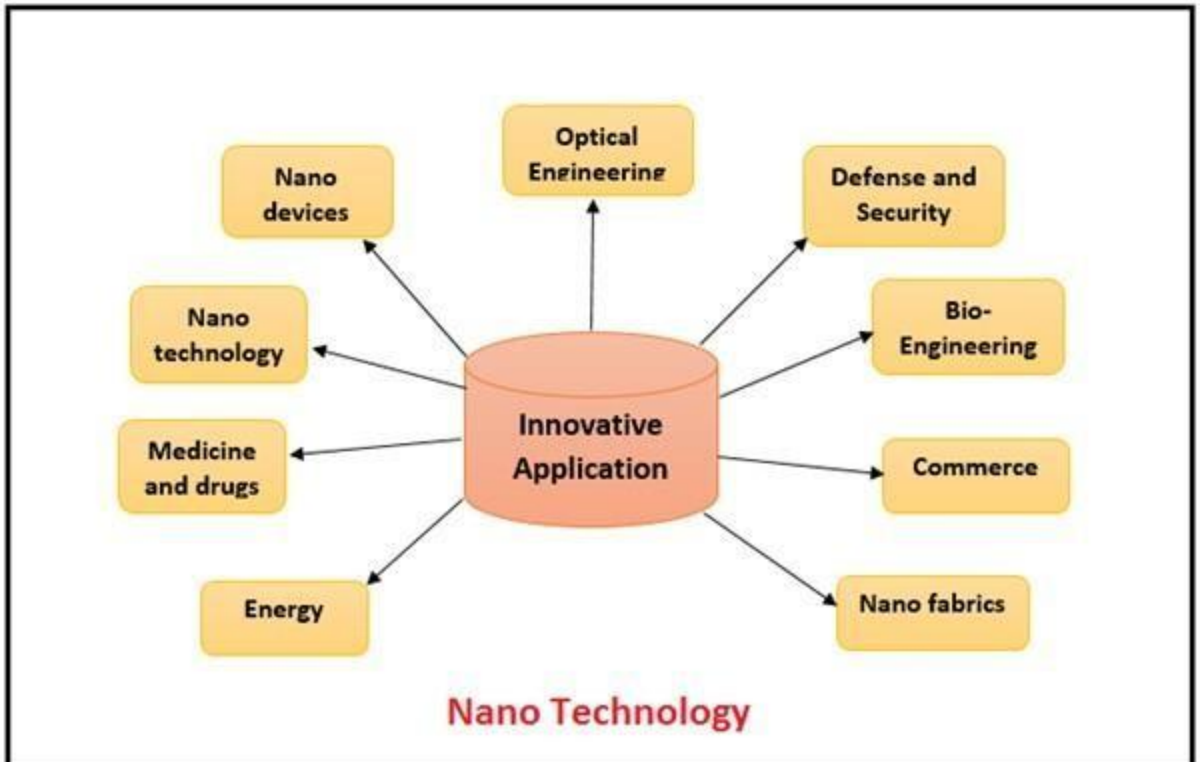
Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometer



Nanomaterials

Pros

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

Sensor **sensitivity & selectivity** improvement

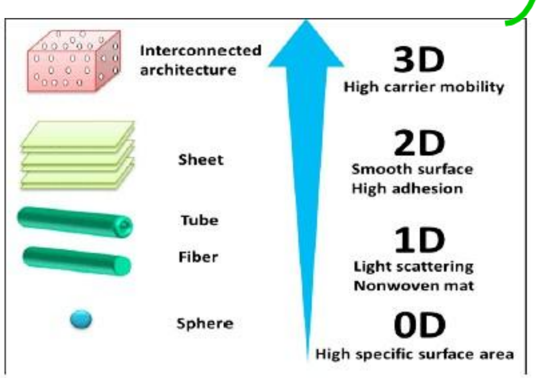
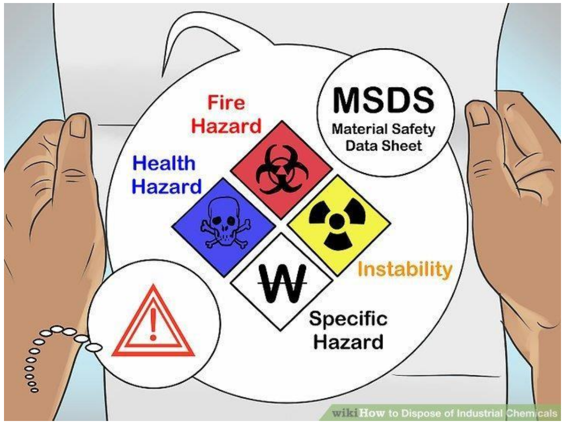


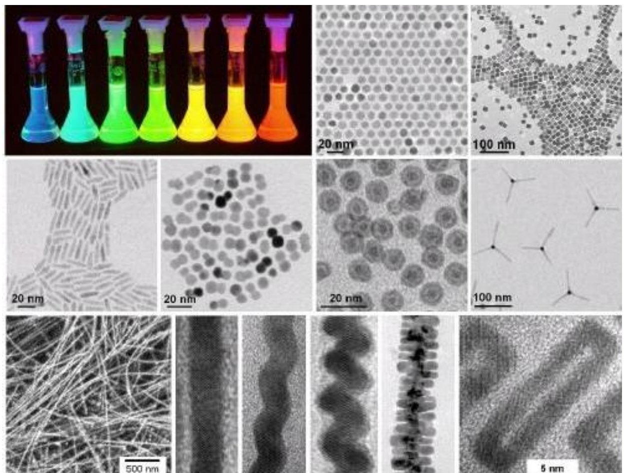
Figure 1: Schematic illustration of structural dimensionality of nanomaterials with expected properties.

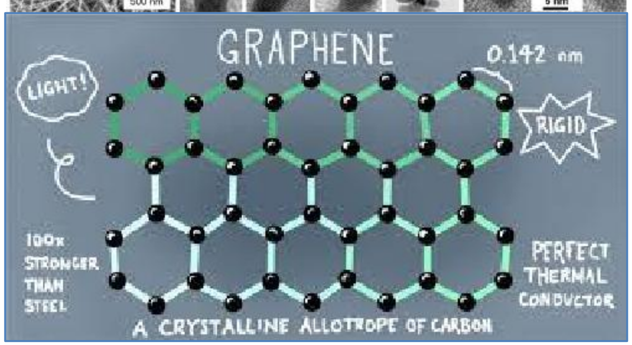


Potential drawbacks

- ? Waste disposal
- ? Potential toxicity

Nanomaterials employed in electrochemical sensor

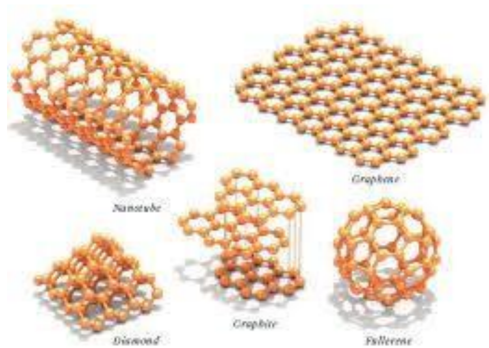


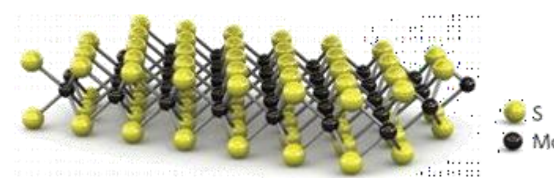


Carbon based nanomaterials:
- Nanotubes
- Fullerenes
- Graphene
- Etc…

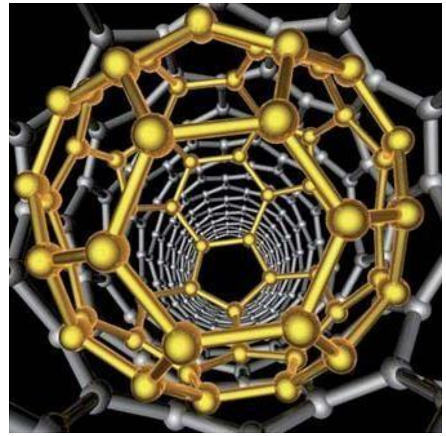
Nanoparticles:
- Metal nanoparticles
- Metal Oxide nanoparticles

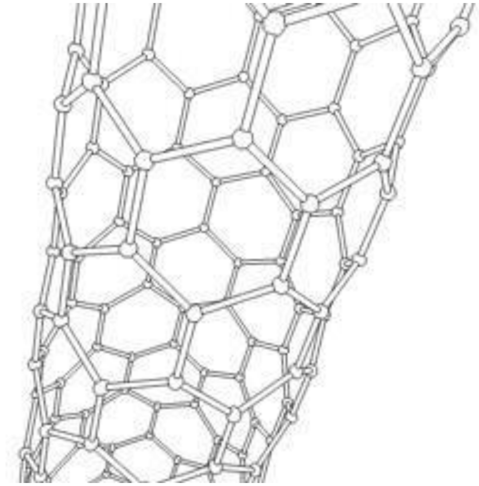
Graphene-like nanomaterials:
- e.g. Transition Metal Dicalchogenised (TMD)





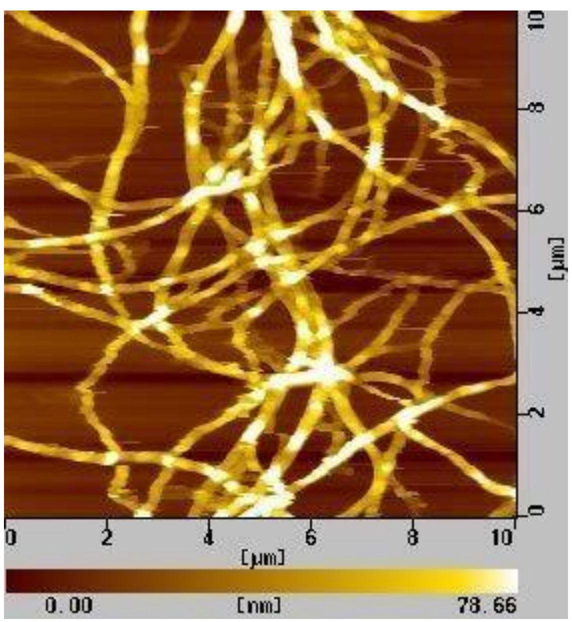
CARBON NANOTUBES

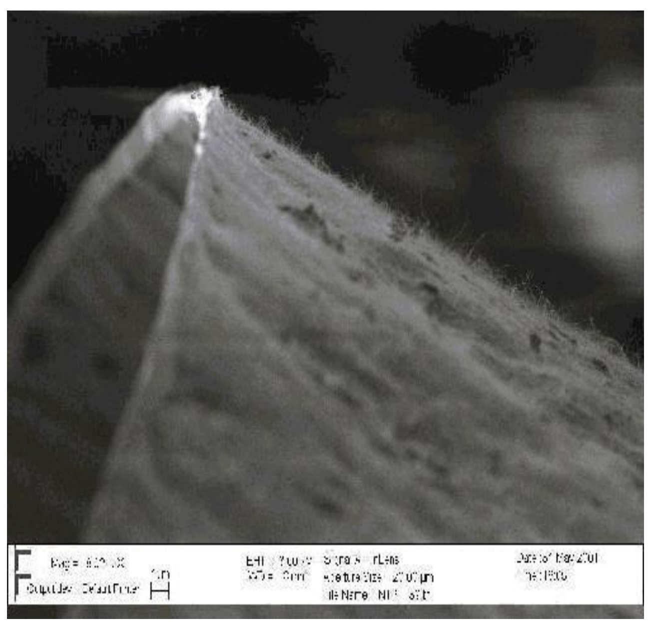


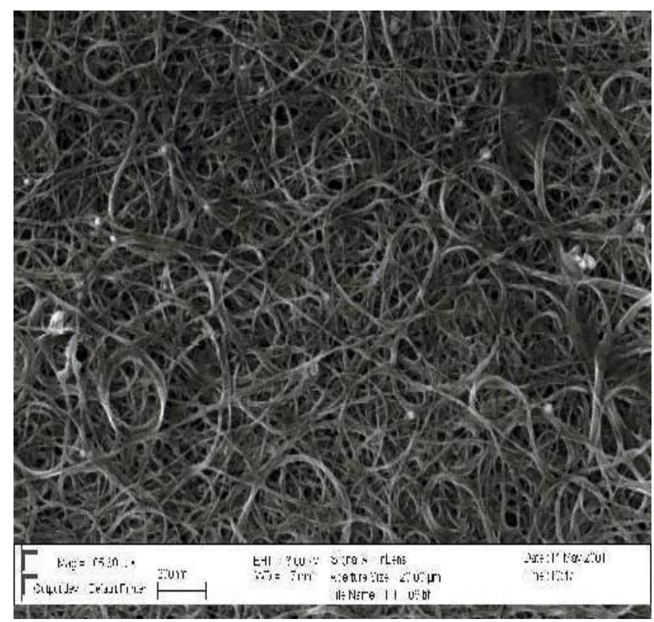


CHARACHERISTICS

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







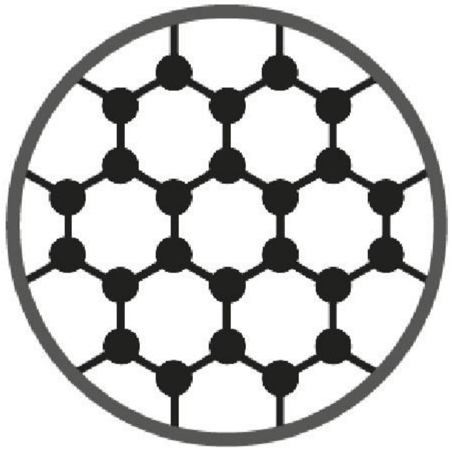
GRAPHENE: THE CARBON-BASED 'WONDER MATERIAL'

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

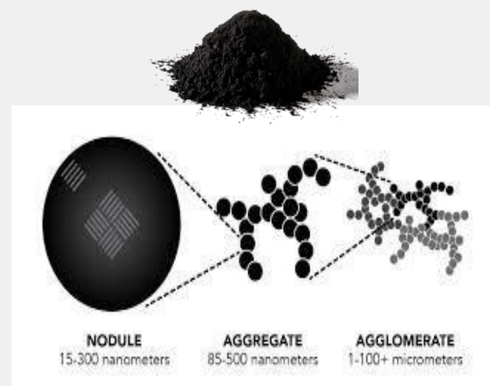
Several biomedical applications are being explored for graphene, including drug delivery, cancer therapy, and its use as a sensor. However, its toxicity profile must be investigated before any clinical uses.

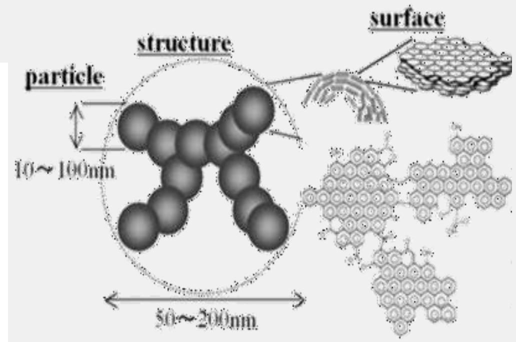
ENERGY STORAGE & COMPOSITES

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.

