Facoltà di Bioscienze e tecnologie agroalimentari e ambientali

UNIVERSITÀ DEGLI STUDI DI TERAMO
UNITE

Application of nanostructured electrochemical sensor for food quality and safety

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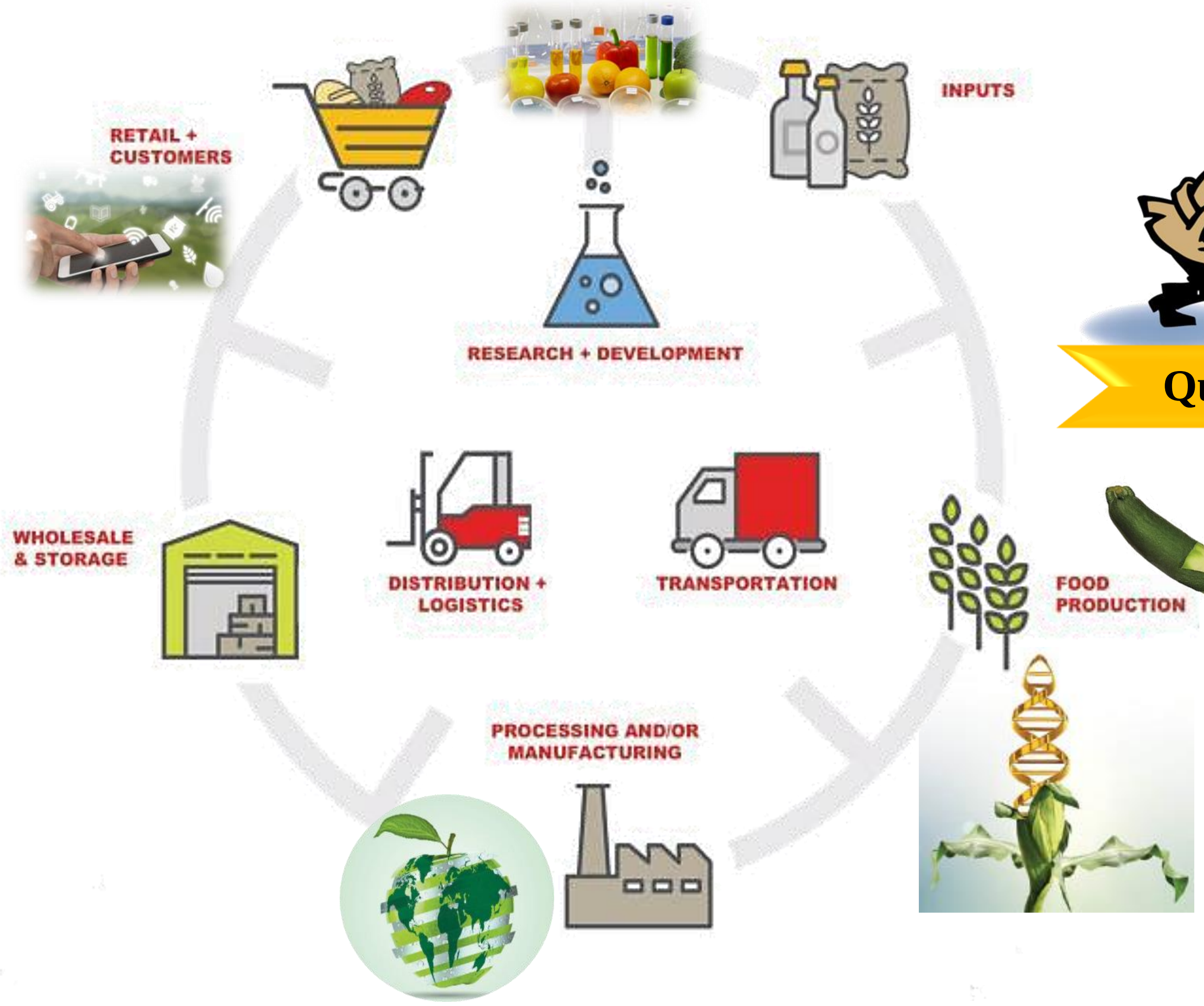
University of Teramo

Food Safety and Quality



Quality and Safety Markers

(Q&S Markers)

Q&S markers

Pesticides


TEATRO NATURALE MOBILE

Trattamenti con dimetoato contro la mosca delle olive: cosa non ha funzionato?

E' l'anno di Bactrocera oleae, se ne parla in frantoio e in ogni dove, con scambi di consigli e opinioni. Tra miti di nuove **mosche delle olive** ogm e la realtà di dover cambiare le abitudini di una vita, anche in oliv…

La Francia vieta l'importazione di ciliegie trattate con l'insetticida dimetoato (utilizzato l'anno scorso per 120 … alia)

28 a…

Prodotti fitosanitari: niente dimetoato contro la mosca del ciliegio

Sicurezza alimentare

Dimetoato, come è andata

Nella riunione tenutasi … aprile scorso (avevam… scusate) la discuss…

BOLOGNA

Legambiente Emilia Romagna lancia l'allerta pesticidi "Troppe sostanze nelle acque e nelle città"

…ntalisti denunciano la presenza di sostanze nocive messe al … del 60% delle analisi trovati fitosanitari

Ambiente

Greenpeace: quanti rischi per gli agricoltori dai pesticidi

Le minacce per la salute dei lavoratori dei campi evidenziate in un rapporto dell'associazione ambientalista. Che ribadisce: serve un'agricoltura ecologicamente sostenibile

(1) Q&S markers

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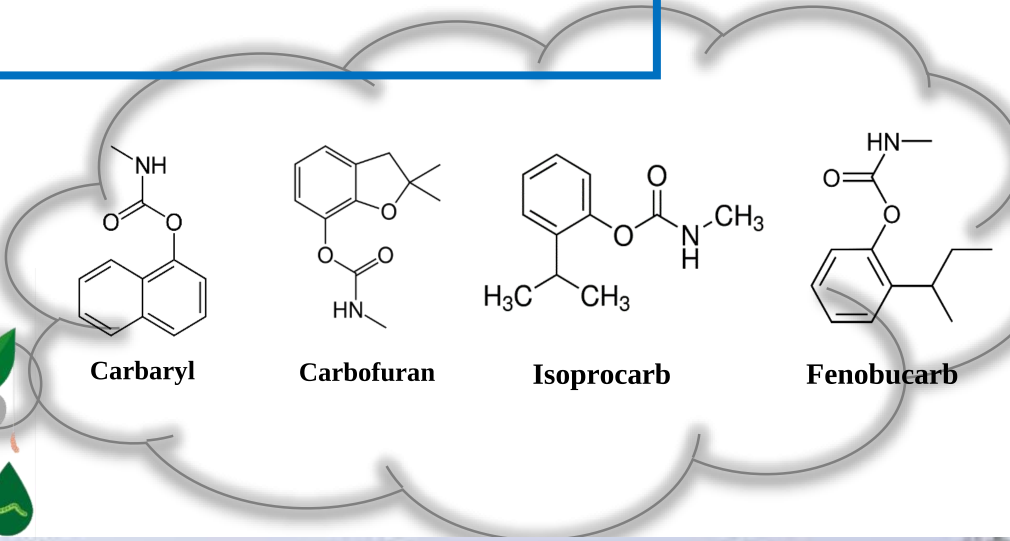
Pesticides

- Control insects and other pests
- Application in terms of dose, timing and frequency
- Regulation (EC) No. 396/2005 and No. 1107/2009 of the European Parliament and the Council
- Maximum Residue Limit



(2) Q&S markers

Heterogeneous class of chemical compounds of considerable interest in the food industry:

Sugars and Phenolic compounds…


Foods nutritional value/energy intake


Rheological properties
(physical and structural attributes)


Consumer perception and sensory character: taste and flavour


key role in shelf-life (reducent ability, hygroscopicity/water control…)


Indicators of quality and ripening degree of horticultural product


Process indicators and substrate (e.g. fermentative process)


Nutritional property / functional food


Sensory characteristics definition
(bitterness, astringency, etc...)


key role in shelf-life


Indicators of quality


Process indicators

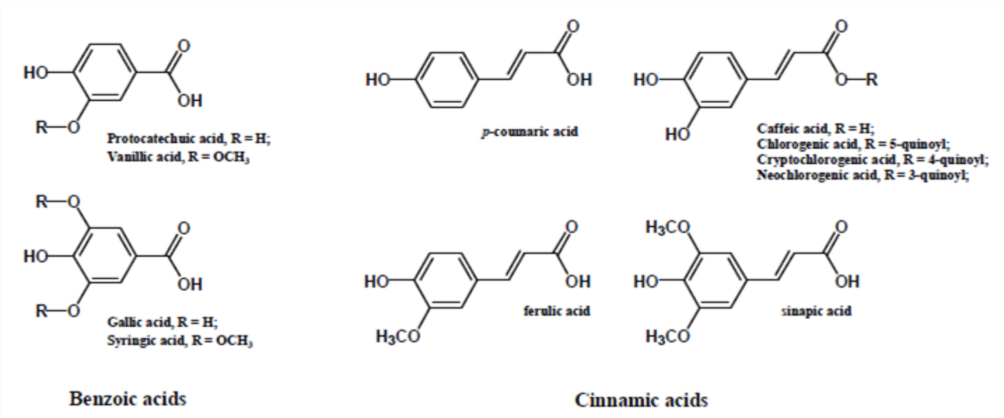

Anti-microbial property

(3) Q&S markers

Phenolic compounds in food

Phenolic acids in food

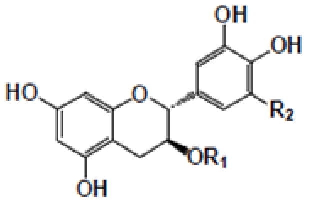
Fruits, vegetables, grains, seeds...



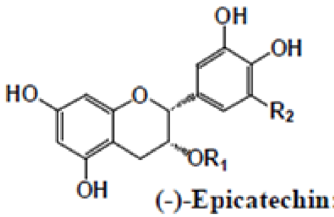
Flavanols

Or flavan-3-ols or catechins.

Black and green tea, apples, blueberries, peaches, pears, strawberries



(+)-Catechin: $R_1 = R_2 = H$;
(+)-Catechin gallate: R_1 = gallyl, $R_2 = H$;
(+)-Gallocatechin: $R_1 = H$, $R_2 = OH$;
(+)-Gallocatechin gallate: R_1 = gallyl, $R_2 = OH$;

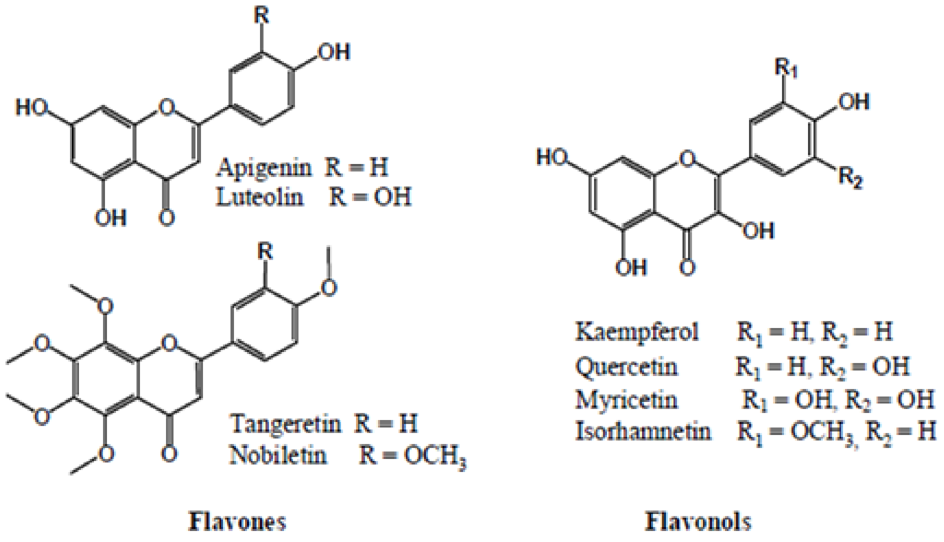


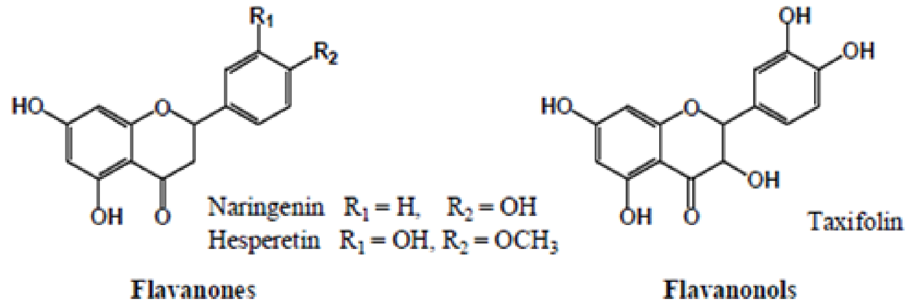
(-)-Epicatechin: $R_1 = R_2 = H$;
(-)-Epicatechin gallate: R_1 = gallyl, $R_2 = H$;
(-)-Epigallocatechin: $R_1 = H$, $R_2 = OH$;
(-)-Epiallocatechin gallate: R_1 = gallyl, $R_2 = OH$;

Flavonoids

Flavones, Flavonols, Flavanones and Flavanonols

Brightly coloured fruits and vegetables: blueberries, plums, apples, cherries, oranges, strawberries, spinach...





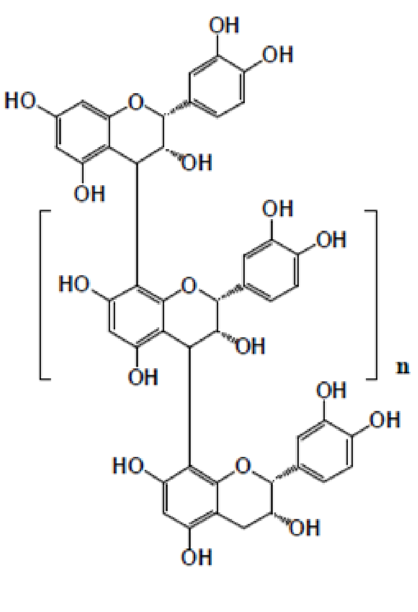
Tsao, R. (2010). *Nutrients*, *2*(12), 1231-1246.

(4) Q&S markers

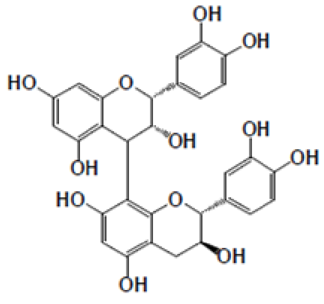
Phenolic compounds in food

Procyanidins

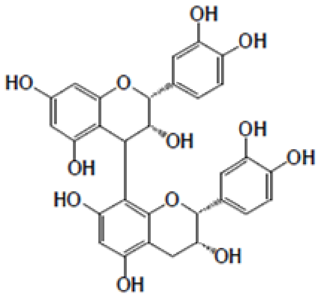
Grapes (seeds and skins), apples, chocolate and cocoa, red wines, blueberries, cranberries, pecans, pistachios



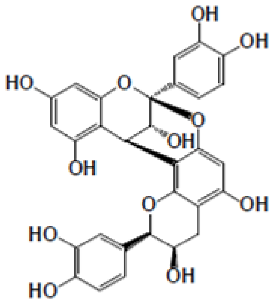
Procyanidins: n > 0;
Oligomeric procyanidins: n = 0-7



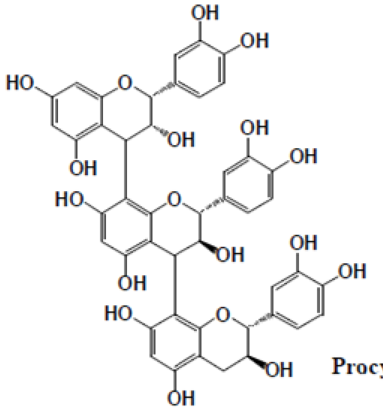
Procyanidin B1



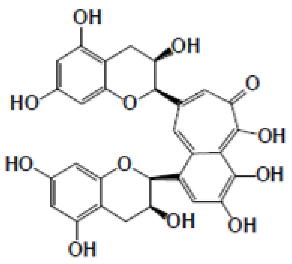
Procyanidin B2



Procyanidin A2



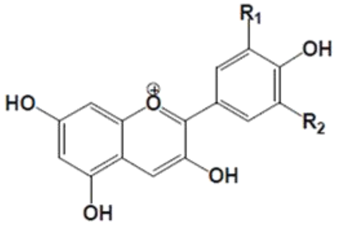
Procyanidin C1



Theaflavin

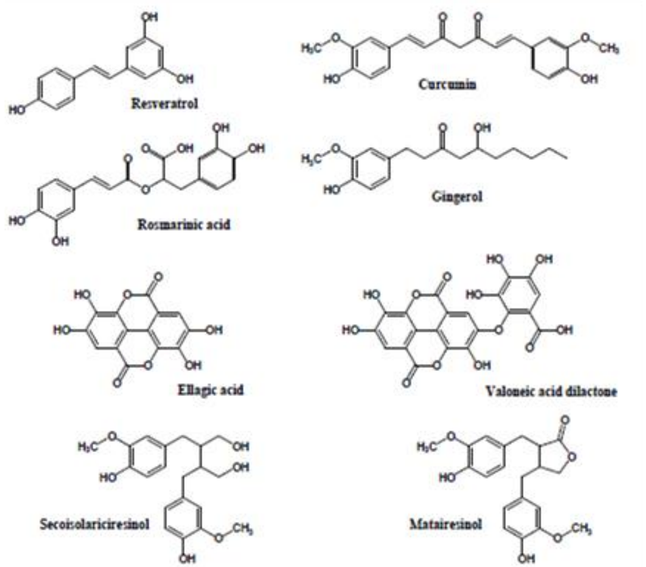
Anthocyanidins

Blue and purple pigments food



Anthocyanidin	R_1	R_2
Cyanidin	-OH	-H
Delphinidin	-OH	-OH
Pelargonidin	-H	-H
Malvidin	$-OCH_3$	$-OCH_3$
Peonidin	$-OCH_3$	-H
Petunidin	-OH	$-OCH_3$

Other important polyphenols…



Tsao, R. (2010). *Nutrients*, *2*(12), 1231-1246.
Neveu, V., Perez-Jiménez, J., Vos, F., Crespy, V., Du Chaffaut, L., Mennen, L., ... & Scalbert, A. (2010). *Database*, *2010*.

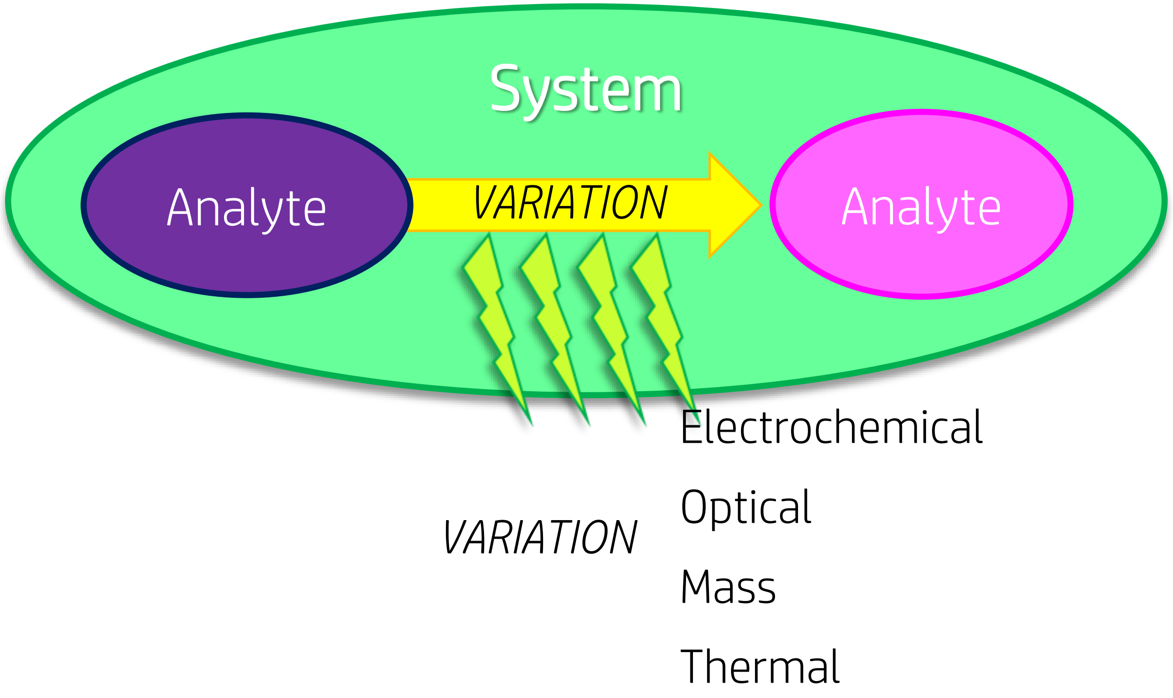
HOW TO DETECT AND GUARANTEE FOOD Q&S?

Quality and Safety Markers

HOW TO DETECT ???

