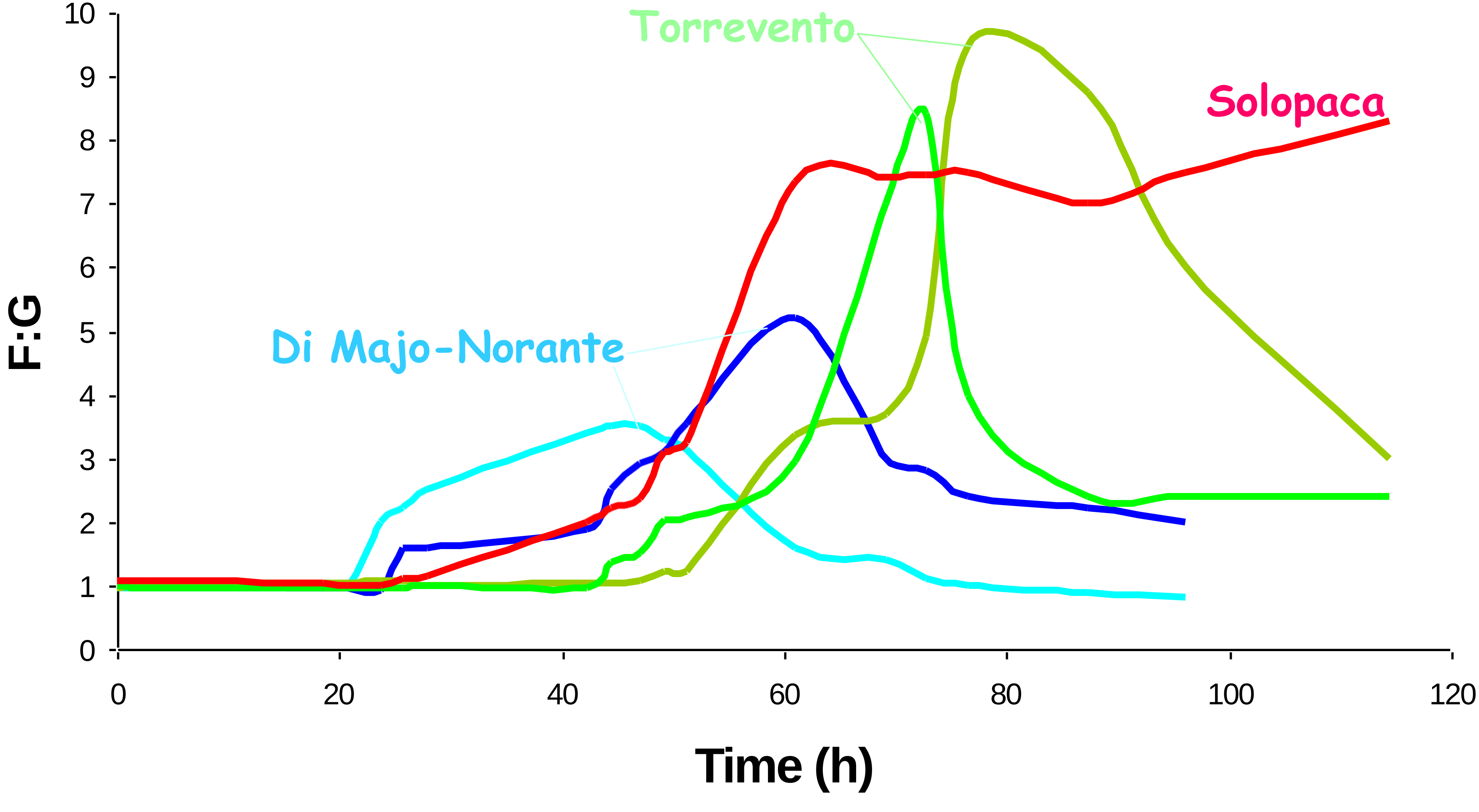


glucose
fructose
ethanol

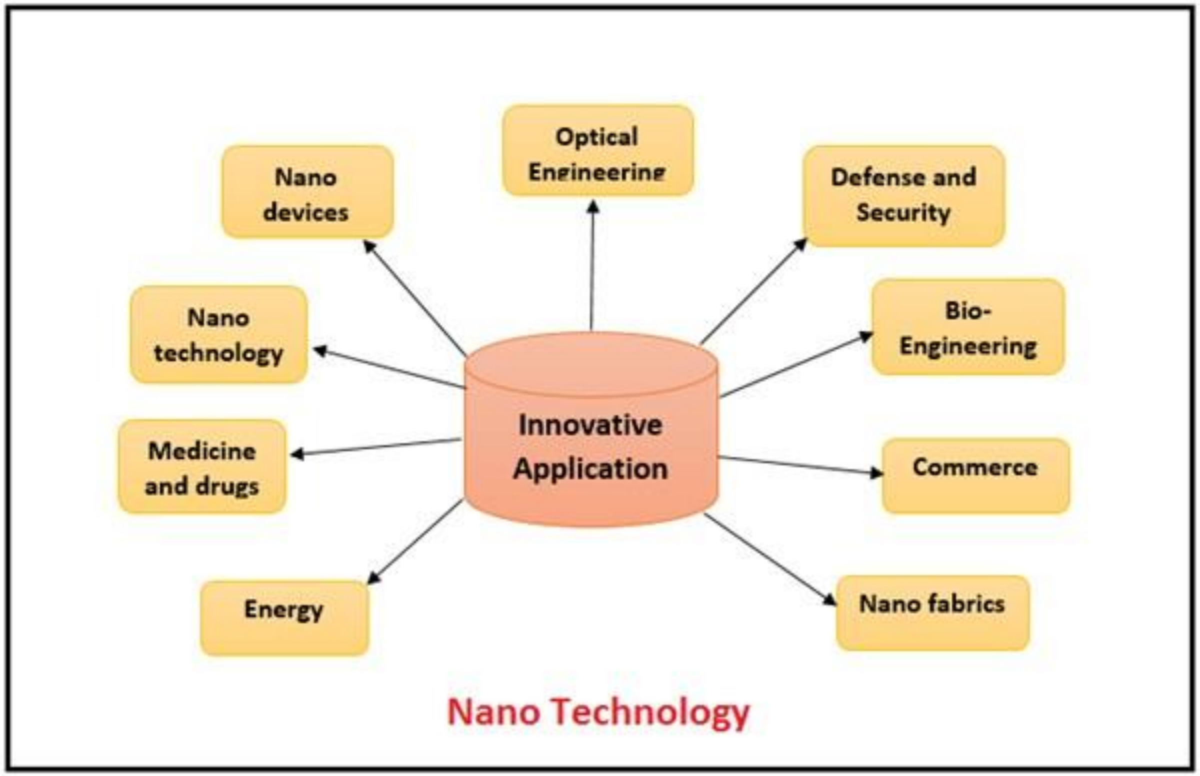


glucose
fructose
ethanol

Fructose:Glucose ratio during alcoholic fermentation



Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometer



Nanomaterials

Pros

- ✓ Different chemical nature
- ✓ Different morphologies
- ✓ High surface/volume ratio
- ✓ High functionalizability
- ✓ Easy interfaceability
- ✓ Size/morphology dependent properties → **tunability**

Sensor **sensitivity & selectivity** improvement

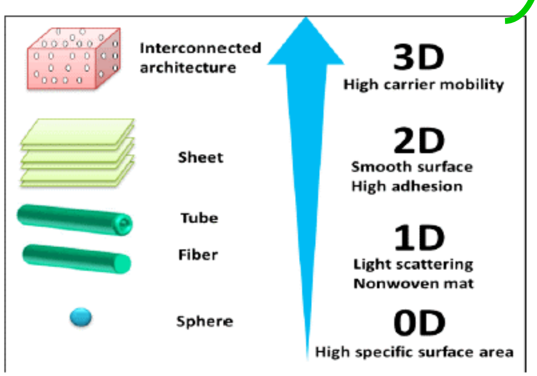
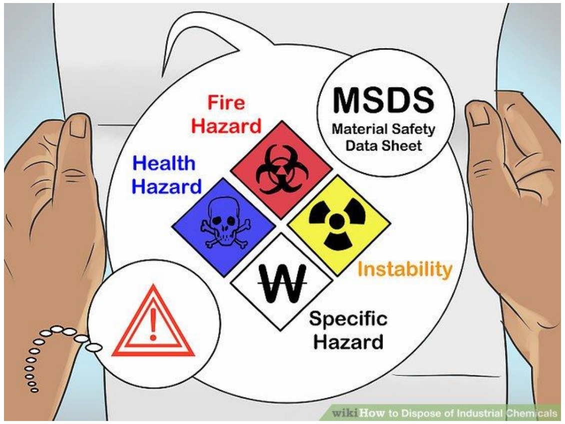


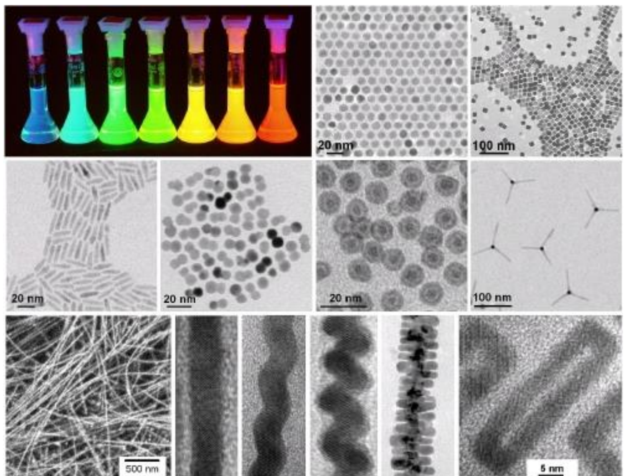
Figure 1: Schematic illustration of structural dimensionality of nanomaterials with expected properties.

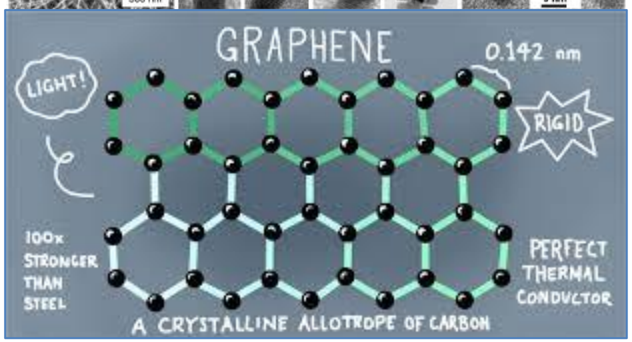


Potential drawbacks

- ? Waste disposal
- ? Potential toxicity

Nanomaterials employed in electrochemical sensor

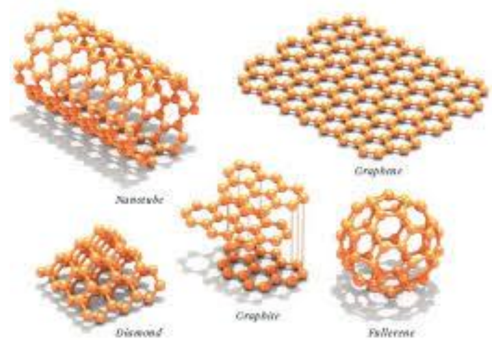


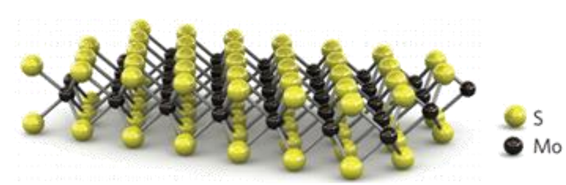


Carbon based nanomaterials:
- Nanotubes
- Fullerenes
- Graphene
- Etc…

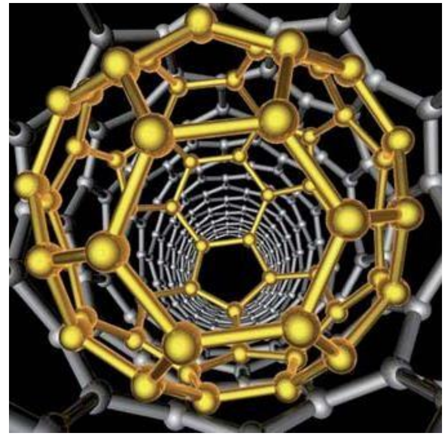
Nanoparticles:
- Metal nanoparticles
- Metal Oxide nanoparticles

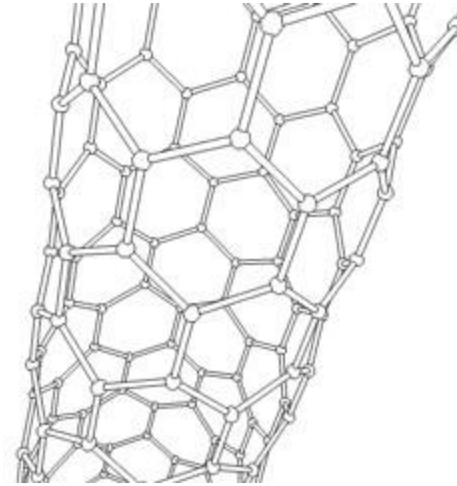
Graphene-like nanomaterials:
- e.g. Transition Metal Dicalchogenised (TMD)





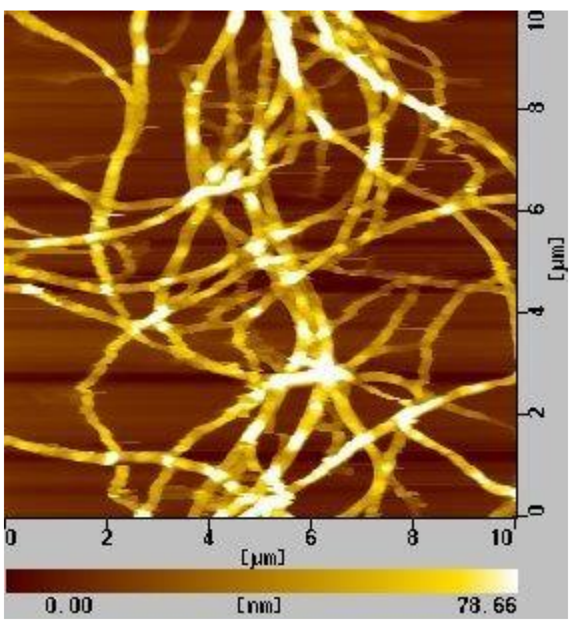
CARBON NANOTUBES

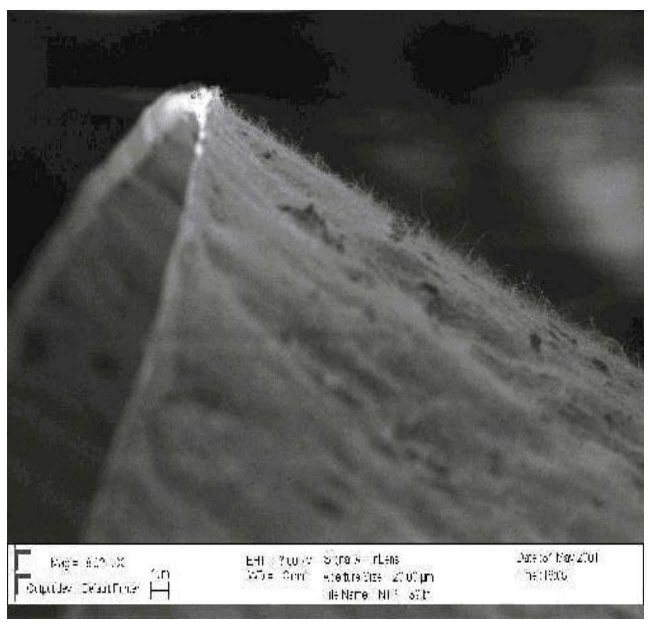


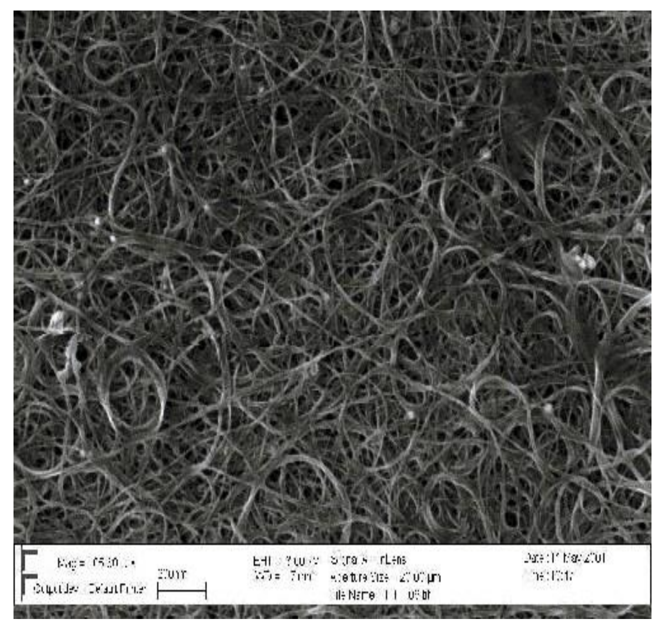


CHARACHERISTICS

- porous structure;
- high mechanichal strenght;
- easy to be modified;







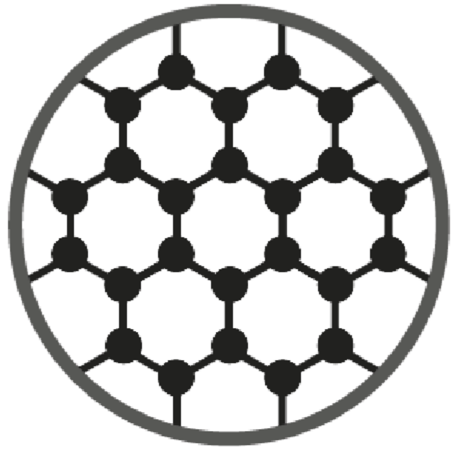
GRAPHENE: THE CARBON-BASED 'WONDER MATERIAL'

Since its discovery in 2003, graphene has been a hot topic in chemistry and materials science research. It's been linked with water purification, electronics, and biomedical applications. However, how close are we really to using graphene in our day-to-day lives? This graphic looks at its properties, uses, and future.

WHAT IS GRAPHENE?