Carbon based nanomaterials
(Carbon Black, CB)

Nano Carbon Black



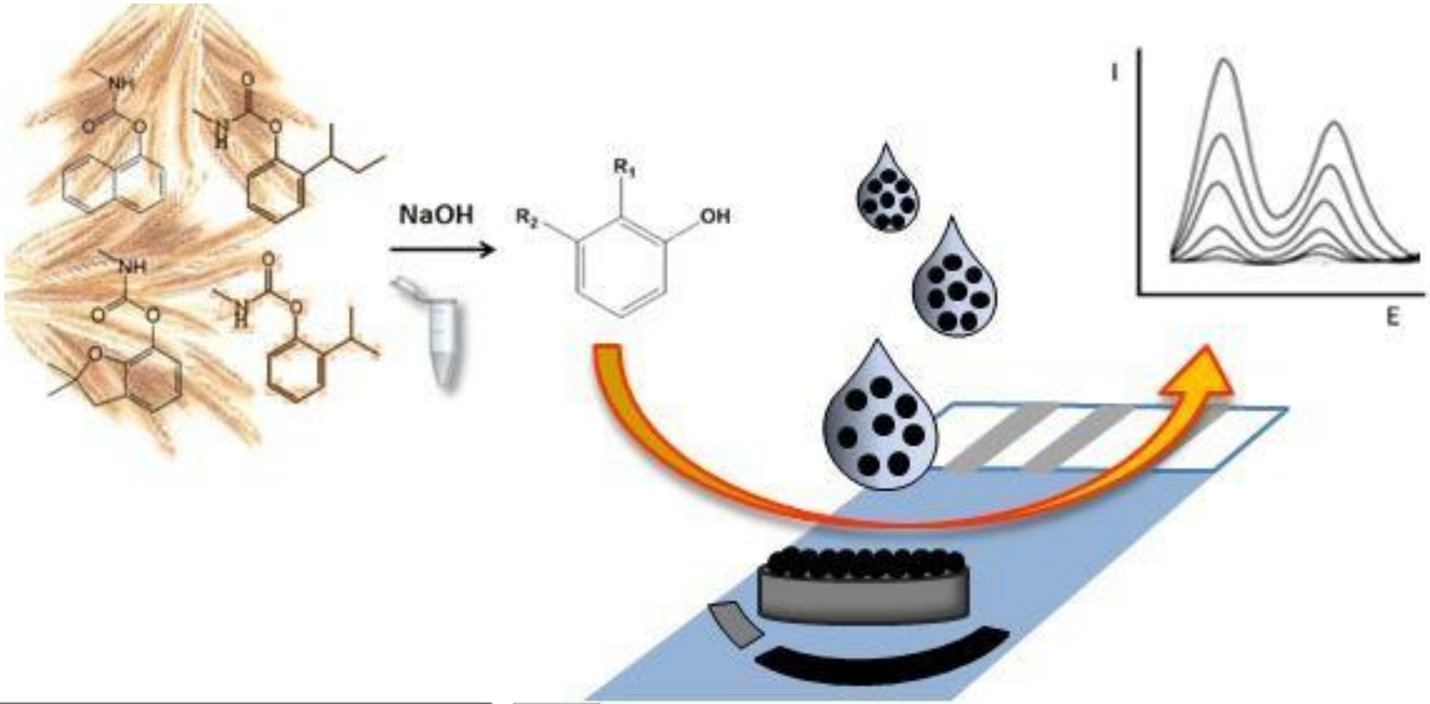


Electrocatalysis	Selectivity
High surface	Sensitivity
Resistance to fouling	Reproducibility
Faster eletron transfer	Improving separation performance

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



Contents lists available at ScienceDirect

Talanta

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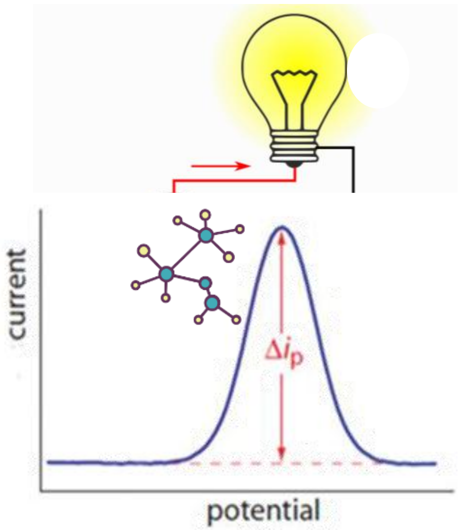
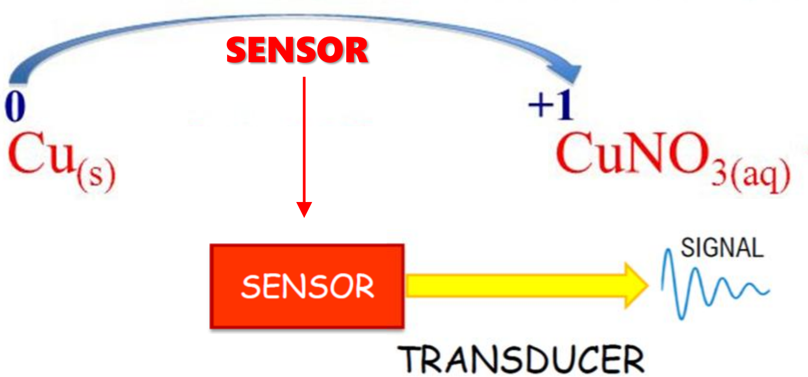
Nano carbon black-based screen printed sensor for carbofuran, isoprocarb, carbaryl and fenobucarb detection: application to grain samples

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

Amperometry – Voltammetry



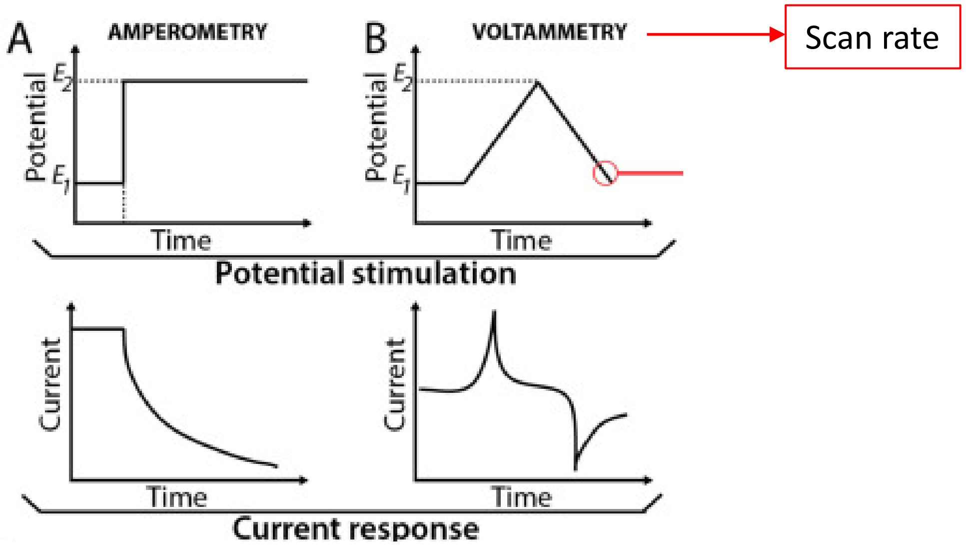


Electron transfer between a redox compound and an electrode (working electrode).
A redox compound is able to exchange electrons at a particular applied potential (applied potential depends on reference electrode)

Signal –current is used to detect/quantify

Amperometry: measurement of current at constant potential

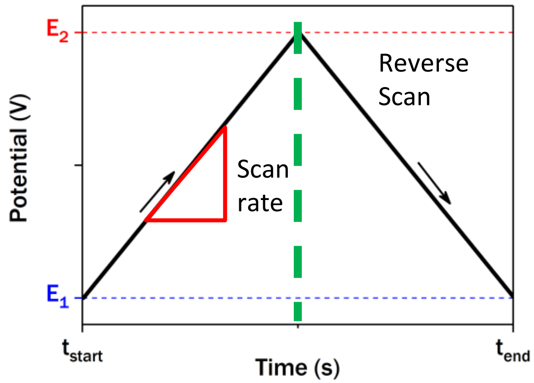
Voltammetry: measument of current with varying potential

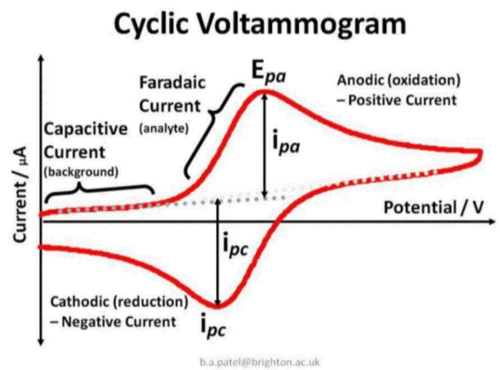


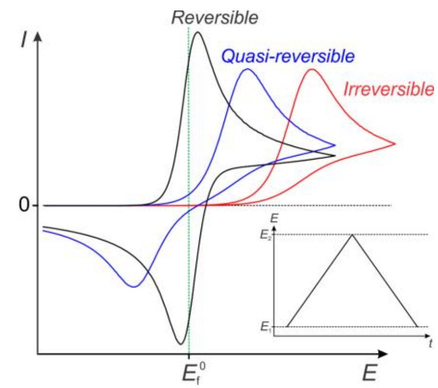
Electroanalytical-based strategies:

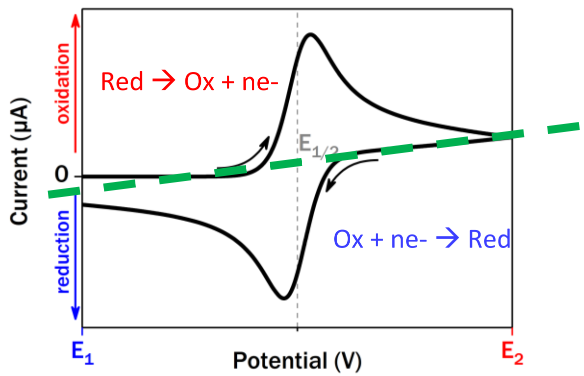
LINEAR SWEEP VOLTAMMETRY and CYCLIC VOLTAMMETRY

LSW → NO REVERSE SCAN!!!







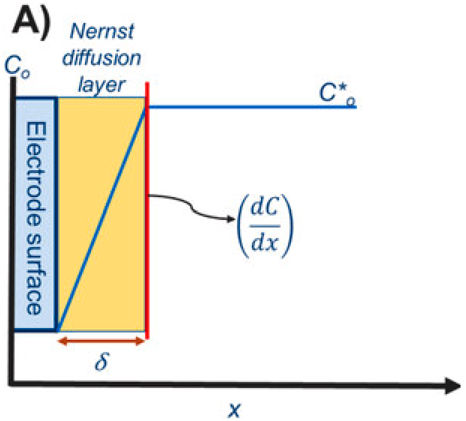


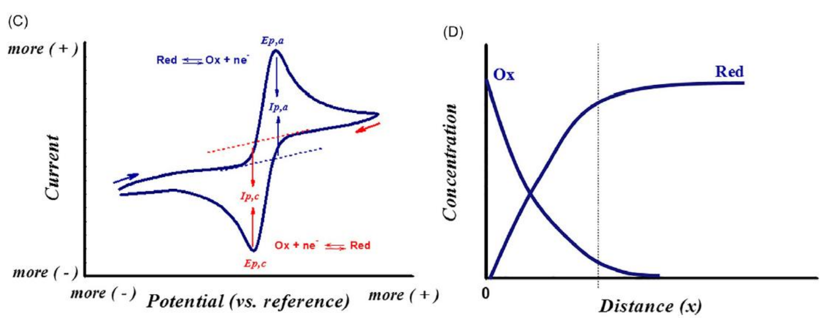
- ip,a: peak current of anodic oxidation,
- Ep,a: peak potential of anodic oxidation,
- ip,c: peak current of cathodic reduction,
- Ep,c: peak potential of cathodic reduction;
- △Ep= | Ep, a − Ep, c |: Peak-to-peak separation
  <u>(for ideal reversible 59/n mV)</u>

Electroanalytical-based strategies: voltammetry and amperometry

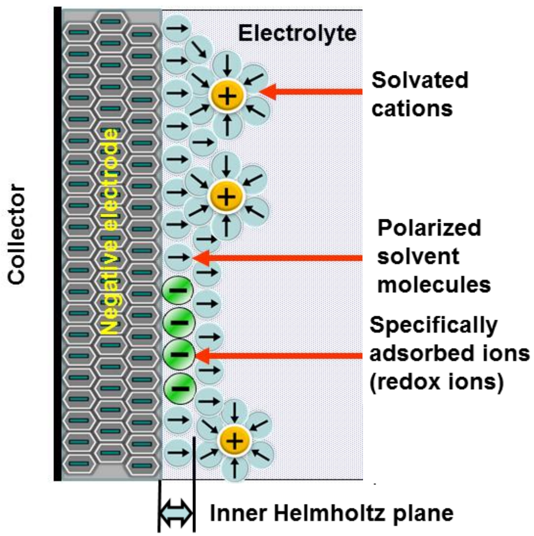
An electrolyte (salt) is necessary, to repress migration to the electrode driven by charge, the analyte should arrive to the electrode surface by diffusion or forced mass transport (pump, stirring) to have reproducible concentration signals

NERNST DIFFUSION LAYER





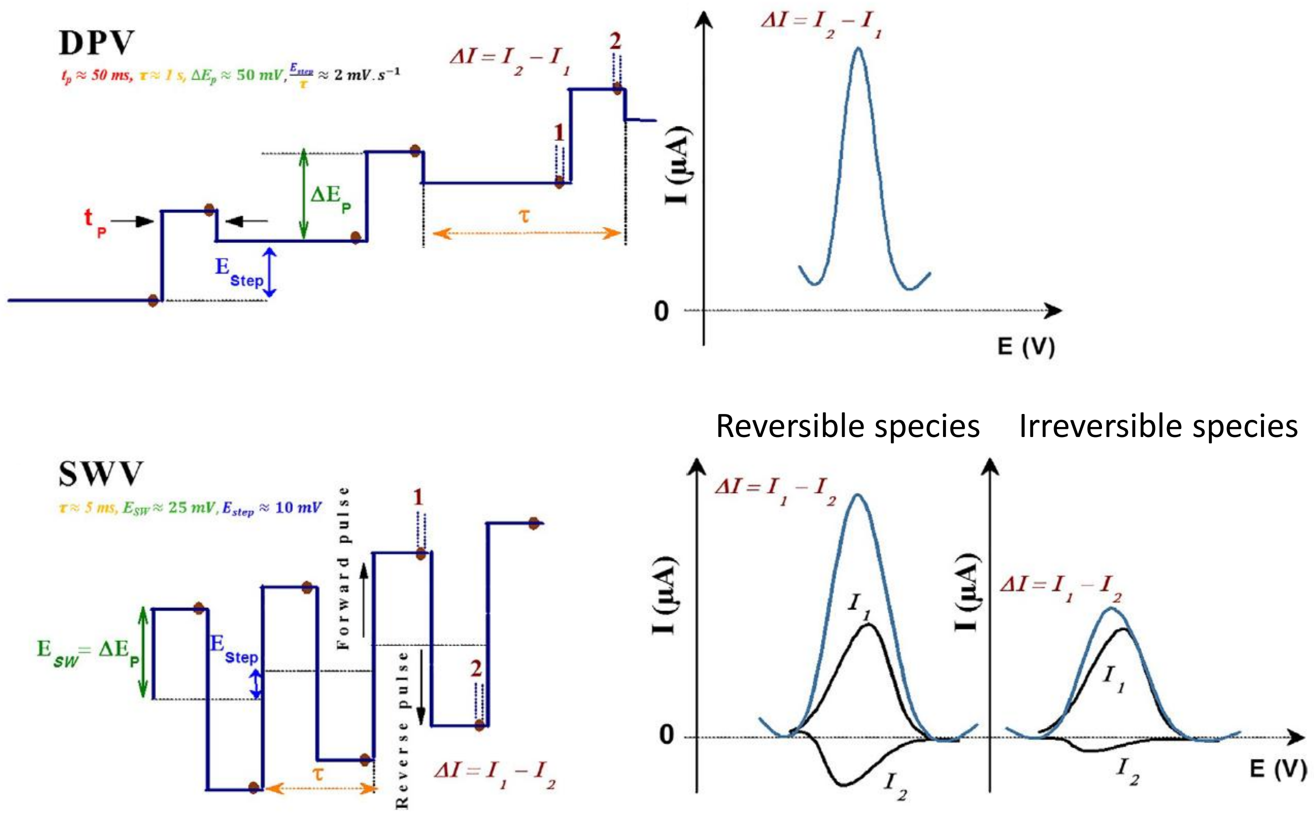
CAPACITIVE CURRENT



!!! PULSE METHODs !!!

Electroanalytical-based strategies:

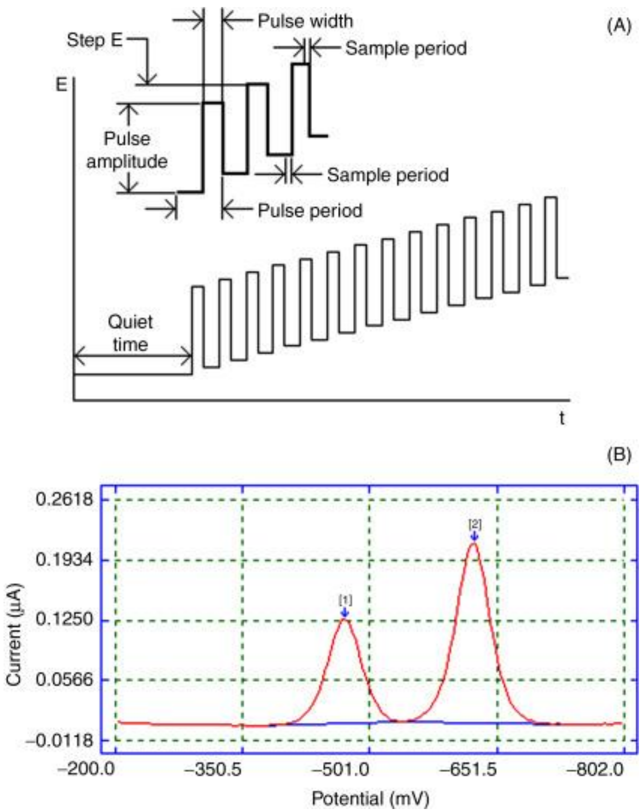
DIFFERENTIAL PULSE VOLTAMMETRIES and SQUARE WAVE VOLTAMMETRY



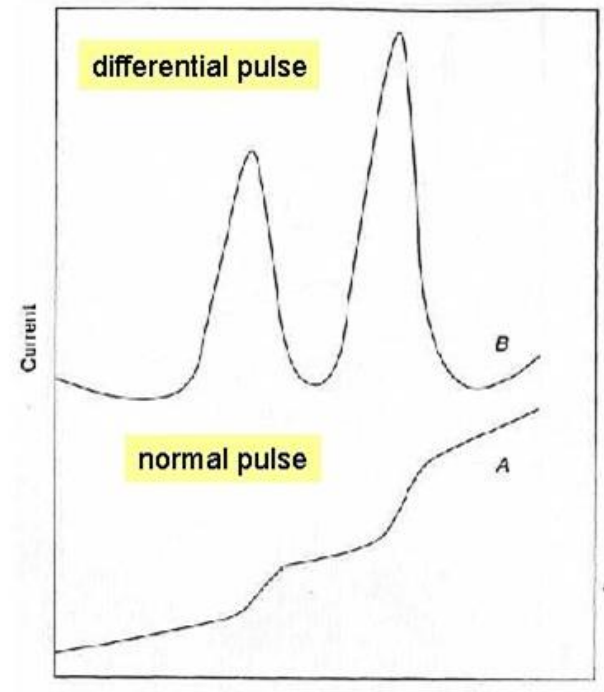
τ is the pulse period, tp is the pulse time, Estep is a potential step, **△Ep is the pulse amplitude**, ESW is the square wave amplitude, and △I is the resulting current.