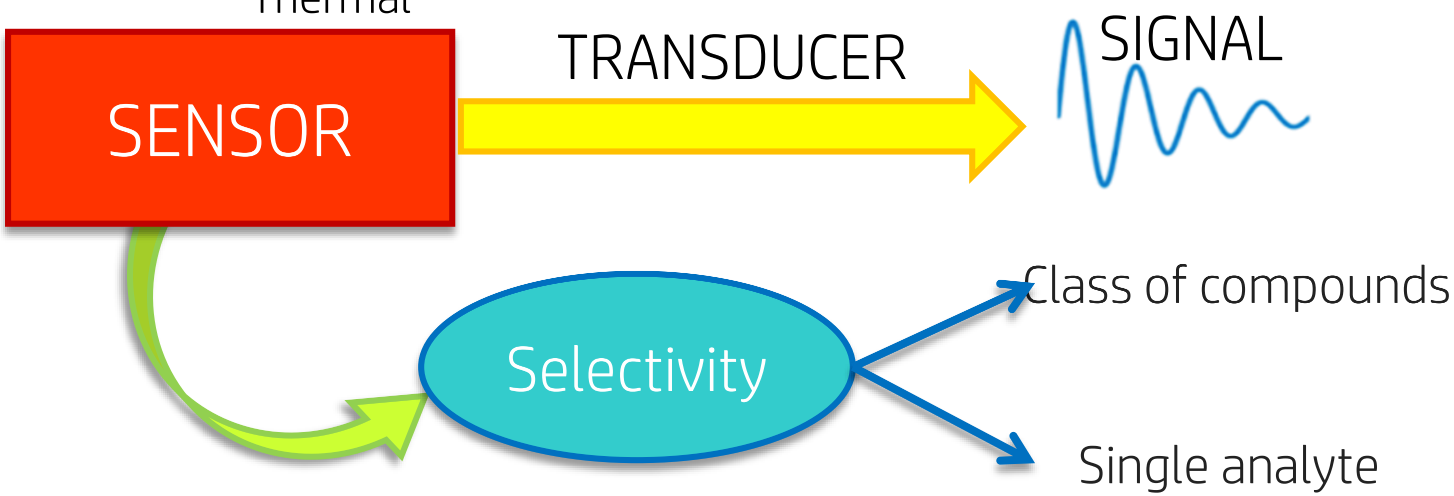
SENSORS

Sensor



… is a device able to catch a physical, chemical or biochemical variation in a system…

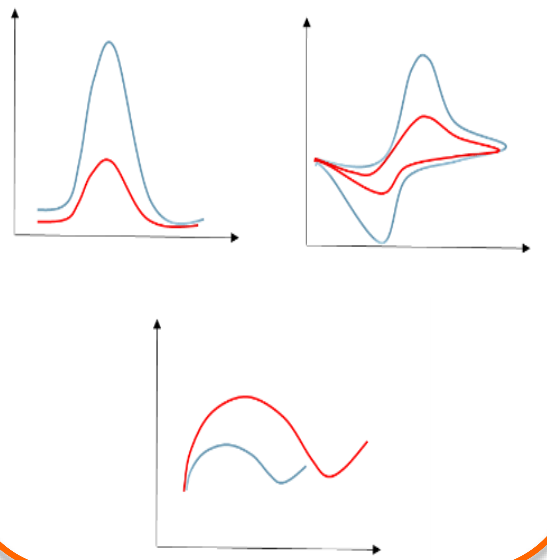
… the sensor devices response is able to give a qualitative and/or quantitative detectable response in an analytical way…



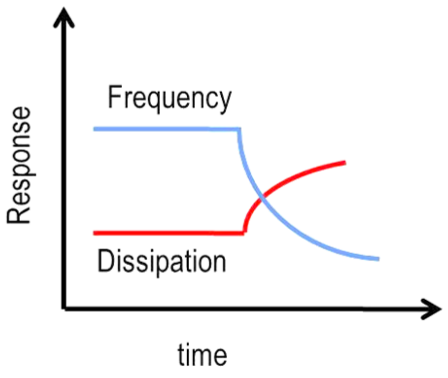
(1) Sensors

TRANSDUCERS

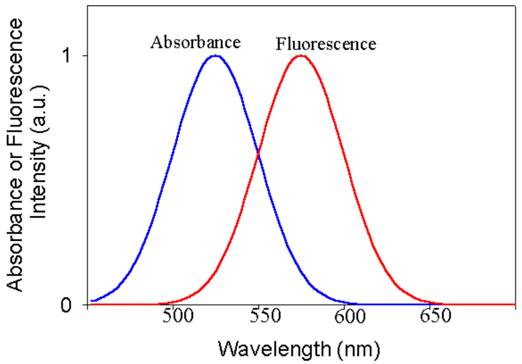
Electrochemical devices



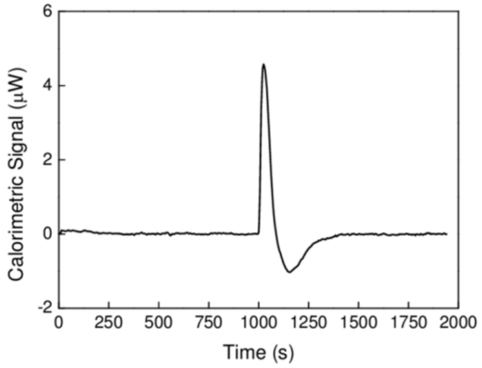
Piezoelectric devices



Optical devices

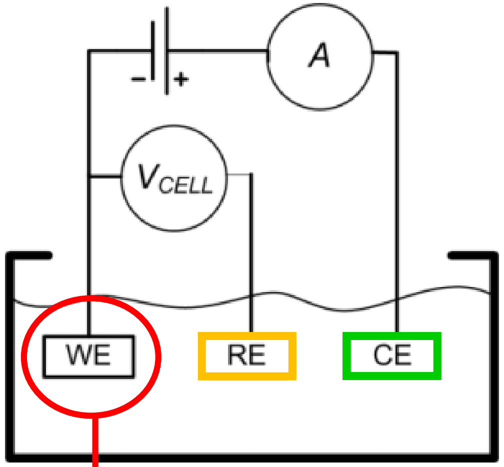


Calorimetric devices

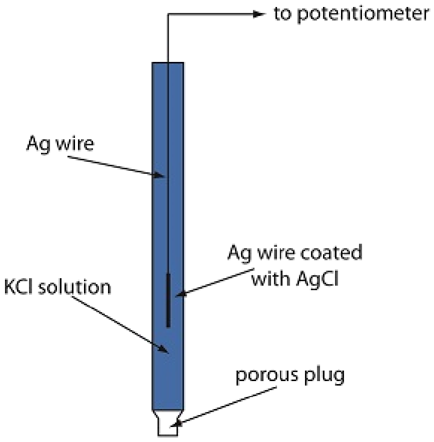


(3) Sensor → TRANSDUCER → *Electrochemical devices*

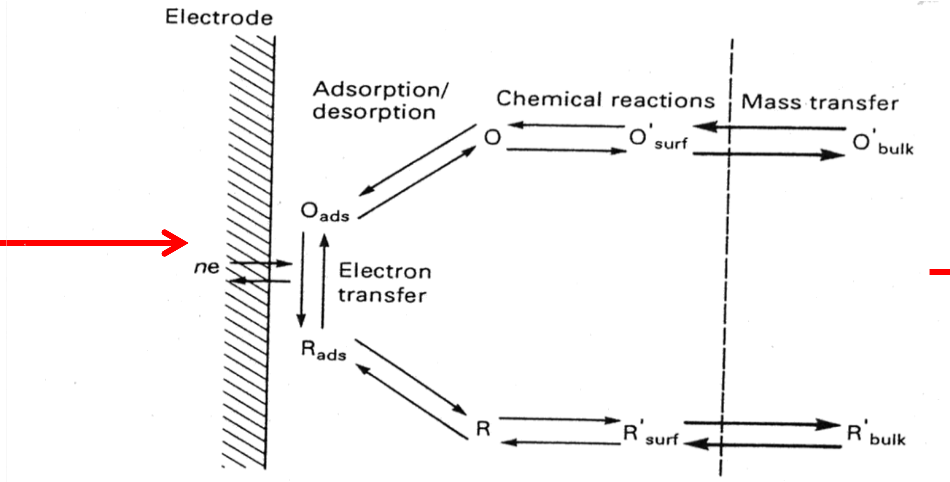
Working electrode (WE)



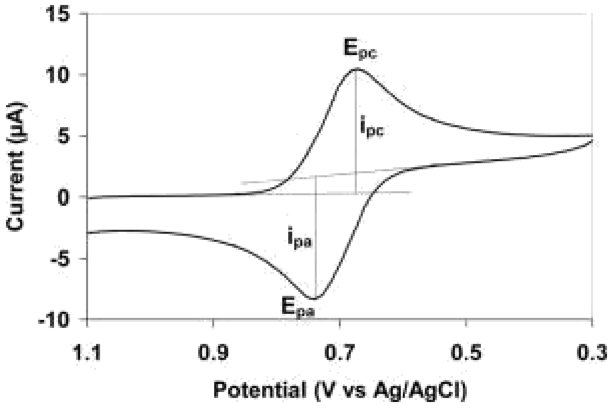
Reference electrode (RE)



Counterelectrode (CE)

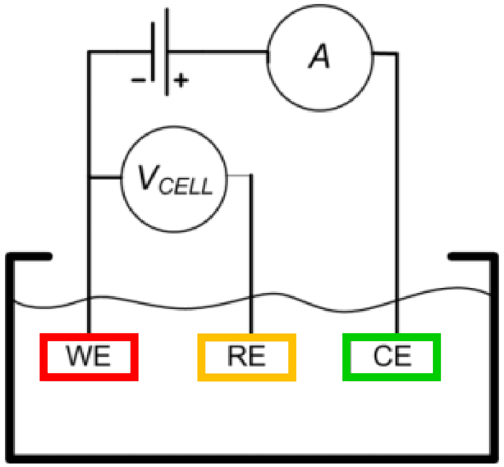


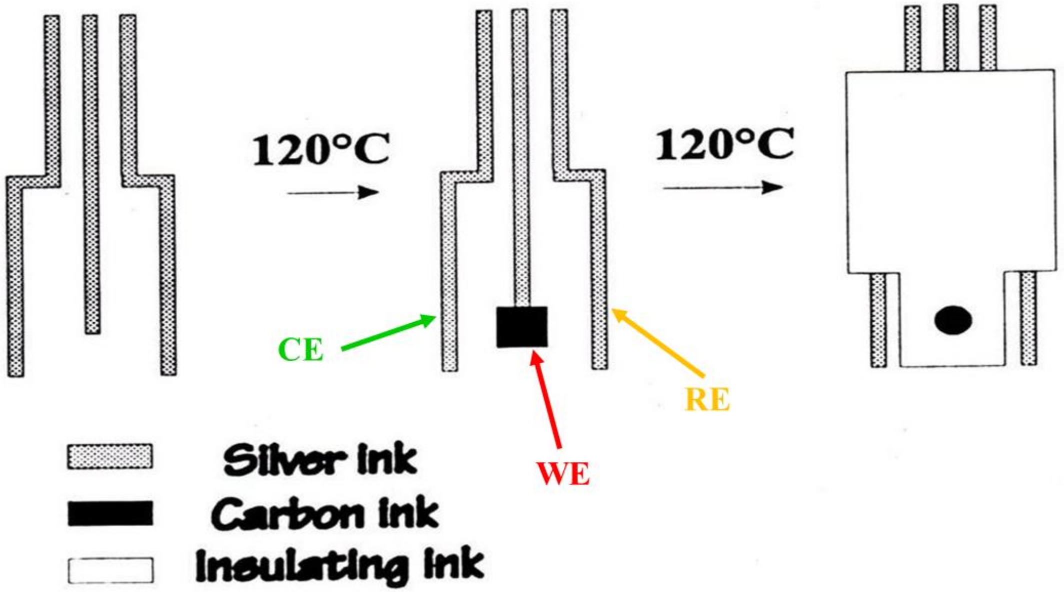
Pathway of surface processes involved in a general electrode reaction

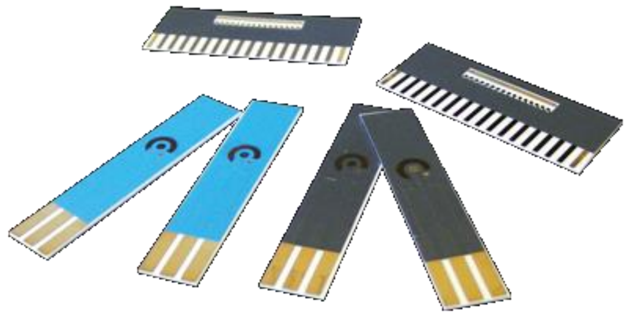


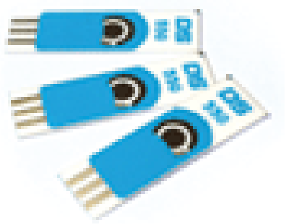
(3) Sensor → TRANSDUCER → *Electrochemical devices*

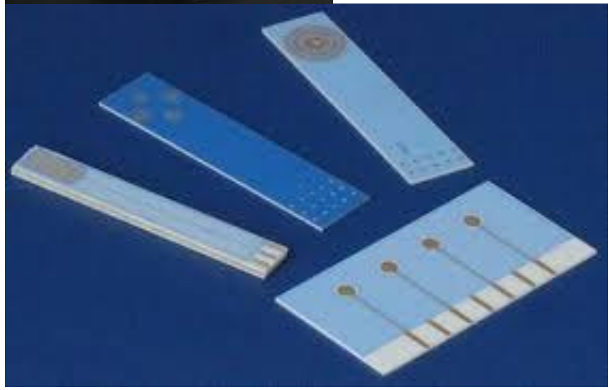
DISPOSABLE SCREEN-PRINTED CARBON ELECTRODES







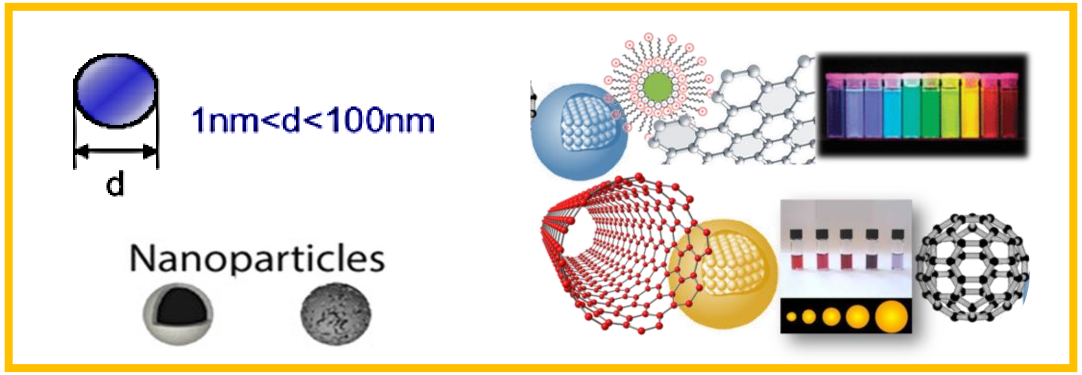


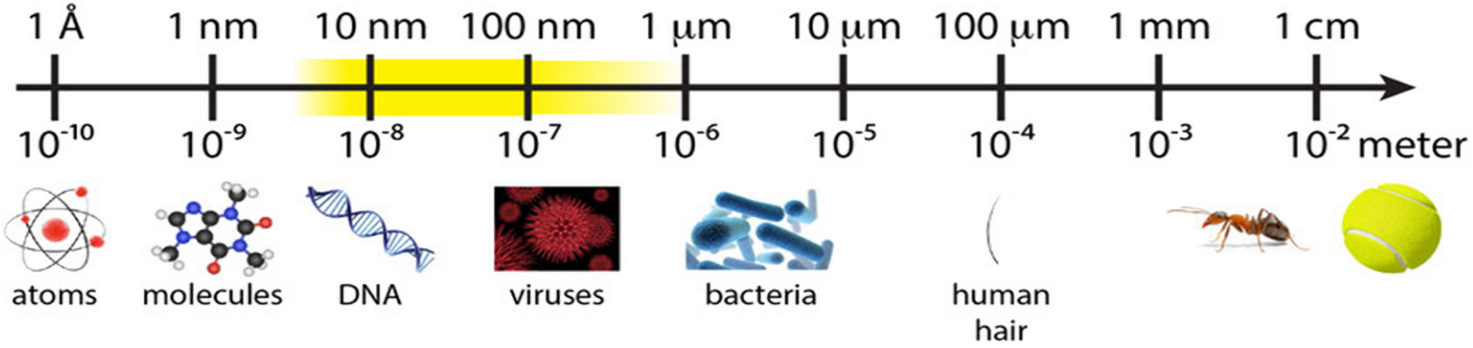


Nanomaterials

- **Nanomaterial is defined by the European Commission Communication* of 7 June 2005 like :**

'means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm'





[*] European Commission, Commission Recommendation of 18 October 2011 on the definition of nanomaterial, Official Journal of the European Union. 2011/696/EU: 38-40, 2011

(1) Nanomaterials

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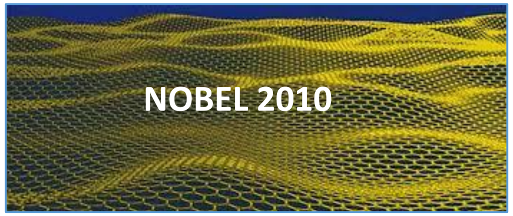
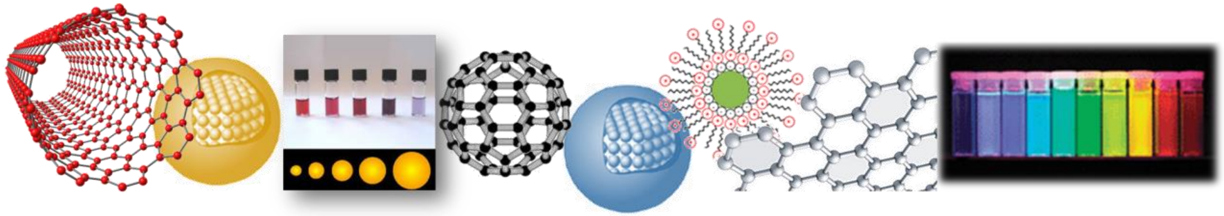
Starting from Romans…

Nanotecnologia romana

I colori cangianti della Coppa di Licurgo, datata IV secolo a.C., sono dovuti a nanoparticelle di oro e argento disperse nella matrice vetrosa.

…till Today… looking towards the future…

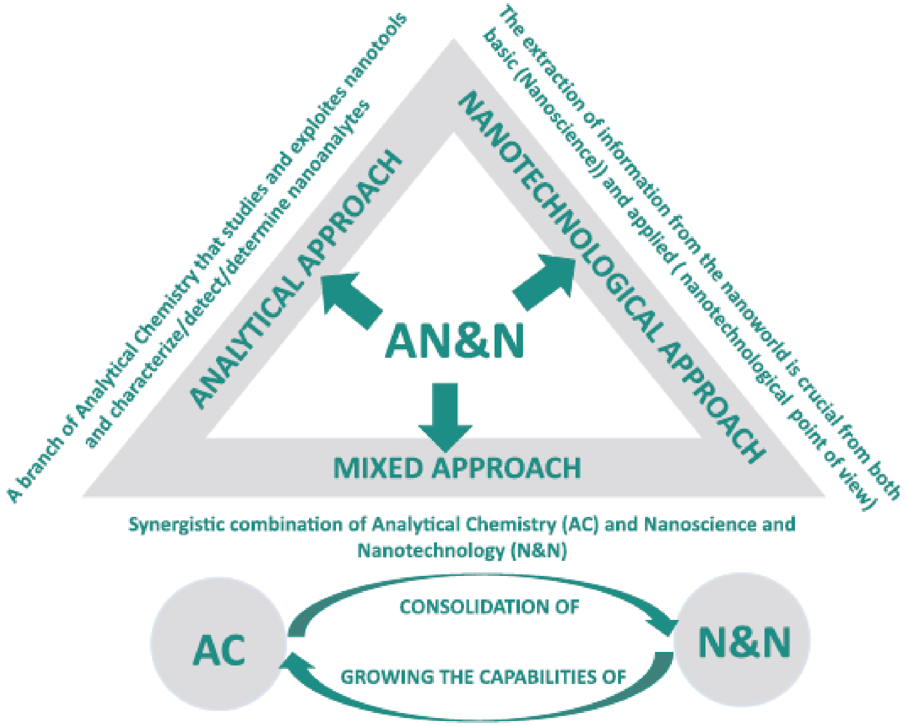


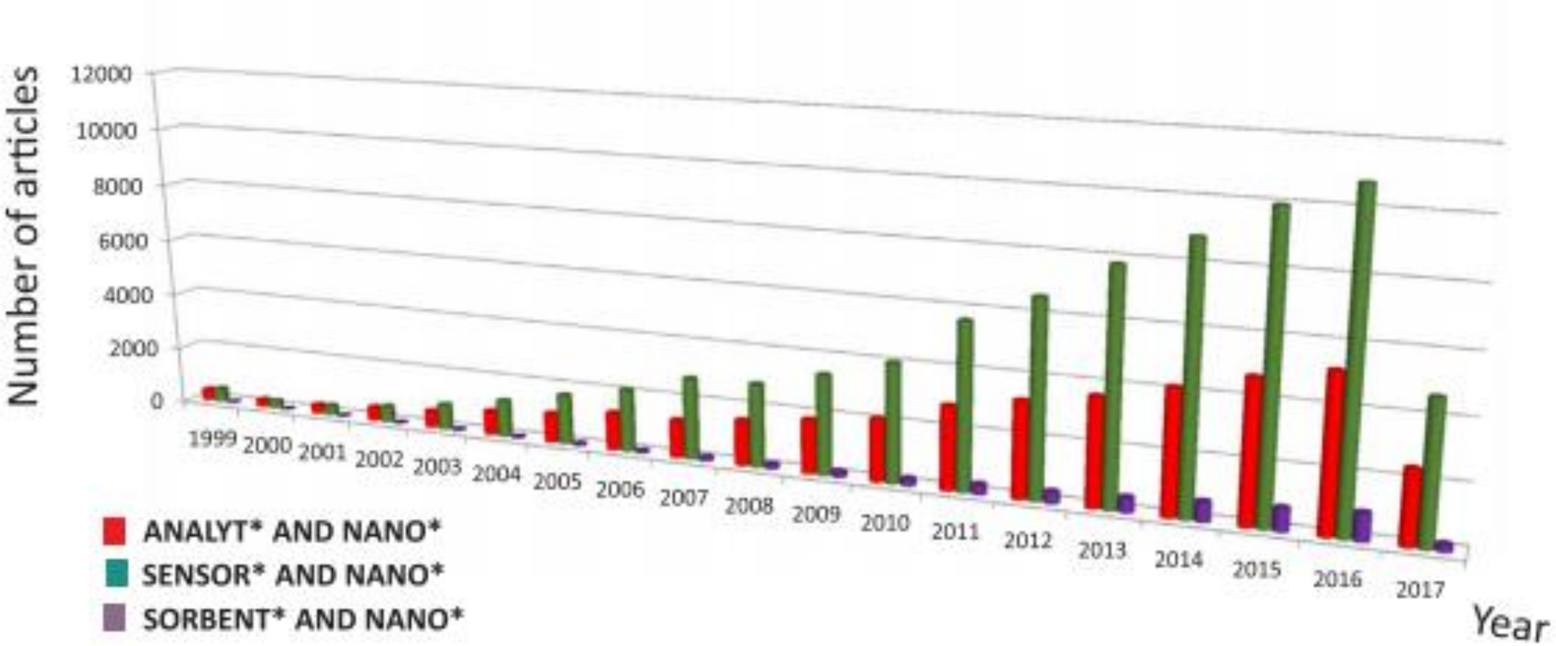


Novoselov, K. S., **Geim**, A. K., Morozov, S. V., Jiang, D. A., Zhang, Y., Dubonos, S. V., ... & Firsov, A. A. (**2004**). *science*, *306*(5696), 666-669.