- SINGLE LAYER OF CARBON ATOMS
- HONEYCOMB-LIKE STRUCTURE
- GRAPHITE IS LAYERS OF GRAPHENE
- ISOLATED IN 2003 IN MANCHESTER

Graphene is a single layer of graphite, the carbon-based material found in pencil leads. Graphite has been known for centuries, but graphene was only isolated in 2003, by shearing layers off of graphite using sellotape. It's a single atom-thick layer of carbon atoms, that are arranged in a flat, hexagonal lattice structure.



THE PROPERTIES OF GRAPHENE

- HIGH ELECTRICAL CONDUCTIVITY
- 200X STRONGER THAN STEEL
- THIN AND LIGHTWEIGHT
- HIGH THERMAL CONDUCTIVITY
- VERY HIGH TRANSPARENCY

Graphene's 'wonder material' reputation stems from its superlative properties. It is a million times thinner than a piece of paper, yet stronger than diamond, and 200 times stronger than steel, due to the strong carbon-carbon bonds. It's also a flexible material, and conducts heat and electricity better than copper. Being only one atom thick, almost 98% of visible light passes through graphene, making it transparent.

POTENTIAL USES OF GRAPHENE

TOUCH SCREENS IN DEVICES

Graphene's transparency and conductivity means that it can be used in displays and touchscreens. However, currently these are more expensive to produce than the currently used material, indium tin oxide.

WATER FILTRATION SYSTEMS

Graphene allows water to pass through it, but not other liquids and gases, so it can be used in water purification. Researchers are working on a device that could be capable of filtering salt from sea water.

IN ELECTRONIC DEVICES

Graphene has been touted as silicon's successor, and has been used to make very fast transistors. However, its conductivity cannot be 'switched off' as silicon's can. Other 2D materials seem more promising.

MEDICAL SENSORS & DRUG DELIVERY

Several biomedical applications are being explored for graphene, including drug delivery, cancer therapy, and its use as a sensor. However, its toxicity profile must be investigated before any clinical uses.

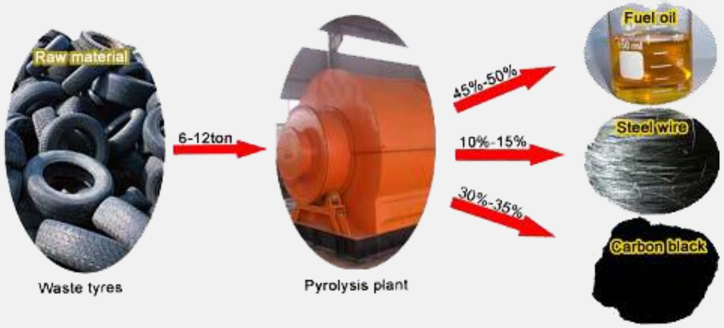
ENERGY STORAGE & COMPOSITES

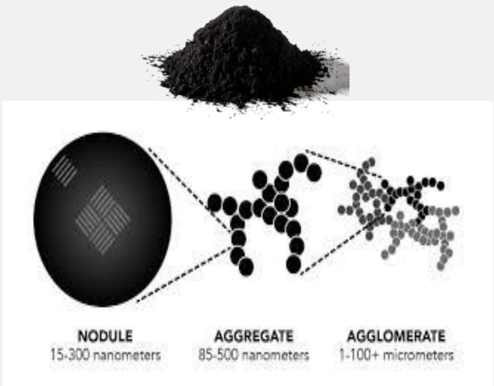
Graphene-based energy storage devices are possible. It can also substitute for graphite in normal batteries, improving efficiency. Additionally, it can be added to materials to make them stronger and more lightweight.

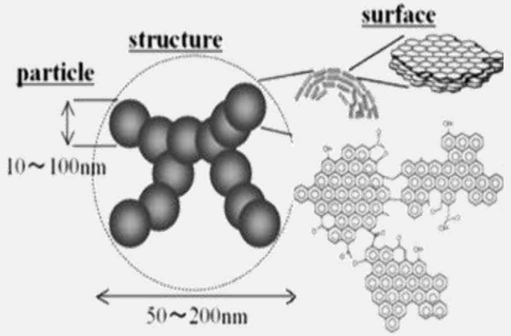
UNITE UNIVERSITÀ DEGLI STUDI DI TERAMO

Carbon based nanomaterials
(Carbon Black, CB)

Nano Carbon Black





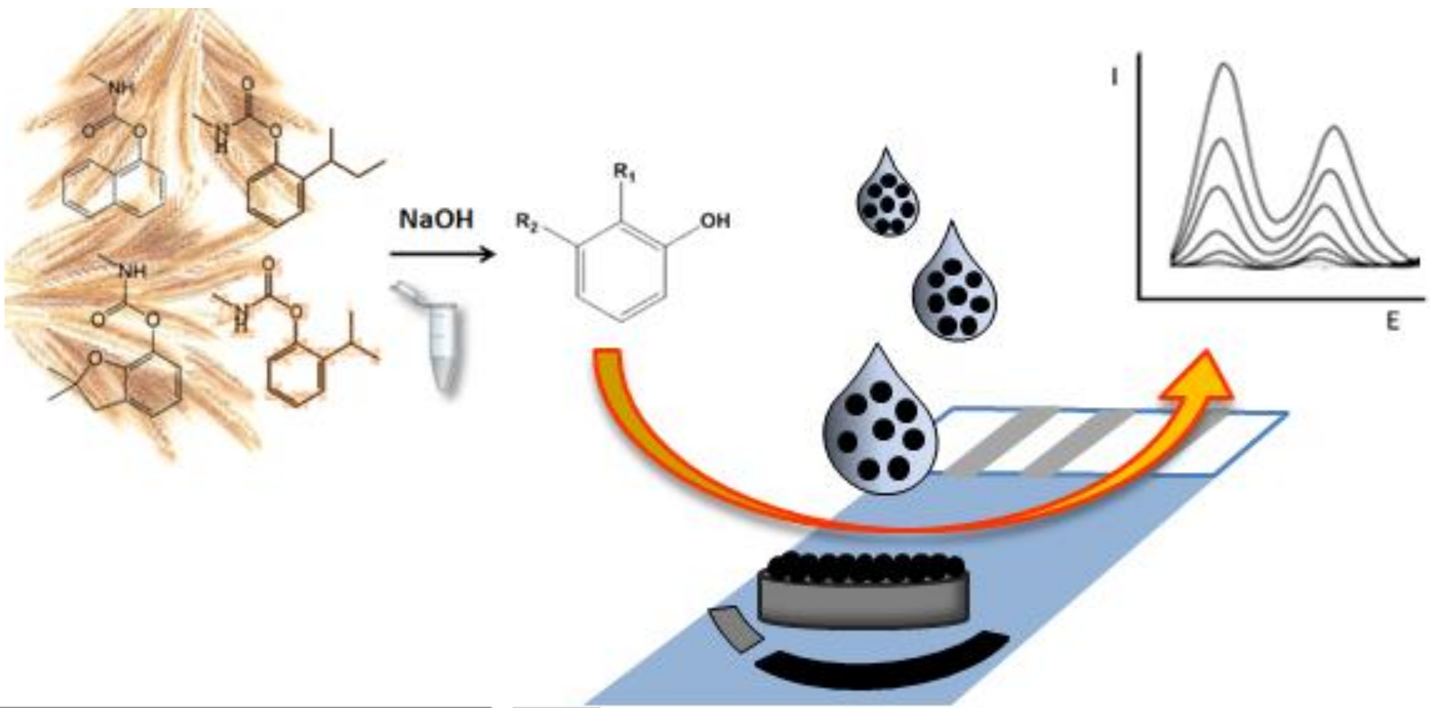


Electrocatalysis →	Selectivity
High surface →	Sensitivity
Resistance to fouling →	Reproducibility
Faster eletron transfer →	Improving separation performance

CB compared with other nanomaterials:

Very low cost
No synthesis
No impurities due to synthesis
Easily dispersible
Large number of defect sites

SPE CBNPs for direct analysis of carbamates in grain samples



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Nano carbon black-based screen printed sensor for carbofuran, isoprocarb, carbaryl and fenobucarb detection: application to grain samples

Flavio Della Pelle, Claudia Angelini, Manuel Sergi, Michele Del Carlo, Alessia Pepe, Dario Compagnone*

Nano carbon black-based screen printed sensor for carbofuran, isoprocarb, carbaryl and fenobucarb detection: application to grain samples

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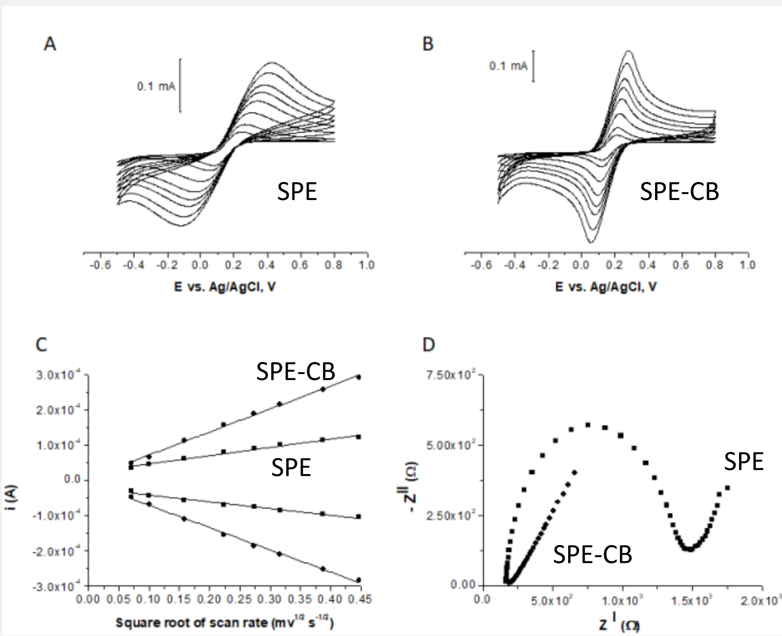
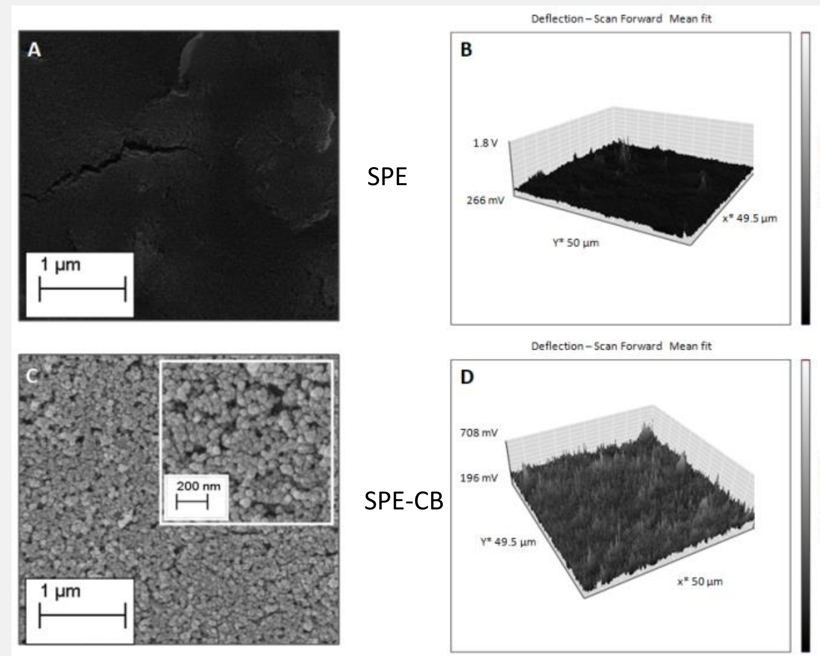
SPE vs. SPE-CB electrochemical performance



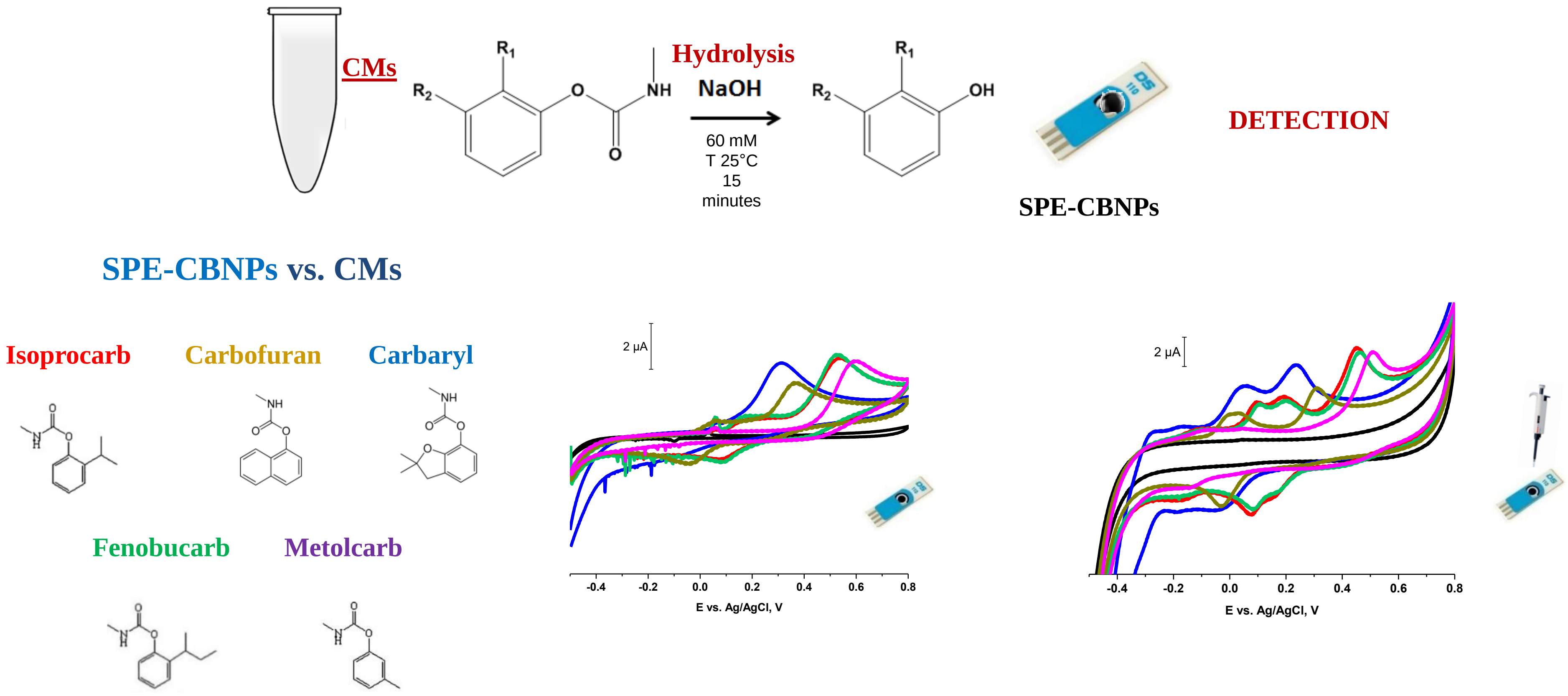
1 mmol L^{-1} **ferricyanide** solution in 0.1 mol L^{-1} KCl of SPE CV performed at 5, 10, 25, 50, 75, 100,150 and 200 mV s^{-1}

SEM

AFM

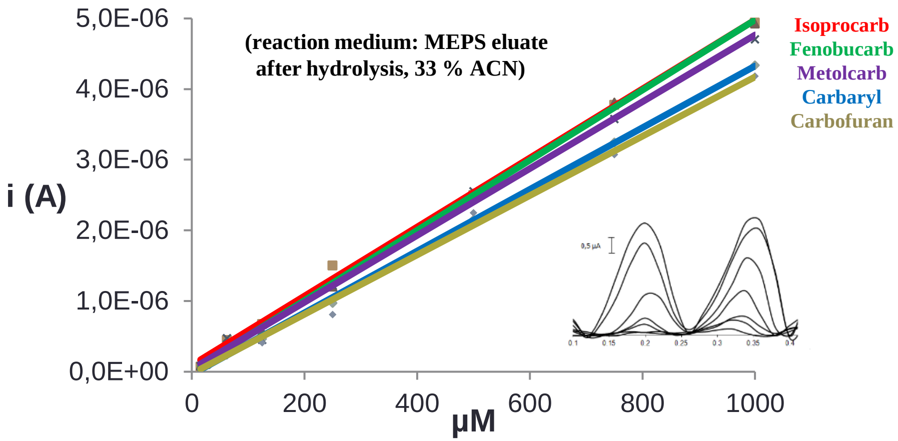


SPE CBNPs for direct analysis of carbamates in grain samples



SPE CBNPs for direct analysis of carbamates in grain samples

SPE-CBNPs CMs Calibration, Reproducibility and Fouling resistance



Analyte	Linear range (µmol L-1)	Regression equation (Y=am + b)	Coefficient of determination (r^2)	Detection limit (µmol L-1)	Quantification limit (µmol L^{-1})
Isoprocarb	0.1-100	y = 3E-08x + 5E-09	**0.9971**	0.6	**0.7**
Carbofuran	0.1-100	y = 6E-08x - 1E-08	**0.9999**	0.4	**0.5**
Carbaryl	0.1-100	y = 6E-08x + 2E-08	**0.9983**	0.4	**0.5**
Fenobucarb	0.1-100	y = 3E-08x - 8E-09	**0.9996**	0.6	**0.7**
Metolcarb	0.1-100	y = 6E-08x + 4E-08	**0.9980**	0.3	**0.4**

Peak intensity (RSD, n=7): < 0.9 %

Peak potential (RSD, n =7): < 4,8 %

Inter electrode reproducibility (RSD, n=10): < 6.6 % p.i and < 3,4 % p.E.