Electroanalytical-based strategies:

DIFFERENTIAL PULSE VOLTAMMETRY



- allows measurement down to 10-8 M concentration
- improved resolution between the species with similar potential (down to 50 mV)



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

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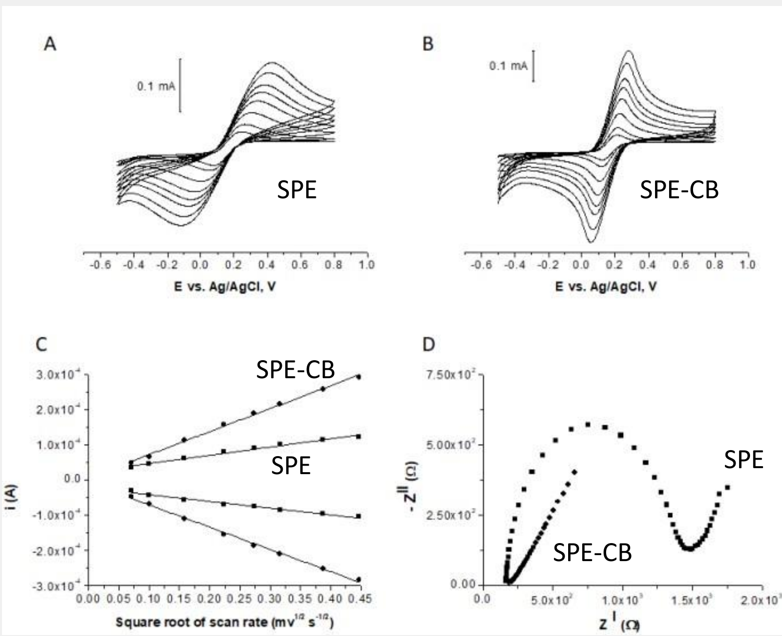
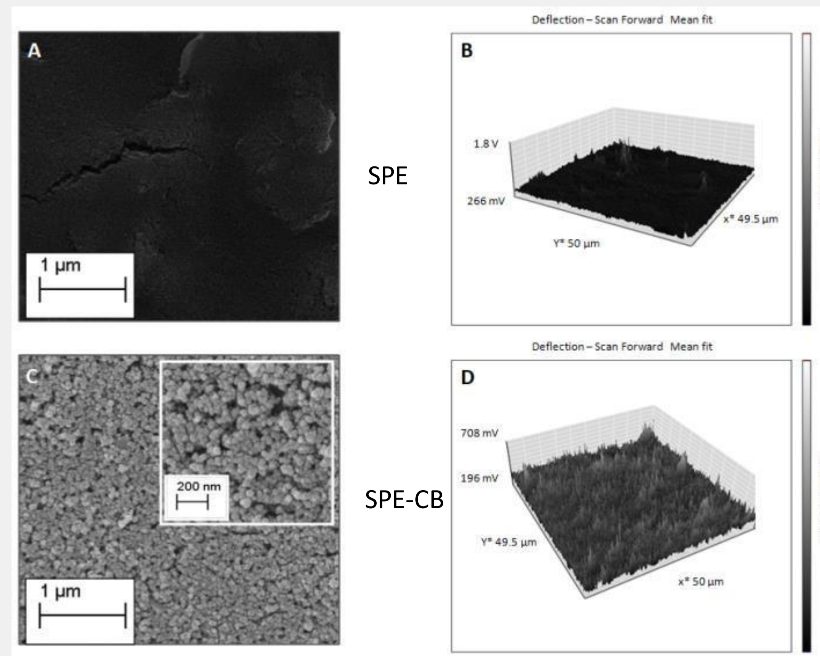
SPE vs. SPE-CB electrochemical performance



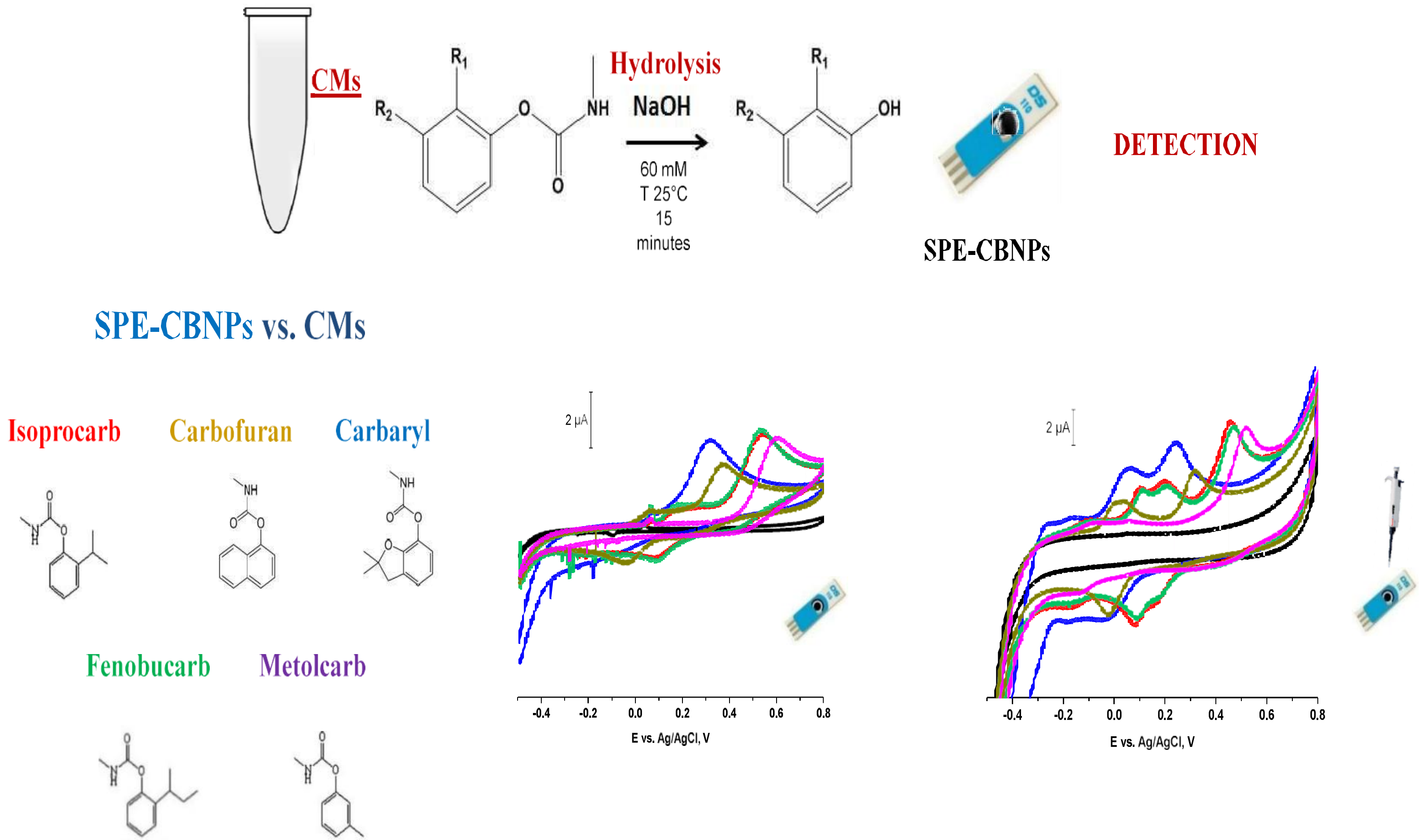
1 mmol L^{-1} **ferricyanide** solution in 0.1 mol L^{-1} KCl of SPE CV performed at 5, 10, 25, 50, 75, 100,150 and 200 mV s^{-1}

SEM

AFM

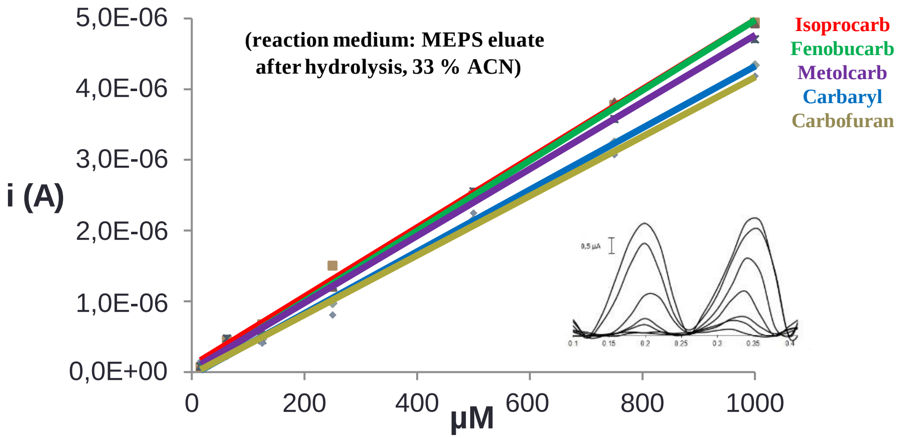


SPE CBNPs for direct analysis of carbamates in grain samples



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

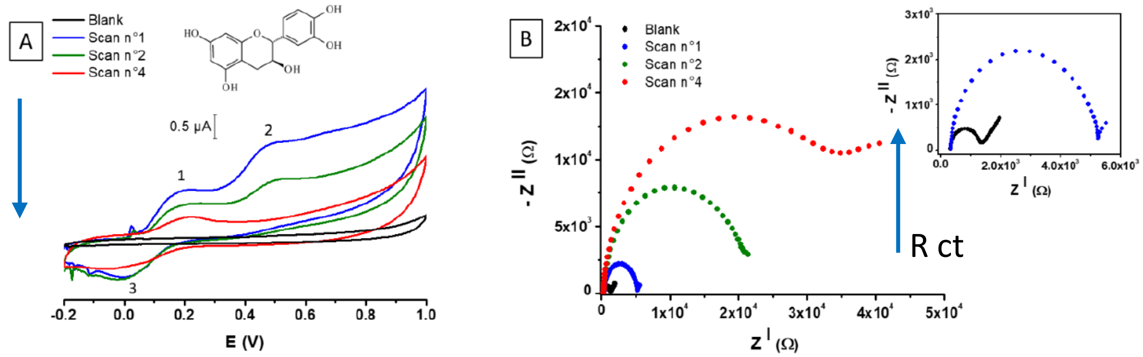
[a] Mean value (n = 3) of three different extracts were employed for the recovery and relative error calculation for both CB-SPE and UHPLC-MS/MS methods.

Electrochemical analytical drawback:

irreversible Passivation /low sensitivity for phenolic compounds

(occur after 1 scan; moreover: low sensitivity and repeatability. Impossible to perform a calibration)

SPE



(A) Catechin 50 µM performed in phosphate buffer (10 mM + 0.1 M KCl at pH 7.0), scan rate of 50 mV s^{-1}.
(B) Nyquist plots of 5 mM $Fe(CN)_6^{4-/3-}$ in 0.1 KCl M performed with the bare SPE after each CVs scan

Carbon Electrodes

...Catechin also adsorbs strongly on the electrode surface and the final oxidation product is not electroactive and blocks the electrode surface...

Janeiro, P., Brett, A.M.O. (2004). Analytica chimica acta, 518(1-2), 109-115.

Della Pelle, F., Rojas, D., Scroccarello, A., Del Carlo, M., Ferraro, G., Di Mattia, C., Martuscelli, M., Escarpa, A., Compagnone, D. (2019). SENSOR ACTUAT B-CHEM, 296, 126651.

Transition Metal Dichalcogenides and their hybrid nanomaterials

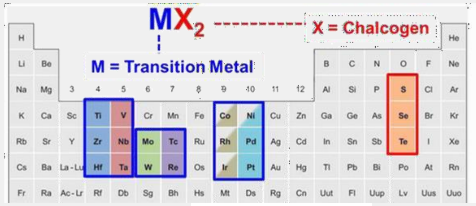
Objective	MoS_2 hybrids	WS_2 hybrids	Group VI Transition Metal Dichalcogenides

Transition Metal Dichalcogenides (TMDs)

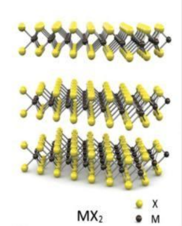
TMDs are a family of 2D nanomaterials with general formula MX_2 (M: Group 4-10 and X: S, Se and Te)

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**

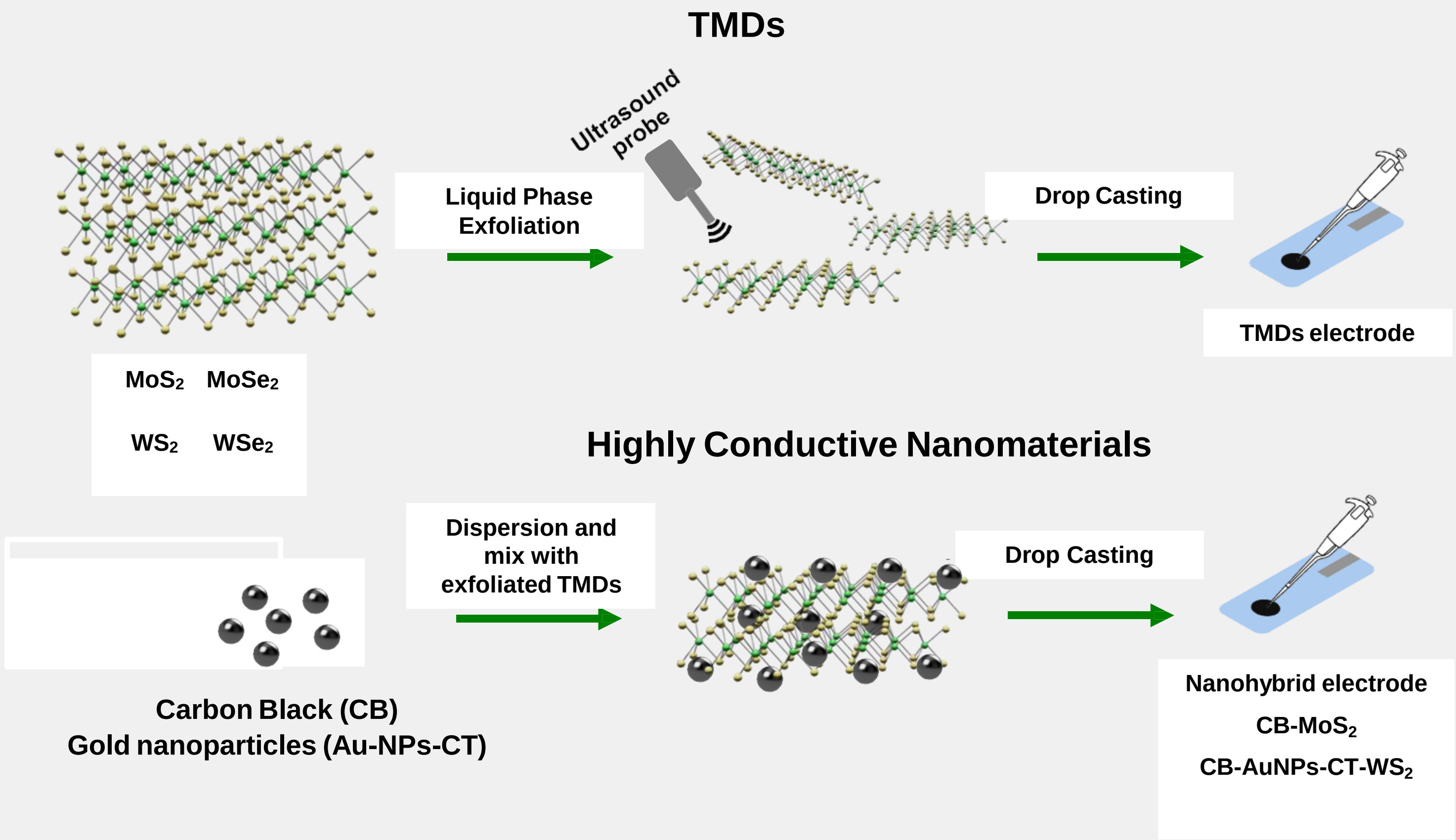
✓TMDs are poor conductive materials

✓Hinder its catalytic capabilities

→ **Nanohybrids materials**

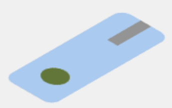
Transition Metal Dichalcogenides and their hybrid nanomaterials

Electrode preparation methods



Transition Metal Dichalcogenides and their hybrid nanomaterials

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



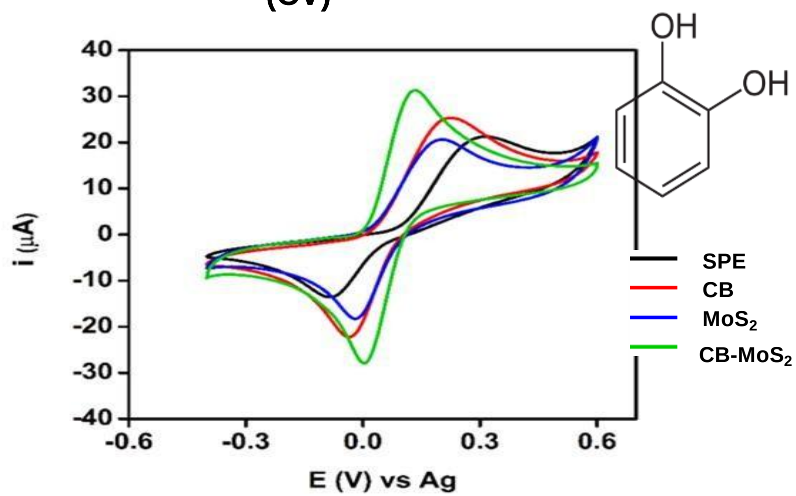
CB-MoS_2

Electrochemical characterization

Catechol as representative redox moiety in food polyphenols

Cyclic Voltammetry (CV)