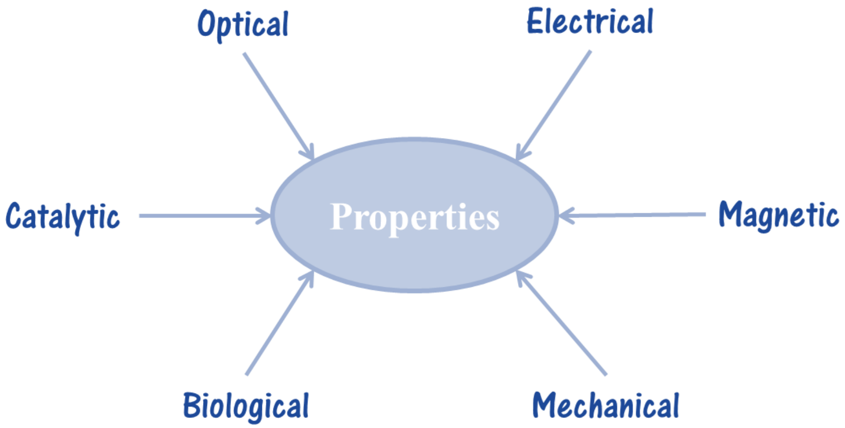
(2) Nanomaterials

Nanomaterials-based Sensors and sensing strategies





Nanomaterials are widely used in various fields of analytical chemistry, because of their unique properties potential



Soriano, M. L., Zougagh, M., Valcárcel, M., & Ríos, Á. (2018). *Talanta*, *177*, 104-121.

(3) Nanomaterials

Pros

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

Sensor **sensitivity & selectivity** improvement

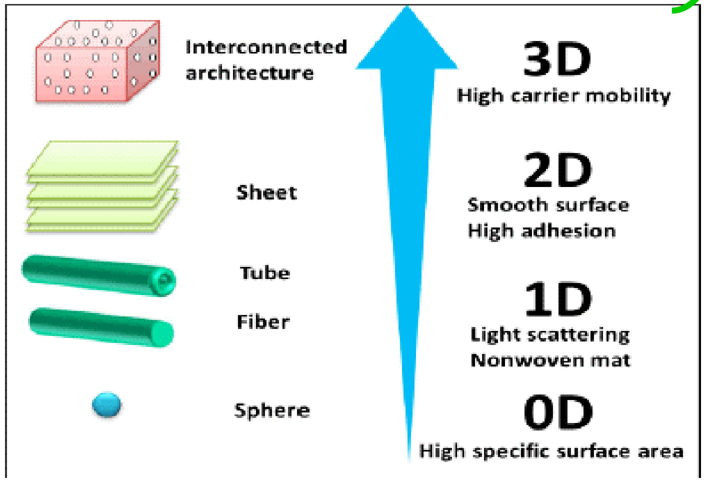
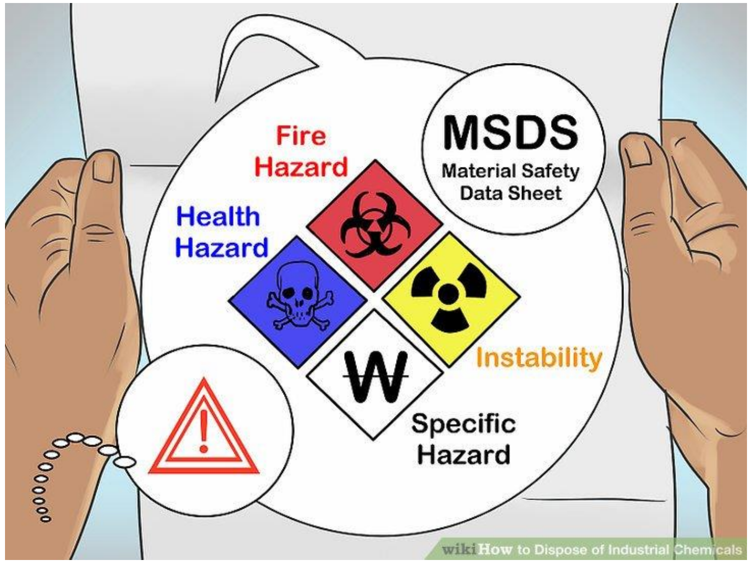


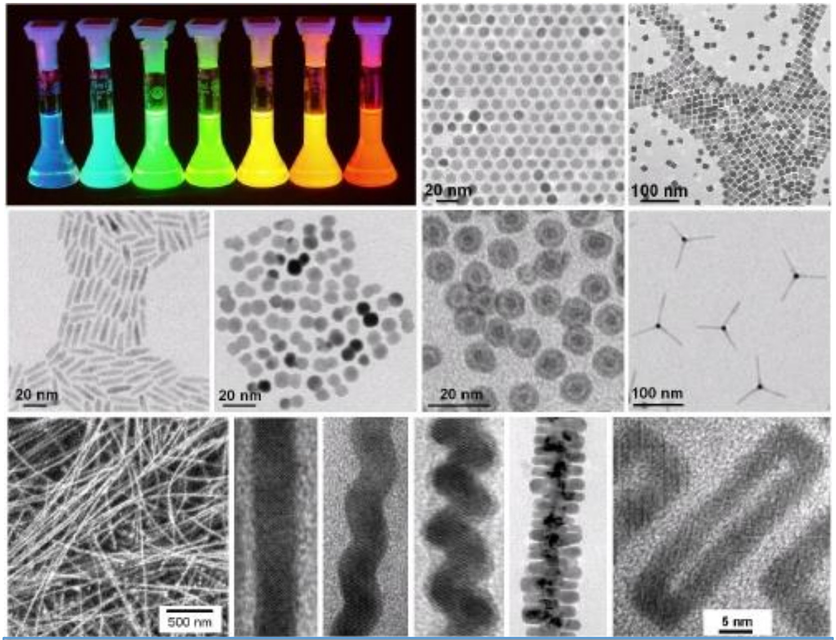
Figure 1: Schematic illustration of structural dimensionality of nanomaterials with expected properties.

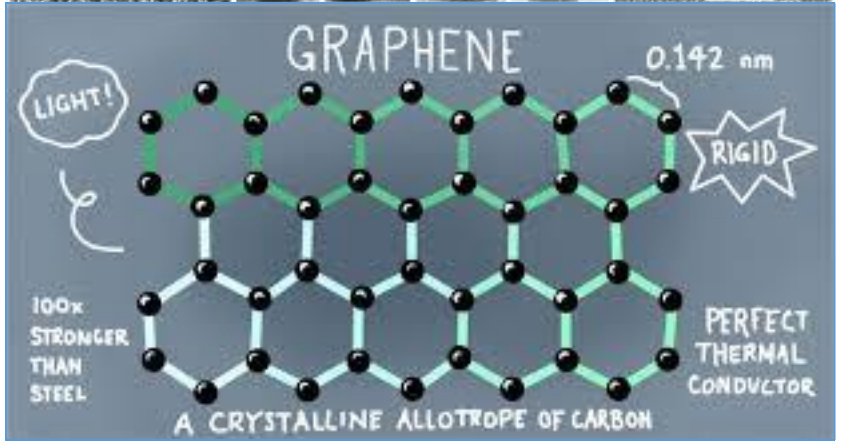


Potential drawbacks

- ? Waste disposal
- ? Potential toxicity

Nanomaterials used in electrochemical sensors





Carbon based nanomaterials:

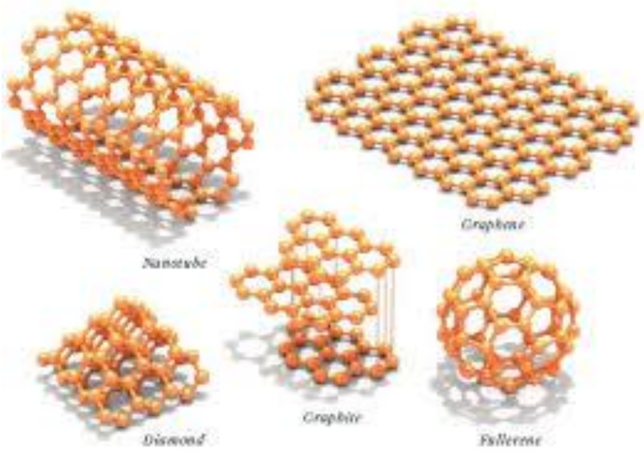
- Nanotubes
- Fullerenes
- Graphene
- Etc…

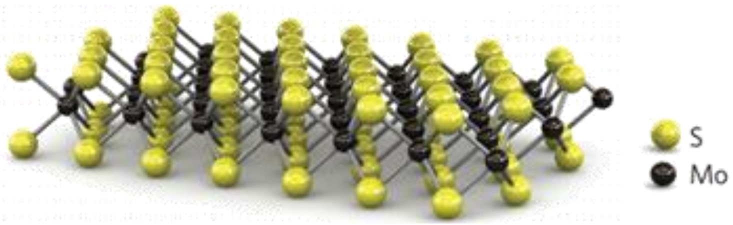
Nanoparticles:

- Metal nanoparticles
- Metal Oxide nanoparticles

Graphene-like nanomaterials:

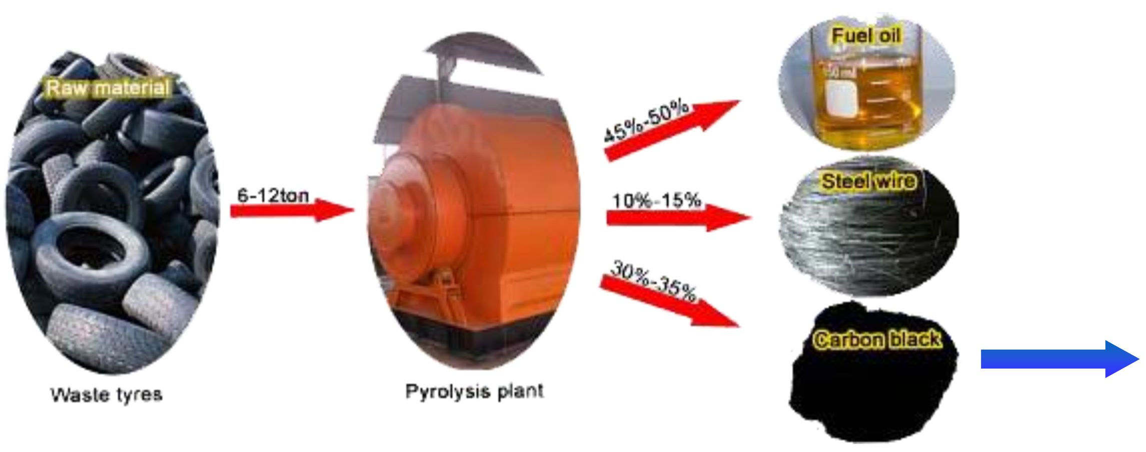
- e.g. Transition Metal Dicalchogenides (TMD)

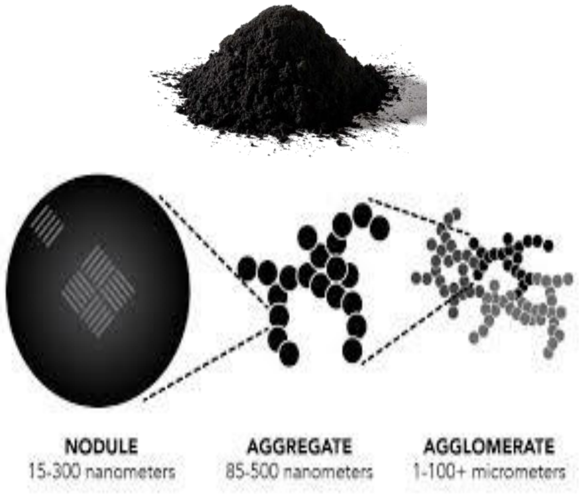


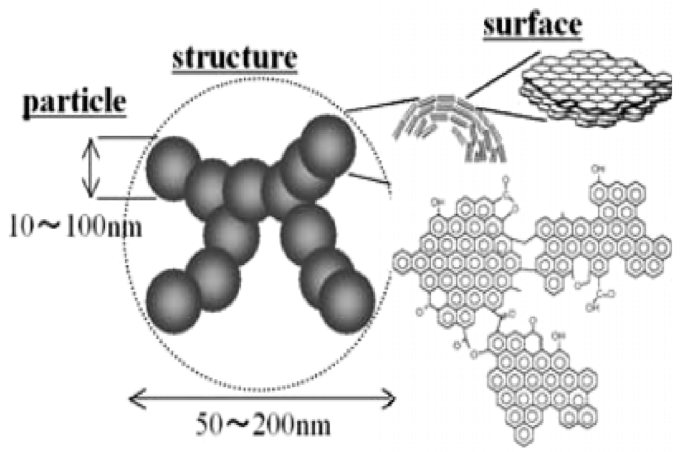


Carbon based nanomaterials (Carbon Black, CB)

Carbon black is a material produced by the incomplete combustion of heavy petroleum products. It is mainly used as a reinforcing filler in tires and other rubber products. In plastics, paints, and inks, carbon black is used as a color pigment







Electrocatalysis → Selectivity

High surface → Sensitivity

Resistance to fouling → Reproducibility

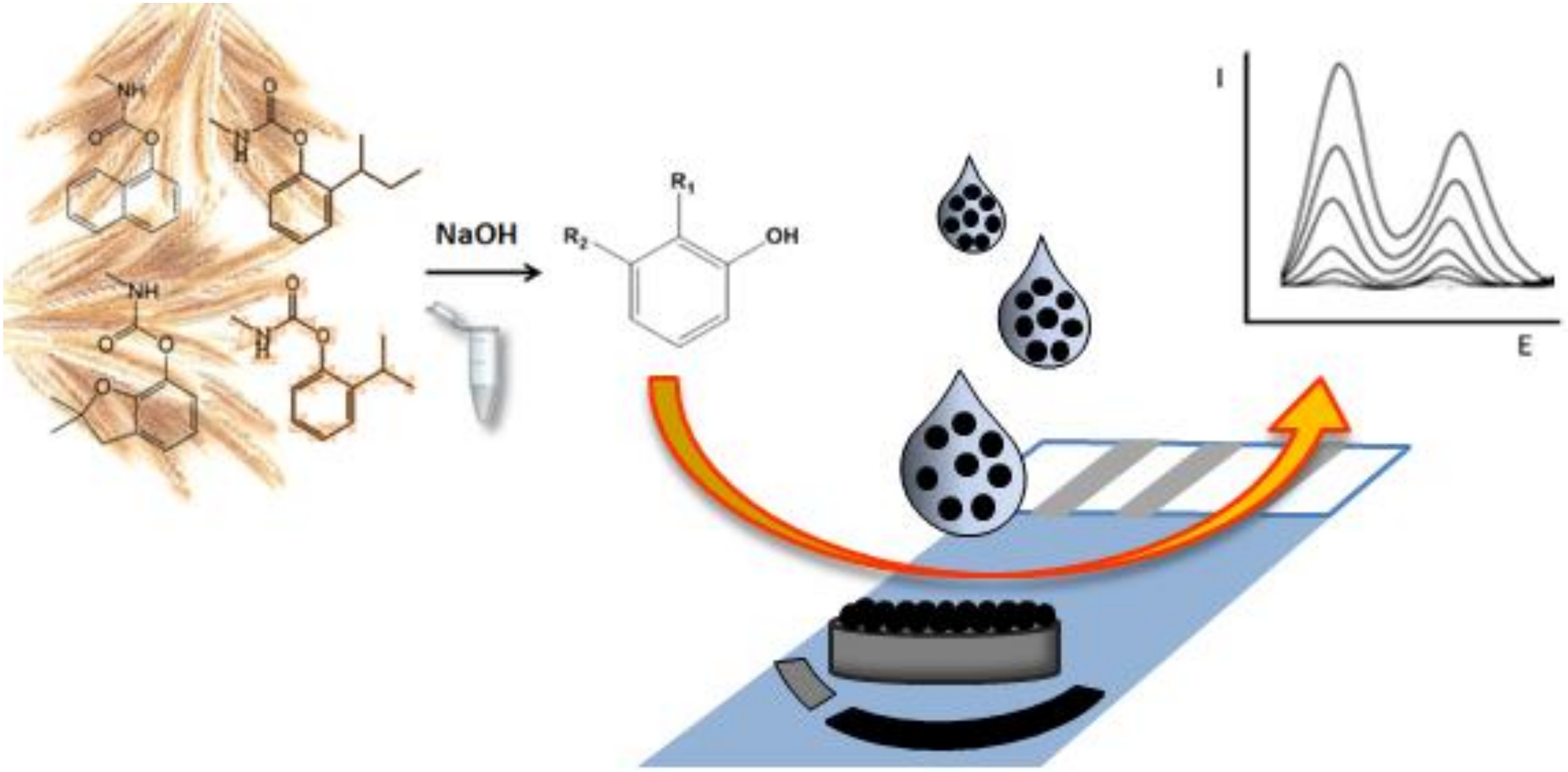
Faster eletron transfer → Improving separation performance

CB compared with other nanomaterials:

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

(1) Carbon based nanomaterials (CB)

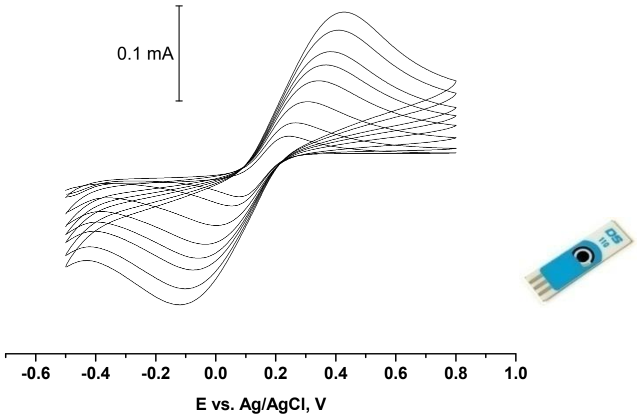
SPE CBNPs for direct analysis of carbamates in grain samples

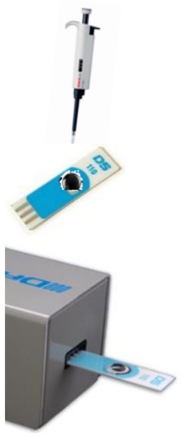


(1) SPE CBNPs for direct analysis of carbamates in wheat

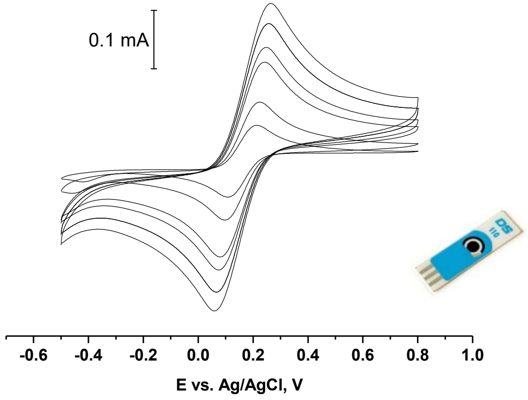
SPE-CBNPs electrochemical behaviour for ferrycianide