Fouling (peaks RSD):
DPV (n = 30, 250 µM) 96 % v.s.32 %
CV (n = 20, 500 µM) 94 % v.s 15 %

Nano carbon black-based screen printed sensor for carbofuran, isoprocarb, carbaryl and fenobucarb detection: application to grain samples

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Recoveries : 78–102%
Correlation: r= 0.952
Accuracy: relative error between 9.0% and −7.8%

Pesticide recoveries in grain samples

Analyte Spiked (mg Kg^{-1})	UHPL C-MS/MS recovery (%)[a]					CB-SPE recovery (%)[a]					Relative error (%)				
	HW	HWO	SW	SWO	MZ	HW	HWO	SW	SWO	MZ	HW	HWO	SW	SWO	MZ
CA															
0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD					
0.25	82 ± 6	87 ± 3	83 ± 9	89 ± 12	82 ± 15	88 ± 1	84 ± 4	76 ± 7	93 ± 8	85 ± 12	− 6.8	3.1	9.0	− 4.1	− 3.8
0.50	85 ± 2	84 ± 13	83 ± 2	81 ± 8	93 ± 7	88 ± 3	88 ± 11	80 ± 5	80 ± 6	90 ± 4	− 3.4	− 4.7	3.4	0.6	3.1
0.75	82 ± 10	78 ± 7	84 ± 1	82 ± 7	80 ± 4	85 ± 5	80 ± 9	87 ± 8	81 ± 9	84 ± 2	− 3.7	− 2.3	− 3.0	1.2	− 5.6
CF															
0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD					
0.25	80 ± 14	102 ± 10	83 ± 10	82 ± 14	81 ± 8	86 ± 9	97 ± 7	86 ± 6	79 ± 10	80 ± 9	− 7.8	4.8	− 3.7	3.4	1.9
0.50	78 ± 7	96 ± 6	78 ± 5	78 ± 5	79 ± 13	81 ± 4	100 ± 2	81 ± 3	80 ± 5	83 ± 11	− 3.3	− 4.8	− 3.6	− 2.9	− 5.6
0.75	79 ± 9	100 ± 9	84 ± 11	99 ± 131	79 ± 16	82 ± 5	100 ± 5	87 ± 7	100 ± 8	84 ± 9	− 3.4	− 0.6	− 3.1	− 0.7	− 6.4
IC															
0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD					
0.25	82 ± 5	80 ± 8	78 ± 8	84 ± 5	79 ± 8	82 ± 5	81 ± 6	82 ± 2	86 ± 9	80 ± 5	− 1.0	− 0.5	− 5.3	− 2.4	− 1.2
0.50	82 ± 7	85 ± 4	79 ± 2	78 ± 8	79 ± 5	81 ± 8	85 ± 4	81 ± 4	82 ± 6	78 ± 8	1.3	− 0.2	− 3.0	− 4.5	1.6
0.75	96 ± 2	96 ± 6	80 ± 3	95 ± 2	92 ± 14	96 ± 4	98 ± 9	80 ± 3	96 ± 4	97 ± 11	0.0	− 2.0	− 4.9	− 1.8	− 5.6
FB															
0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD					
0.25	83 ± 9	87 ± 7	83 ± 15	80 ± 4	87 ± 9	84 ± 5	92 ± 4	80 ± 13	79 ± 4	88 ± 3	− 0.9	− 5.3	8.0	4.5	− 0.9
0.50	79 ± 12	78 ± 9	97 ± 2	78 ± 5	80 ± 9	78 ± 8	82 ± 11	102 ± 0	78 ± 2	78 ± 6	7.7	− 5.7	− 5.2	4.7	5.1
0.75	89 ± 11	78 ± 8	102 ± 7	94 ± 13	79 ± 13	84 ± 11	81 ± 10	99 ± 3	96 ± 9	84 ± 11	5.6	− 4.1	3.3	− 2.5	− 6.8

[a] Mean value (n = 3) of three different extracts were employed for the recovery and relative error calculation for both CB-SPE and UHPLC-MS/MS methods.

Transition Metal Dichalcogenides and their hybrid nanomaterials

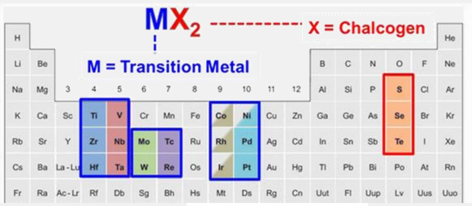
Objective	MoS_2 hybrids	WS_2 hybrids	Group VI Transition Metal Dichalcogenides

Transition Metal Dichalcogenides (TMDs)

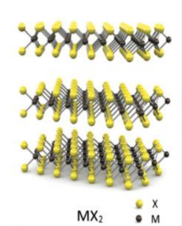
TMDs are a family of 2D nanomaterials with general formula MX_2 (M: Group 4-10 and X: S, Se and Te)

Arranged in a multilayered structure held by weak van der Walls forces

TMDs nanosheets easily prepared by exfoliation



TMDs general structure



Polyphenols electrochemical sensing

Limitations using common electrodes

- Tendency to passivation (so called Fouling)

Nanomaterials

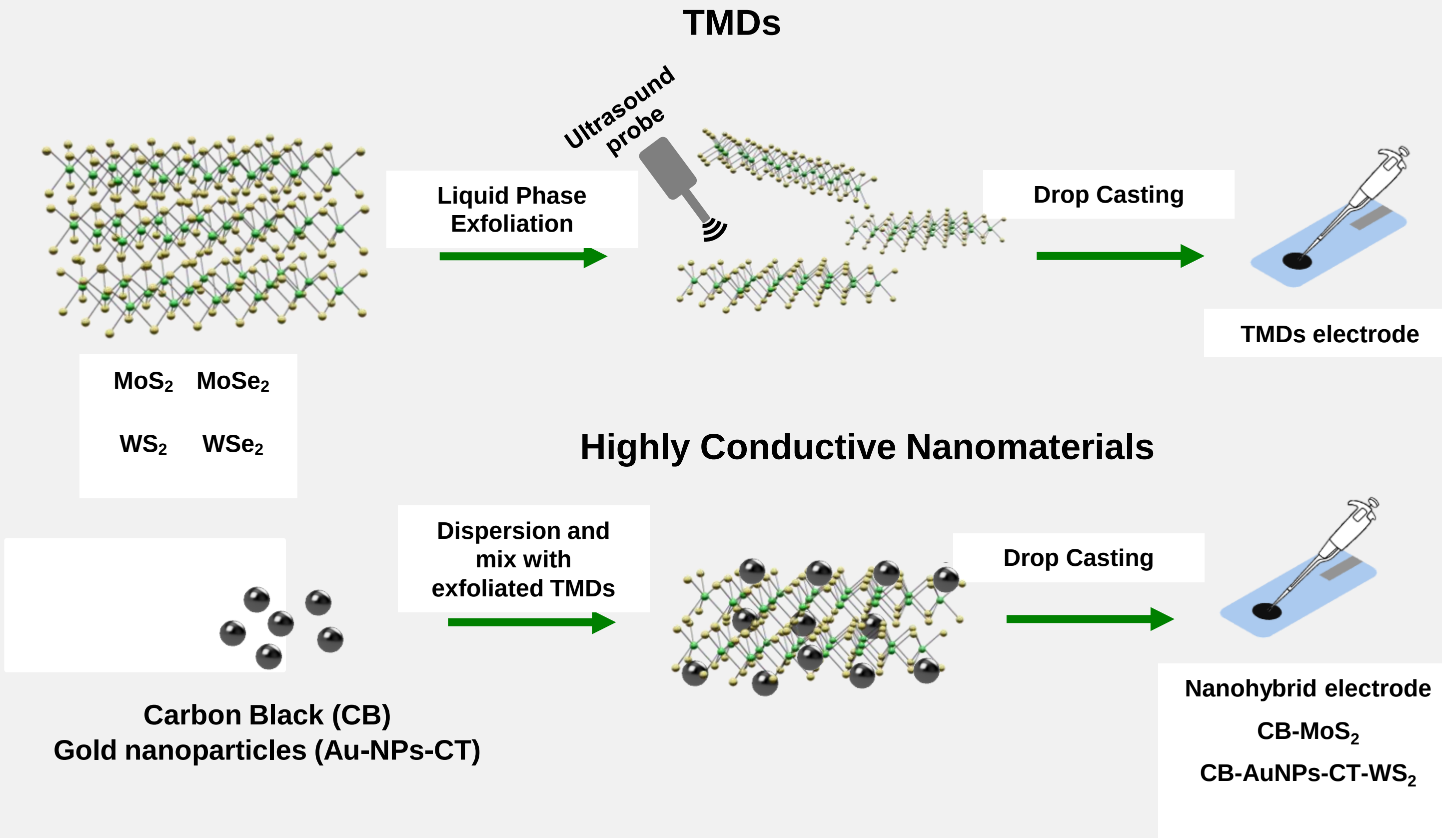
✓TMDs are poor conductive materials

✓Hinder its catalytic capabilities

Nanohybrids materials

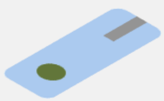
Transition Metal Dichalcogenides and their hybrid nanomaterials

Electrode preparation methods



Transition Metal Dichalcogenides and their hybrid nanomaterials

Objective | **MoS_2 hybrids** | WS_2 hybrids | Group VI Transition Metal Dichalcogenides



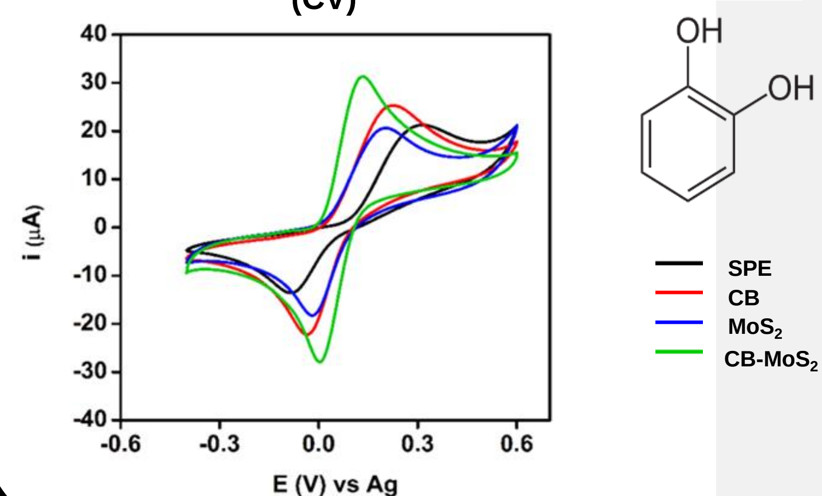
CB-MoS_2

Electrochemical characterization

Catechol as representative redox moiety in food polyphenols

Cyclic Voltammetry (CV)

Catechol



Catechol moiety is present in highly antioxidant polyphenols

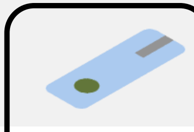
CB–MoS_2 nanohybrids shows an enhanced and synergistic electrocatalytic effect towards catechol

D. Rojas, F. Della Pelle, M. Del Carlo, E. Fratini, A. Escarpa, D. Compagnone. Microchim. Acta. 186 (2019) 363.

Transition Metal Dichalcogenides and their hybrid nanomaterials

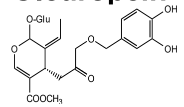
Objective | **MoS_2 Nanohybrids** | WS_2 Nanohybrids | Group VI Transition Metal Dichalcogenides

Application of CB-MoS_2 electrochemical sensors to different food matrices

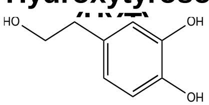


Olive oil

Oleuropein

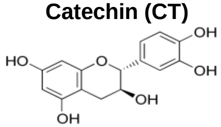


Hydroxytyrosol

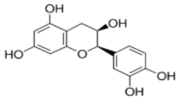


Cocoa

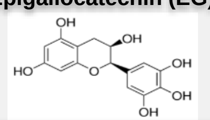
Catechin (CT)



Epicatechin (EP)



Epigallocatechin (EG)



✓ **Catalytic effect extensive to complex structures**

Correlation matrix: electrochemical sensor and well stablished analysis

CB-MoS_2	HPLC-UV	ABTS	AuNPs	FC
Olive Oil	0.995	-	-	-
Cocoa	-	0.966	0.949	0.972

✓ **Antifouling effect: nanohybrid n=50 measurements vs n=1 carbon**

D. Rojas, F. Della Pelle, M. Del Carlo, E. Fratini, A. Escarpa, D. Compagnone. Microchim. Acta. 186 (2019) 363.

F. Della Pelle, **D. Rojas**, A. Scroccarello, M. Del Carlo, G. Ferraro, C. Di Mattia, M. Martuscelli, A. Escarpa, D. Compagnone, Sensors Actuators B Chem. 296 (2019) 126651.

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Co-funded by: University of Teramo, Region Abruzzo

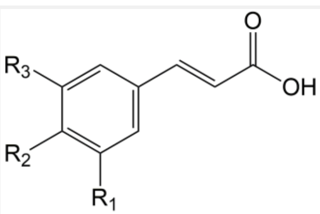
Transition Metal Dichalcogenides and their hybrid nanomaterials

Objective	MoS_2 Nanohybrids	WS_2 Nanohybrids	Group VI Transition Metal Dichalcogenides

WS_2 nanohybrids electrochemical behavior towards different hydroxycinnamic acids (hCNs)

CB-AuNPs-CT-WS_2

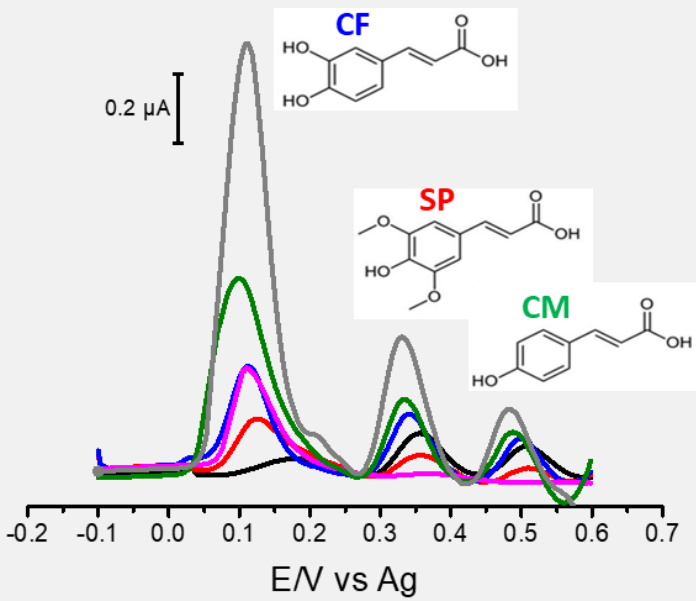
hCNs general structure



R_1=R_2=OH Caffeic Acid

R_1=R_3=OCH_3 R_2=OH Sinapic Acid

R_2=OH Coumaric Acid



- ✓ **Synergistic electrocatalytic effect**
- ✓ **Effective voltametric separation**
- ✓ **Antifouling (97% signal retention (n=15))**

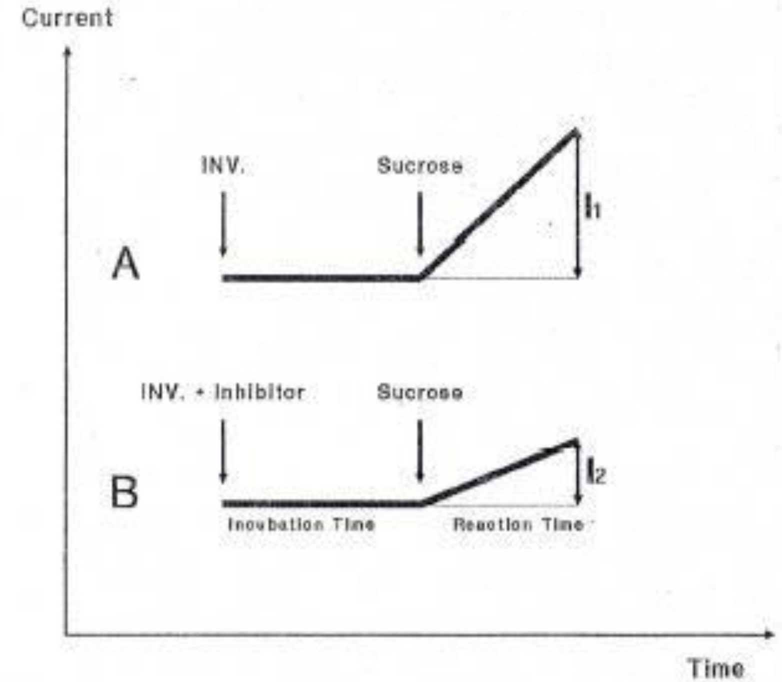
F. Della Pelle, **D. Rojas**, F. Silveri, G. Ferraro, E. Fratini, A. Scroccarello, A. Escarpa, D. Compagnone. Microchim. Acta. 187 (2020) 296.

Biosensors based on enzyme inhibition

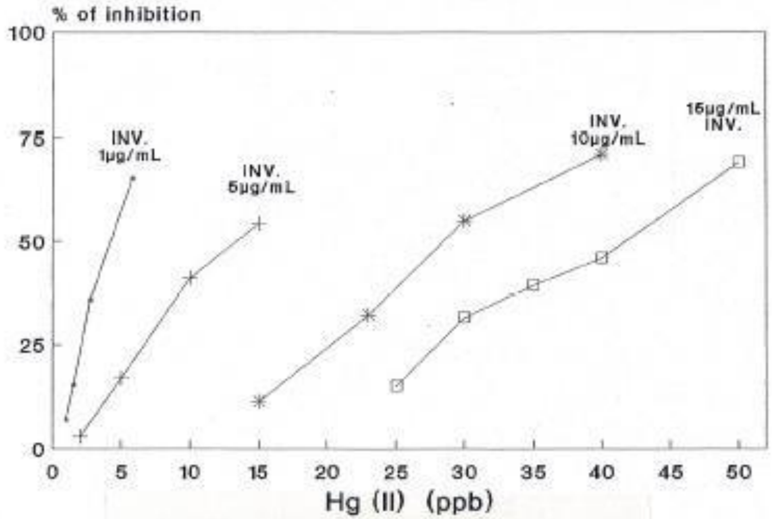
There is a great demand for rapid and sensitive analytical methods for the determination of mercury and related compounds in environmental samples. The environmental risk and toxicological concern of mercury and its compounds, especially methylmercury, have stimulated the research into various new methods of trace analysis.

Many enzymes are inhibited specifically by low concentrations of certain chemical substances.