Catechol



Catechol moiety is present in highly antioxidant polyphenols

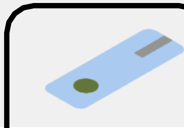
CB–MoS_2 nanohybrids shows an enhanced and synergistic electrocatalytic effect towards catechol

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

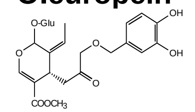
Objective | **MoS_2 Nanohybrids** | WS_2 Nanohybrids | Group VI Transition Metal Dichalcogenides

Application of CB-MoS_2 electrochemical sensors to different food matrices

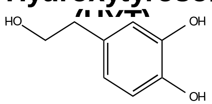


Olive oil

Oleuropein

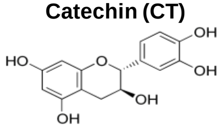


Hydroxytyrosol

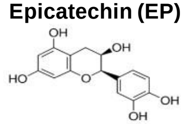


Cocoa

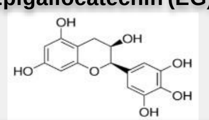
Catechin (CT)



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

Università degli Studi di Teramo
Universidad de Alcalá
REP-EAT
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 713714
Co-funded by: University of Teramo, Region Abruzzo

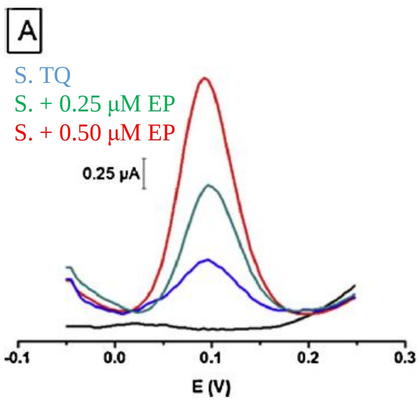
Real sample analysis: n = 59 cocoa powder samples

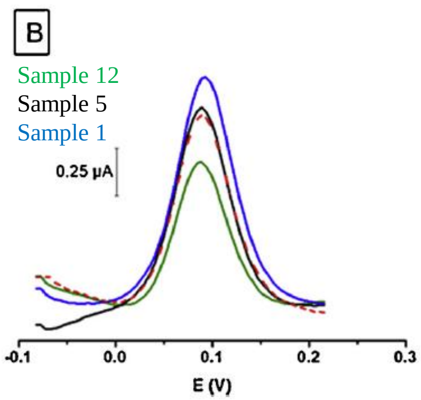
UNIVERSITÀ DEGLI STUDI DI TERAMO
UNITE

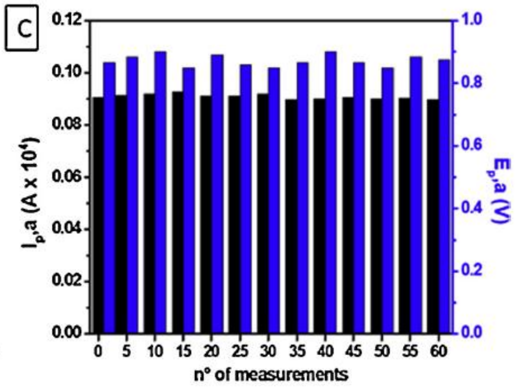
Recoveries

Repeatability during n=59 sample analysis

DPV conditions:
pulse width 50 ms, pulse amplitude 20 mV.







From 94% to 103%
The sensor is exploitable for catechins determination in complex samples

Signal recovery 99%
After n= 59 samples measured

RSD Ip,a < 0.9% and Ep,a< 5.2
10 µM epicatechin signal, obtained during the whole samples analysis

SPE-CB-MoS_2 has a regenerable electrode surface
59 cocoa samples consecutive analysis

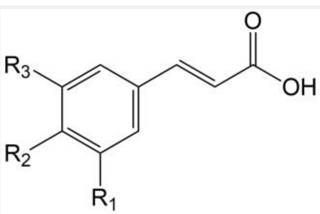
Della Pelle, F., Rojas, D., Scroccarello, A., Del Carlo, M., Ferraro, G., Di Mattia, C., Martuscelli, M., Escarpa, A., Compagnone, D. (2019). SENSOR ACTUAT B-CHEM, 296, 126651.

Transition Metal Dichalcogenides and their hybrid nanomaterials

WS_2 nanohybrids electrochemical behavior towards different hydroxycinnamic acids (hCNs)

CB-AuNPs-CT-WS_2

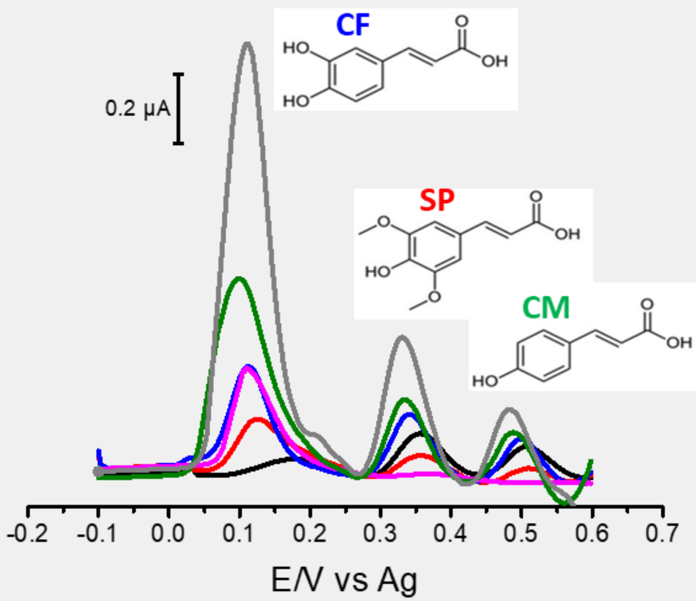
hCNs general structure



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))**

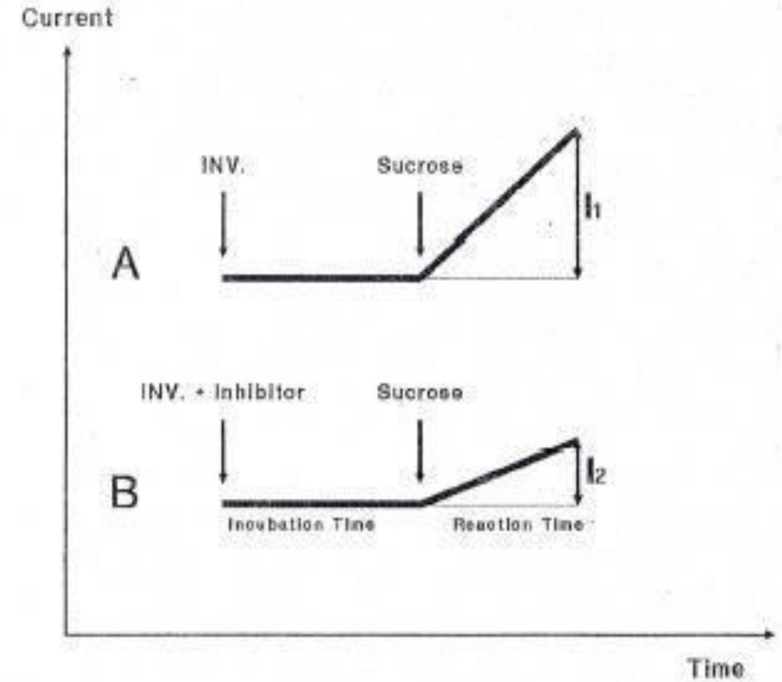
F. Della Pelle, **D. Rojas**, F. Silveri, G. Ferraro, E. Fratini, A. Scroccarello, A. Escarpa, D. Compagnone. Microchim. Acta. 187 (2020) 296.

Biosensors based on enzyme inhibition

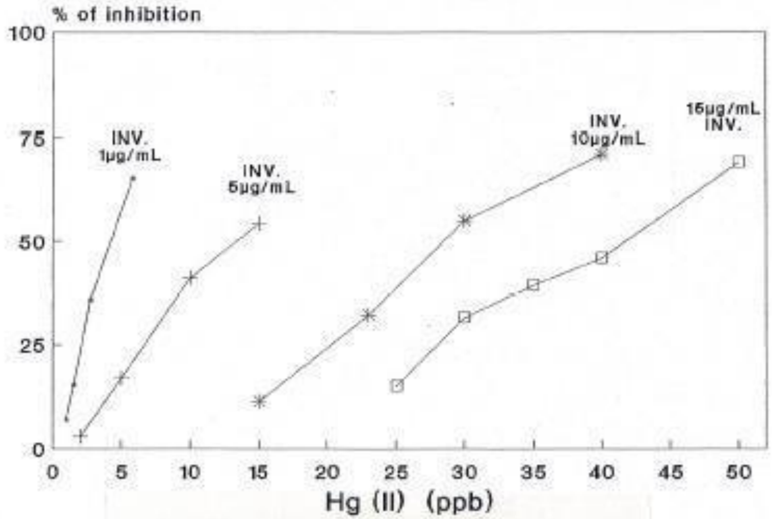
There is a great demand for rapid and sensitive analytical methods for the determination of mercury and related compounds in environmental samples. The environmental risk and toxicological concern of mercury and its compounds, especially methylmercury, have stimulated the research into various new methods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

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

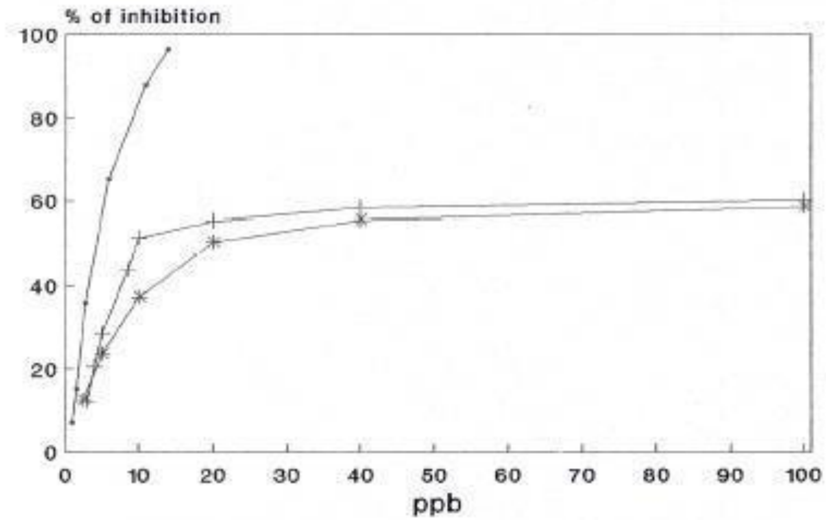
Toxicity of mercury depends on its chemical form. For example methyl mercury is more toxic than HgII (1).



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

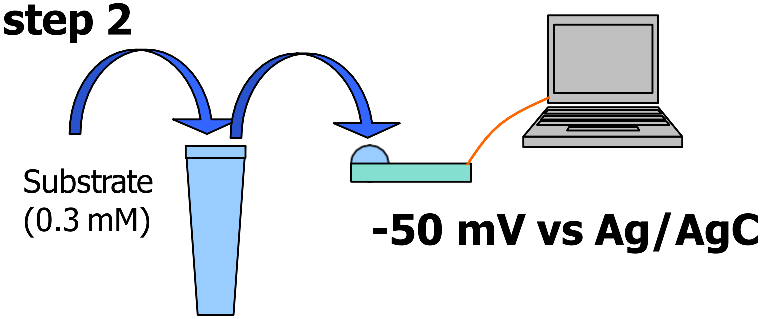
step 1

0.125 U/ml AChE

1 mL buffer +
standard or sample

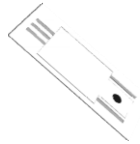
10’ incubation

step 2



120’’

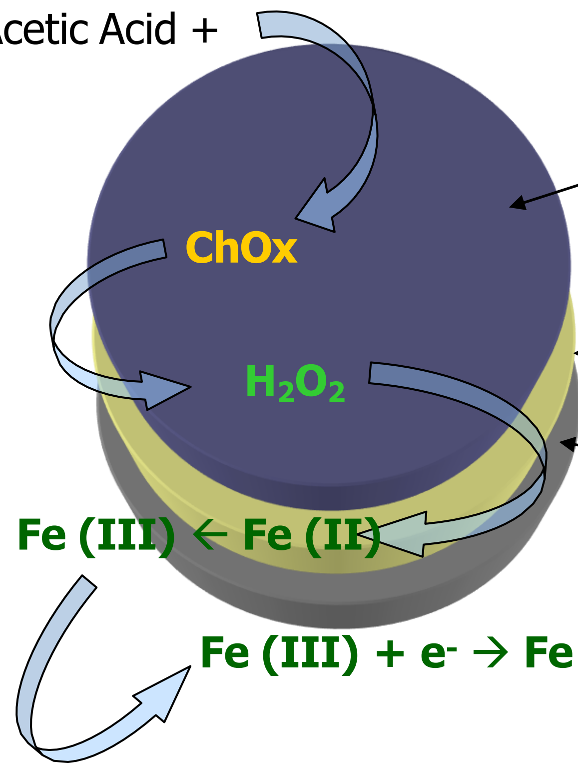
$$RA\% = 100 * \frac{(I_0 - Is)}{I_0}$$



Screen printed electrode

Working electrode reactions pathway

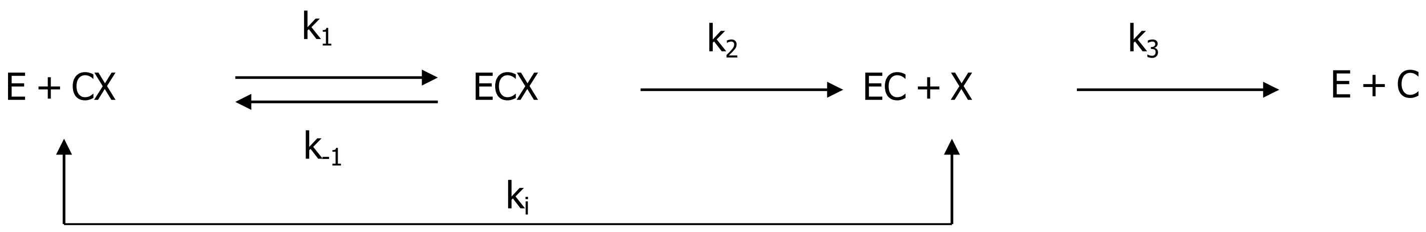
Acetylcholine + H_2O → Acetic Acid + **Choline** (AChE)



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

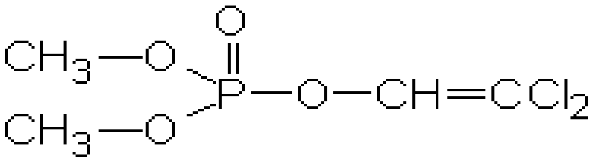
Diclorvos (organophosphate) **anticolinesterasic**

Mechanism of AChE inhibition



E = enzyme; CX = carbamate or organophosphate; X = leaving group; $K_d = k_{-1} / k_1 k_2$ 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.