Carbon SPE

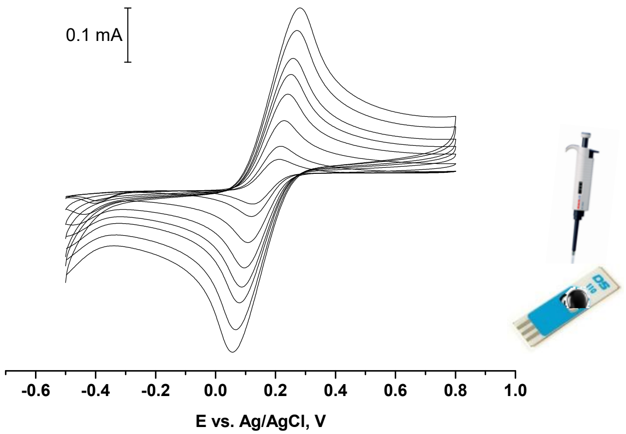


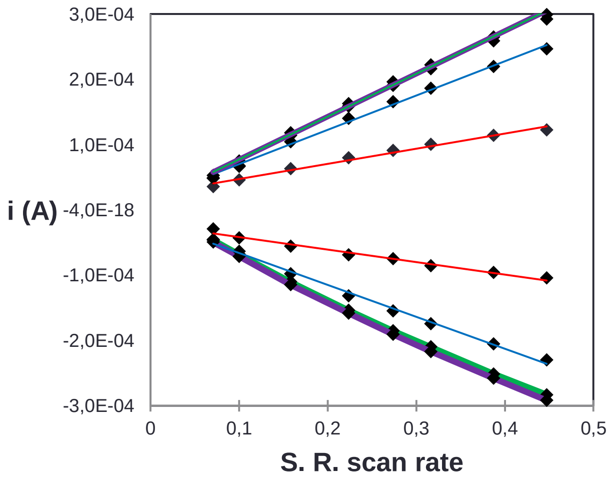


Graphene/Carbon SPE (DS110-GPH)

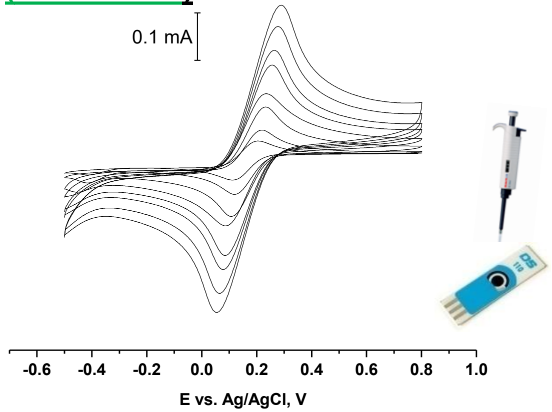


Carbon-CB SPE





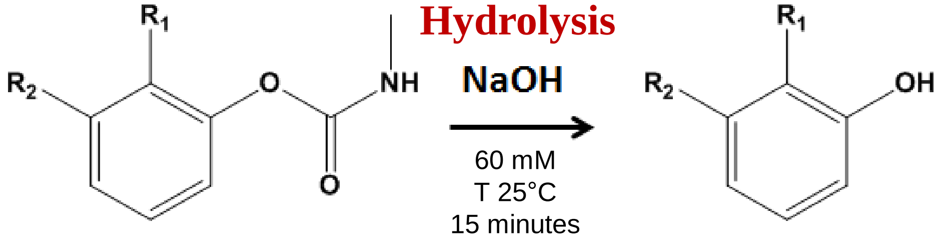
Graphene/Carbon-CB SPE (DS110-GPH)



CB modified SPE demonstrates a better electron transfer

(2) SPE CBNPs for direct analysis of carbamates in grain samples

CMs

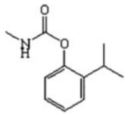


DETECTION

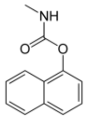
SPE-CBNPs

SPE-CBNPs vs. CMs

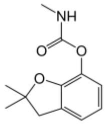
Isoprocarb



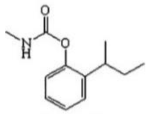
Carbofuran



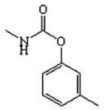
Carbaryl

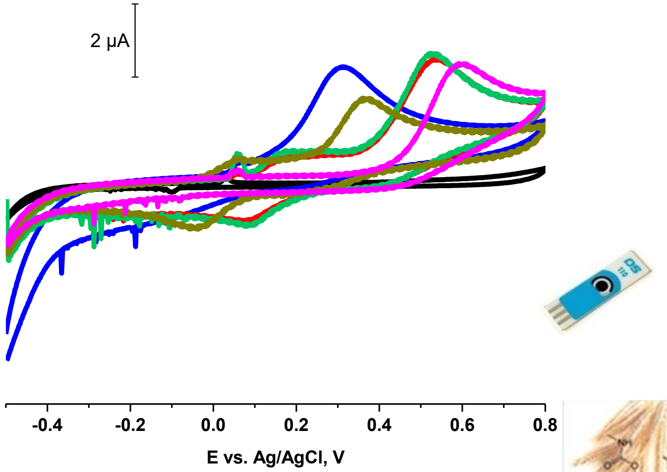


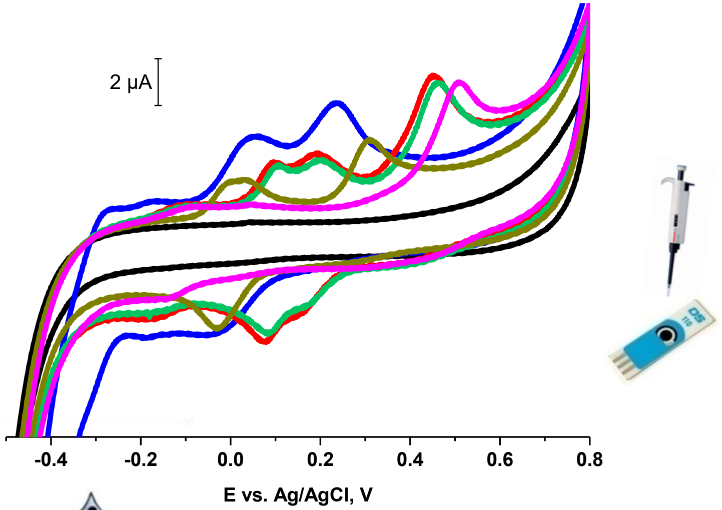
Fenobucarb

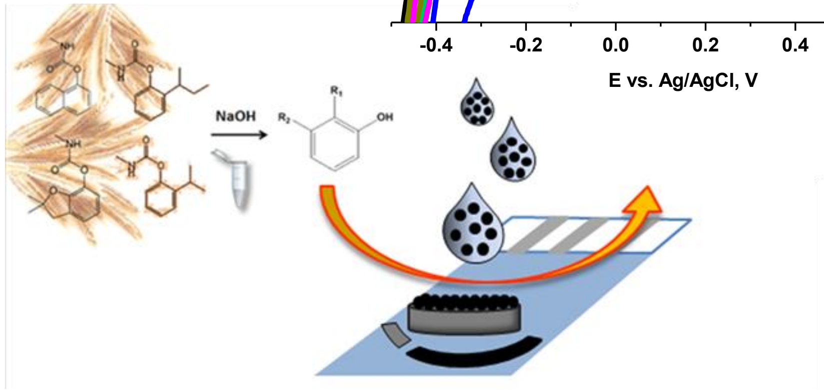


Metolcarb









(3) SPE CBNPs for direct analysis of carbamates in grain samples

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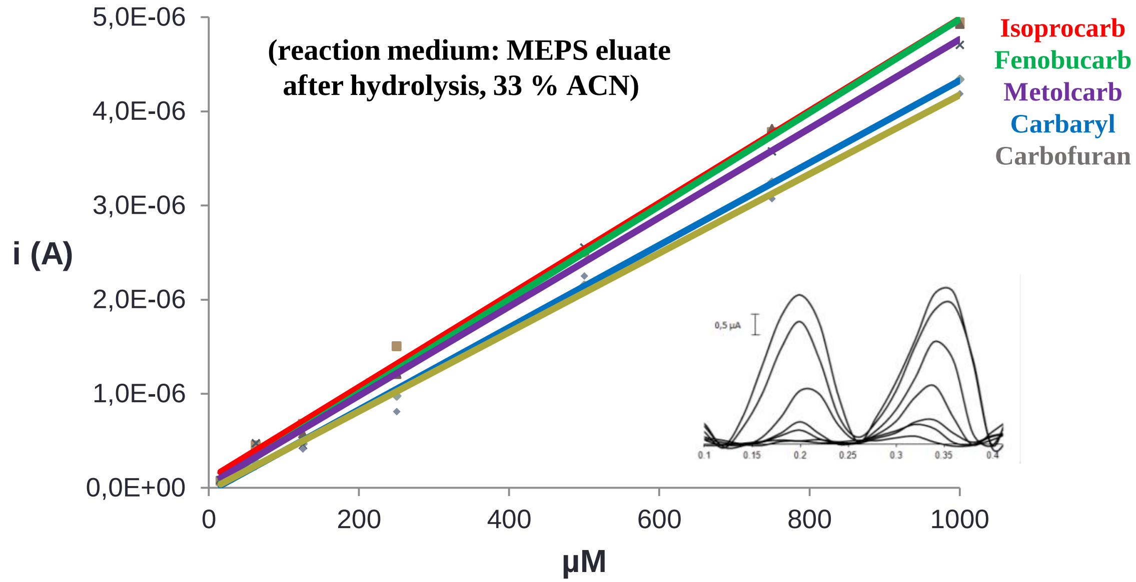
SPE-CBNPs CMs Calibration, Reproducibility and Fouling resistance



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 %

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

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 (Hard wheat, organic hard wheat soft wheat, organic soft wheat, maize)

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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

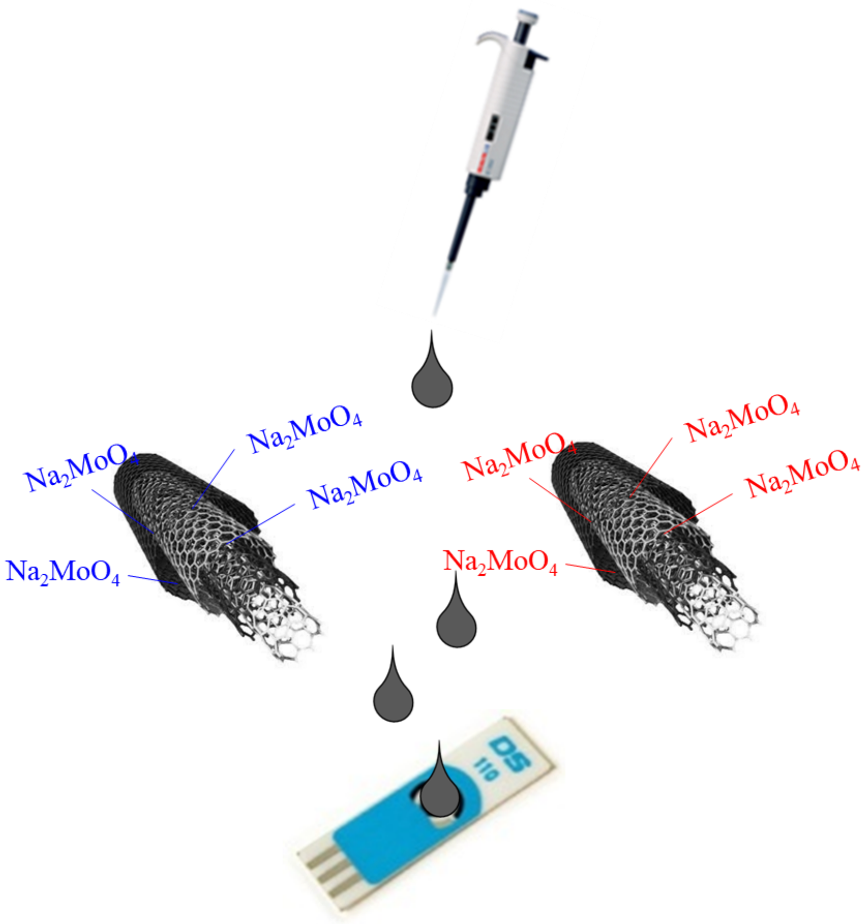
Analyte Spiked (mg Kg^{-1})	UHPL C-MS/MS recovery (%)[a]					CB-SPE recovery (%)[a]					Relative error (%)				
	HW	HWO	SW	SWO	MZ	HW	HWO	SW	SWO	MZ	HW	HWO	SW	SWO	MZ
CA															
0	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD					
0.25	82 ± 6	87 ± 3	83 ± 9	89 ± 12	82 ± 15	88 ± 1	84 ± 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.

Carbon based nanomaterials (Carbon nanotubes, CNTs)

Flow injection analysis (FIA) of olive oil polyphenols

The $-NH_2$ functionalized CNTs exhibited also improved reversibility with respect to the -COOH functionalized CNTs



$-NH_2$ bear

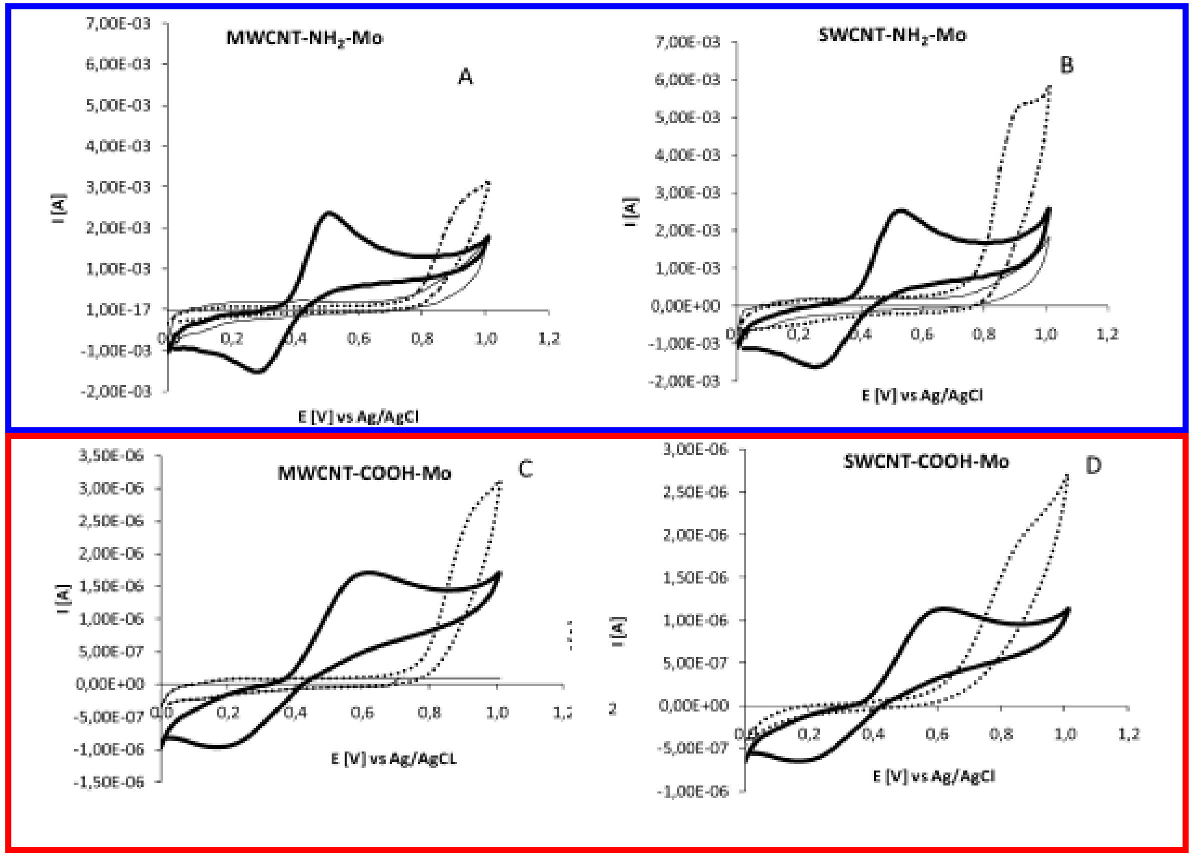
—— Catechol

- - - Tyrosol

-COOH bear

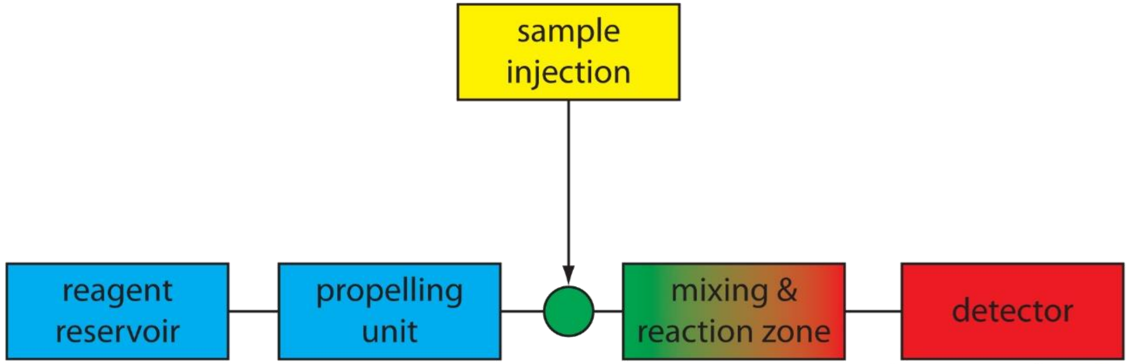
—— Catechol

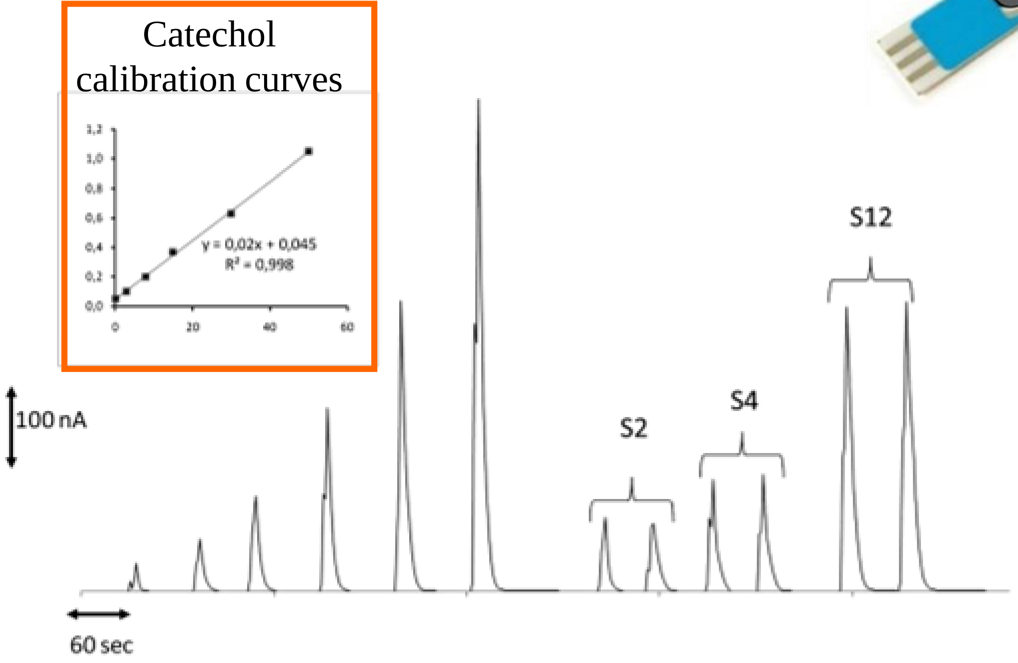
- - - Tyrosol



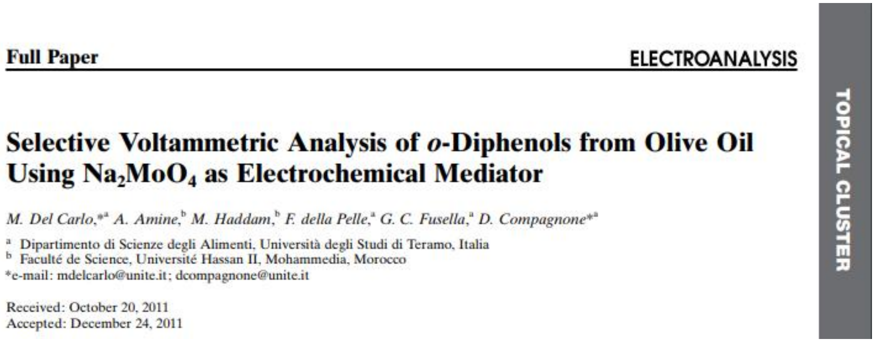
Comparison of the mediated electrochemical response of CNTs chemically modified nanosensor to catechol and tyrosol

(1) Flow injection analysis





Amperometric FIA record of catechol standards and two replicates (S2, S4, and S12).