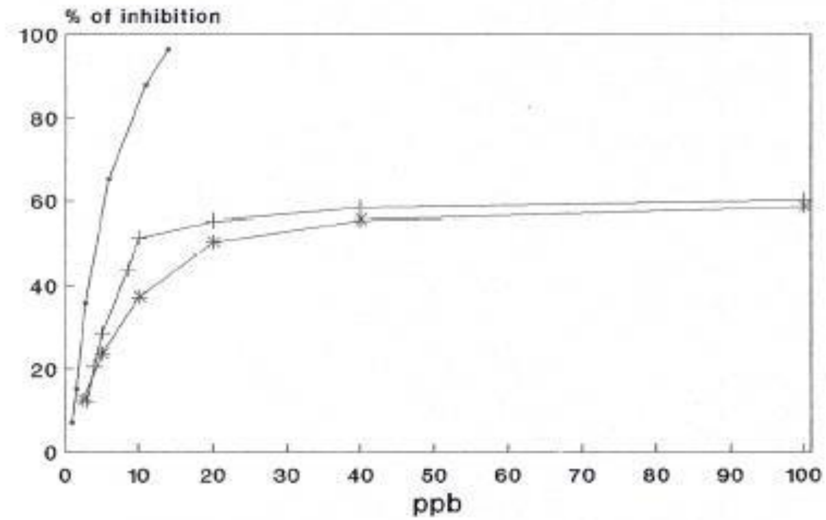
Toxicity of mercury depends on its chemical form. For example methyl mercury is more toxic than HgII (1).



Typical current-time curves obtained in the absence (A) and in the presence (B) of inhibitor.



Calibration curves of Hg(II) with different enzyme concentrations. 5mM sucrose, phosphate buffer pH 6.0. 10 minutes incubation time.



Calibration curves of Hg(II) (.), MetHg (+) and EtHg (*). 1 µg/mL invertase; 5 mM sucrose; phosphate buffer pH 6.0; 10 min. incubation time.

Biosensor for organophosphate and carbamates pesticides (phytochemicals)

High acute toxicity (200.000 deaths/year in the 80s)

High chronic toxicity

Moderate persistence

Mechanism of action:
inhibition of acetylcholinesterase (AChE)

Classical methods:

GC-NPD o GC-MS, LC-MS

Scheme of the measurement

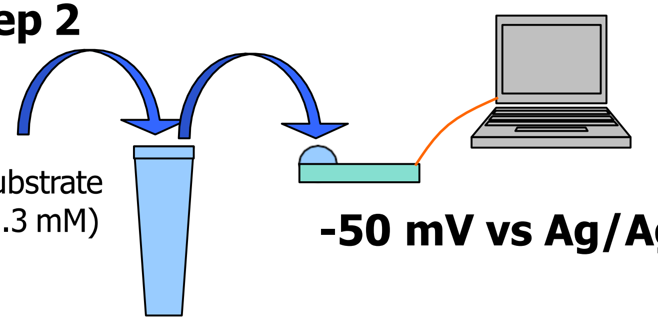
step 1

0.125 U/ml AChE

1 mL buffer +
standard or sample

10’ incubation

step 2

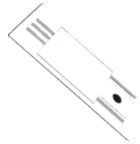


Substrate
(0.3 mM)

-50 mV vs Ag/AgCl

120’’

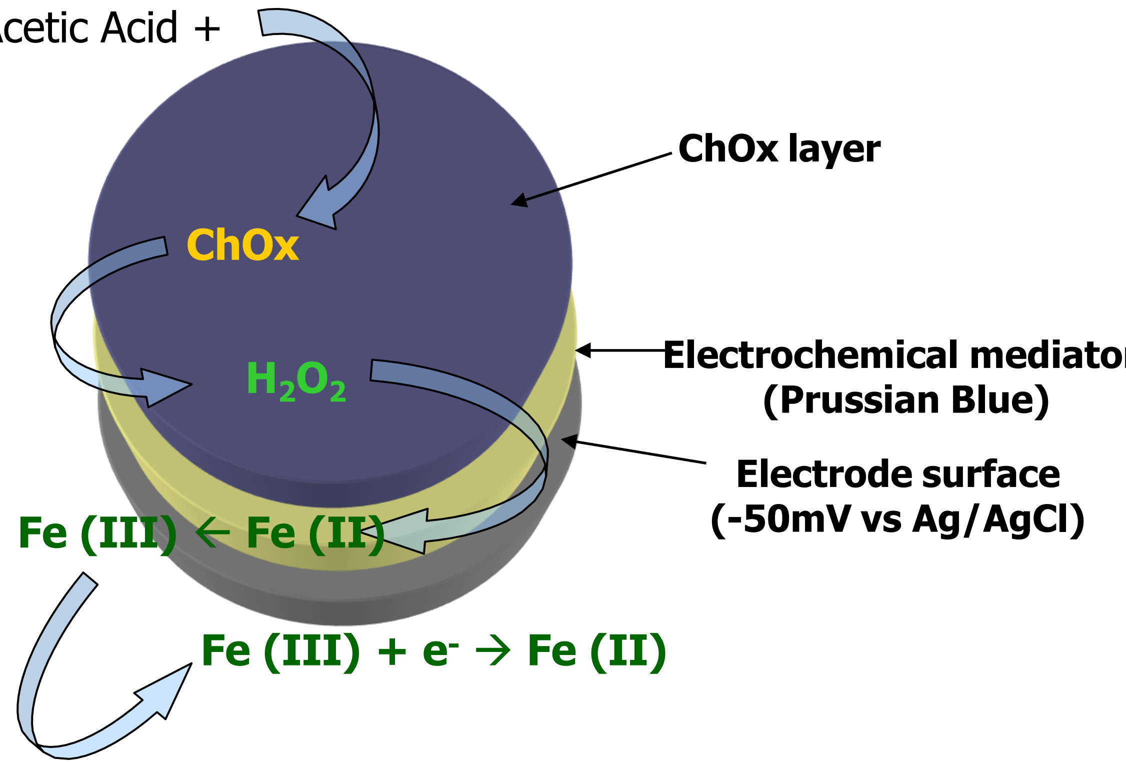
$$RA\% = 100 * \frac{(I_0 - Is)}{I_0}$$



Screen printed electrode

Working electrode reactions pathway

Acetylcholine + H_2O → Acetic Acid + **Choline** (AChE)



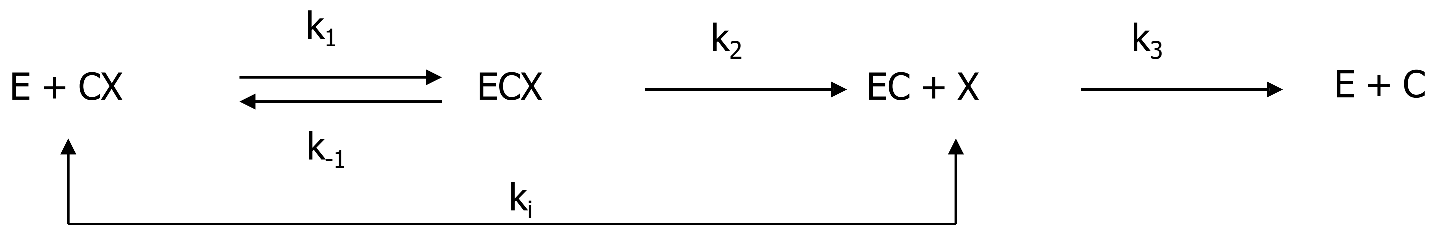
Project PON target molecules:

Ability to detect at ng/mL;
Precision = 10%;
Total analysis time = 20 min

Diclorvos (organophosphate)
Pirimifos-metile (thiophosphate)

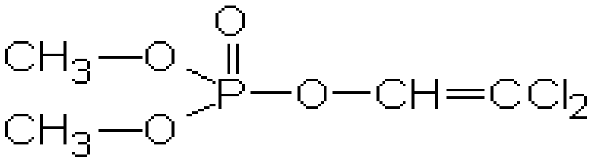
anticolinesterasic

Mechanism of AChE inhibition



E = enzyme; CX = carbamate or organophosphate; X = leaving group; $K_d = k_{-1} / k_1k_2$ carbamoylation or phosphroylation rate constant; k_3 = decarbamylation or dephosphorilation rate constant; k_i = bimolecular rate constant

Dichlorvos



Solubility in water: **16 g/l**

2,2-Dichlorovinyl dimethyl phosphate

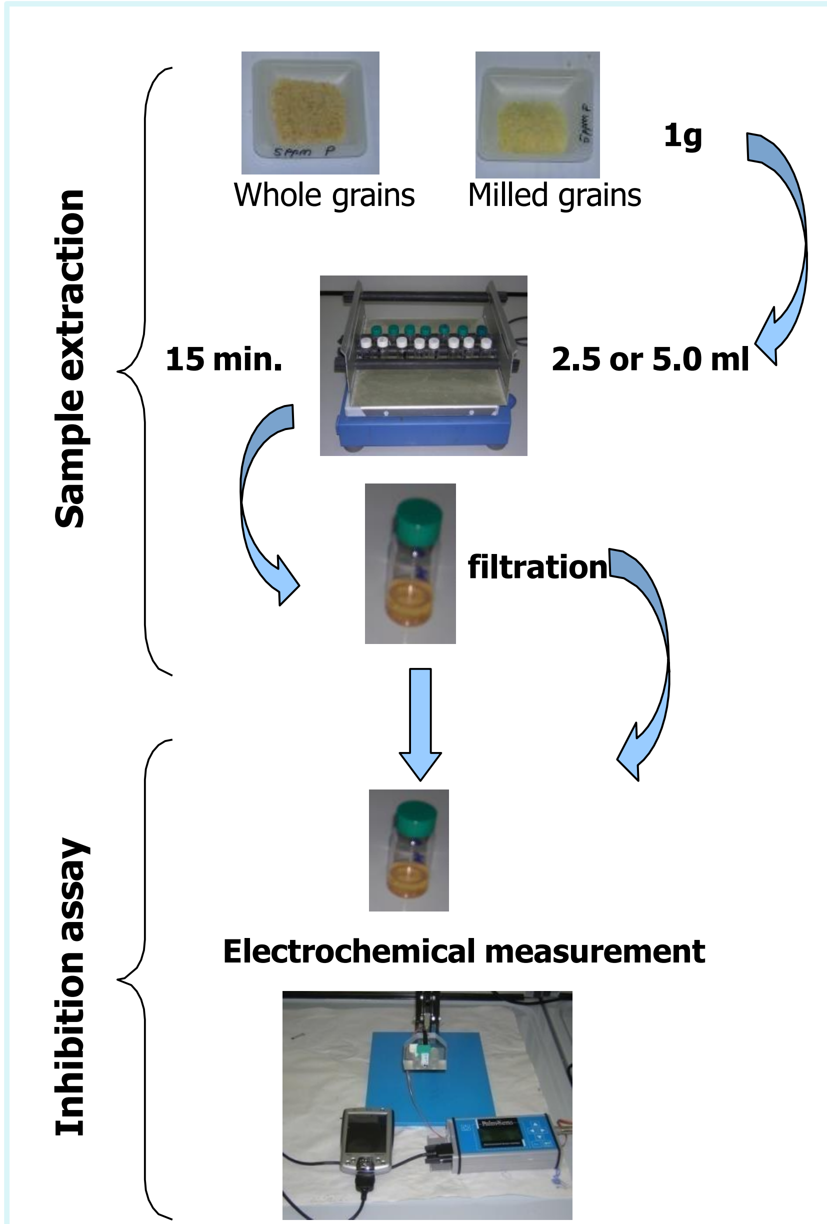
- Commercial formulation **Didivane®** is used as broad spectrum grain protectant insecticide.
- Effective in controlling a wide range of insects that attack stored grain products.
- It provides long-term protection against re-infestation from insects.

The European Union regulates the maximum adsmissible level in **durum wheat** at **2 mg/Kg** (European Directive 2001/57/CE)

Quantitative Usage for dichlorvos

The annual agricultural use of dichlorvos was estimated as 248,000/year during 90' (ATSDR, 1997). Estimates done in late 1990s indicate that 60% of dichlorvos used worldwide was for plant protection, 30% was for public hygiene and vector control, and **10% to protect stored crops (WHO, 1999)**.

Extraction + assay protocol

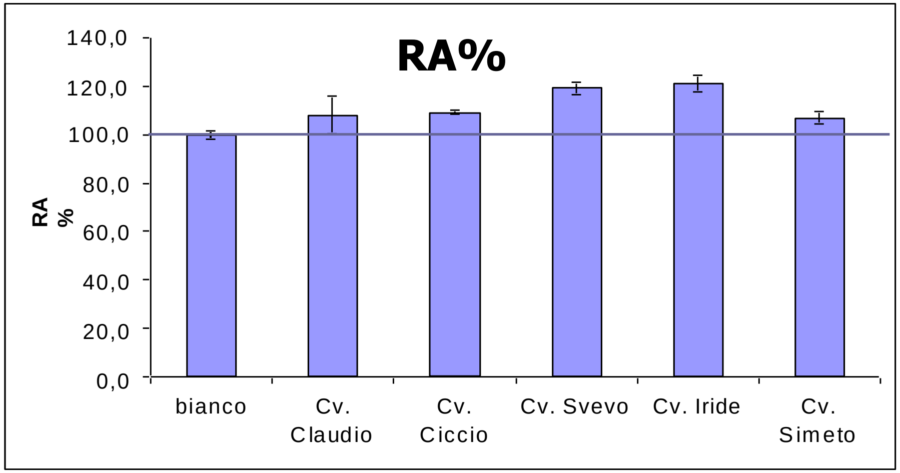


Matrix effect on the RA% and the I%

Experimental conditions:
<u>Extraction in **measuring buffer** (1g/10ml)</u>

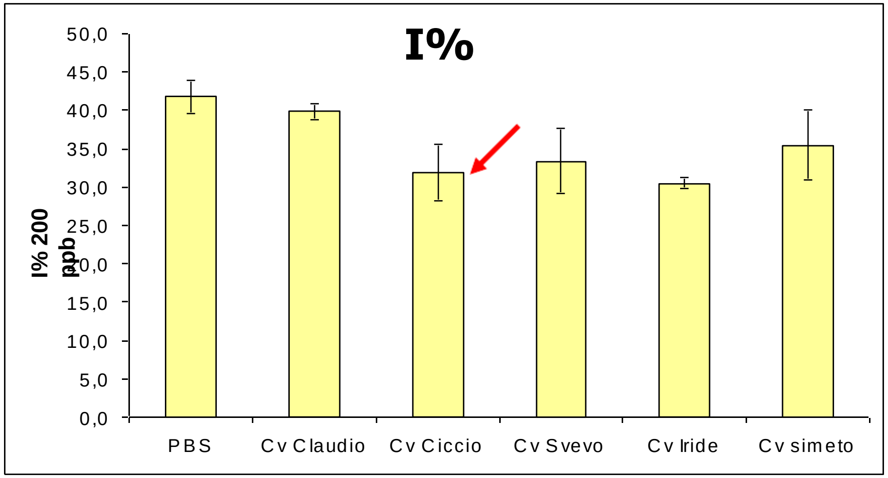
Phosphate buffer pH 7.4, KCl 100 mM
10% matrix
AChE 0.125 U/ml, Ach 0.3 mM
Incubation time: 10 min.

$$RA\% = 100 - (I_0 - I_s / I_0) * 100$$

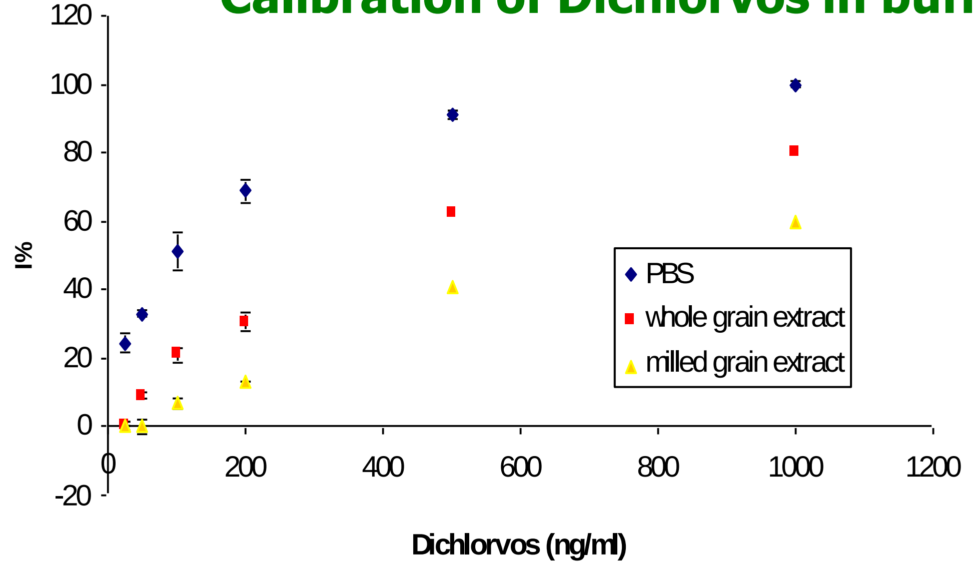


Experimental conditions:

Phosphate buffer pH 7.4, KCl 100 mM
10% matrix
AChE 0.125 U/ml, Ach 0.3 mM
200 ng/ml dichlorvos
Incubation time: 10 min.