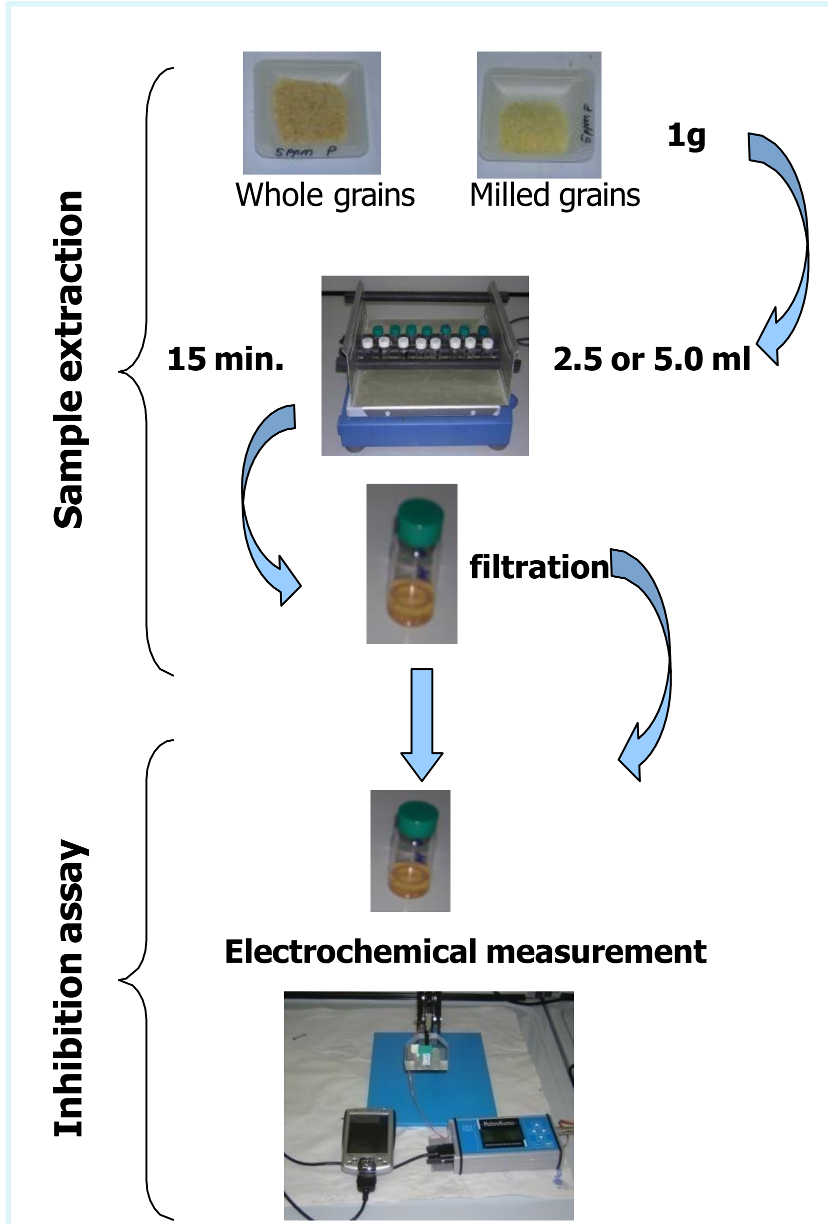
The European Union regulates the maximum adsmissible level in **durum wheat** at **2 mg/Kg** (European Directive 2001/57/CE)

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

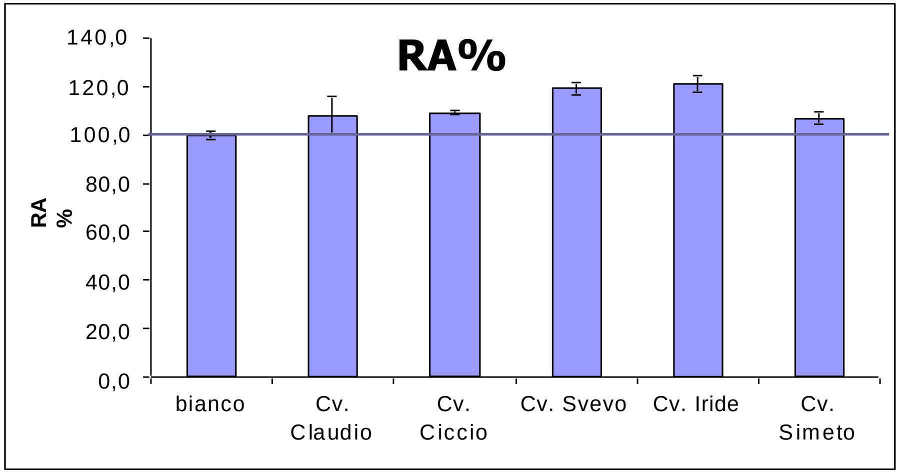


Matrix effect on the RA% and the I%

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

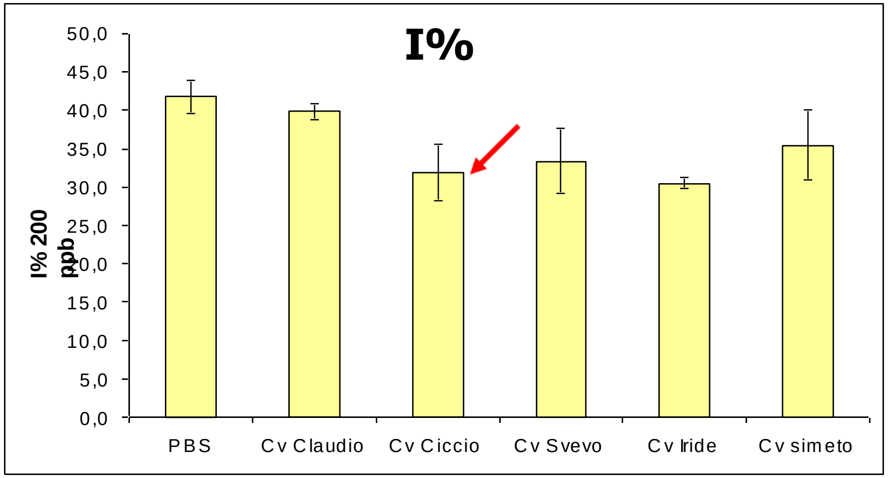
Phosphate buffer pH 7.4, KCl 100 mM
10% matrix
AChE 0.125 U/ml, Ach 0.3 mM
Incubation time: 10 min.

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

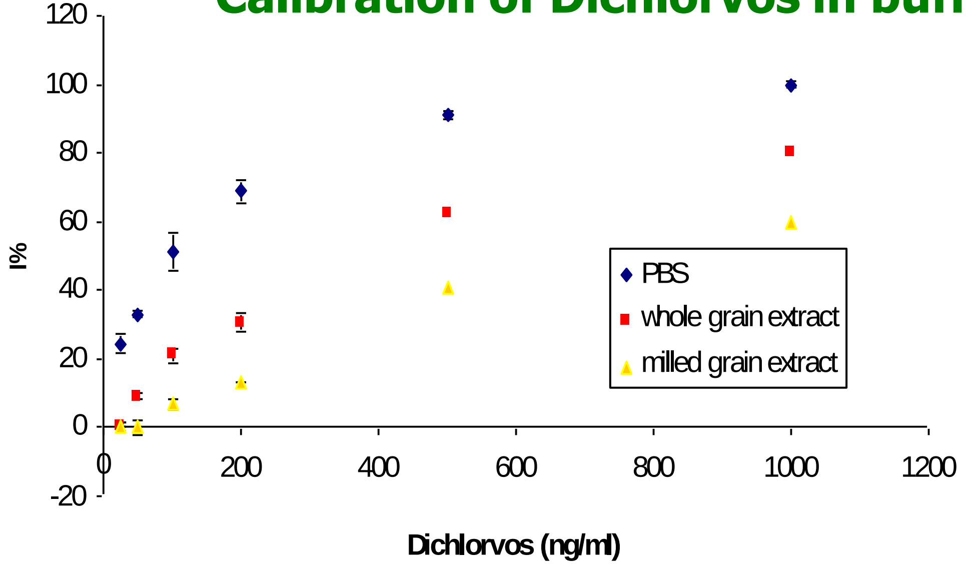


Experimental conditions:

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

- **LOD = 2 x SD of no ihnibition measurement**
- **$I_{50\%}$ = 50% of inhibition**

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

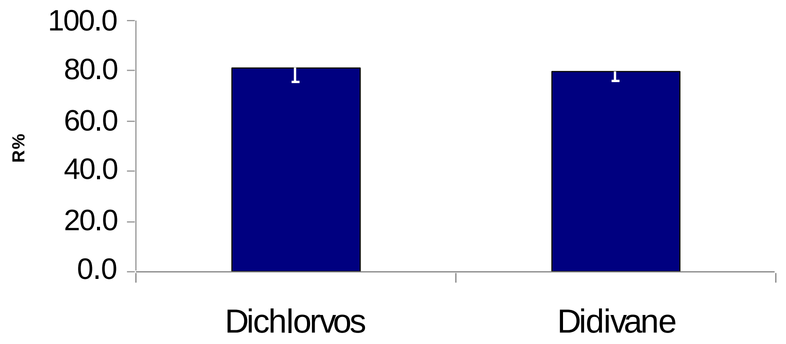
LOD = 1.3 mg/Kg

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



Mean I%: 21.0±1.3 — **Mean recovery: 81.3 ±5.8** (Dichlorvos)

Mean I%: 19.2±1.2 — **Mean recovery: 79.5 ±3.5** (Didivane)

Milled grains

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

Dichlorvos
Mean I%: 9.3±1.9
Mean recovery: 81.3 ±16.1

Didivane
Mean I%: 10.2±2.1
Mean recovery: 89.5 ±19.0

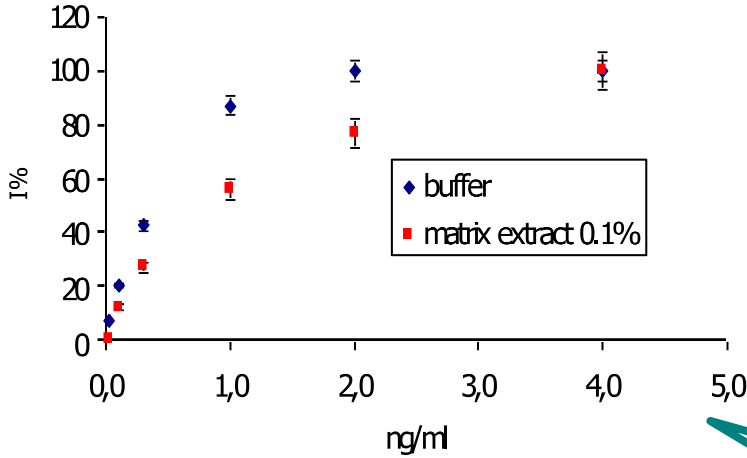
$I\%_{LOD}$=8% !!

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%

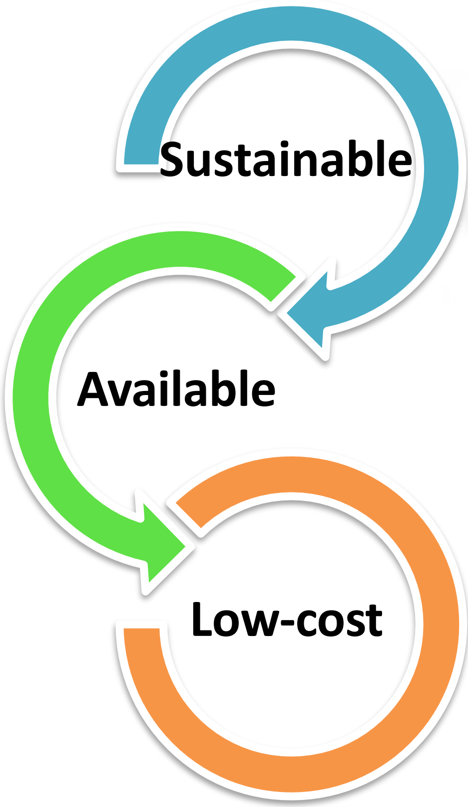
R=0.995
LOD= 0.065 ng/ml
$I_{50\%}$=0.85 ng/ml

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

Paper as substrate



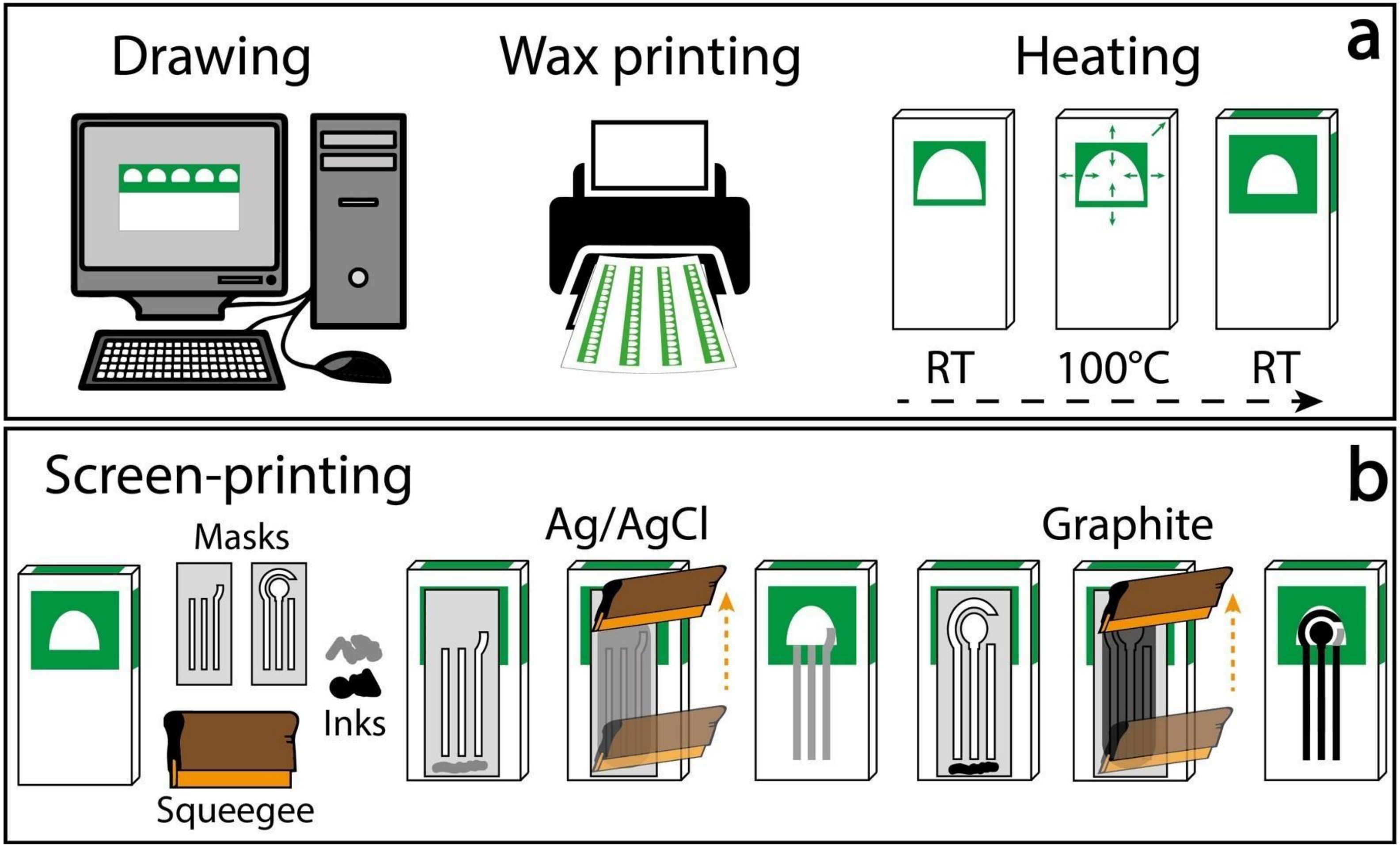
Paper can…
Store
Filter
React

Drawbacks…
Reagents diffusion…
Electrical noise! ☹

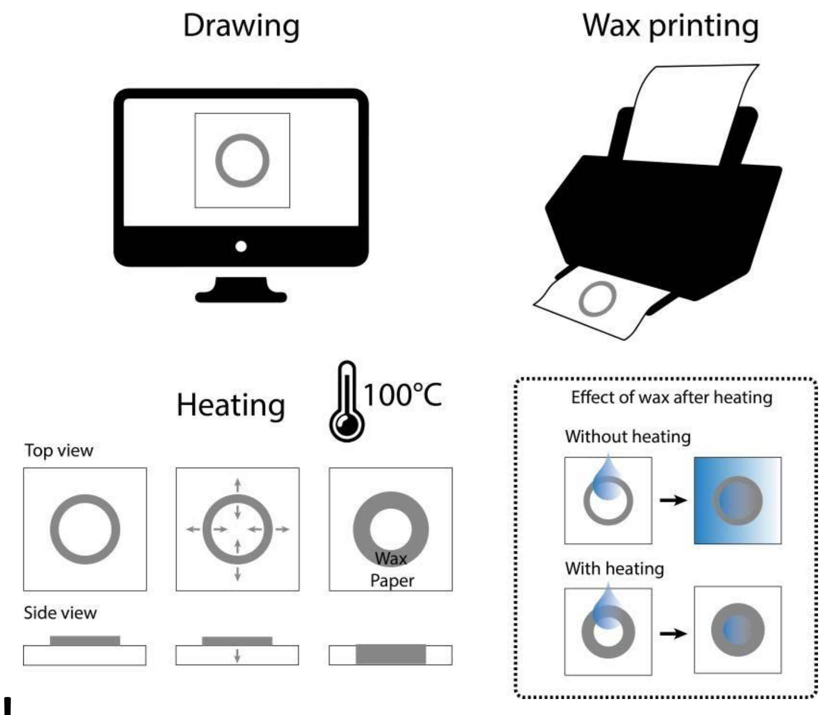
An hydrophobic
barrier
is needed…

From Paper to E-Paper

Few and easy steps



Hydrophilicity matters



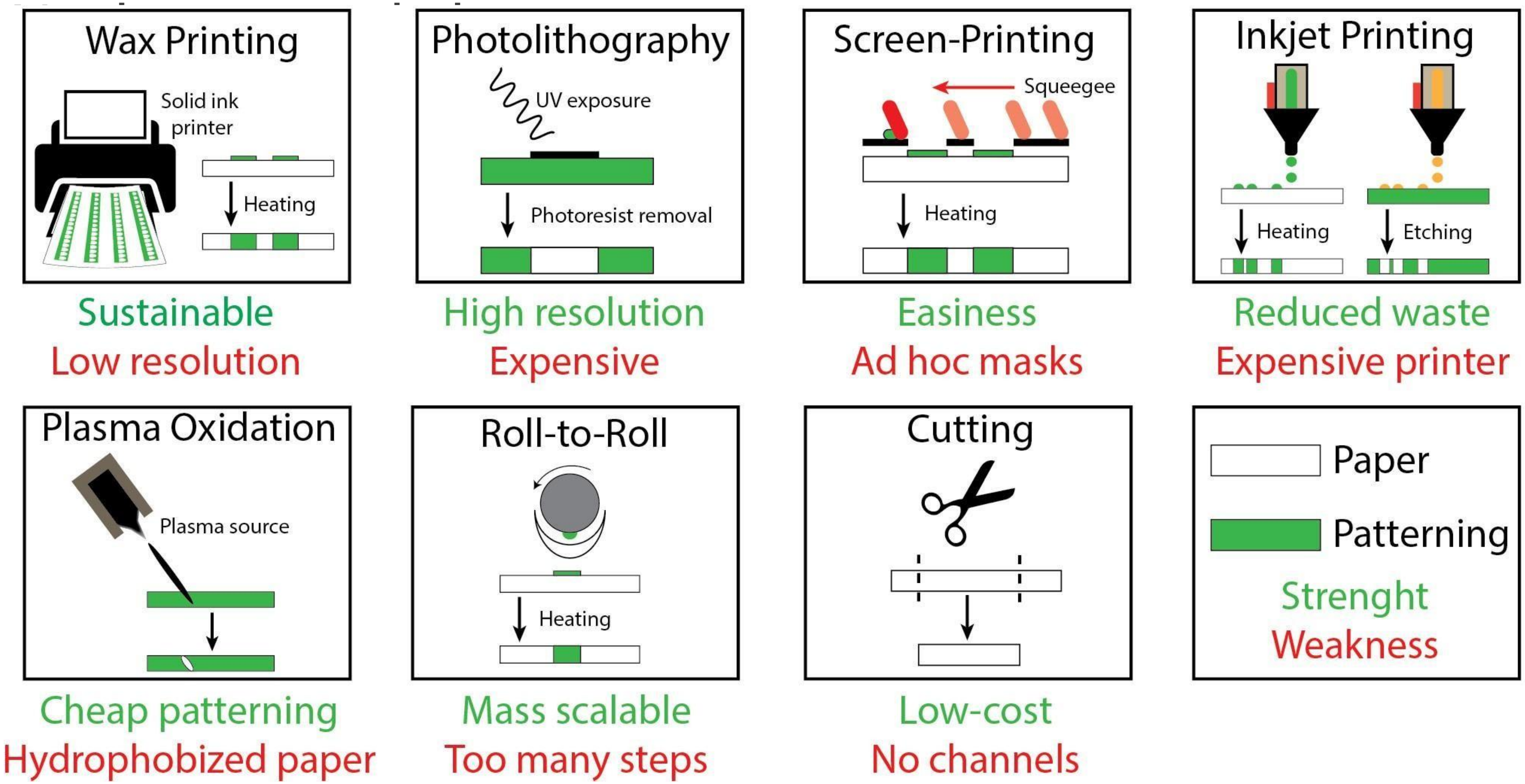
... also the cost!