Full Paper ELECTROANALYSIS

TOPICAL CLUSTER

Selective Voltammetric Analysis of *o*-Diphenols from Olive Oil Using Na_2MoO_4 as Electrochemical Mediator

M. Del Carlo,[a] A. Amine,[b] M. Haddam,[b] F. della Pelle,[a] G. C. Fusella,[a] D. Compagnone*[a]*

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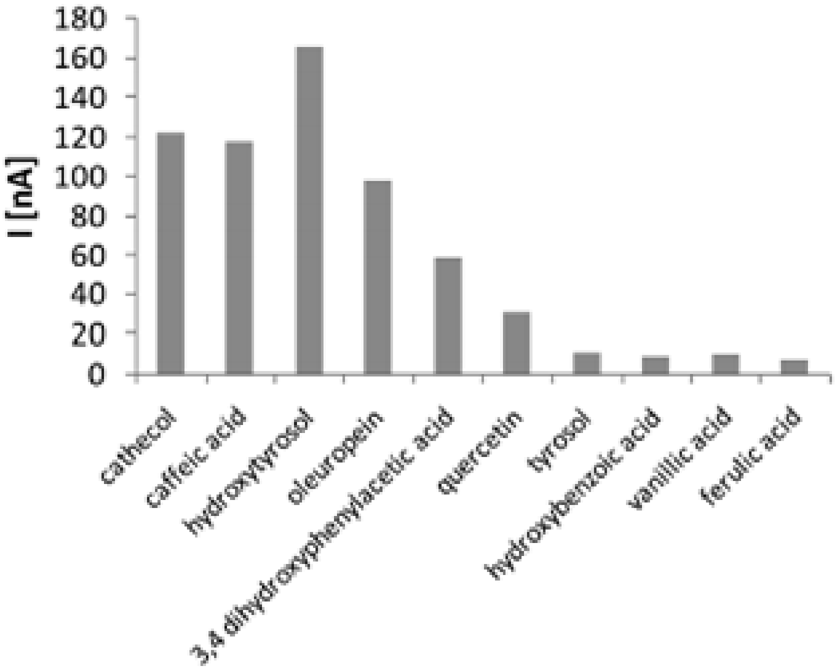
Received: October 20, 2011
Accepted: December 24, 2011

Selectivity of the FIA amperometry method using a potential of + 380 mV; standard concentration was 20 µmol L^{-1}



Microfluidic LAB on CHIP strategy

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Why CE microchips?	**Why Electrochemical Detection?**
High speed of separation **(seconds to few minutes!)** High efficiency & sample processing Low sample/reagent consumption **(from nL to pL!)** Extremely low waste generation **("enviromental friendly")** Portability **(point of care testing)** Disposability Highly multiplexed systems "Lab-on-a-chip"	Inherent miniaturization without lossing of performance **High compatibility with microfabrication technologies (easy to integrate)** **High compatibility with nanotechnologies ("easy "to integrate, and creativity!)** High sensitivity (some times approaching to fluorescence) Independence of optical path lenght and sample turbidity Not expensive!

Microfluidic LAB on CHIP strategy

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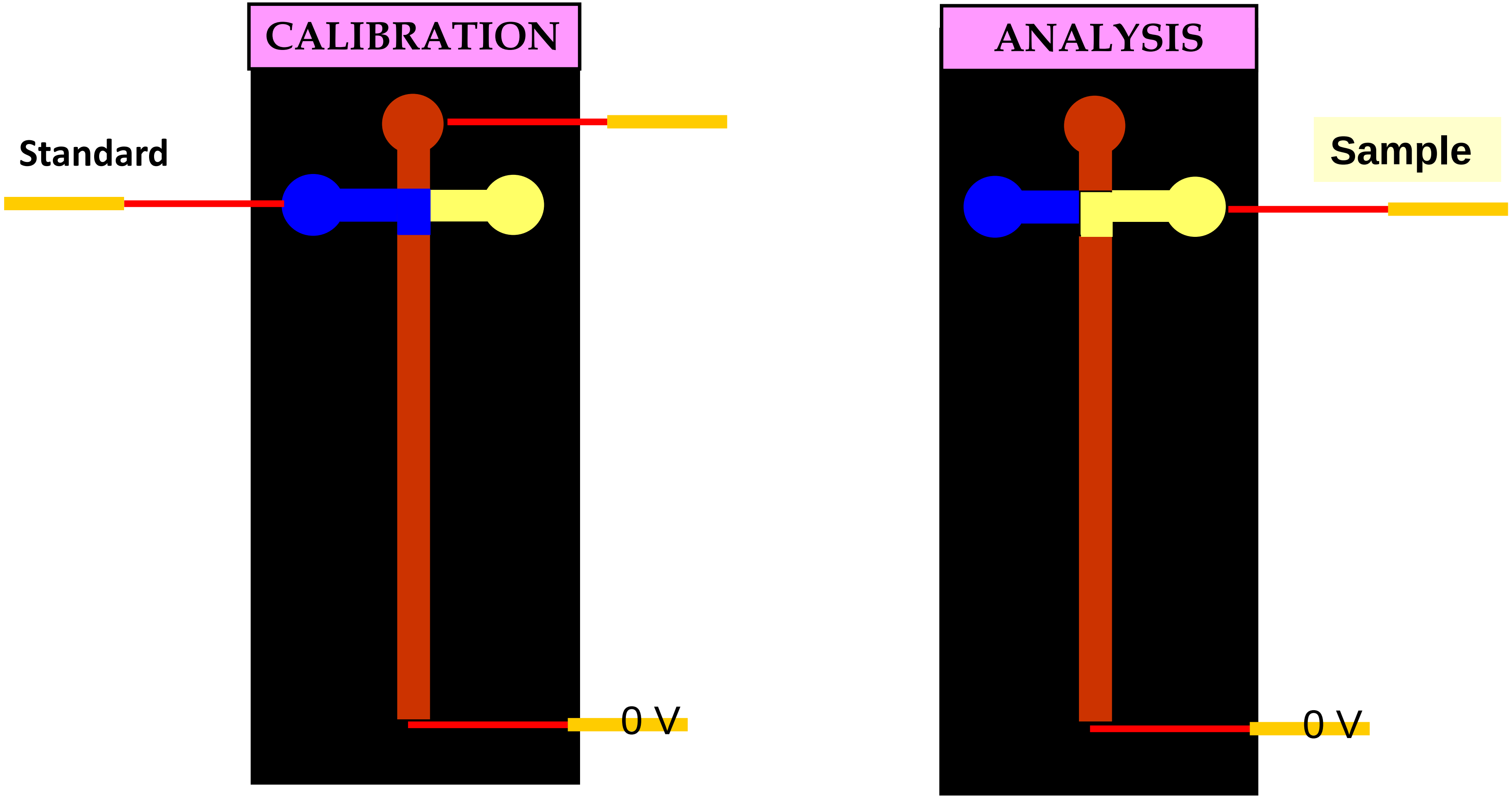
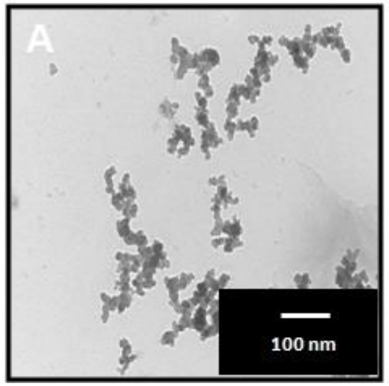
Microfluidic chips for reliable analytical determinations integrating a simplified calibration protocol

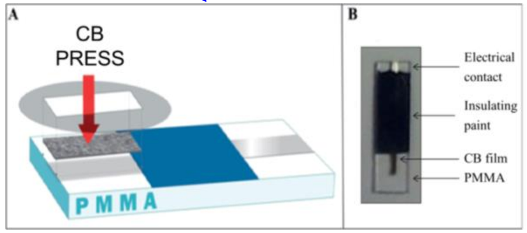


Microfluidic LAB on CHIP strategy

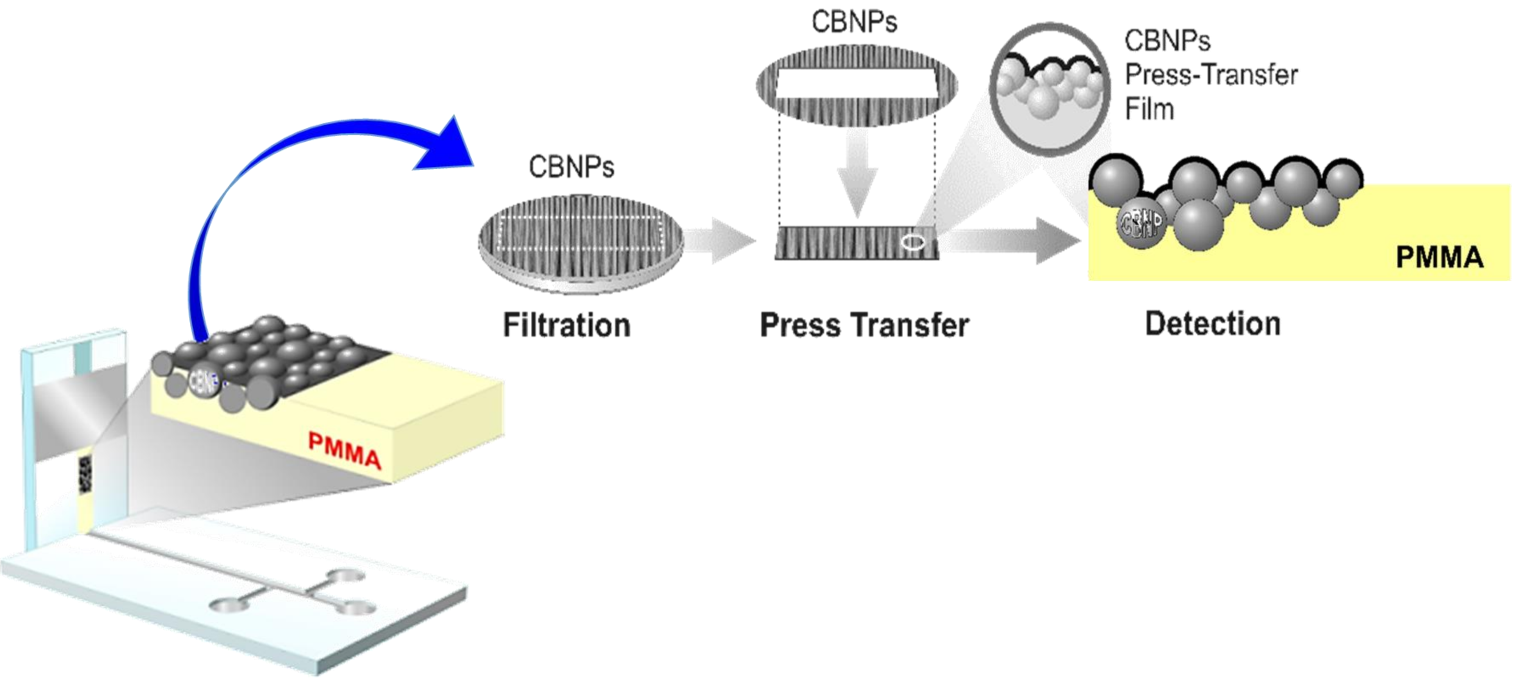
Is CB press transferable?



- **CBNPs Ø** ≤ 30 nm



Few nanomaterials can be transferred to pressure (SWCNTs) on plastic supports !!



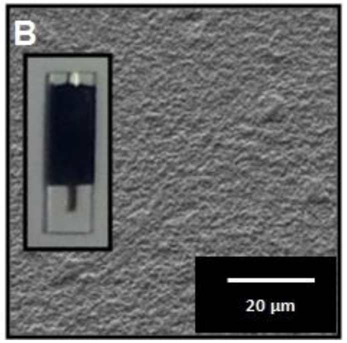
Fabrication strategy

(5) Microfluidic LAB on CHIP strategy

CBNPs Press-transferred transducer characterization

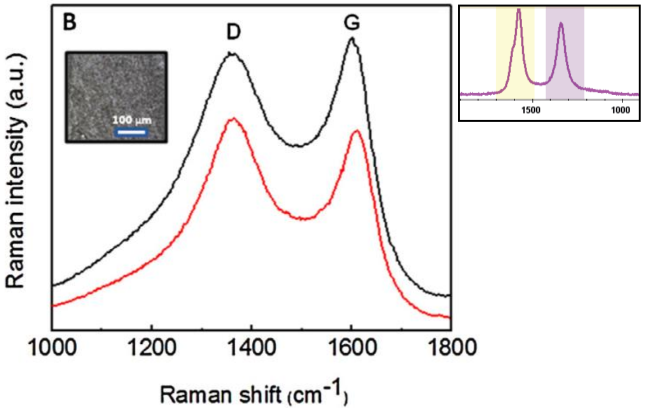
FE-SEM

(Field emission scanning electron microscopy)



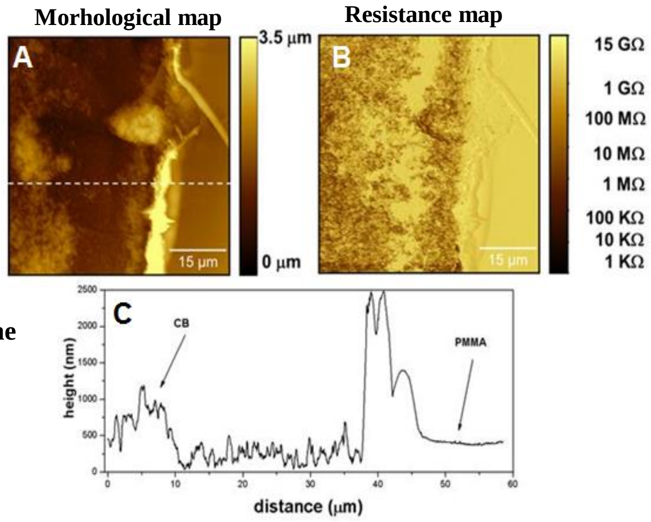
Raman spectroscopy

CBNPs (Red) CBPTE-5 surface (black).

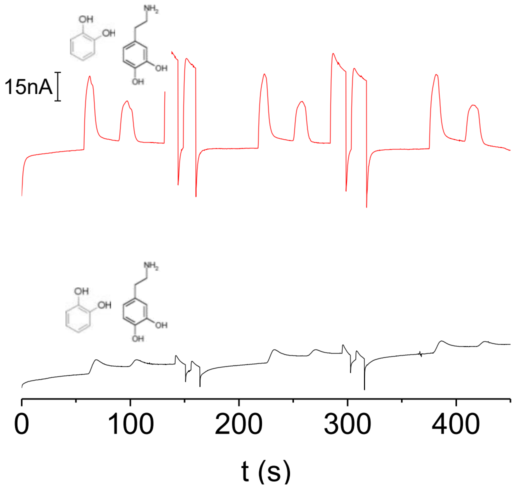


AFM at the interface

(contact mode)

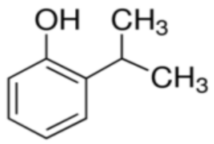


Dashed line

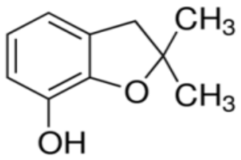


Detection potential +0.40 V !!

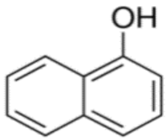
Microfluidic LAB on CHIP strategy



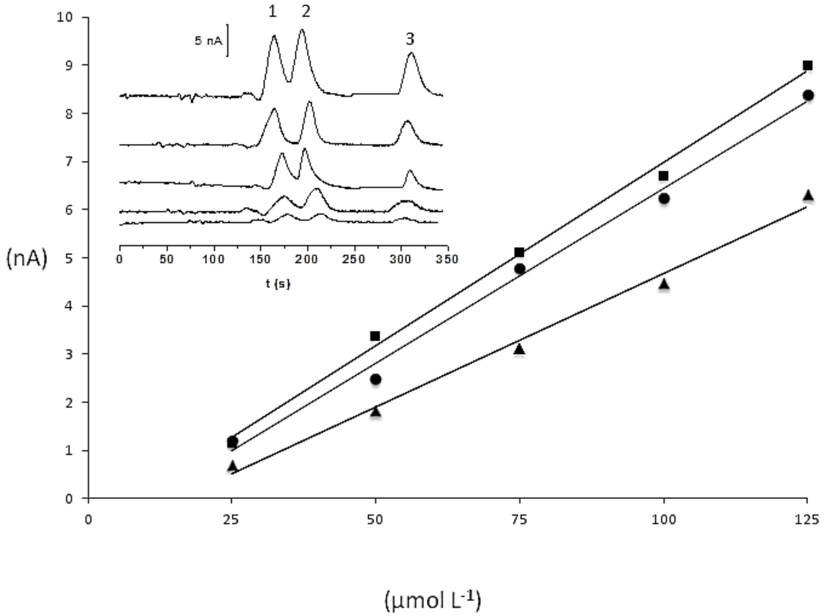
1 peak: Isprocarb
(2-isopropylphenol)

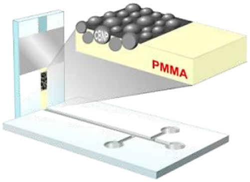


2 peak: Carbofuran
(2 3-dihydro-2 2-dimethyl-7-hydroxy benzofuran)



3 peak: Carbaryl
(1-napthol)





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 (1)	25-125	Y = 0.0726x – 0.830	**0.993**	26	32
Carbofuran (2)	25-125	Y = 0.0760x – 0.632	**0.996**	22	28
Carbaryl (3)	25-125	Y= 0.0555x – 0.876	**0.992**	34	32

Microfluidic LAB on CHIP strategy

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CBNPs Press-transferred microfluidic carbamates real samples analysis

Pesticide	Lake water[1]				River water[1]				Irrigation water[1]			
	Spiked (µM)	Determined (µM)	Recovery (mean)	RSD (%)	Spiked (µM)	Determined (µM)	Recovery (mean)	RSD (%)	Spiked (µM)	Determind (µM)	Recovery (mean)	RSD (%)
Isoprocarb	0	< LOQ	**-**	-	0	< LOQ	**-**	-	0	< LOQ	**-**	
	50	44.28	**87**	8	50	52.62	**105**	8	50	44.97	**90**	8
	100	90.43	**90**	5	100	95.94	**96**	10	100	94.15	**94**	5
Carbofuran	0	< LOQ	**-**	-	0	< LOQ	**-**	-	0	< LOQ	**-**	
	50	45.87	**92**	11	50	53.04	**106**	9	50	52.97	**106**	11
	100	89.09	**89**	9	100	90.61	**91**	8	100	97.18	**97**	9
Carbaryl	0	< LOQ	**-**	-	0	< LOQ	**-**	-	0	< LOQ	**-**	
	50	44.74	**90**	11	50	45.73	**92**	9	50	44.83	**90**	10
	100	88.88	**89**	9	100	87.53	**88**	7	100	88.79	**89**	8

[1] Tests carried out in triplicate.

Graphene-like nanomaterials

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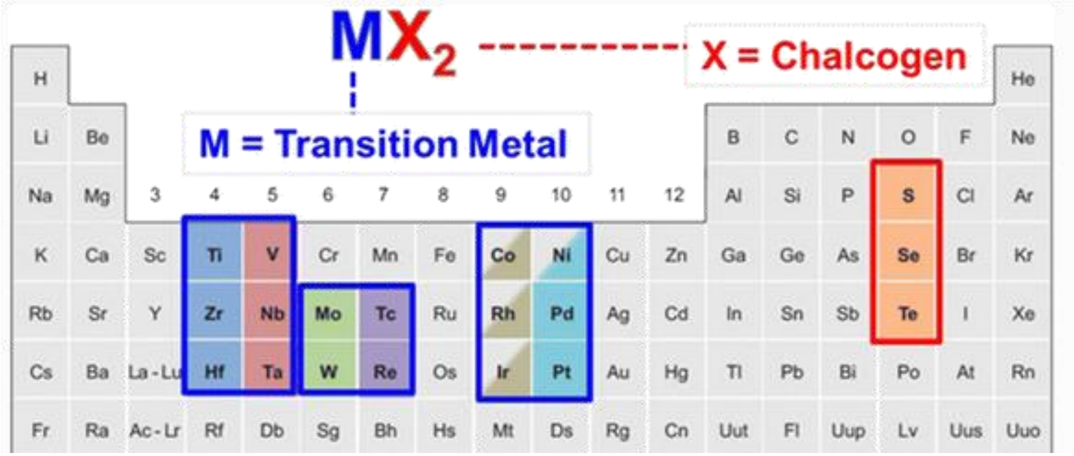
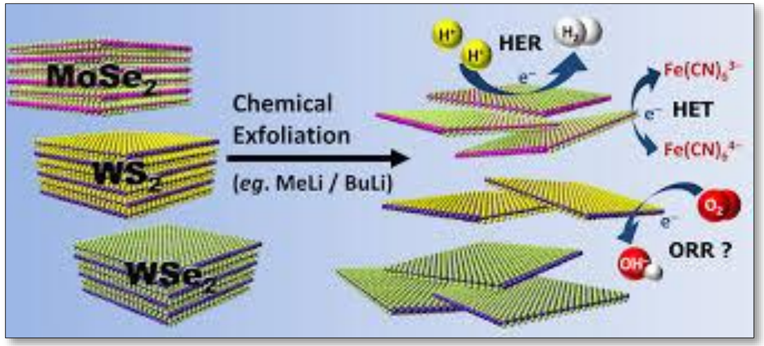
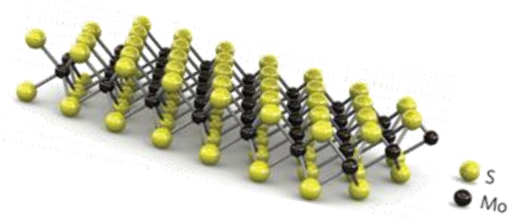
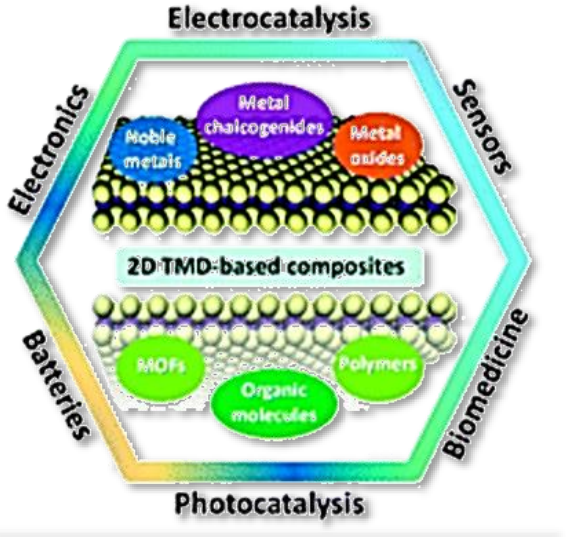
Graphene-like two-dimensional layered nanomaterials, transition metal dichalcogenides (TMDs)





Eng, A. Y. S., Ambrosi, A., Sofer, Z., Simek, P., & Pumera, M. (2014). Electrochemistry of transition metal dichalcogenides: strong dependence on the metal-to-chalcogen composition and exfoliation method. *ACS nano*, *8*(12), 12185-12198.