Calibration of Dichlorvos in buffer and 10% matrix



Buffer

$$y = -1035.26 + \frac{1124.83}{\left\{1 + e\left[-\frac{(x + 776.54)}{303.60}\right]\right\}}$$

R=0.998
LOD= 8 ng/ml
$I_{50\%}$=230 ng/ml

Whole grains extract (10%)

$$y = -463.20 + \frac{566.30}{\left\{1 + e\left[-\frac{(x + 755.36)}{489.98}\right]\right\}}$$

R=0.992
LOD= 45 ng/ml
$I_{50\%}$=360 ng/ml

LOD = 0.45 mg/Kg

milled grains extract (10%)

$$y = -20.86 + \frac{83.82}{\left\{1 + e\left[-\frac{(x - 276.15)}{218.04}\right]\right\}}$$

R=0.998
LOD= 130 ng/ml
$I_{50\%}$=650 ng/ml

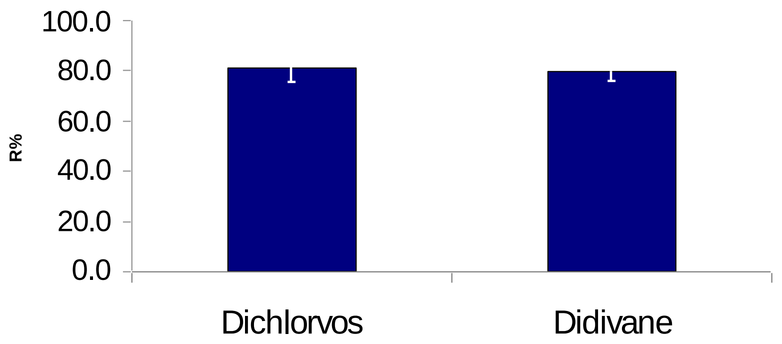
LOD = 1.3 mg/Kg

Recovery from spiked samples (2 mg/Kg)

Experimental conditions:

Spiked samples
Extraction:1g **whole grains sample** in 10ml buffer
AChE 0.125 U/ml, Ach 0.3 mM
Incubation time: 10 min.
n=5

Whole grains



Dichlorvos	Didivane
Mean I%: 21.0±1.3	**Mean I%: 19.2±1.2**
Mean recovery: 81.3 ±5.8	**Mean recovery: 79.5 ±3.5**

Experimental conditions:

Spiked samples
Extraction:1g **milled grains sample** in 10ml buffer
AChE 0.125 U/ml, Ach 0.3 mM
Incubation time: 10 min.
n=5

Milled grains

Dichlorvos	**Didivane**
Mean I%: 9.3±1.9	**Mean I%: 10.2±2.1**
Mean recovery: 81.3 ±16.1	**Mean recovery: 89.5 ±19.0**

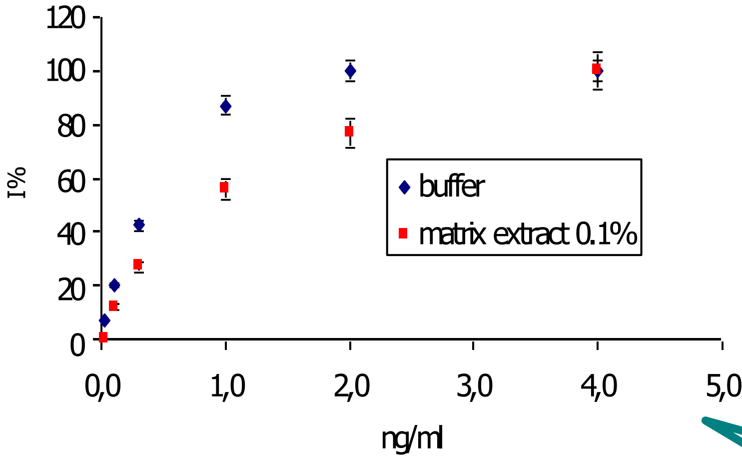
$I\%_{LOD}$=8% !!

Use of recombinant acetylcholinesterase (rAChE)

rAChE: Mutant AChE from Drosophila melanogaster Clone B3 specific for dichlorvos
Fournier D et al. Protein Engineering, Vol. 15, No. 1, 43-50, January 2002

Buffer

R=0.997
LOD= 0.045 ng/ml
$I_{50\%}$=0.37 ng/ml



milled wheat Extract 0.1%

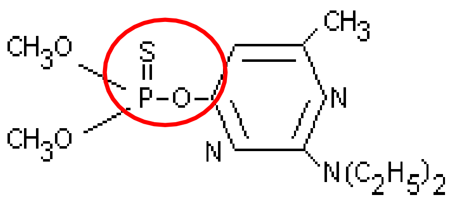
R=0.995
LOD= 0.065 ng/ml
$I_{50\%}$=0.85 ng/ml

LOD= 0.065 mg/Kg

Milled wheat Extract 0.1%

	Mean I% ±SD	Calc. Conc. measuring soln. (ng/ml)	Mean recovery±SD (mg/Kg)
Dichlorvos (n=3)	70.2±4.5	1.5	75.0±4.8
Didivane (n=3)	69.2±7.3	1.45	72.5±7.6

Pirimiphos methyl



Solubility in water: **5 mg/l**
S. methanol, ethanol, acetone: all proportions

(O-[2-(diethylamino)-6-methyl-4-pyrimidinyl]O,O-dimethylphosphorothioate)

- Commercial formulation Actellic® is used as broad spectrum grain protectant insecticide.
- Effective in controlling a wide range of insects that attack stored grain products.
- It provides long-term protection against re-infestation from insects.

The European Union regulates the maximum adsmissible level in durum wheat at **5 mg/Kg** (European Directive 2001/57/CE)

Quantitative Usage Analysis for Pirimiphos-Methyl (EPA 1989-1997)

Total annual USA usage was 12,000 pounds active ingredient (a.i.). Total usage is allocated mainly to **stored corn grain** (39%), **stored sorghum grain** (15%), **corn seed** (5%) and **sorghum seed** (5%).

In **Europe** it is mainly used for wheat, corn, barley (45% in Scotland and ireland) storage.

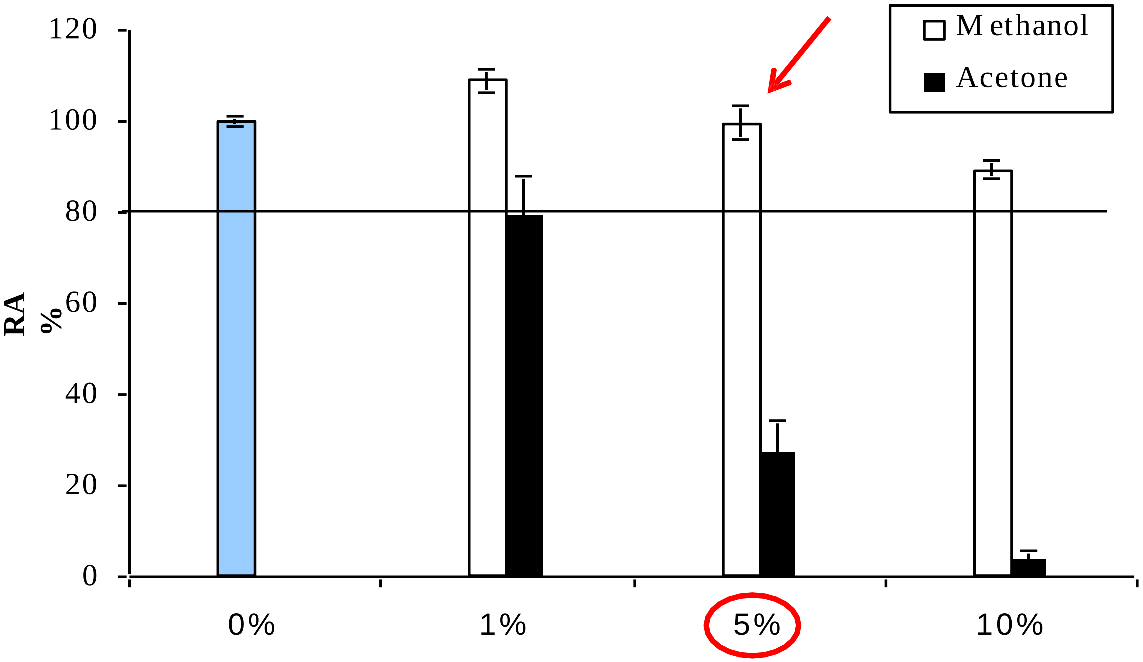
In **italy** the major durum wheat transforming brands indicate pirimiphos methyl as a pest control chemical for post-harvest storage.

Effect of methanol and acetone on the Residual Activity of AChE

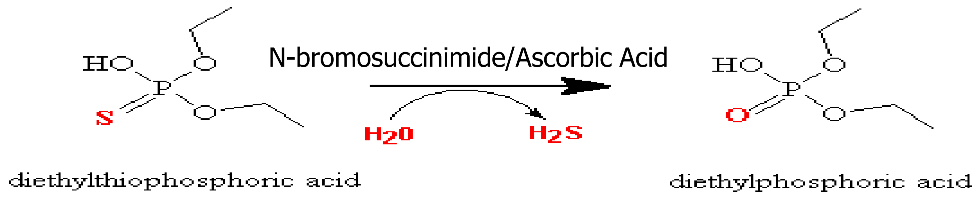
Experimental conditions:

Phosphate buffer pH 7.4, KCl 100 mM
AChE 0.125 U/ml, Ach 0.3 mM
Incubation time: 10 min.

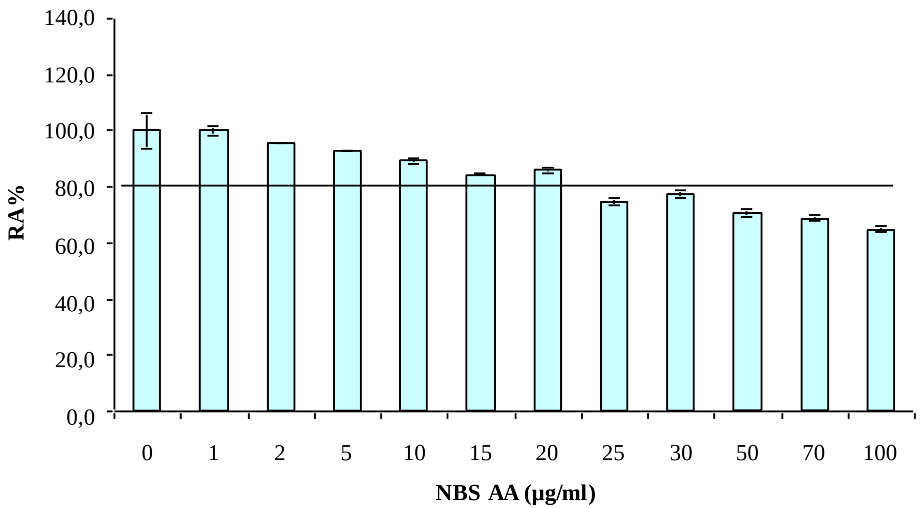
$$RA\% = 100 - (I_0 - I_s / I_0) * 100$$



Oxidation of pirimiphos methyl



Influence of NBS and AA concentration on the blank response evaluated as RA%.



Inhibition obtained with 250 ng/ml of pirimiphos methyl using different concentration of NBS and AA.

NBS-AA µg/ml	I% (n=3)	SD	CV%
5	31.5	2.2	6.9
10	28.6	2.4	8.3
25	28.2	3.1	10.9

Paper as substrate

Paper can…

Store

Filter

React

Drawbacks…

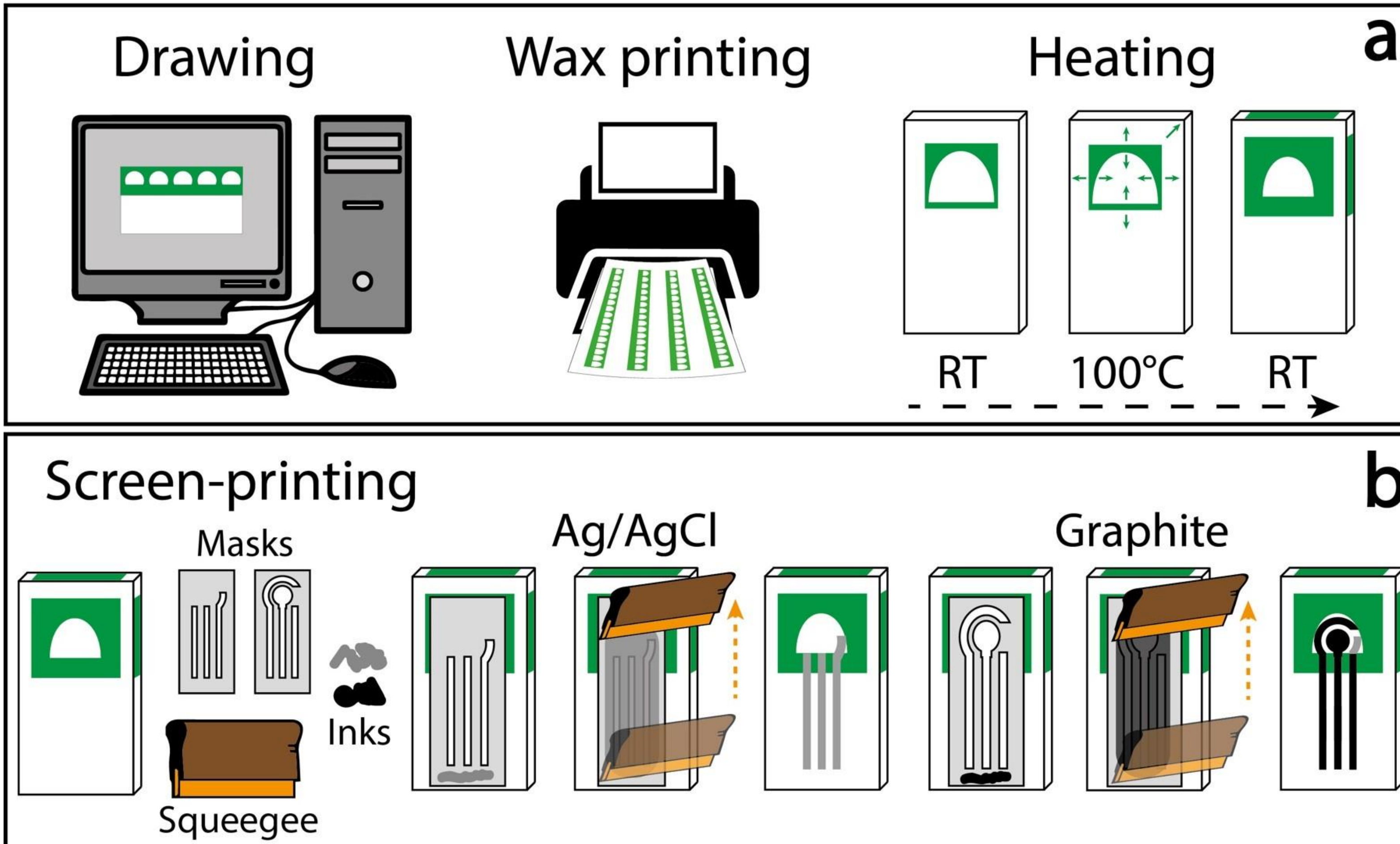
Reagents diffusion…

Electrical noise! ☹

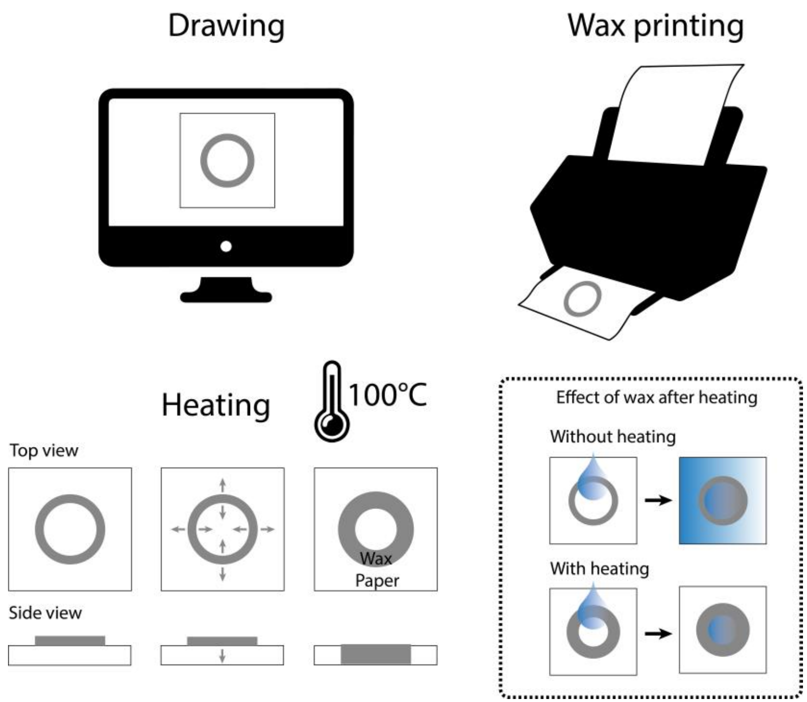
An hydrophobic barrier is needed…

From Paper to E-Paper

Few and easy steps



Hydrophilicity matters



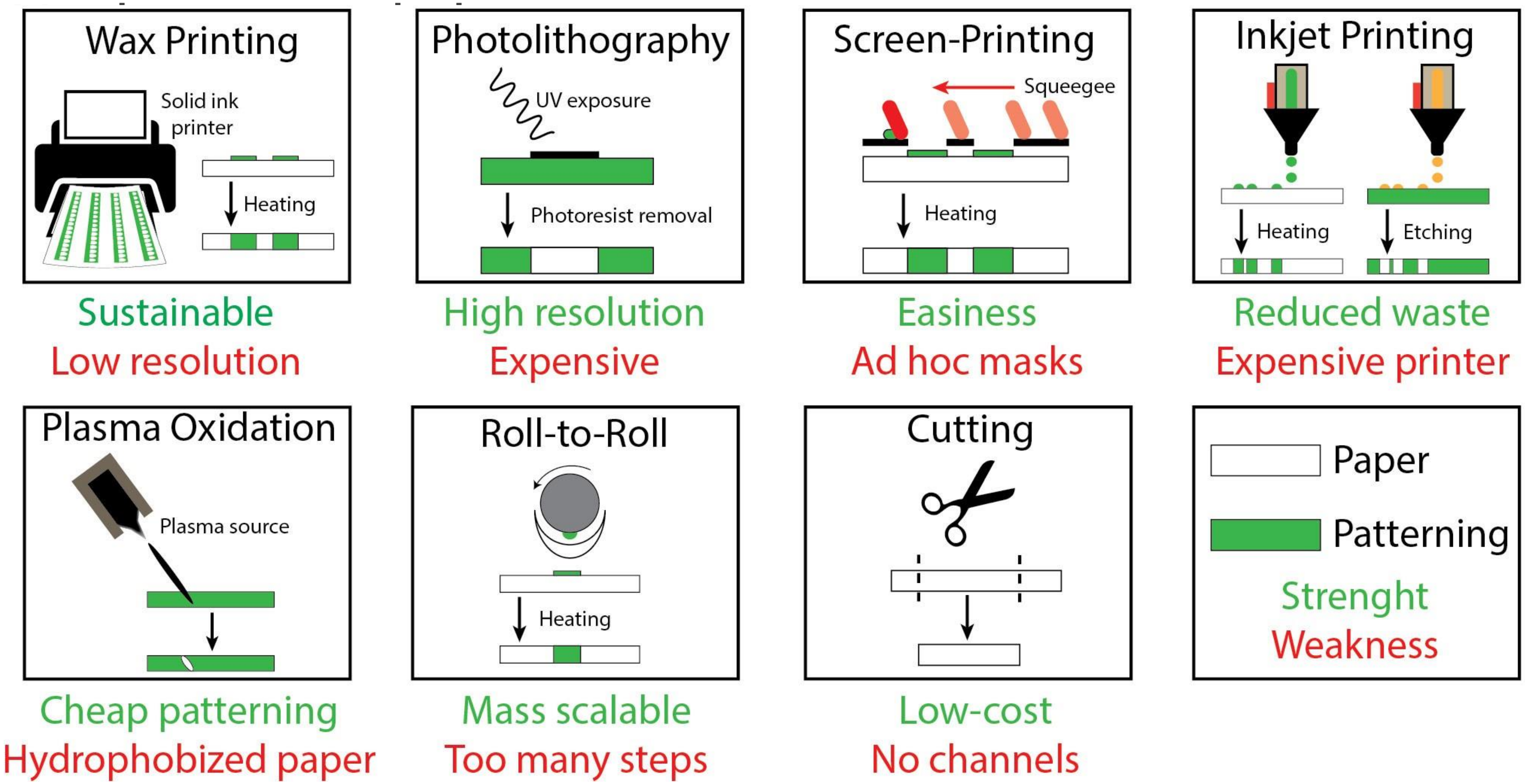
... also the cost!