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	/

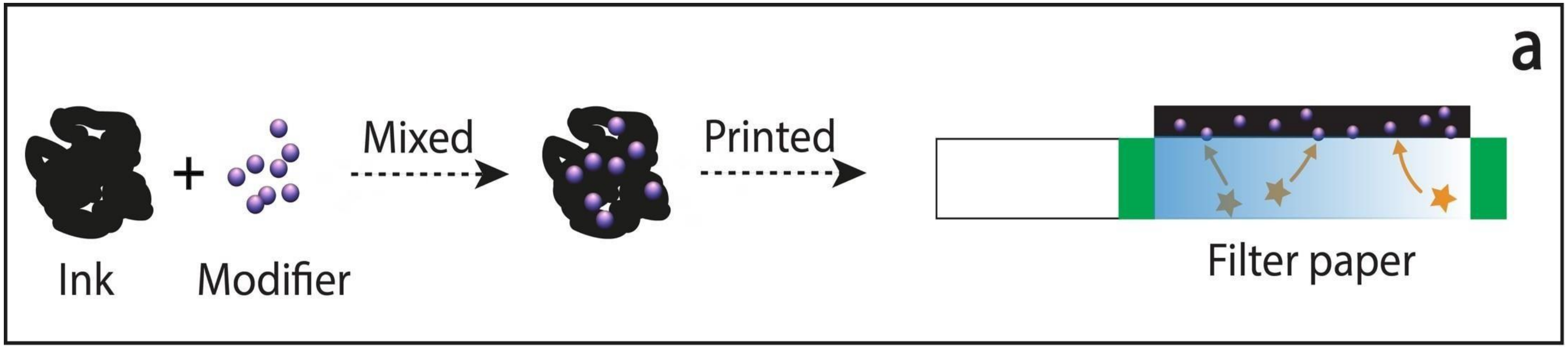
[a] Insulator ink.
[b] Wax.
[c] Calculated as 1 – [Office paper/Other] × 100.

It depends on what you need and you have!

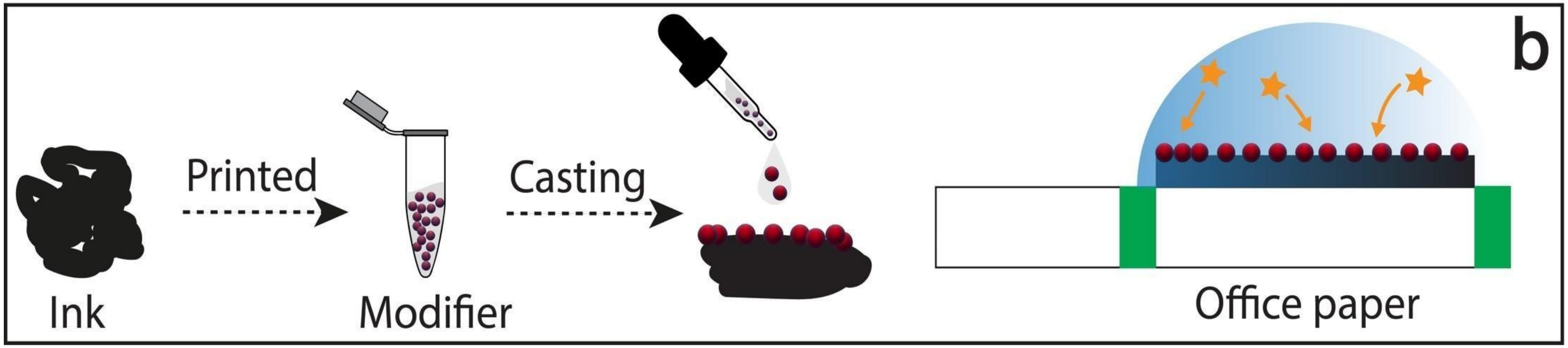


Which E-Paper?

Porous

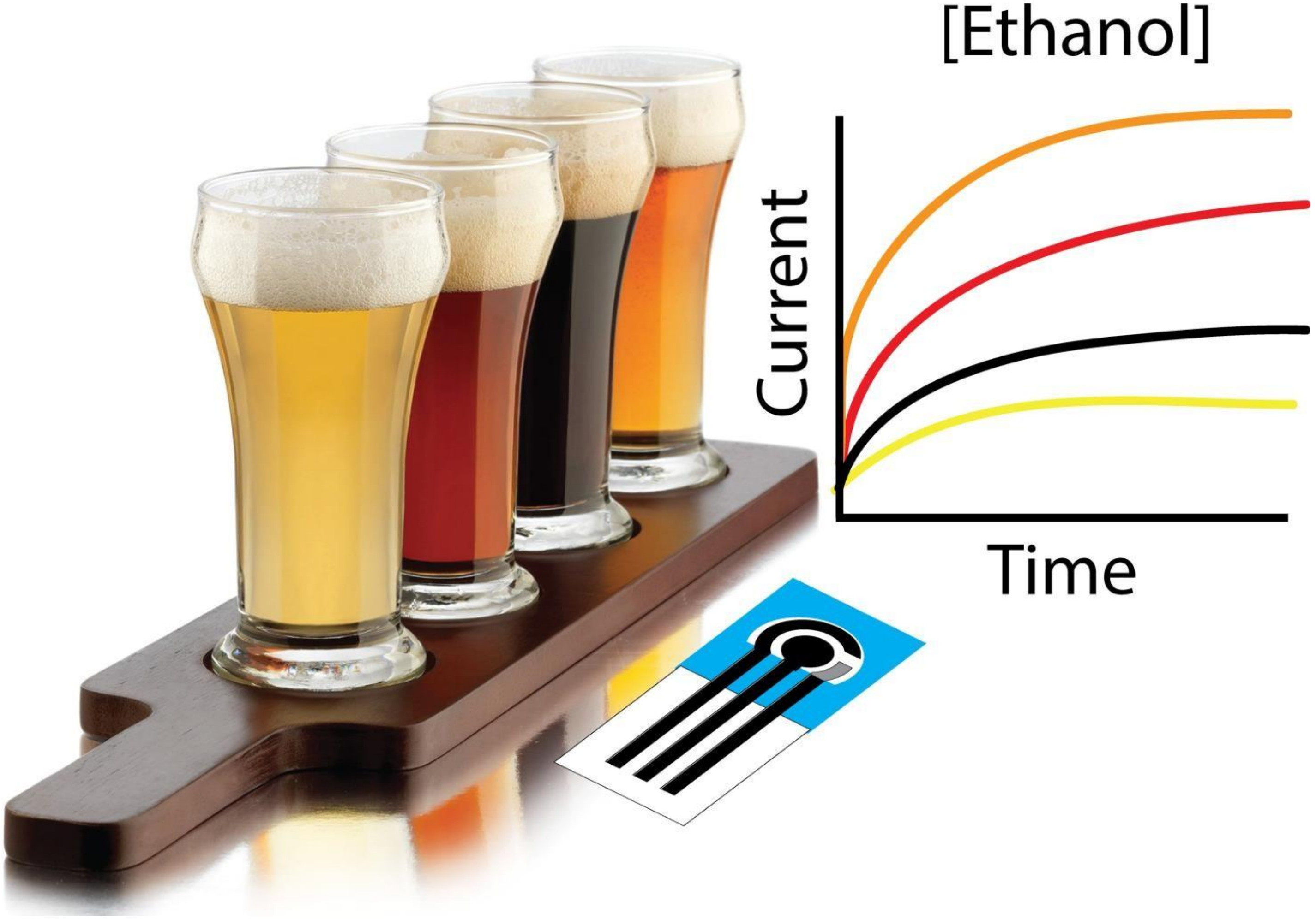


Non porous



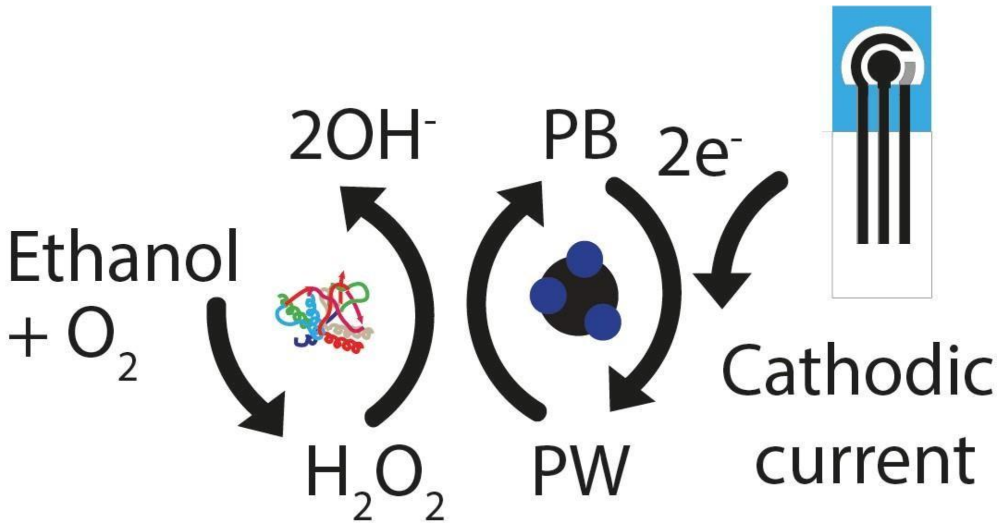
Anyway, paper is the substrate… we need to make these strips ad-hoc

Office paper for ethanol

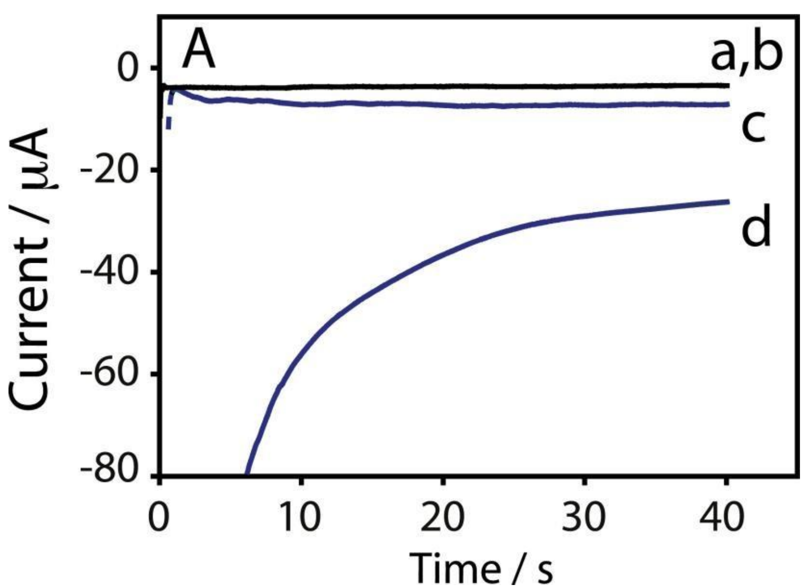


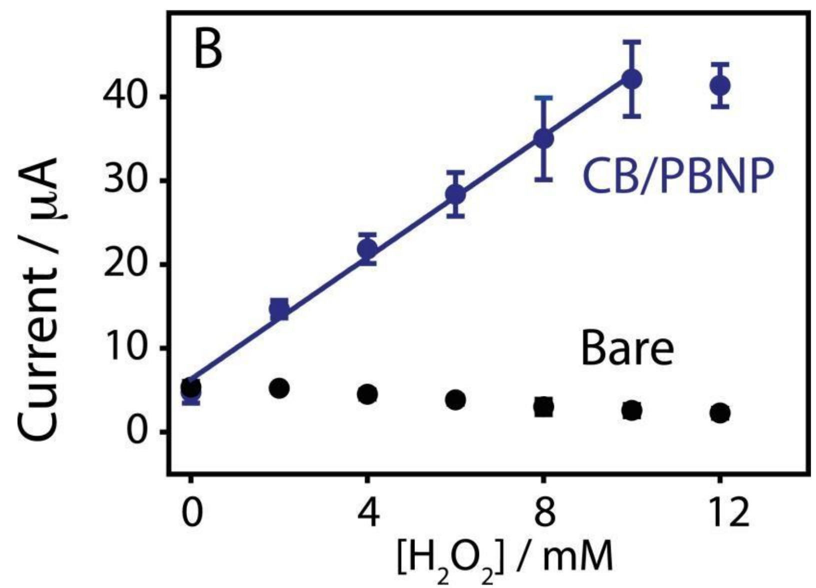
S. Cinti et al. Anal. Chim. Acta 960 (2017) 123-130