Tan, C., & Zhang, H. (2015). Two-dimensional transition metal dichalcogenide nanosheet-based composites. *Chemical Society Reviews*, *44*(9), 2713-2731.

- TMDs nanosheets Easy to prepare
- Unique electrical, optical , and mechanical properties
- Large surface area, low cost, stability
- Metallic and semi-conducting electrical capabilities
- Widely in employed in hydrogen evolution reaction (HER) and energy storage
- Few applications in (bio)sensors employed in food analysis
- Tunable electrocatalytic properties /intercalatable morphologies

(2)Graphene-like nanomaterials

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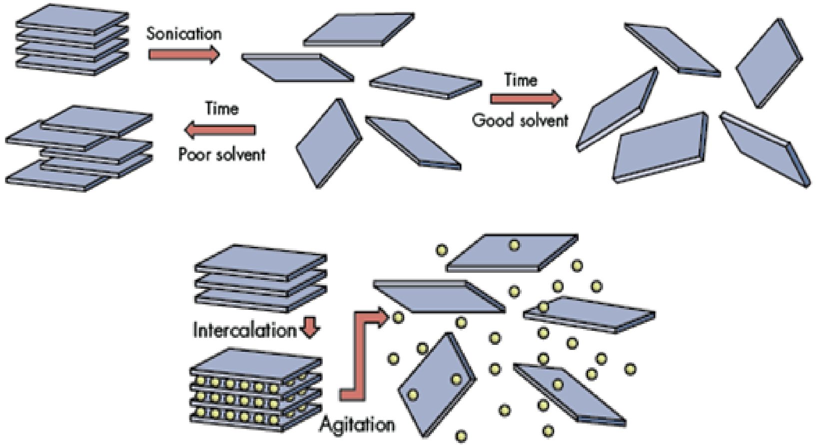
TMDs and TMDs-based nanocomposite for sensor and biosensors

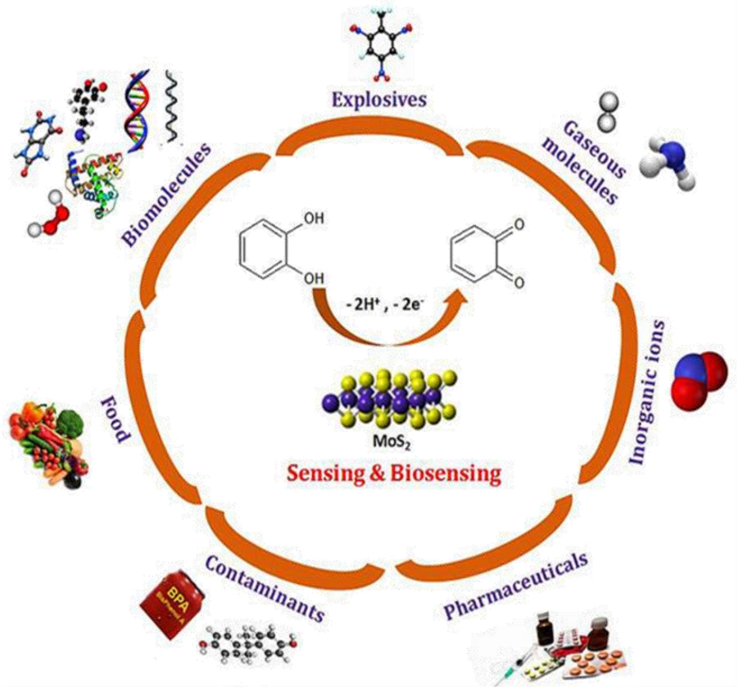
2D NMs can form heterostructures with layers of varied materials and with a thickness of one or two atoms, and thus synergistically improve their physicochemical properties.



Exfoliation using intercalating materials/ appropriate solvent
(single- or few-layer TMDs nanosheets)

TMDs-based nanocomposites/ Hybrid nanoarchitectures

These strategies avoiding restacking, narrow potential window, low conductivity, fouling, etc.
improving the general electrochemical performance



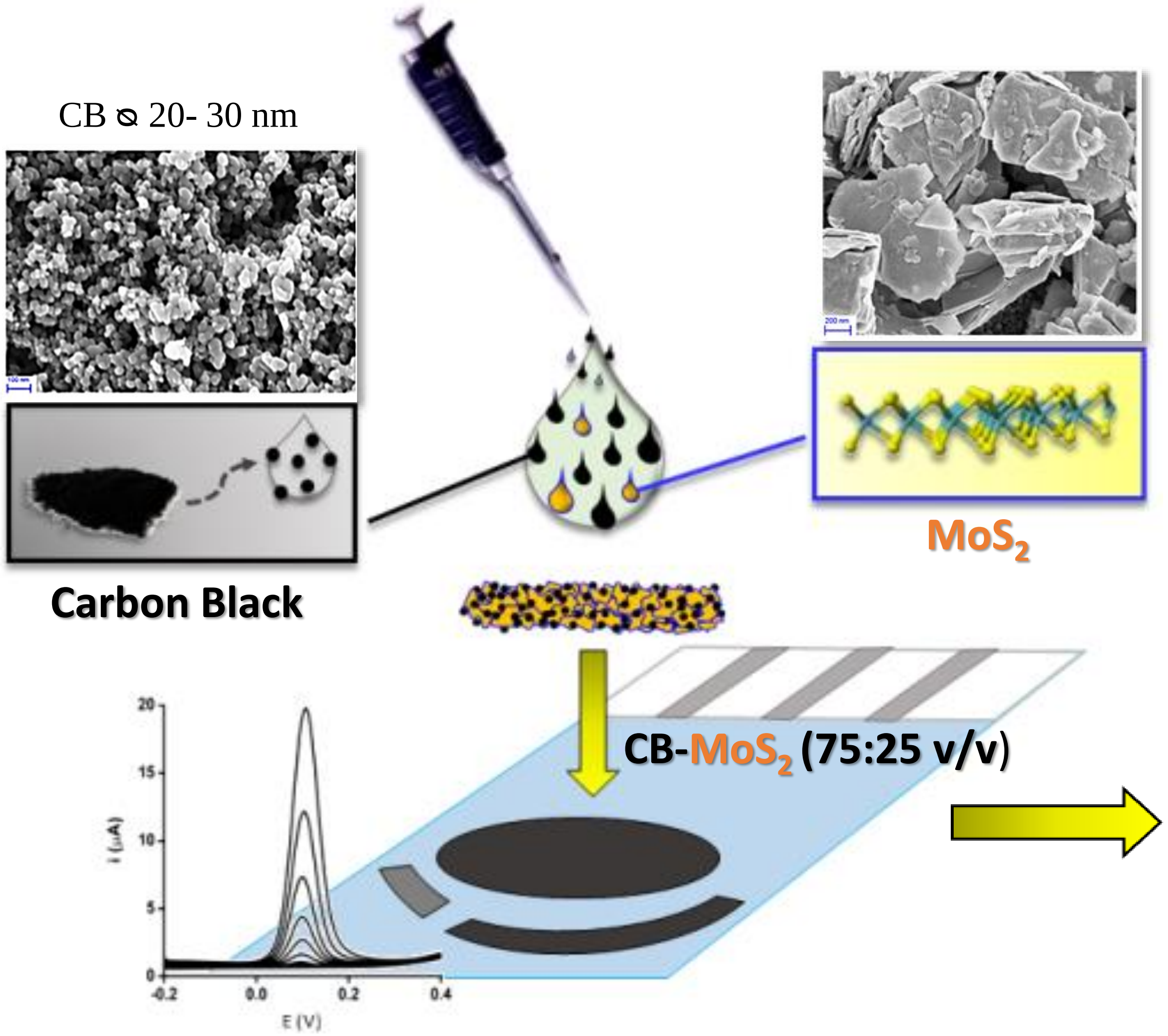
TMDs-based sensors and biosensors growing field and holds great promise

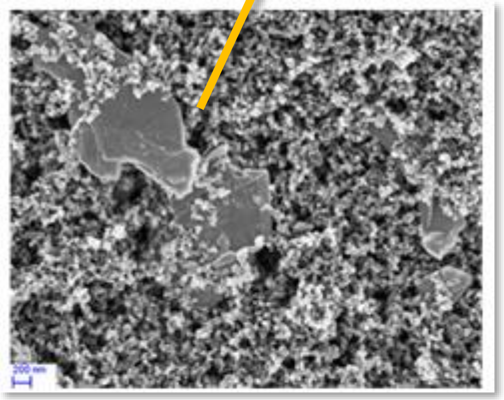
Alarcon-Angeles, G., Palomar-Pardavé, M., & Merkoçi, A. (2018). 2D Materials-Based Platforms for Electroanalysis Applications. *Electroanalysis*, *30*(7), 1271-1280.
Sinha, A., Tan, B., Huang, Y., Zhao, H., Dang, X., Chen, J., & Jain, R. (2018). MoS 2 Nanostructures for Electrochemical Sensing of Multidisciplinary Targets: A Review. *TrAC Trends in Analytical Chemistry*.

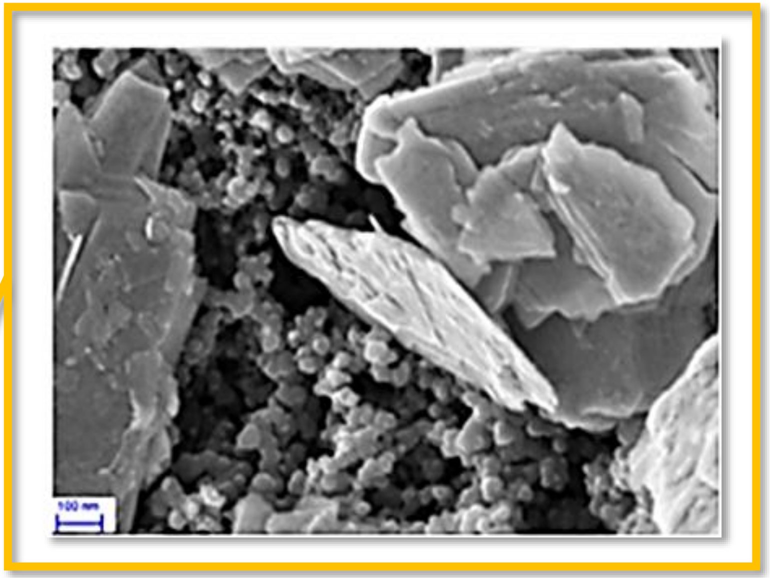
Graphene-like nanohybrids materials

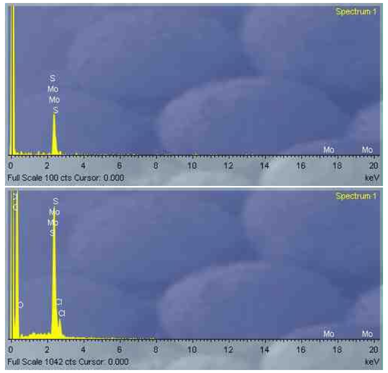
UNIVERSITÀ DEGLI STUDI DI TERAMO
UNITE

Effective nanocomposite carbon black(CB)-molybdenum disulphide (MoS_2) as novel screen-printed electrodes modifier for sensing applications









EDS spectra of SPEs modified with A) Exfoliated MoS_2, B) CB-MoS_2 composite at 75:25. The small peak of Cl is associated with external contamination.

Graphene-like nanohybrids materials

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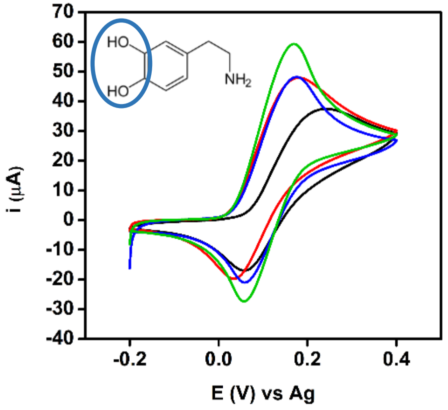
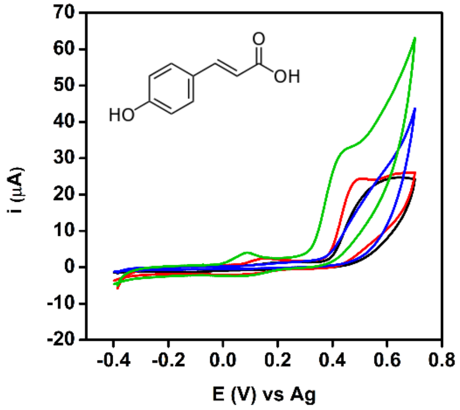
Electrochemical response towards common electroactive species

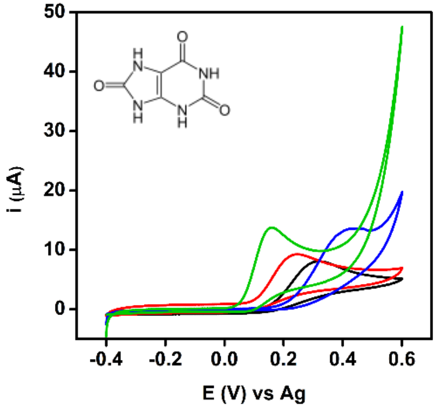
Dopamine



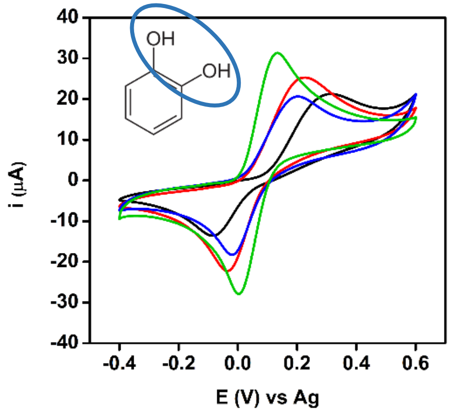
Coumaric acid



Ascorbic Acid

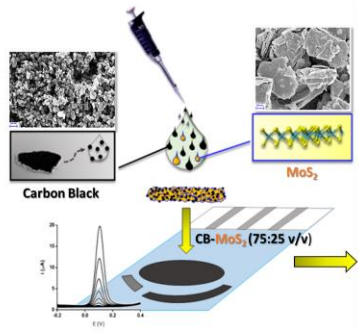


Catechol



SPE
CB
MoS_2
CB-MoS_2

CVs of 1 mmol L^{-1} of each compound at a scan rate of 50 mV s^{-1}.



•Dopamine and Catechol showed an improvement in the peak-to-peak separation and increased peak intesities.

•Coumaric acid and ascorbic acid showed a negative shift and improved peak intensities.

•SPE-CB-MoS2 anodic peak intensity decrease was in the ≤2 % and ≤ 10% for Catechol/Dopamine and Uric acid/Coumaric acid, respectively, after 10 scans

(6) Graphene-like nanohybrids materials

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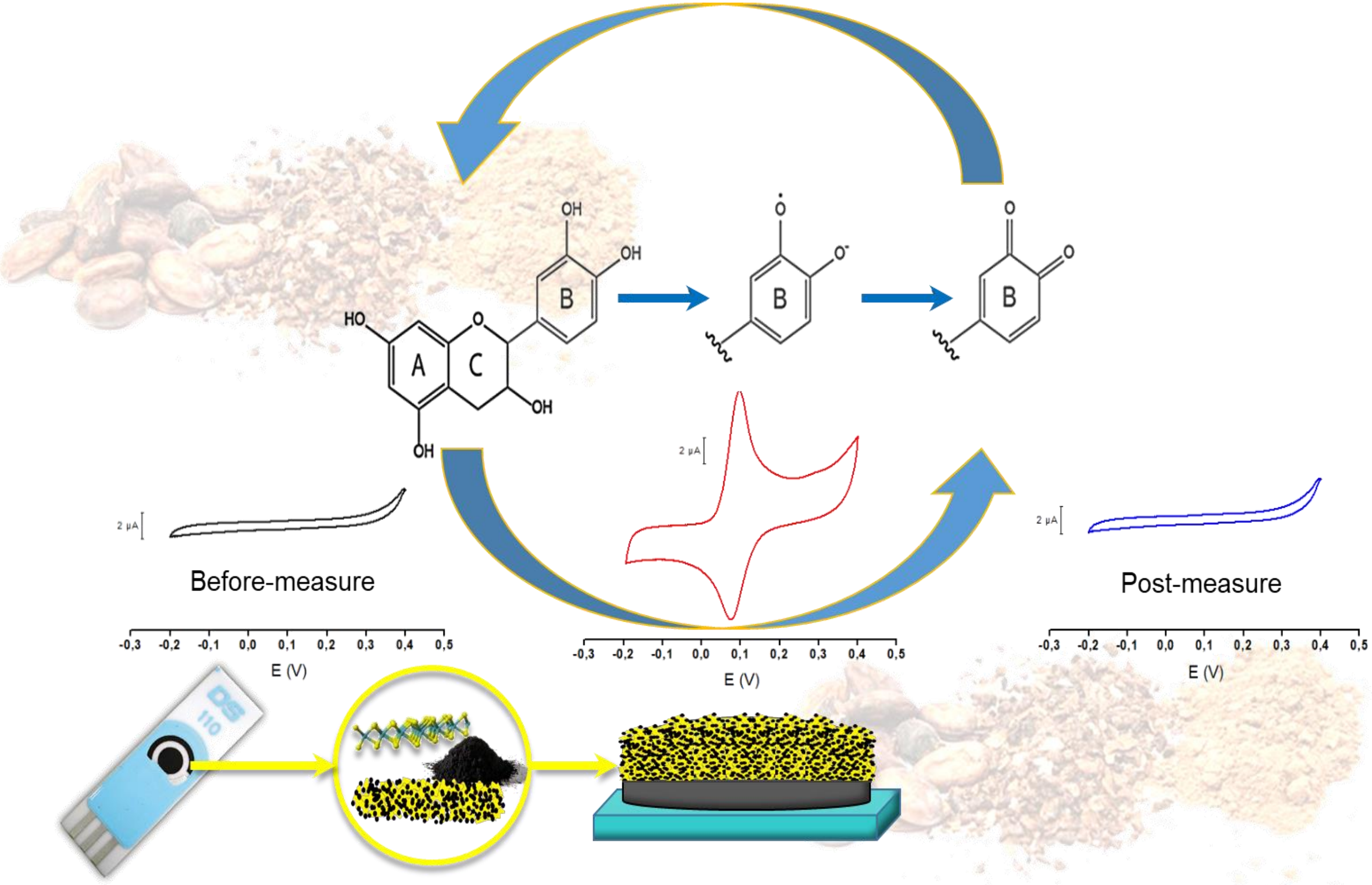
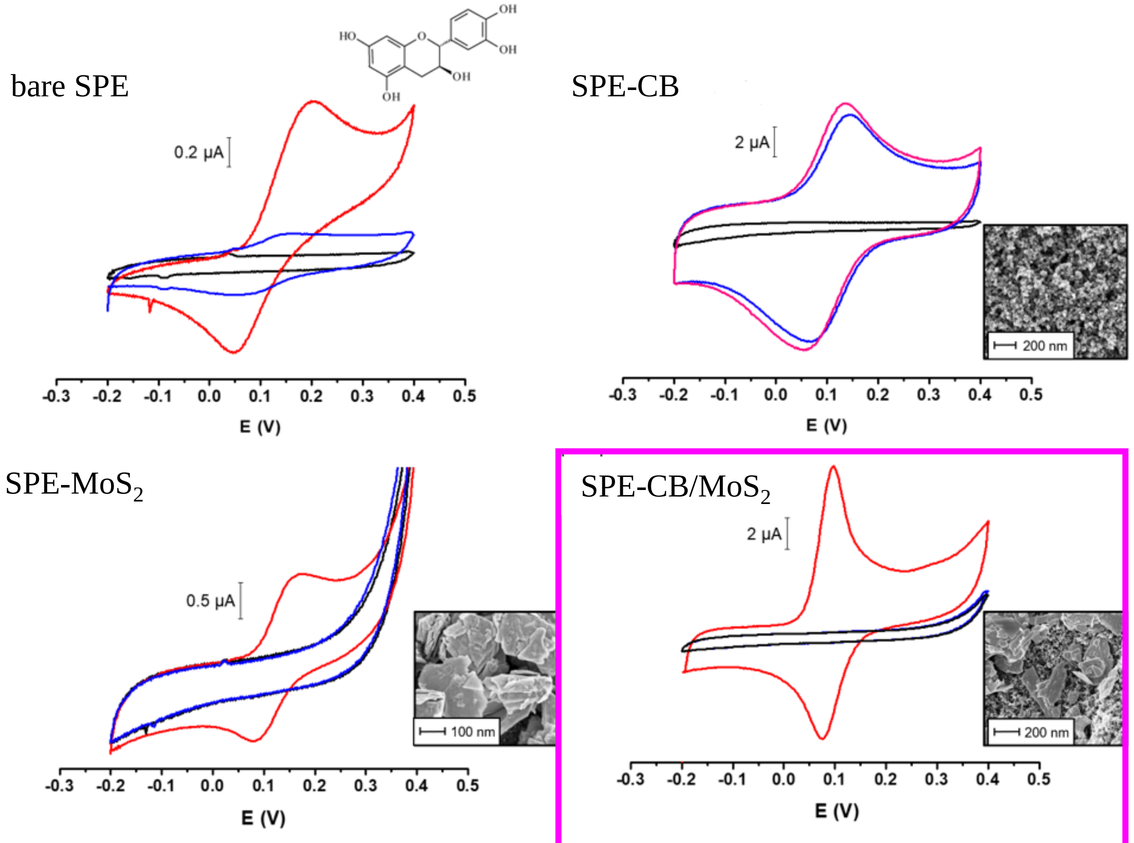
A case of study: Cocoa polyphenols