Costs of the components for producing one device (all the costs have to be intended in Euro).

Substrate	Ag/AgCl ink	Carbon ink	Insulator	Substrate	Total cost	Saving[c]
Polyester	0.010	0.007	0.003[a]	0.013	0.033	45%
Whatman #1			0.001[b]	0.007	0.025	30%
Office paper			0.001[b]	0.0001	0.018	/

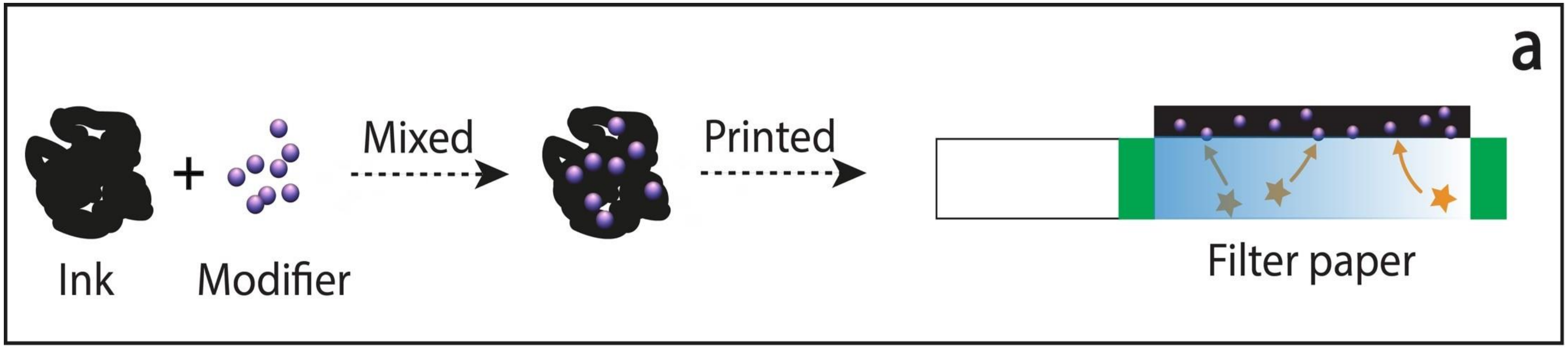
[a] Insulator ink.
[b] Wax.
[c] Calculated as 1 – [Office paper/Other] × 100.

It depends on what you need and you have!

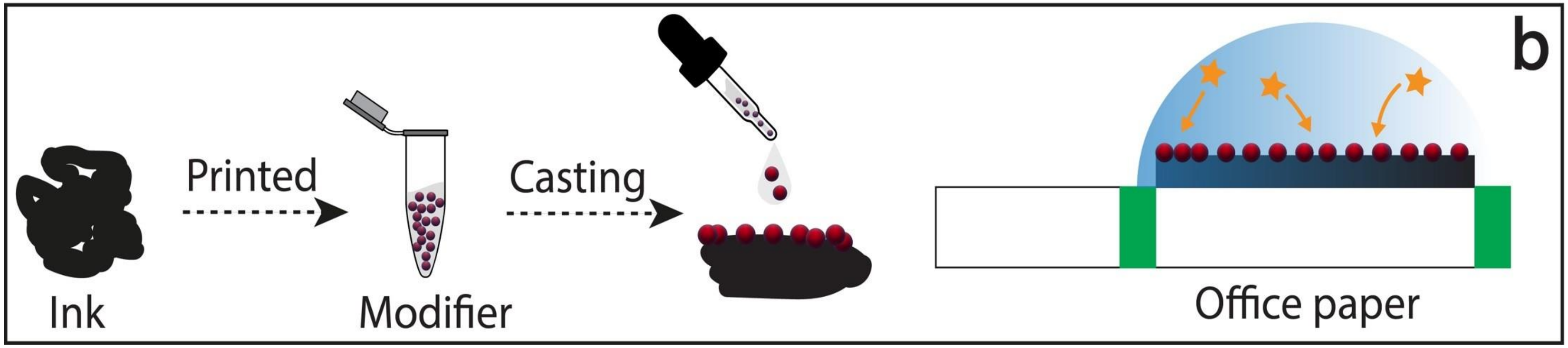


Which E-Paper?

Porous

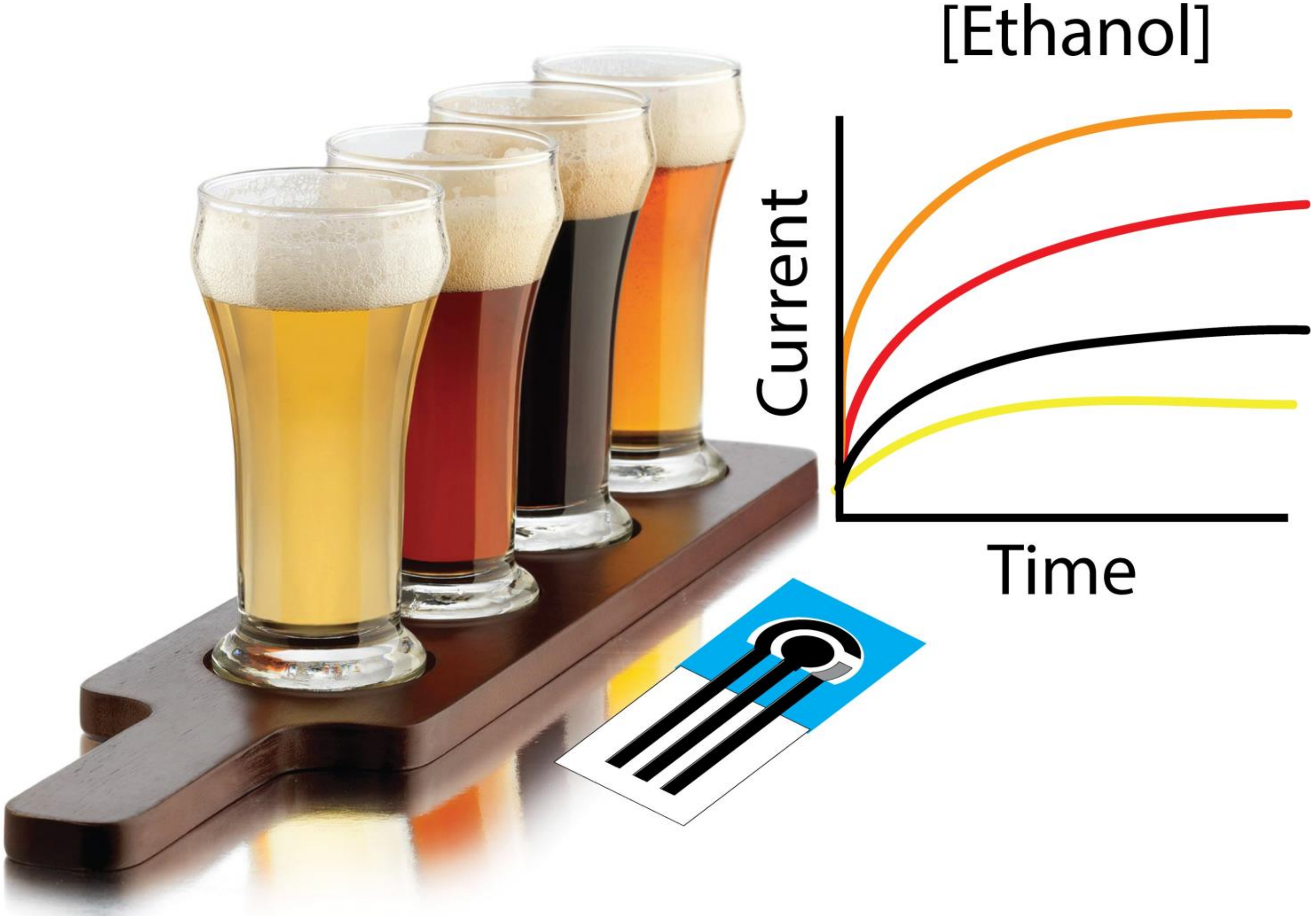


Non porous



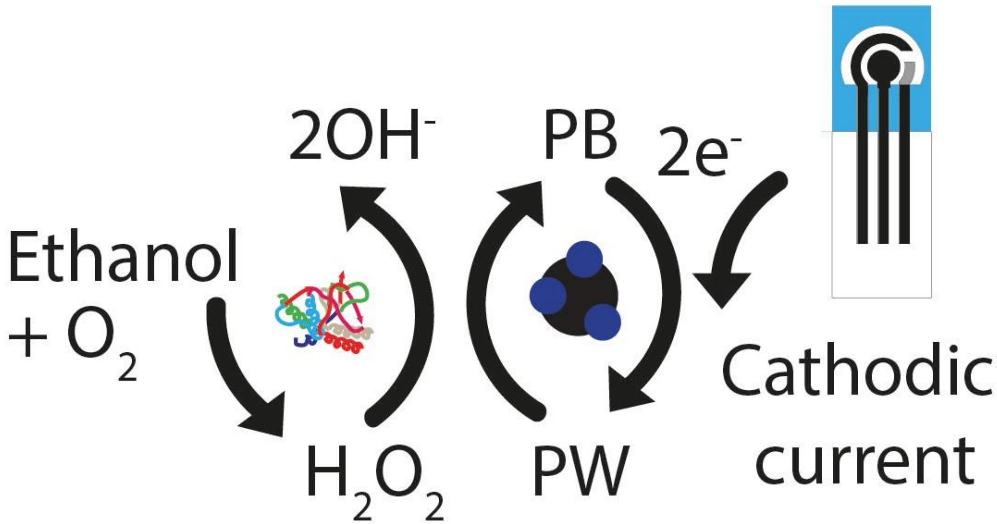
Anyway, paper is the substrate… we need to make these strips ad-hoc

Office paper for ethanol

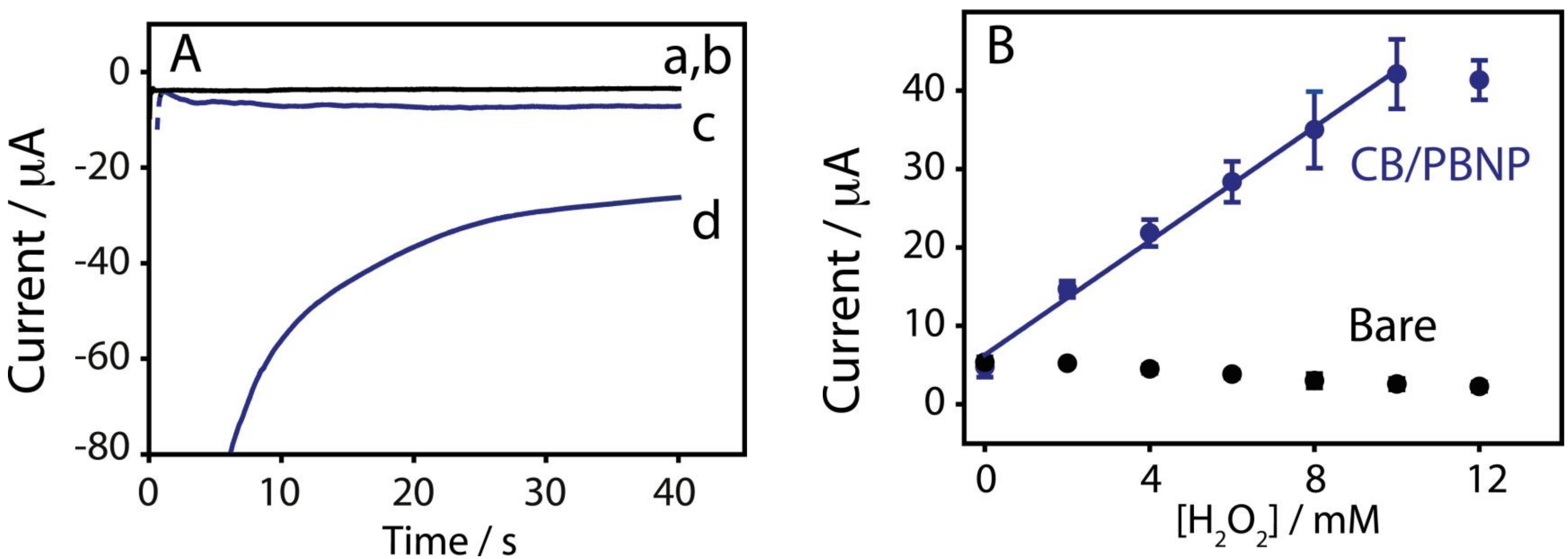


S. Cinti et al. Anal. Chim. Acta 960 (2017) 123-130

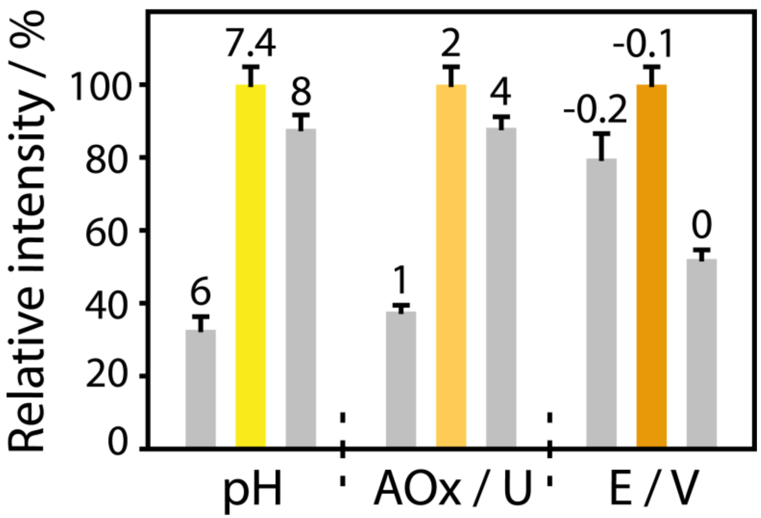
Detection mechanism



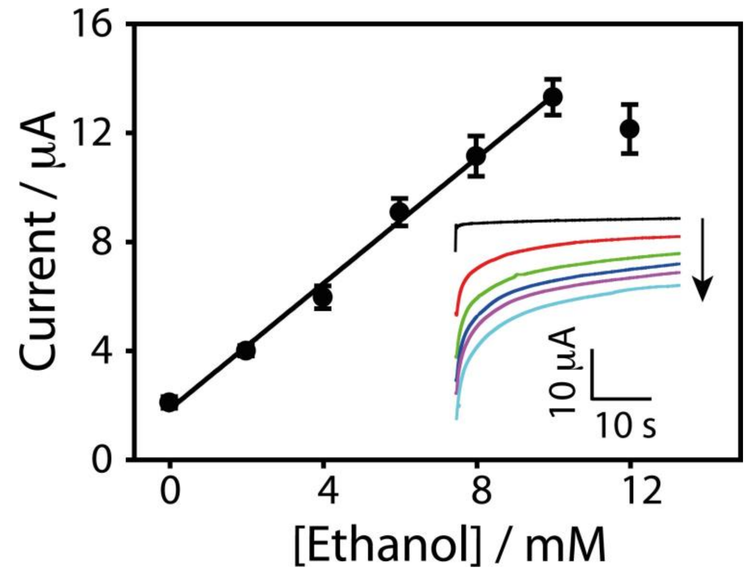
- Office paper
- Carbon Black
- Prussian Blue
- Alcohol oxidase



Optimization



Calibration curve



LOD = 0.5 mM

Linear range up to 10 mM

RSD = 8 %

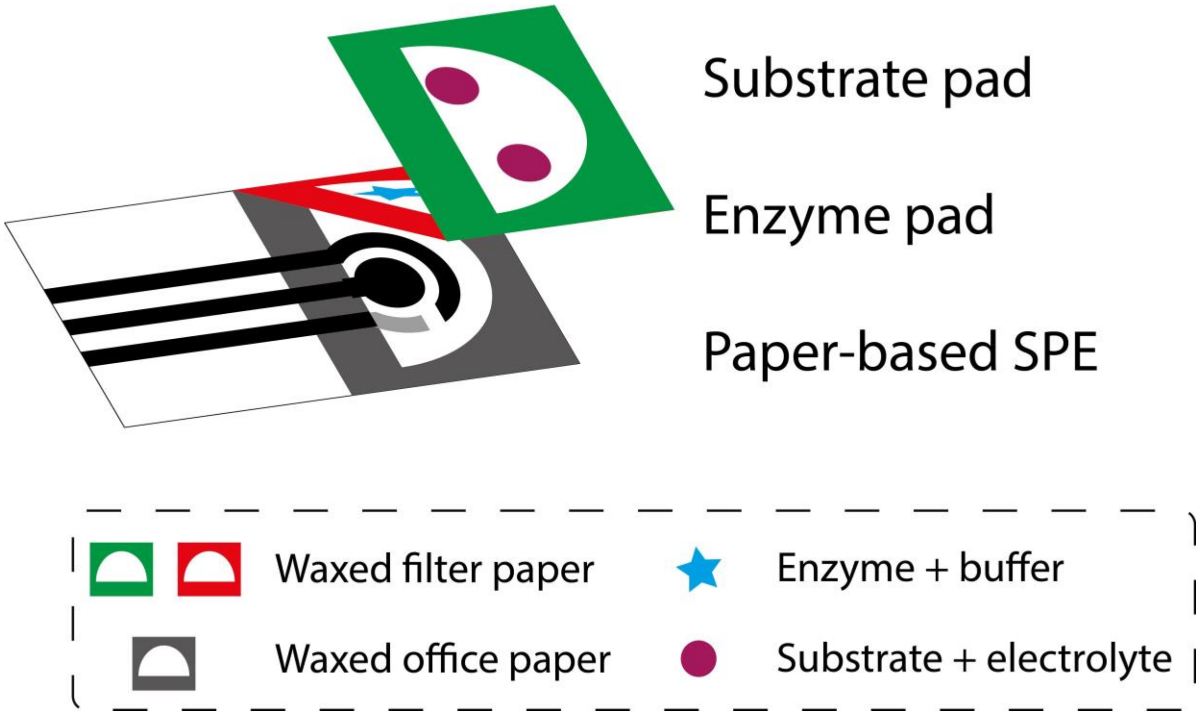
Accordance with label

Detection of ethanol in commercial beers.