Detection mechanism

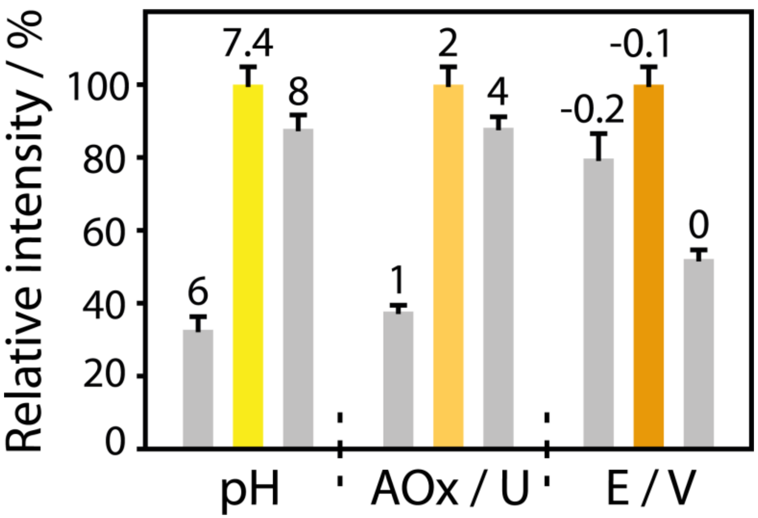


- Office paper
- Carbon Black
- Prussian Blue
- Alcohol oxidase

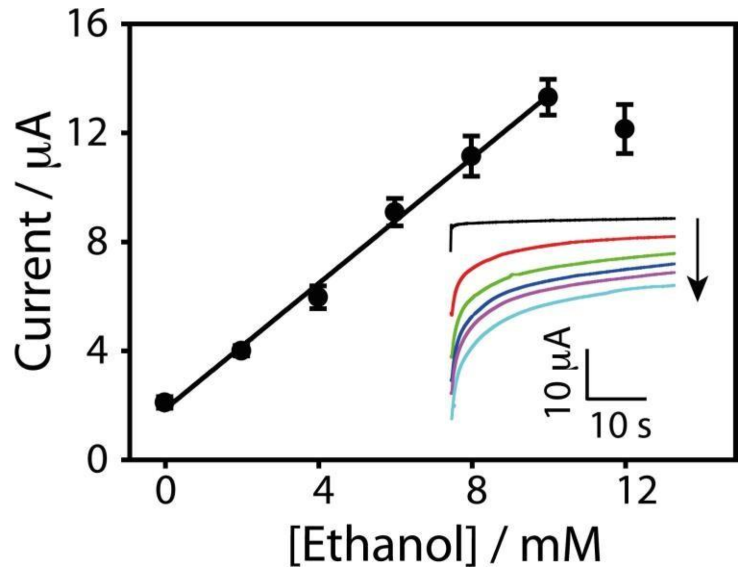




Optimization



Calibration curve



LOD = 0.5 mM

Linear range up to 10 mM

RSD = 8 %

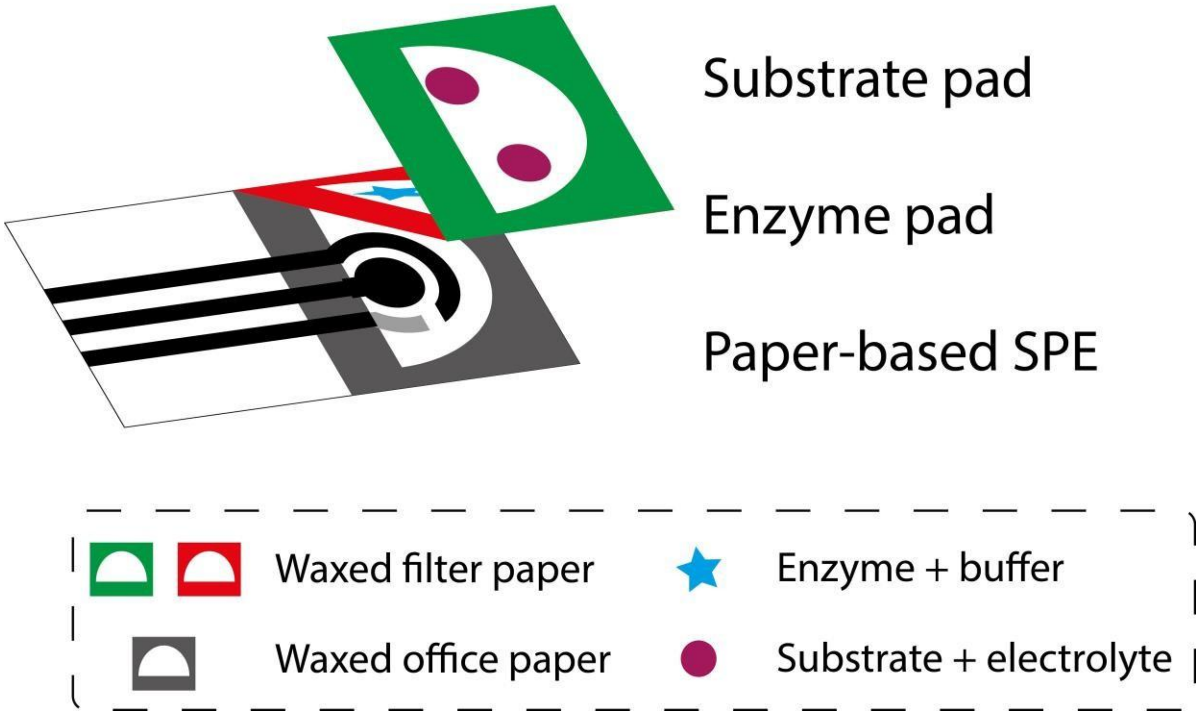
Accordance with label

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

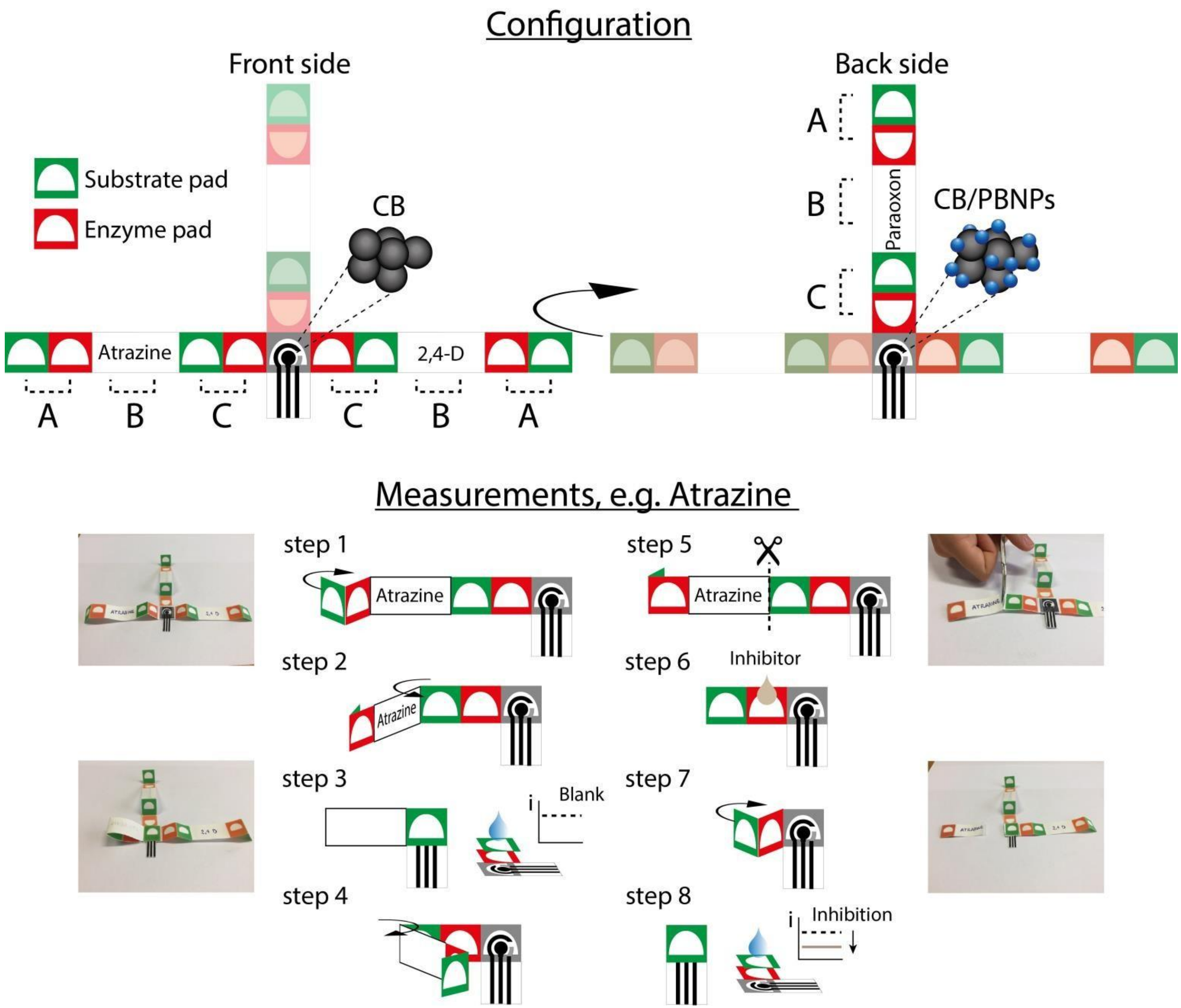
3-D paper origami for pesticides

Filter paper + office paper

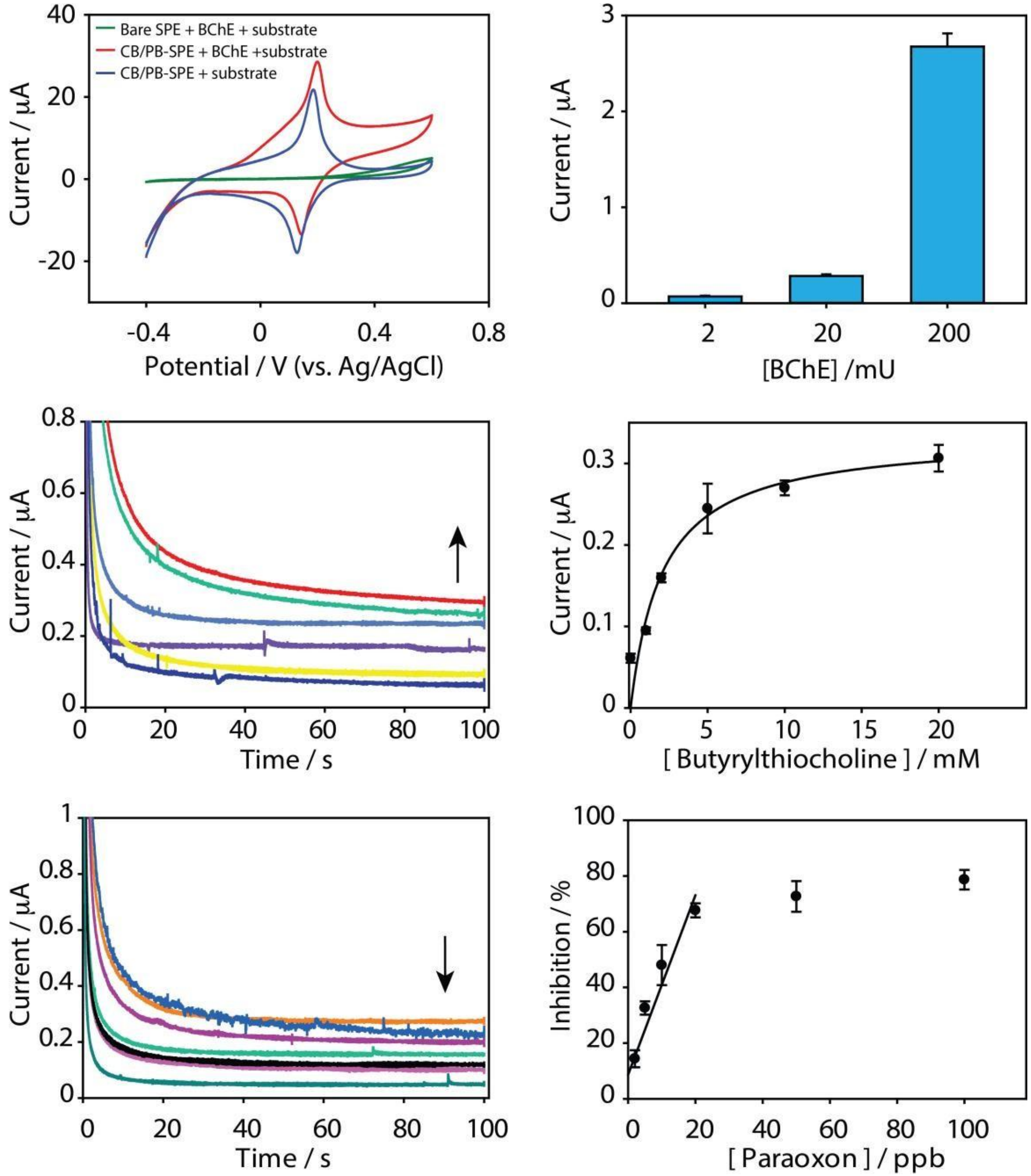


Paraoxon, **2,4-dichlorophenoxyacetic acid**, and **atrazine** by inhibition of **butyrylcholinesterase**, **alkaline phosphatase,** and **tyrosinase**

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
Atrazine
2,4-D
A
B
C
C
B
A
A
B
C
Paraoxon
CB/PBNPs
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

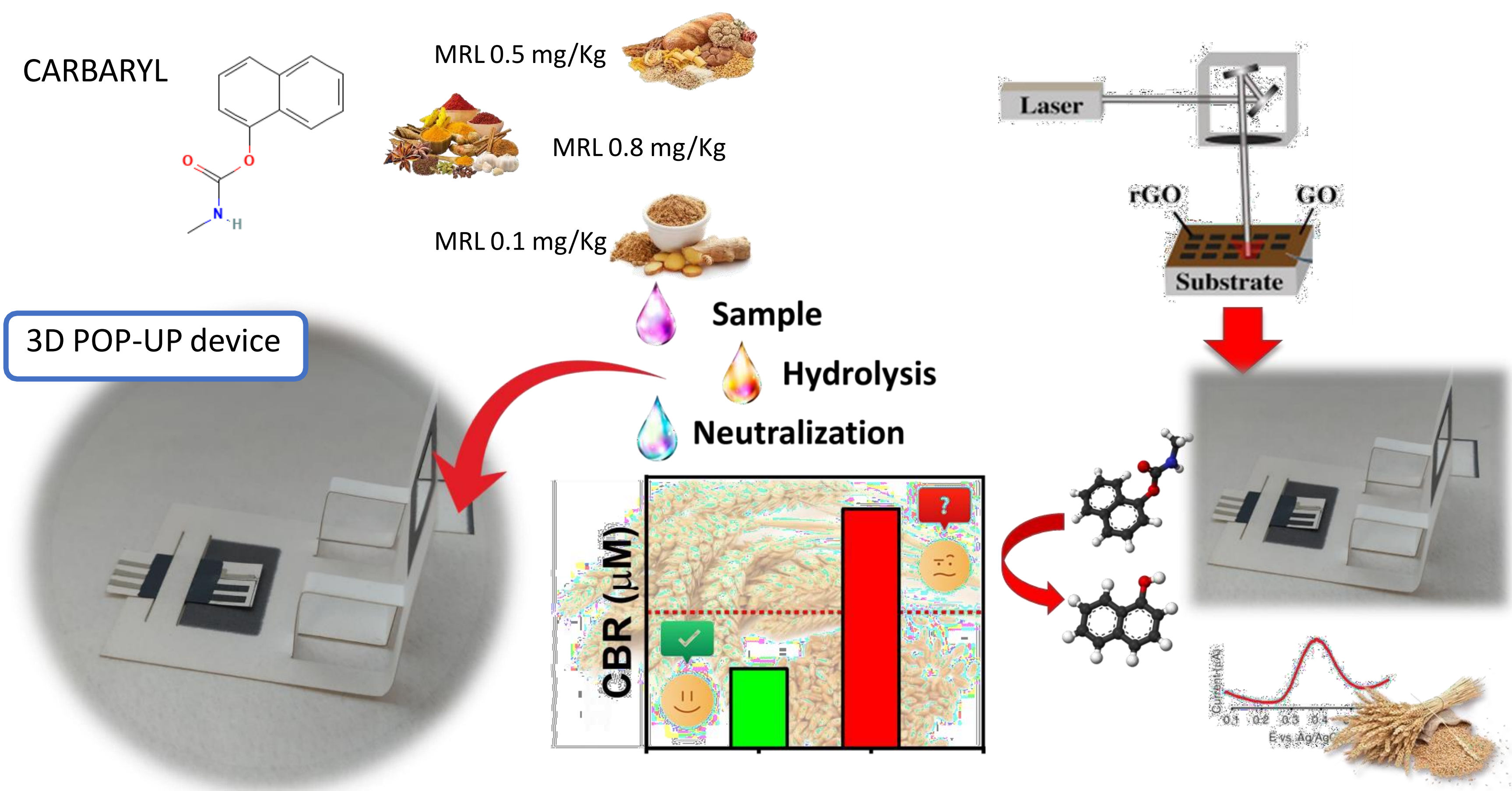
RSD = 11%

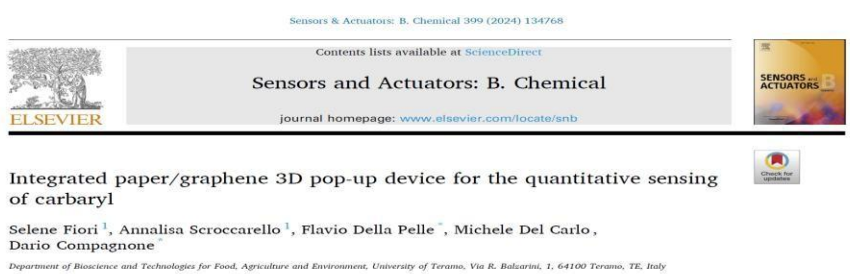
<u>Real sample: River water</u>

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

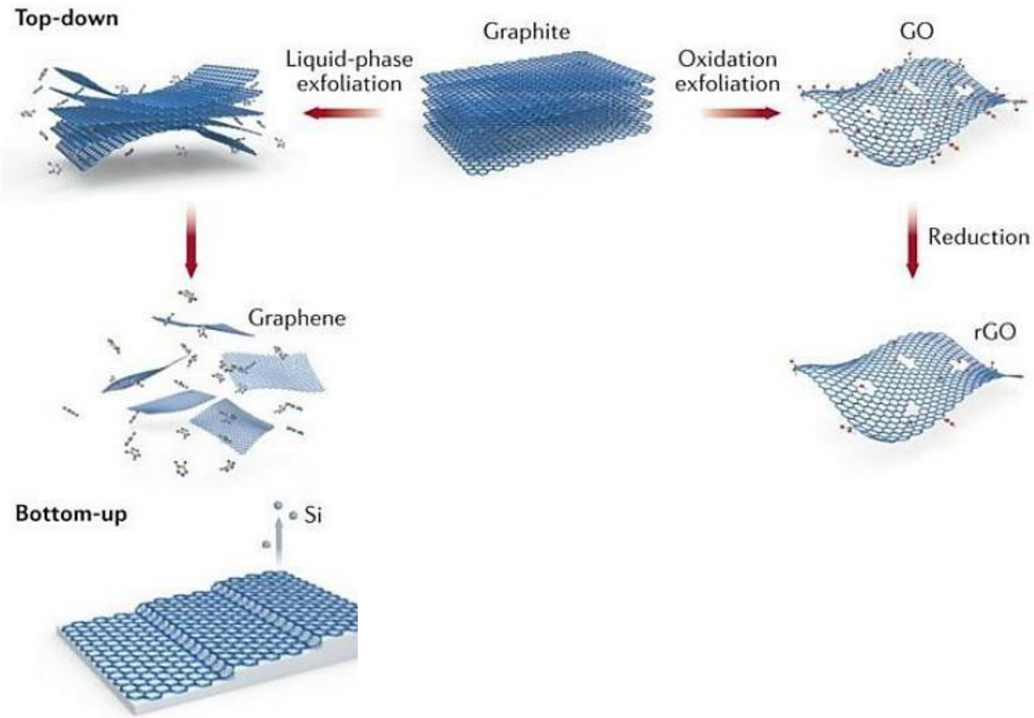
Integrated paper/graphene 3D pop-up device for the quantitative sensing of carbaryl

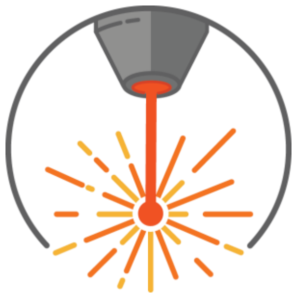
Selene Fiori [1], Annalisa Scroccarello [1], Flavio Della Pelle [*], Michele Del Carlo, Dario Compagnone [*]