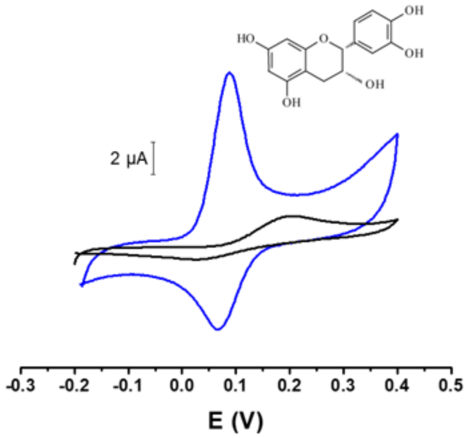
Graphene-like nanohybrids materials

CATECHIN

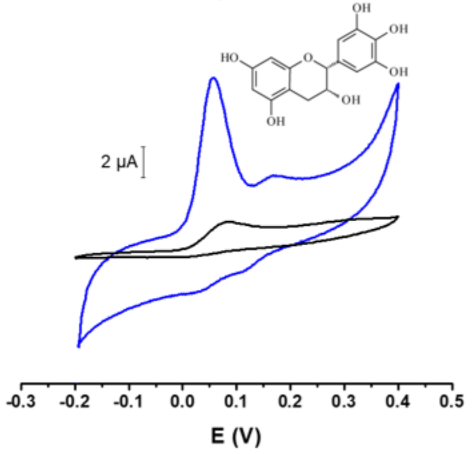


Anti-Fouling properties

EPICATECHIN



EPIGALLOCATECHIN



Graphene-like nanohybrids materials

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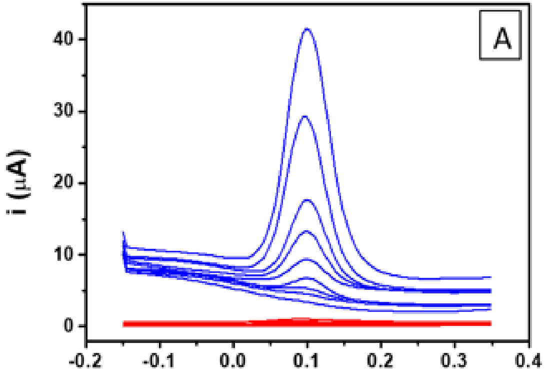
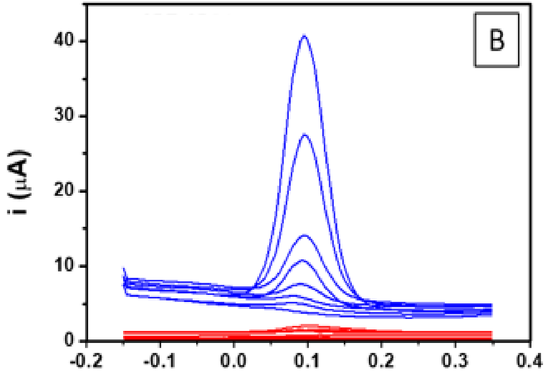
Standard calibration curve

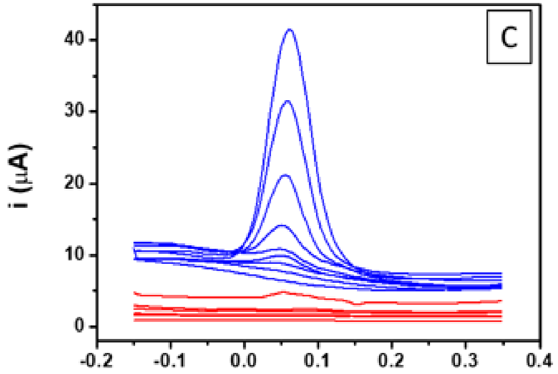
EPICATECHIN



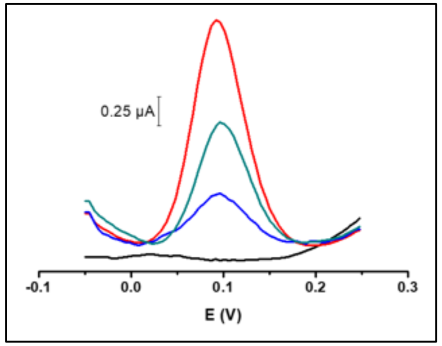
CATECHIN



EPIGALLOCATECHIN



Fortified cocoa samples



+ 0,25 µM catechin

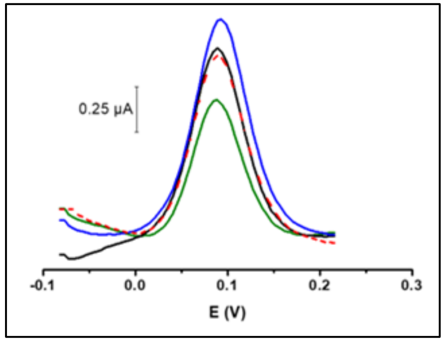
+ 0,5 µM catechin

Cocoa mix

Analytical characteristics of the SPE-CB/MoS_2 sensor employed for CT, EP, and EG detection.

	Linear Range ($\mu mol\ L^{-1}$)	R^2	Sensitivity ($\mu A\ L\ \mu mol^{-1}$)	LOD ($\mu mol\ L^{-1}$)
CT	0.2-25	0.998	1.12	0.18
EP	0.2-25	0.998	1.18	0.17
EG	0.2-25	0.998	1.10	0.18

[1]LODs were calculated as 3σ/slope ratio, where σ is the standard deviation of the mean value for 10 voltammograms of the blank. Analytical characteristics calculated using the mean value of three calibration curves.



Low polyphenols content

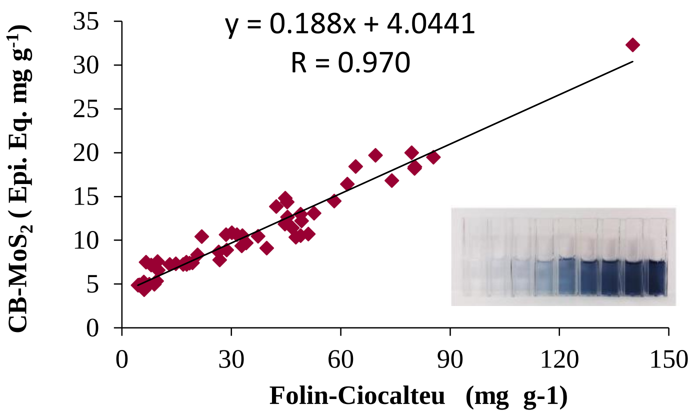
Medium polyphenols content

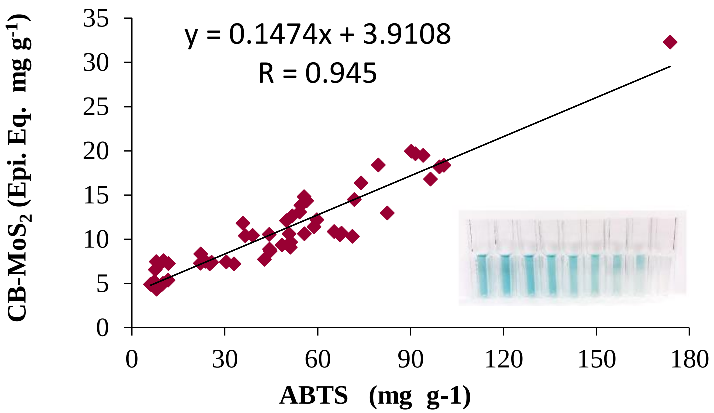
High polyphenols content

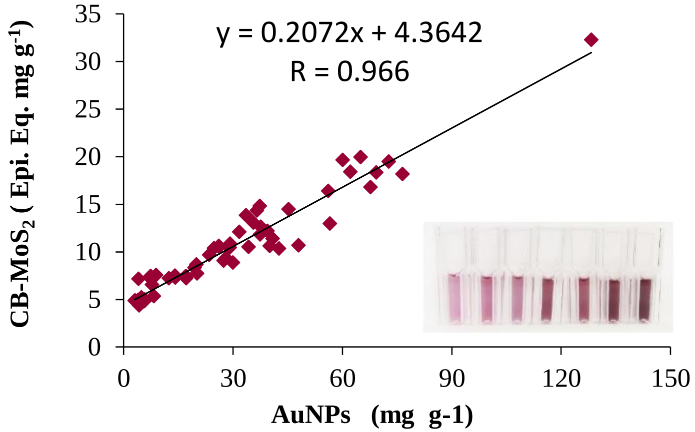
n= 5 repetition after n° 59 cocoa measurement

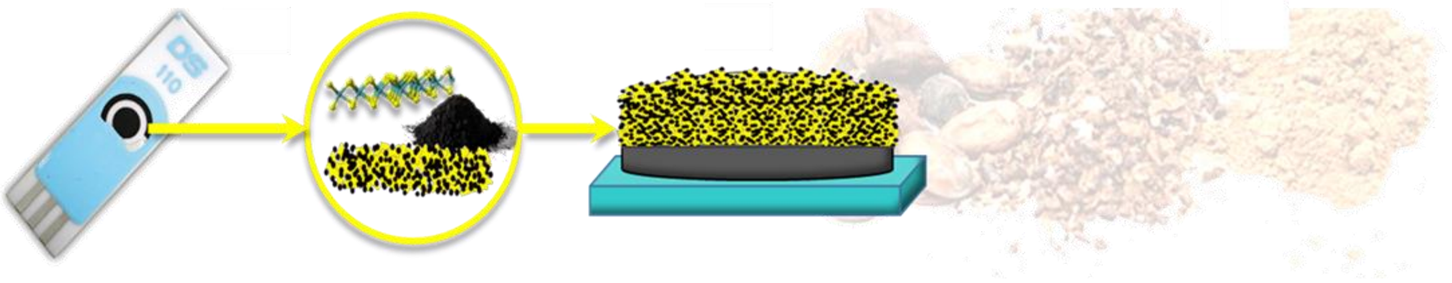
Graphene-like nanohybrids materials

Data correlation
Optical assay vs. Electrochemical
n= 59 sample



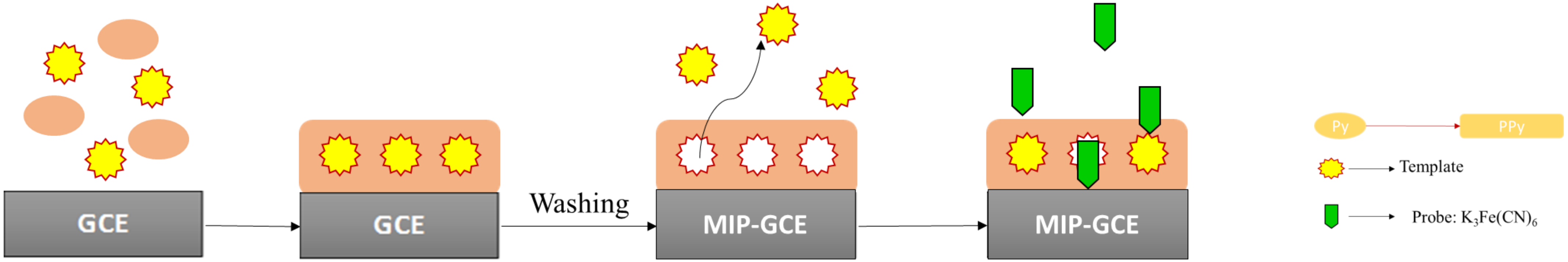


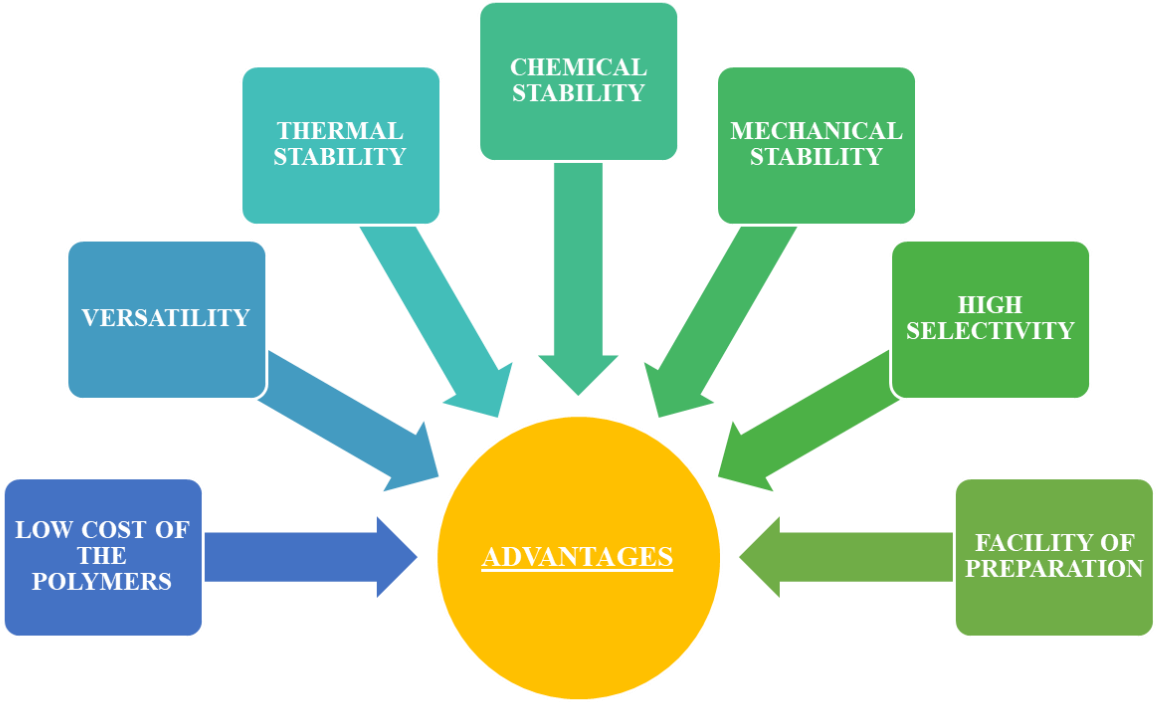




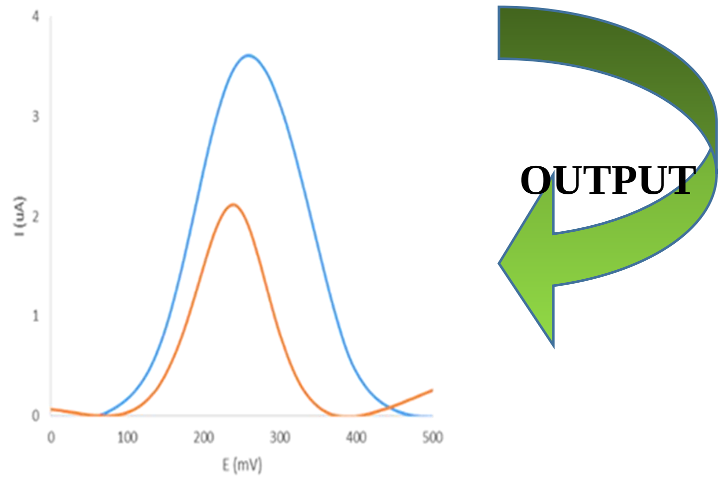
Molecular imprinted polymer (MIP) based sensing

A **molecularly imprinted polymer** (MIP) is a polymer that has been processed using the molecular imprinting technique which leaves cavities in the polymer matrix with an affinity for a chosen "template" molecule.



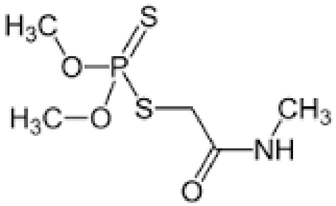


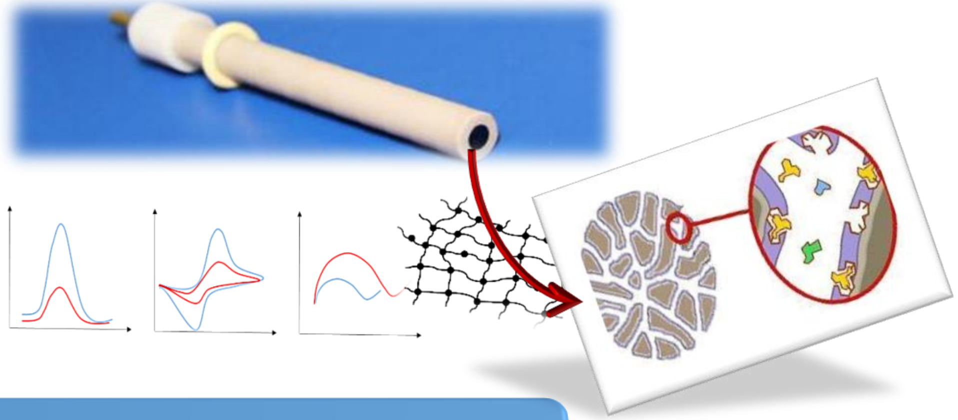
REBINDING & MEASURE



(1) MIP based sensing

MIP-MEPS based sensing strategy for the selective assay of dimethoate. Application to wheat flour samples





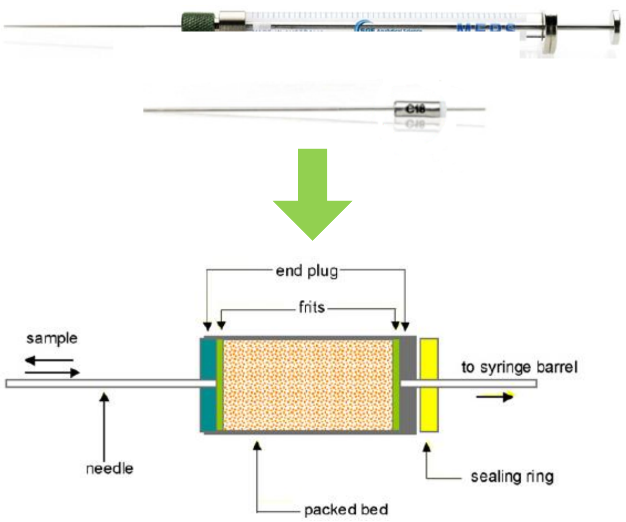
DIMETHOATE MONITORING IN WHEAT FLOUR

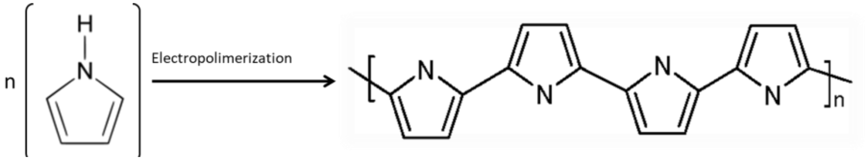
SAMPLE PREPARATION

ANALYTE DETECTION

MICROEXTRACTION BY PACKED SORBENT (MEPS)