Beer	Lager Best Bräu, Poland	Weiss Franziskaner, Germany	Pilsner Ceres, Denmark	Alcohol free Tourtel, Italy
				
Label [ethanol]/$\%_{vol}$ (M)	4.7% (0.805 M)	5% (0.856 M)	4.6% (0.787 M)	<0.5% (0.086 M)
Found [ethanol]/$\%_{vol}$ (M)	4.7 ± 0.4 (0.805 ± 0.075)	5.0 ± 0.4 (0.86 ± 0.07)	4.4 ± 0.2 (0.75 ± 0.04)	0.34 ± 0.03 (0.059 ± 0.004)
RSD/%	9.3	8.1	5.3	6.8

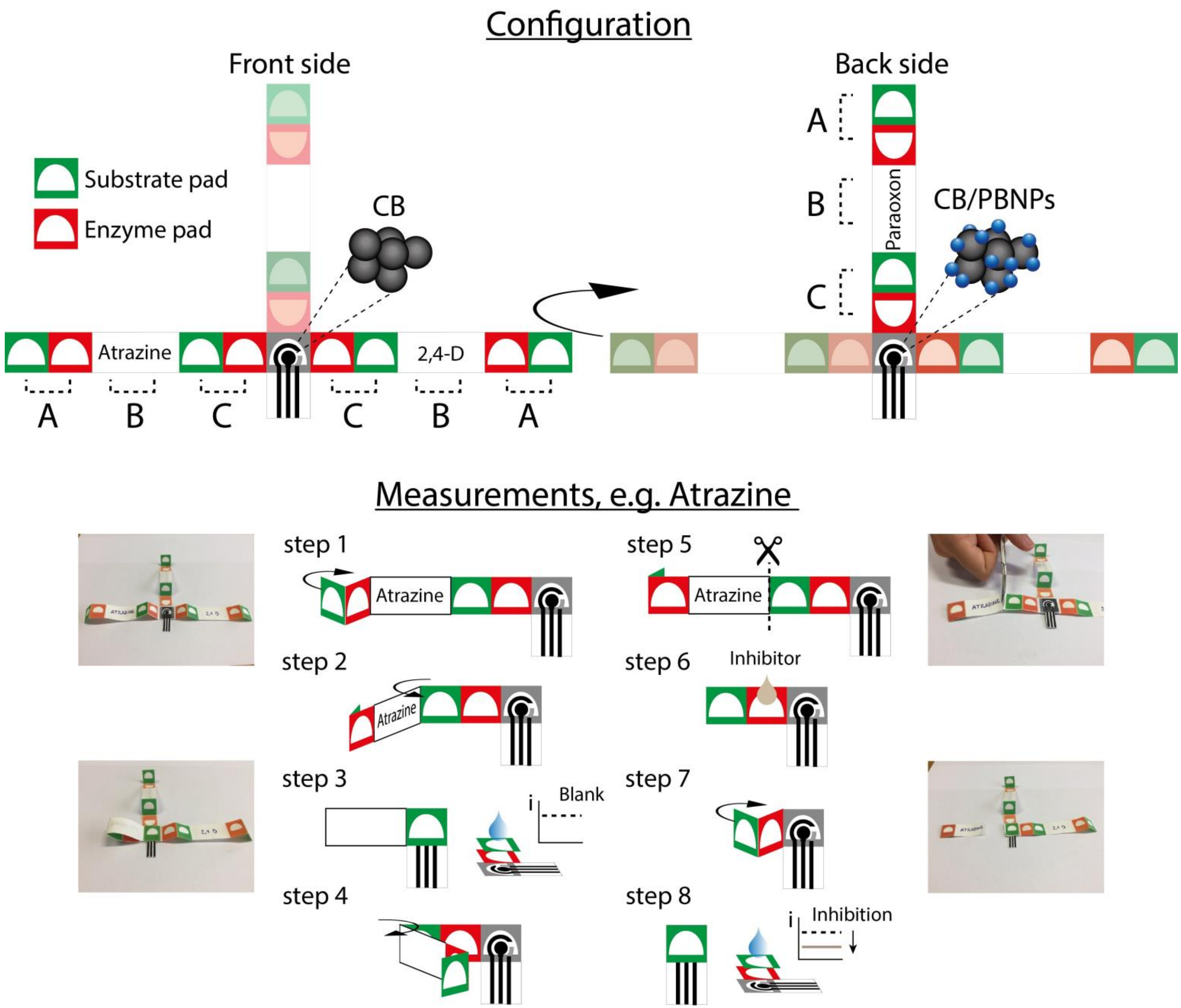
3-D paper origami for pesticides

Filter paper + office paper



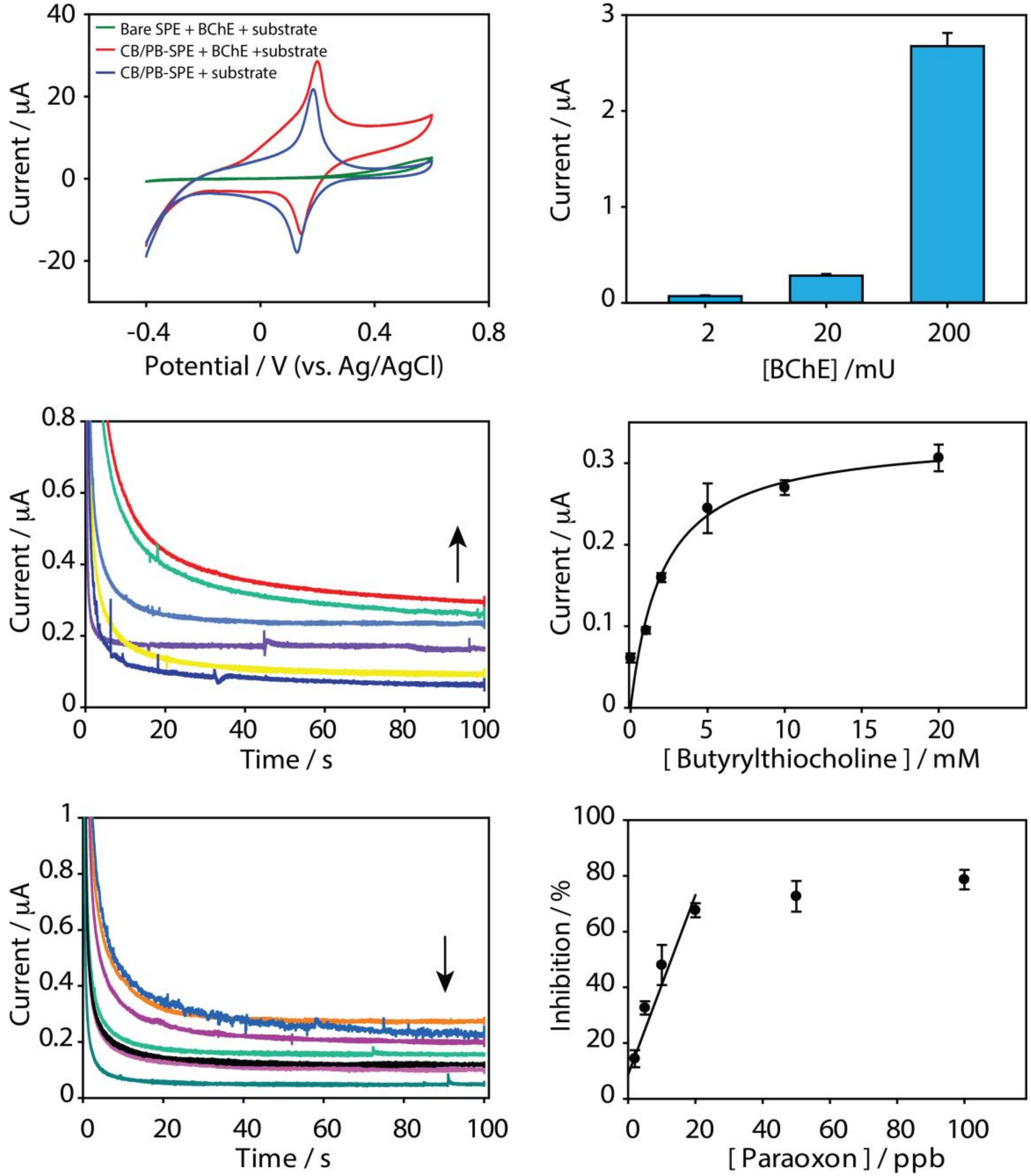
Paraoxon, **2,4-dichlorophenoxyacetic acid**, and **atrazine** by inhibition of **butyrylcholinesterase**, **alkaline phosphatase,** and **tyrosinase**

F. Arduini et al. Biosens. Bioelectron. (2018) DOI:10.1016/j.bios.2018.10.014



Configuration
Front side
Back side
Substrate pad
Enzyme pad
CB
CB/PBNPs
Atrazine
2,4-D
Paraoxon
A
B
C
C
B
A
A
B
C
Measurements, e.g. Atrazine
step 1
Atrazine
step 2
Atrazine
step 3
i
Blank
step 4
step 5
Atrazine
step 6
Inhibitor
step 7
step 8
i
Inhibition

E.g. paraoxon detection



LOD = 2 ppb

Linear range up to 30 ppb

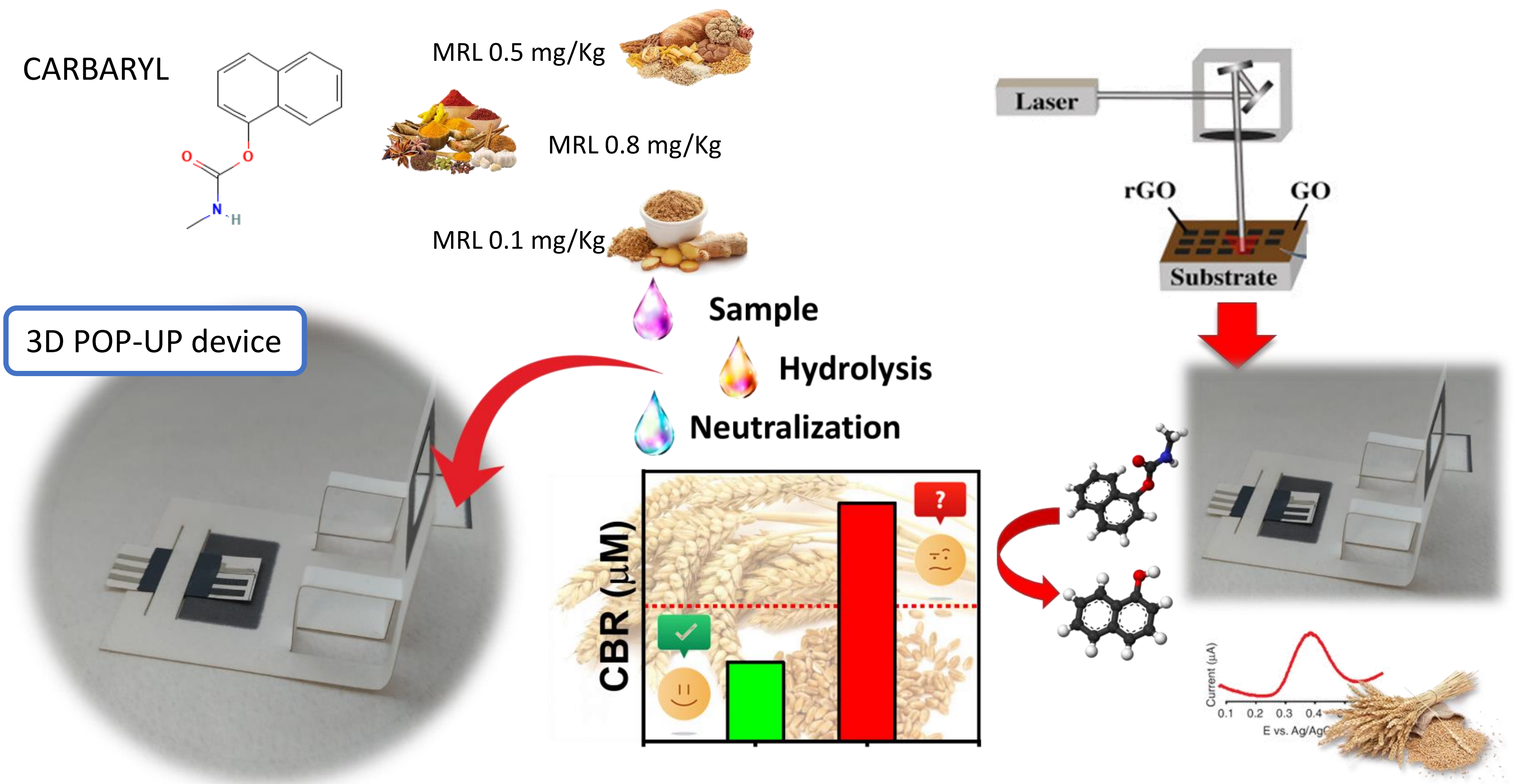
RSD = 11%

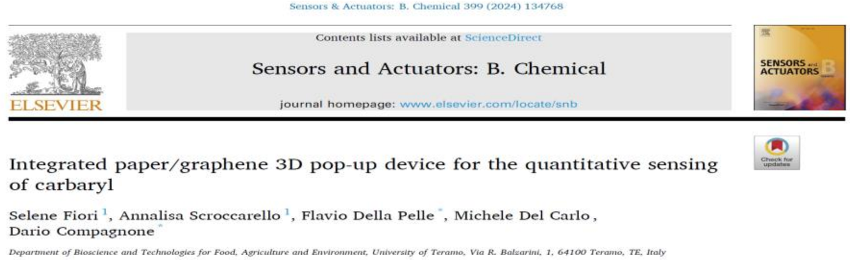
Real sample: River water

Linear up to 30 ppb

Recoveries: 90 and 88% (10 and 20 ppb)

Paper + laser induced graphene + electrochemistry





Sensors & Actuators: B. Chemical 399 (2024) 134768

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journal homepage: www.elsevier.com/locate/snb

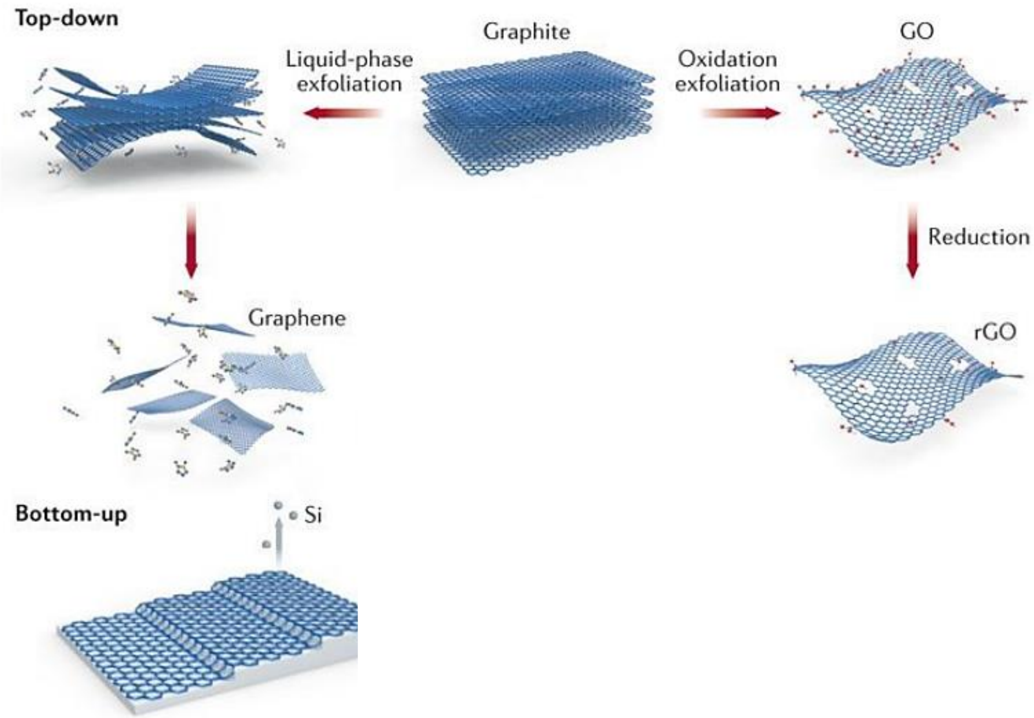
Integrated paper/graphene 3D pop-up device for the quantitative sensing of carbaryl

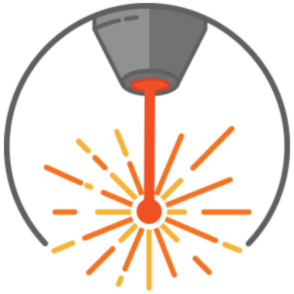
Selene Fiori [1], Annalisa Scroccarello [1], Flavio Della Pelle [*], Michele Del Carlo, Dario Compagnone [*]

Department of Bioscience and Technologies for Food, Agriculture and Environment, University of Teramo, Via R. Balzarini, 1, 64100 Teramo, TE, Italy