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

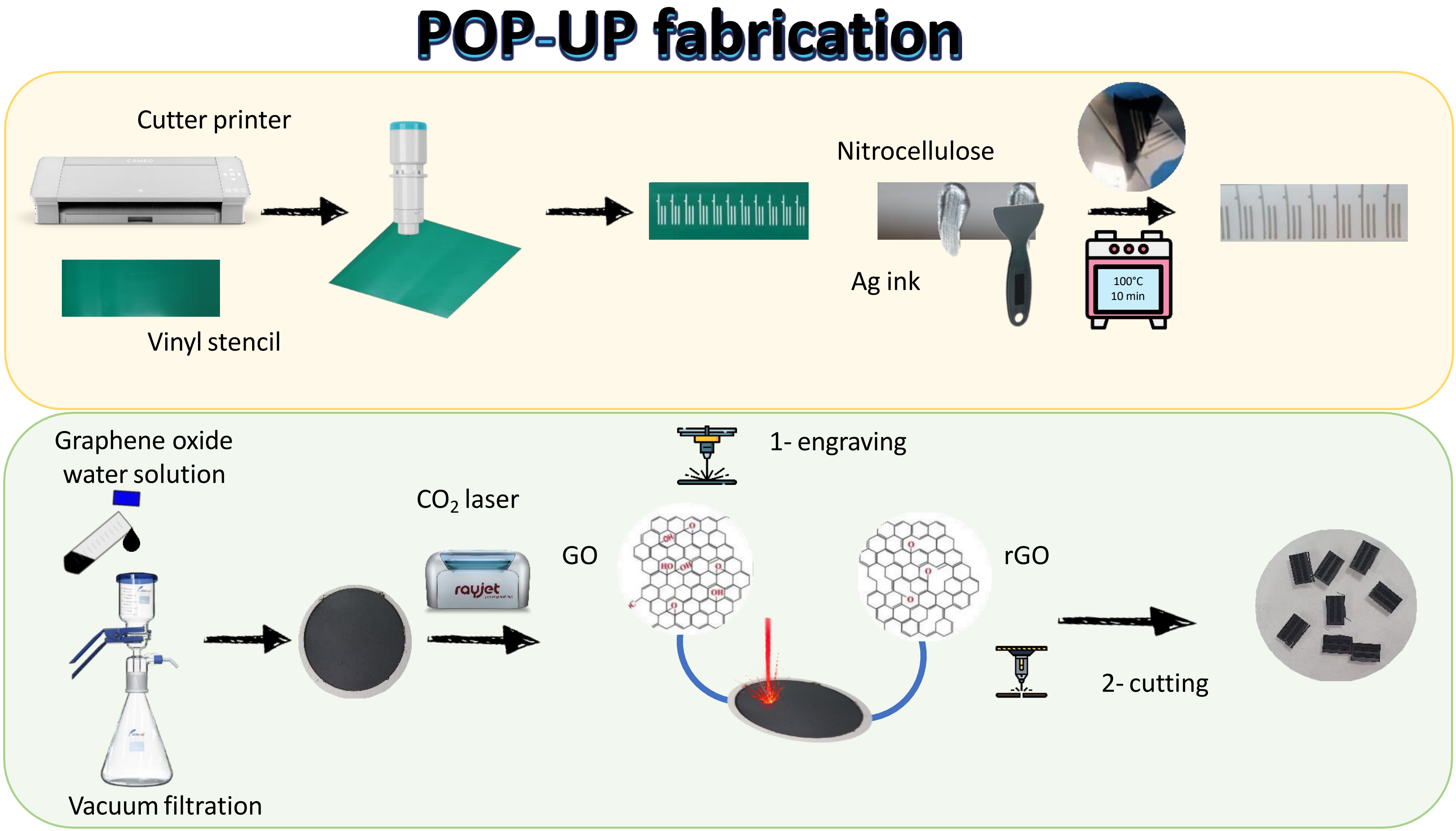
Laser induced graphene

Graphene

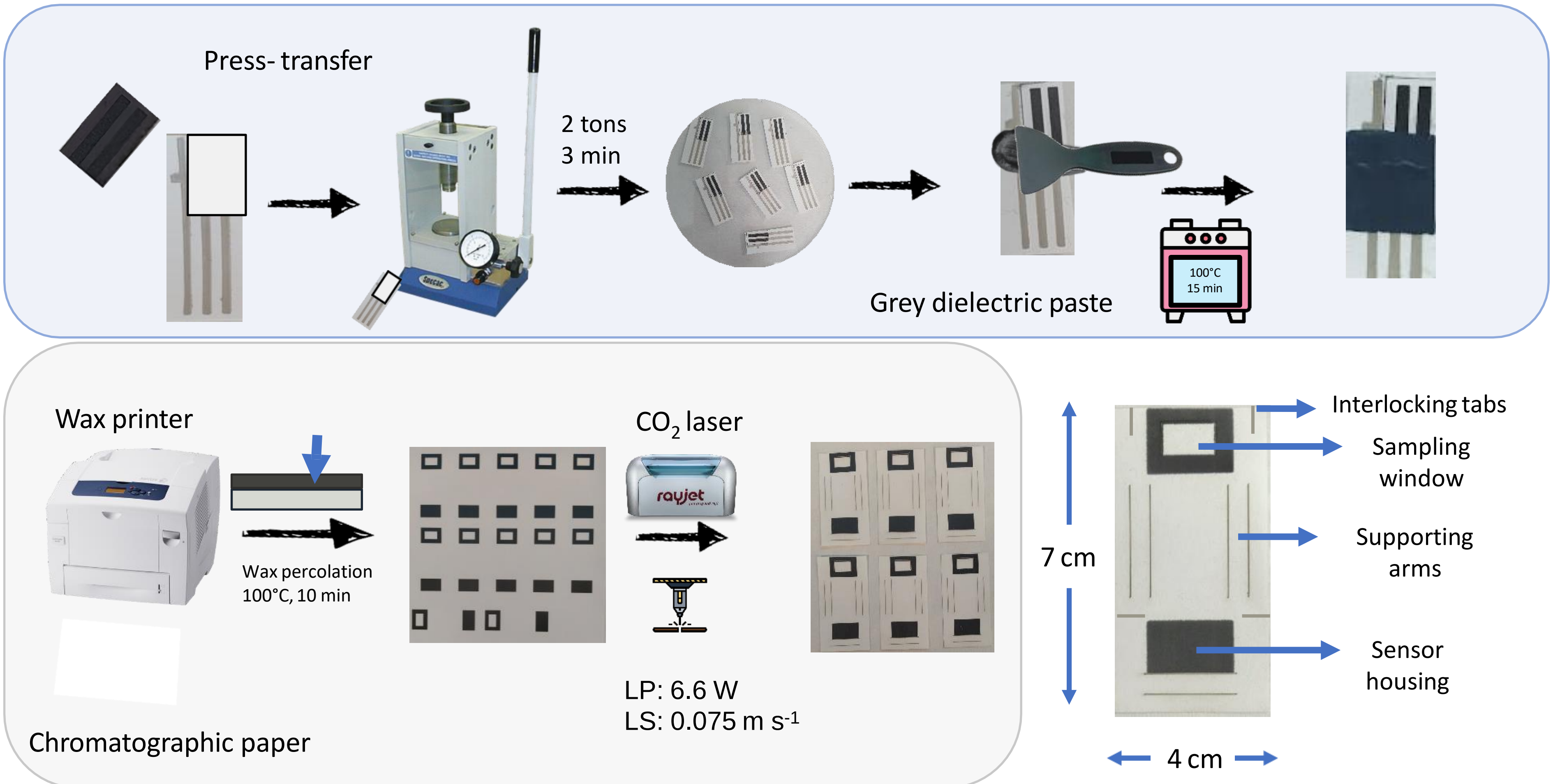




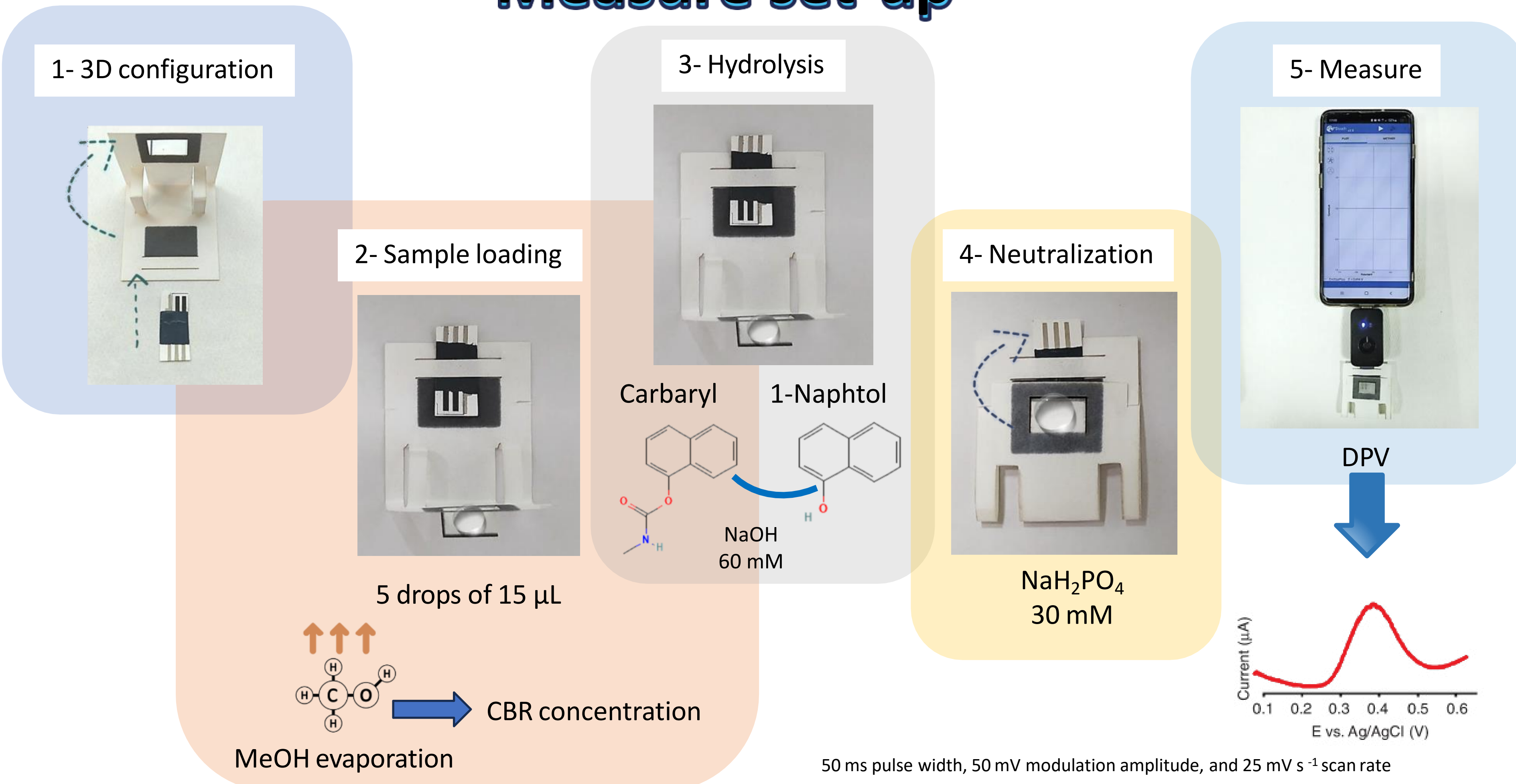
Laser induced graphene


POP-UP fabrication
Cutter printer
Vinyl stencil
Nitrocellulose
Ag ink
100°C
10 min
Graphene oxide
water solution
CO2 laser
GO
1- engraving
rGO
2- cutting
Vacuum filtration

POP-UP fabrication



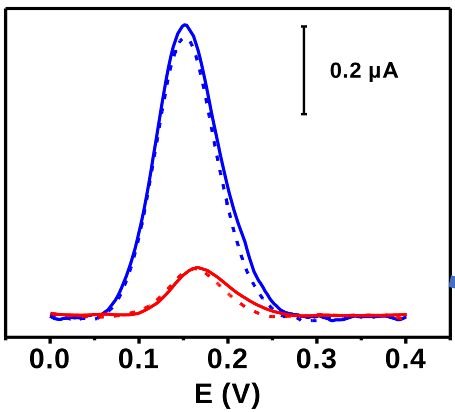
Measure set-up

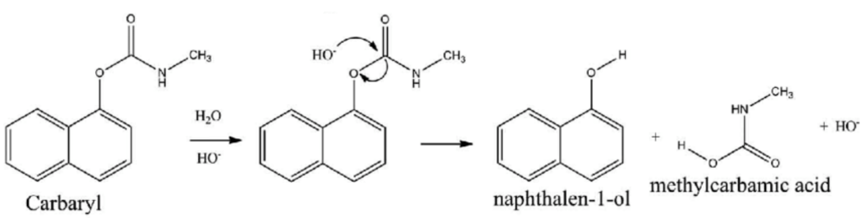


Analytical performances

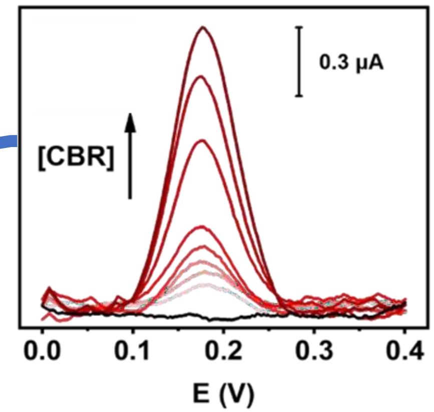
Solid line → CBR hydrolyzed on the POP-UP device
Dashed line → 1-NP used as control

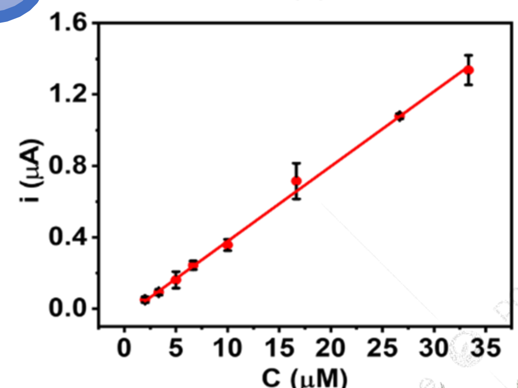
5 µM and 25 µM





Quantitative hydrolysis



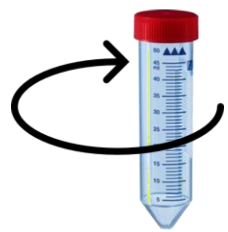


LR: 1.5 - 33 µM
R^2= 0.9950
RSD ≤ 10%, n=3
LOD: 0.4 µM

LOD < MRL in grains

Sample analysis

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

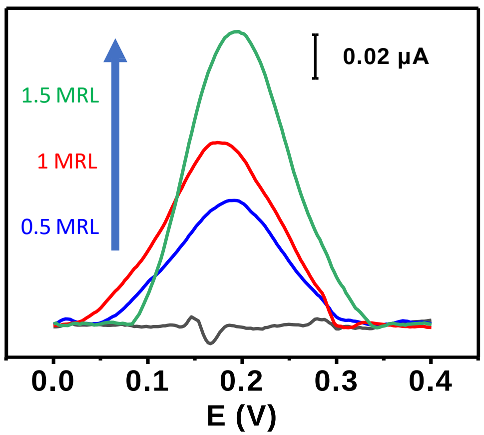


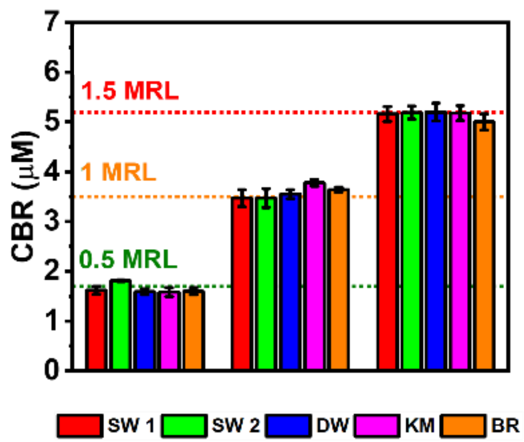
5 mg in 10 mL of methanol

Extraction under orbital stirring for 5 min at 4000 g

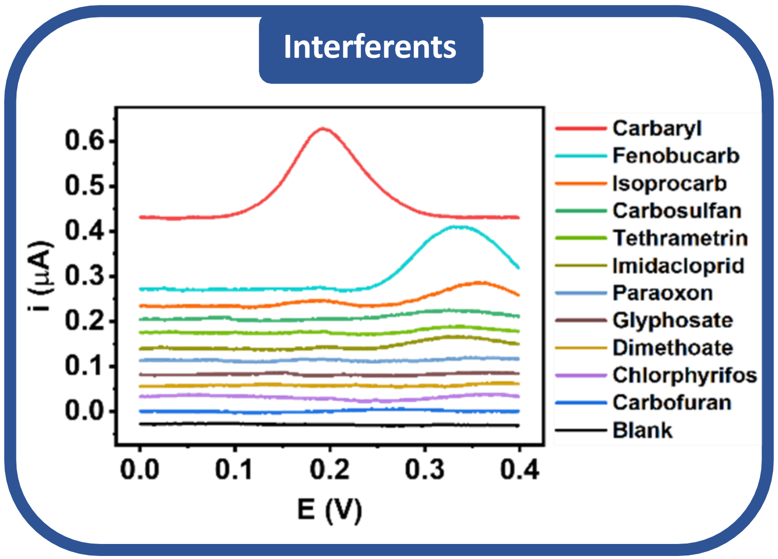
Carbaryl MRL in grains: 3.5 µM

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

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

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

SENZYTEC 1 portable laboratory

Biosensori per l'Industria Alimentare