Laser induced graphene

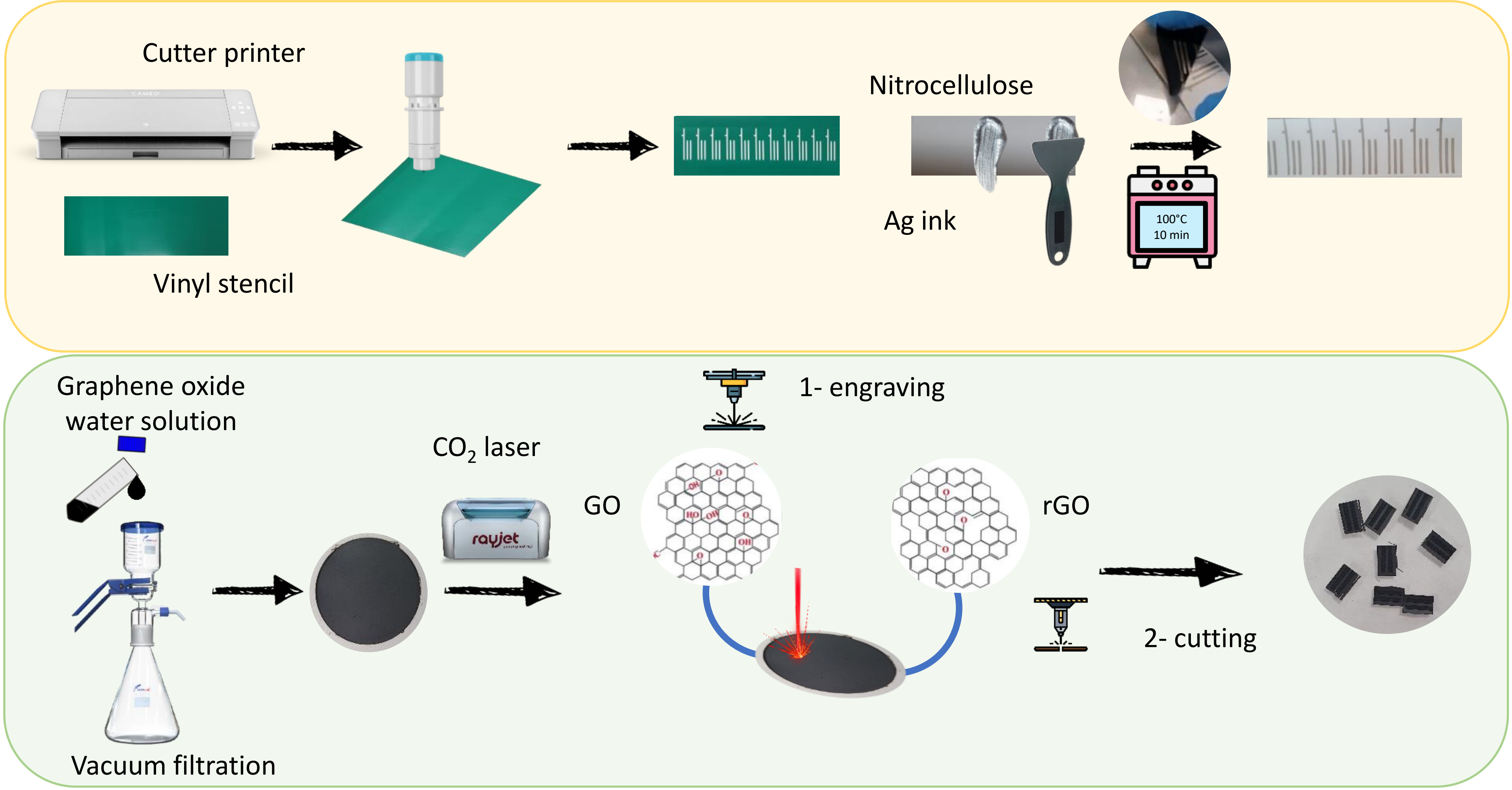
Graphene

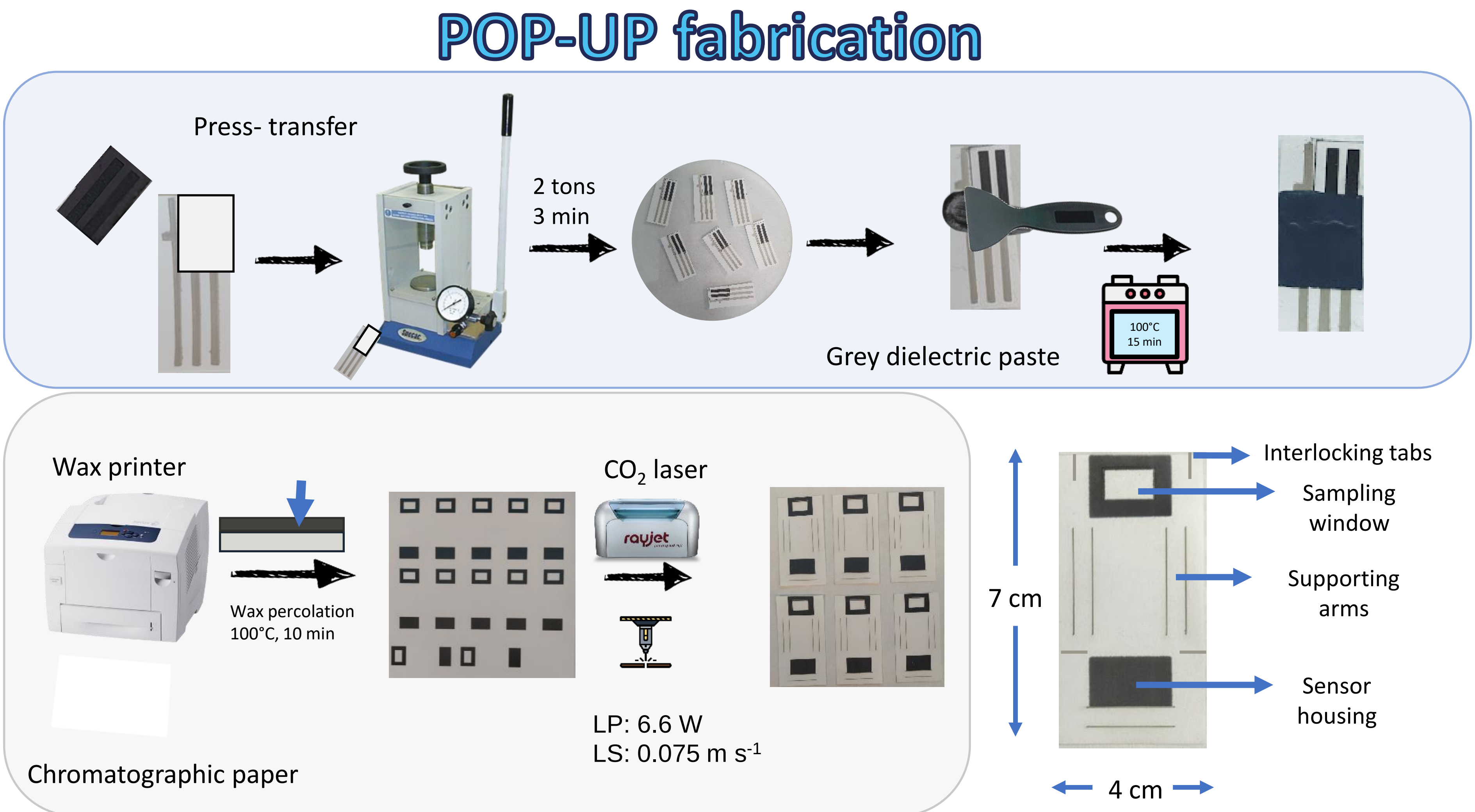




Laser induced graphene

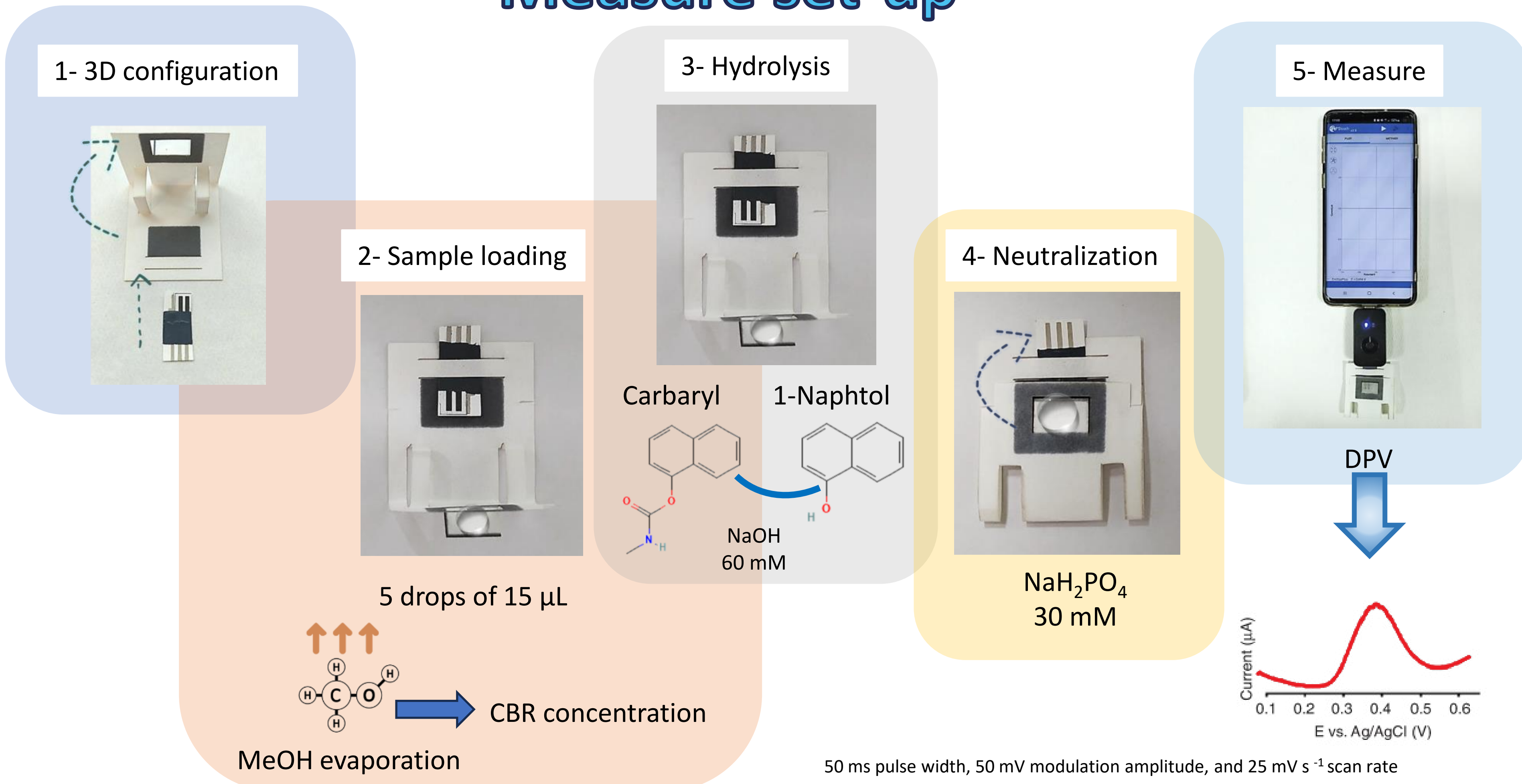
POP-UP fabrication





POP-UP fabrication
Press- transfer
2 tons
3 min
Grey dielectric paste
100°C
15 min
Wax printer
Wax percolation
100°C, 10 min
Chromatographic paper
CO_2 laser
LP: 6.6 W
LS: 0.075 m s^{-1}
7 cm
4 cm
Interlocking tabs
Sampling window
Supporting arms
Sensor housing

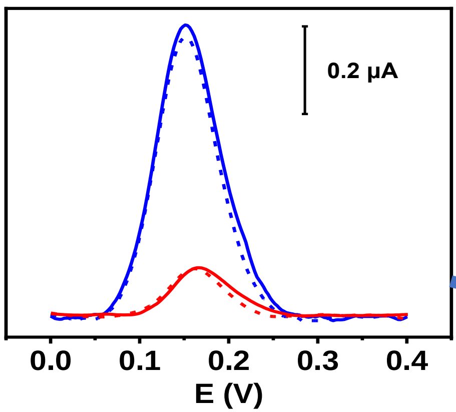
Measure set-up



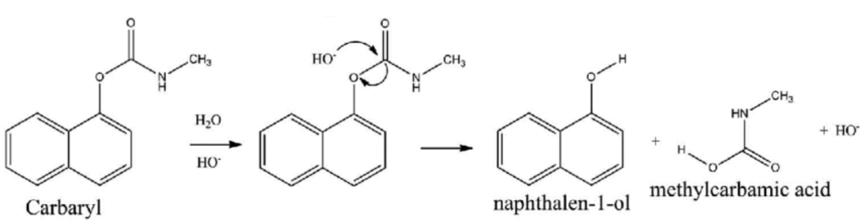
Analytical performances

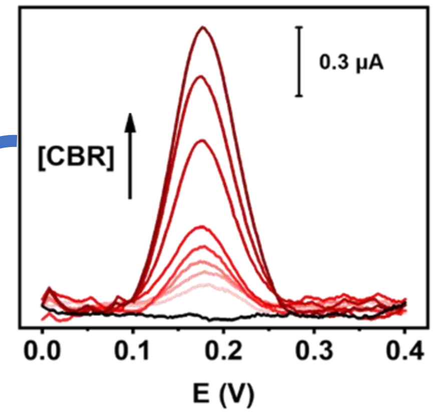
Solid line → CBR hydrolyzed on the POP-UP device
Dashed line → 1-NP used as control

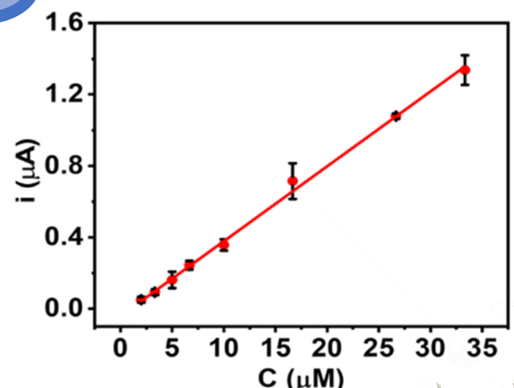
5 μM and 25 μM



Quantitative hydrolysis





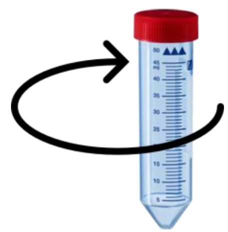


LR: 1.5 - 33 μM
R^2= 0.9950
RSD ≤ 10%, n=3
LOD: 0.4 μM

LOD < MRL in grains

Sample analysis

Soft wheat 1 (SW1)
Soft wheat 2 (SW2)
Durum wheat (DW)
Kamut (KM)
Barley (BR)

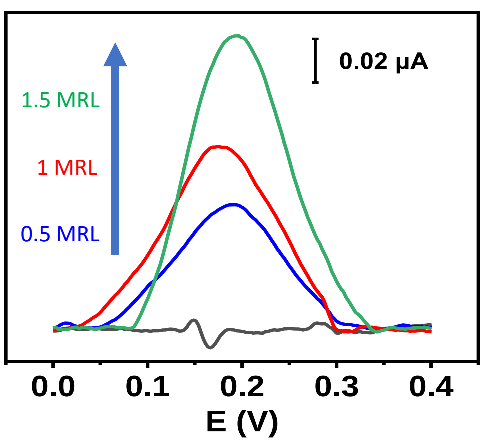


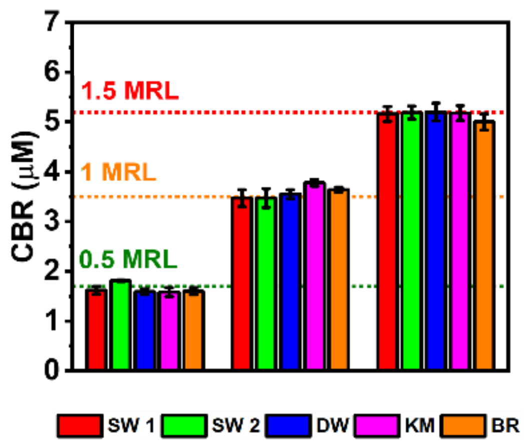
5 mg in 10 mL of methanol

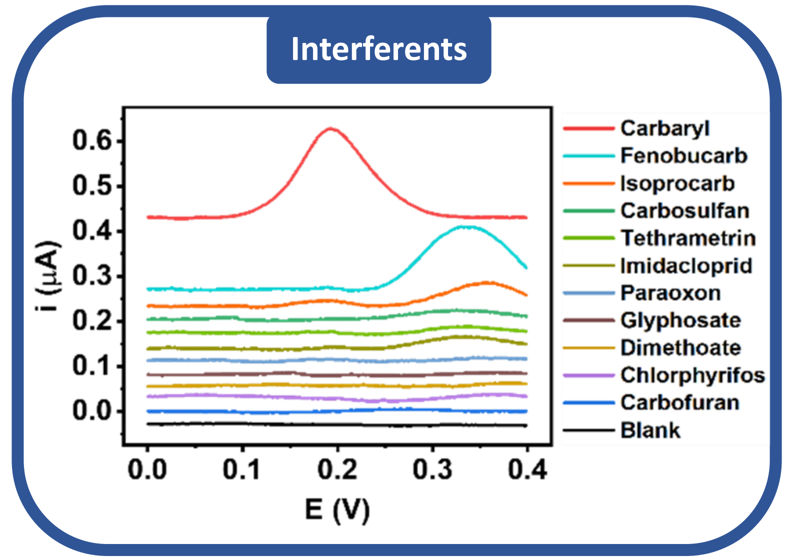
Extraction under orbital stirring for 5 min at 4000 g

Carbaryl MRL in grains: 3.5 µM

CBR fortification at:
0.5 MRL (1.7 µM)
1 MRL (3.5 µM)
1.5 MRL (5.2 µM)







Recovery: 93-108% (RSD ≤ 6%, n = 3)

Multianalita (zuccheri, alcol, acidi organici) Universal Sensor

Etanolo

Analox instruments

$$Ethanol + O_2 \xrightarrow{Alcohol\ Oxidase\ (AOD)} Acetaldehyde + H_2O_2$$

Acido lattico, monouso
(Sens-Lab)

$$L-Lactate + O_2 \xrightarrow[(LOD)]{L-Lactate\ Oxidase} Pyruvate + H_2O_2$$

Gwent Sensors Ltd.

Glucose, Lactate, Ethanol, Methanol, Ammonia, Glycerol, Sucrose, Lactose and Glutamine

$$Sucrose \xrightarrow{invertase} (\alpha-D-Glucose) \xrightarrow{buffer,\ ph5} \beta-D-Glucose + Fructose$$

$$\beta\text{-}D-Glucose + O_2 \xrightarrow[(GOD)]{Glucose\ Oxidase} D\text{-}Gluconic\ Acid + H_2O_2$$

SENZYTEC 1 portable laboratory

Biosensori per l'Industria Alimentare