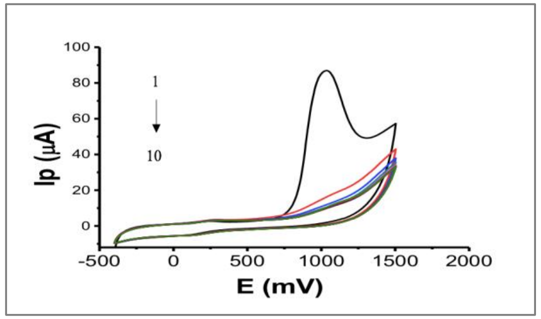
MIP-GLASSY CARBON ELECTRODE

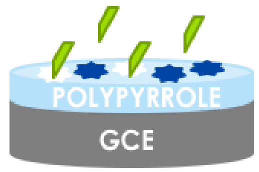


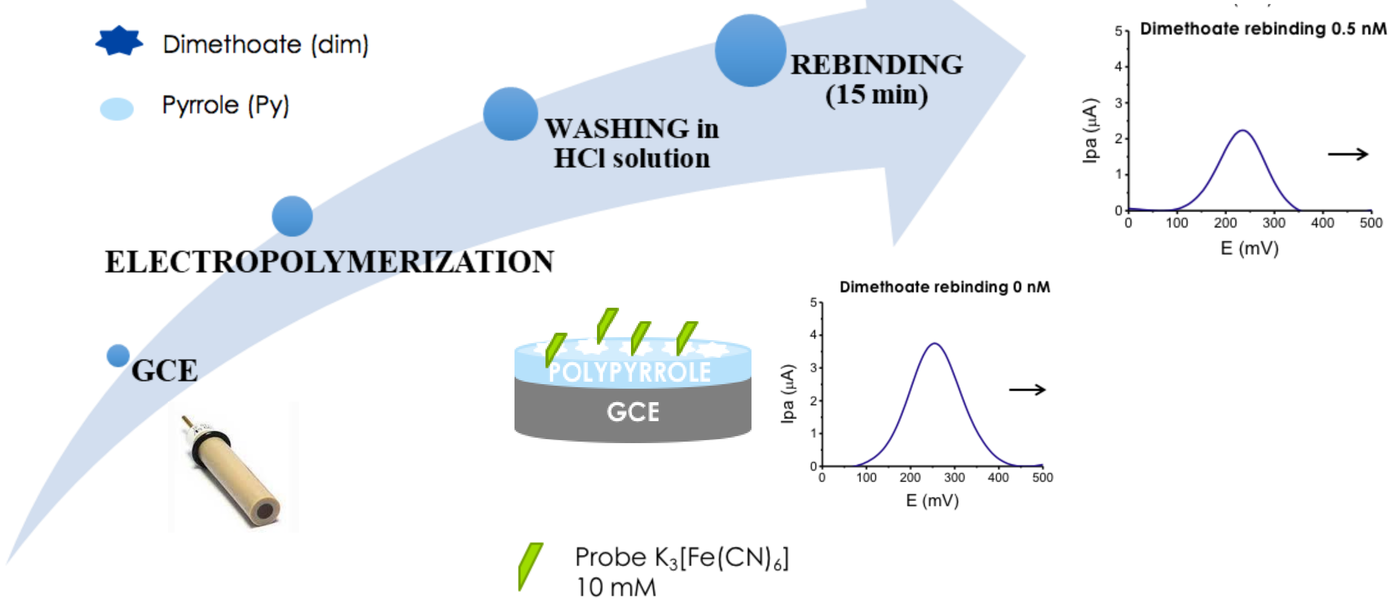


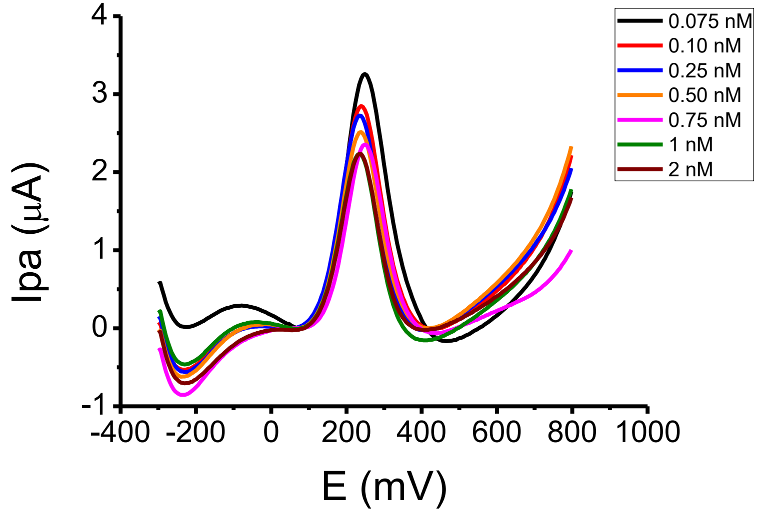
(2) MIP based sensing

Strategy

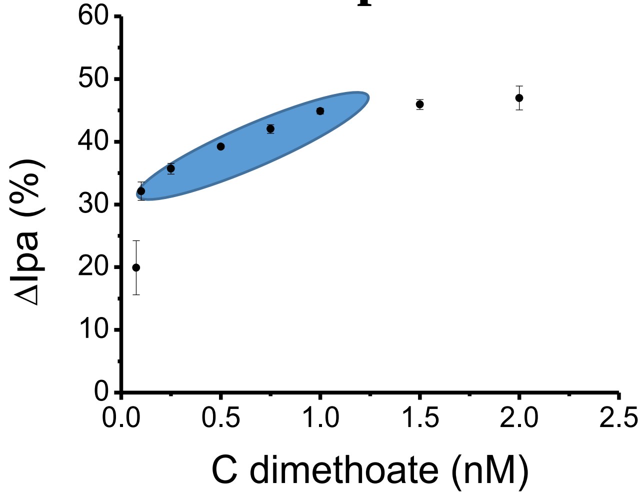








Dose-response curve



(3) MIP based sensing

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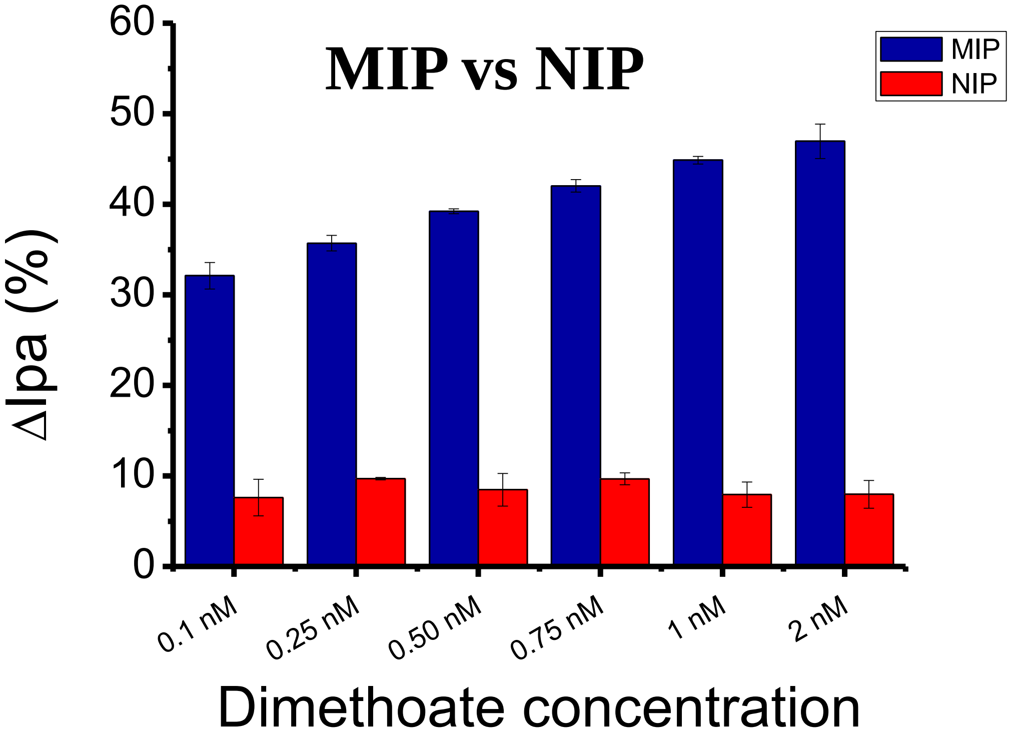
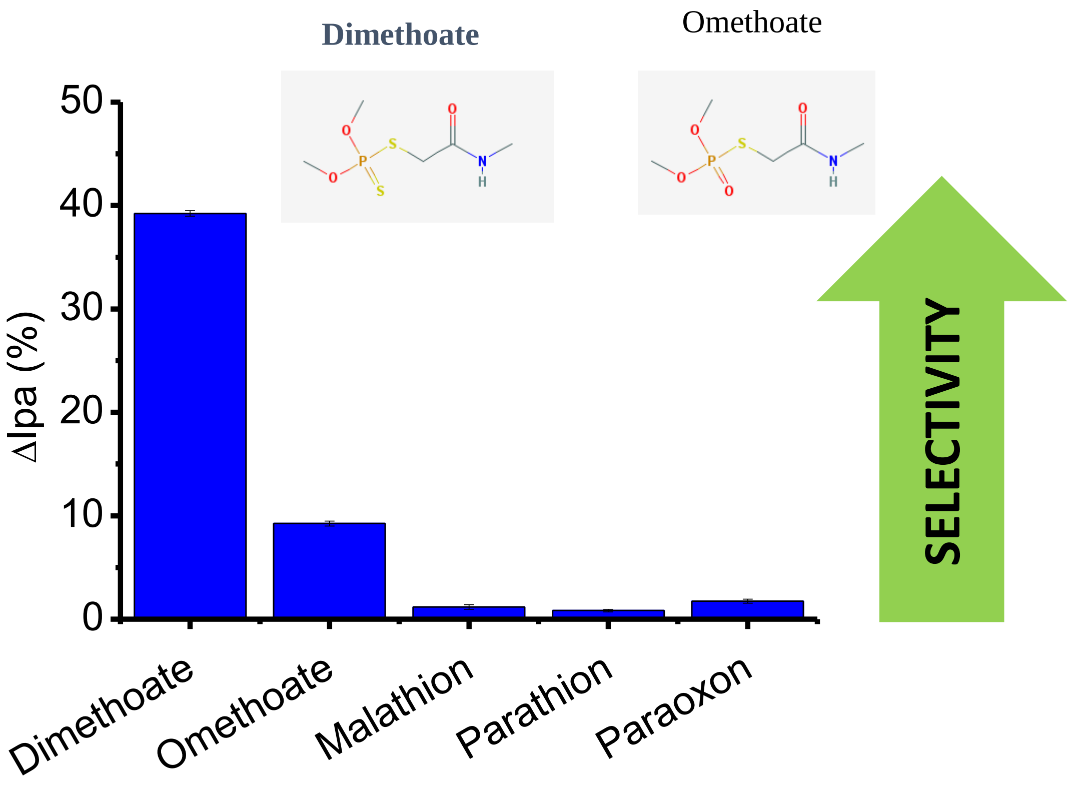
ΔIpa (%)	Repeatability (RSD %)	Reproducibility (RSD %)
0.5 nM dimethoate (n=3)	0.7	2.7
1 nM dimethoate (n=3)	0.9	5.5

ΔIpa (%) for malathion, parathion and paraoxon after the rebinding step was negligible; **omethoate** gave a response of **23%**.





(4) MIP based sensing

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MIP-MEPS based sensing strategy for the selective assay of dimethoate. Application to wheat flour samples

D. Capoferri[a], M. Del Carlo[a,1], N. Ntshongontshi[b], E.I. Iwuoha[b], M. Sergi[a], F. Di Ottavio[a], D. Compagnone[a,*,1]

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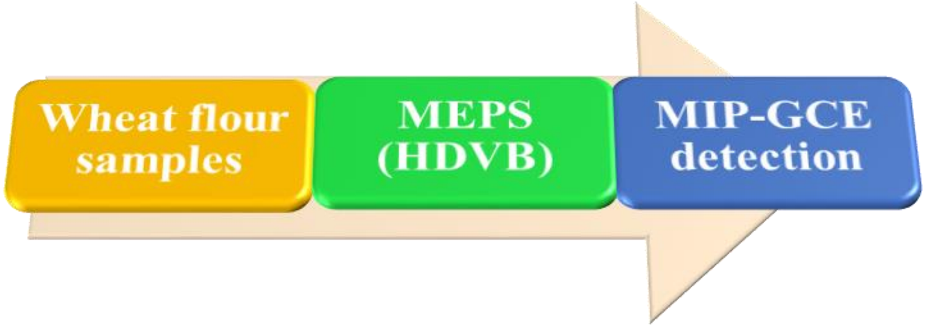
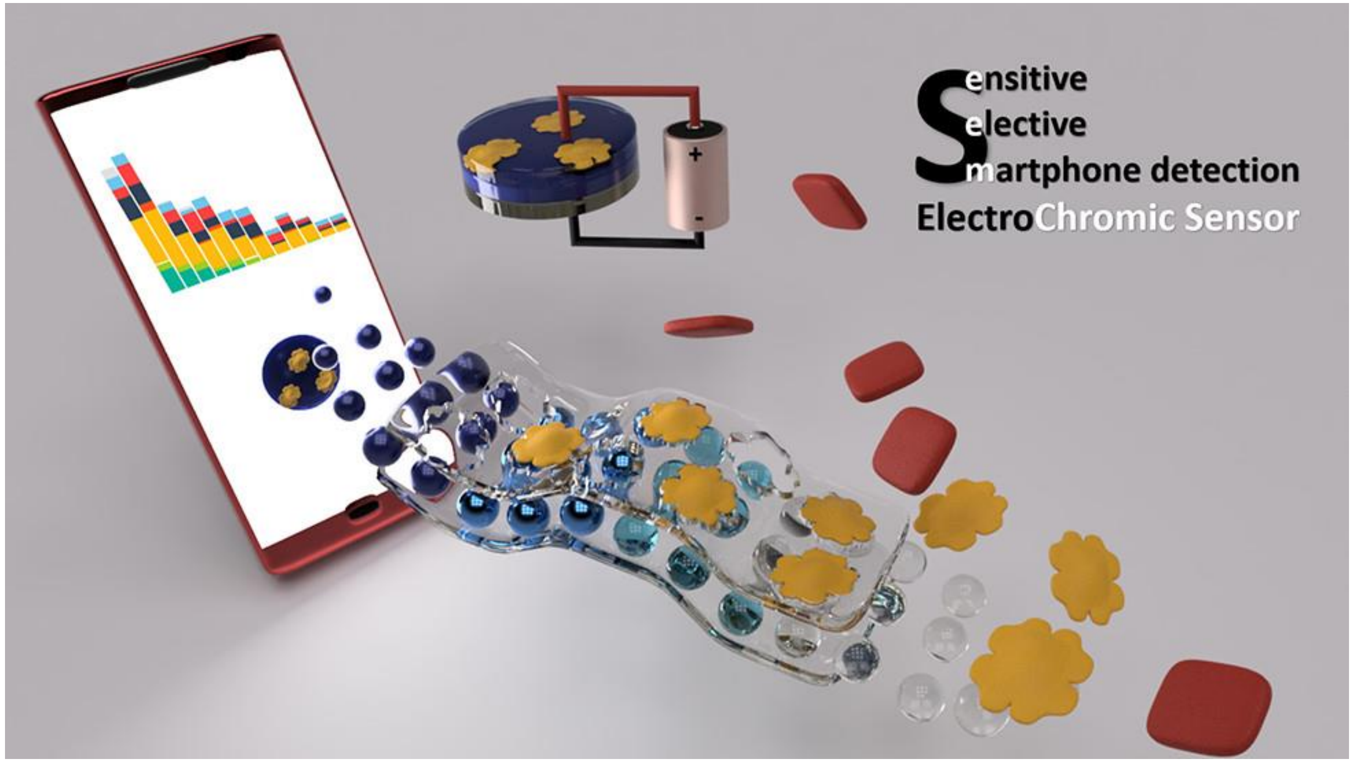


Wheat flour samples: MIP vs. UHPLC-MS/MS

Samples	MIP-GCE RELATIVE ERROR (%) of dimethoate concentration (μg kg^{-1})	MIP-GCE SD of dimethoate concentration (μg kg^{-1})
Wheat flour spiked with dimethoate 0.5 MRL	+13.5	0.52
Wheat flour spiked with dimethoate 0.5 MRL + mix	+4.6	2.37
Wheat flour spiked with dimethoate MRL	-21.1	1.24
Wheat flour spiked with dimethoate MRL + mix	-21.2	1.36
Wheat flour spiked with dimethoate 1.5 MRL	+16.7	0.74
Wheat flour spiked with dimethoate 1.5 MRL + mix	-0.4	1.69
Wheat flour spiked with dimethoate MRL + omethoate (1:1)	+3.5	2.70

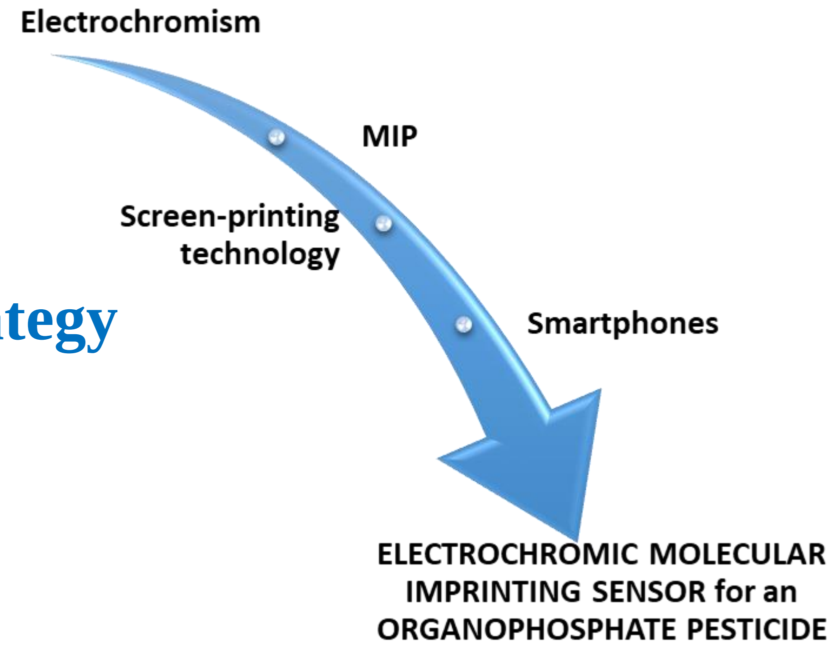
(5) MIP based sensing

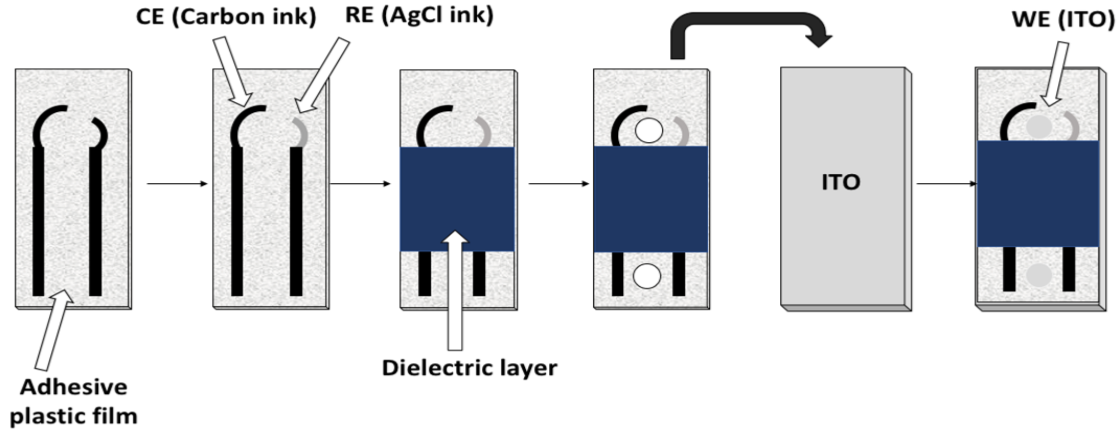
Electrochromic Molecular Imprinting Sensor for Visual and Smartphone-Based Detections

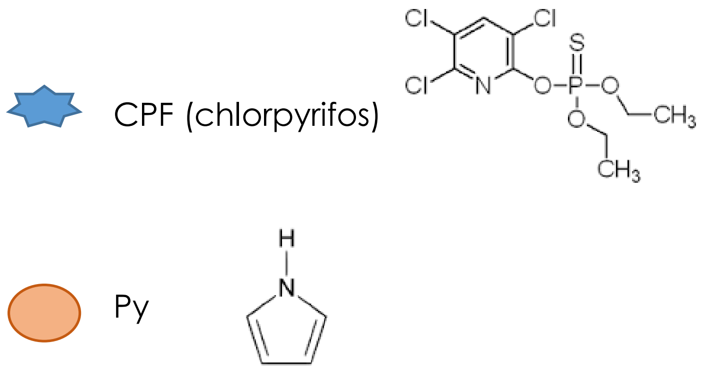


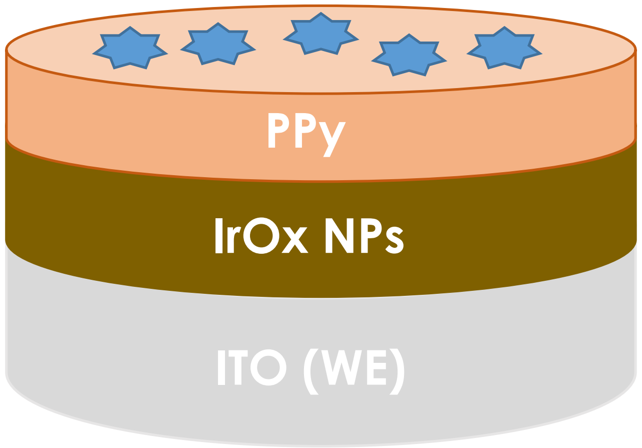
(6) MIP based sensing

Strategy

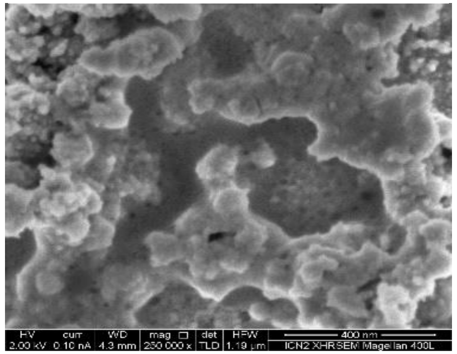








MIP/IrOx NPs – ITO SPE



(7) MIP based sensing

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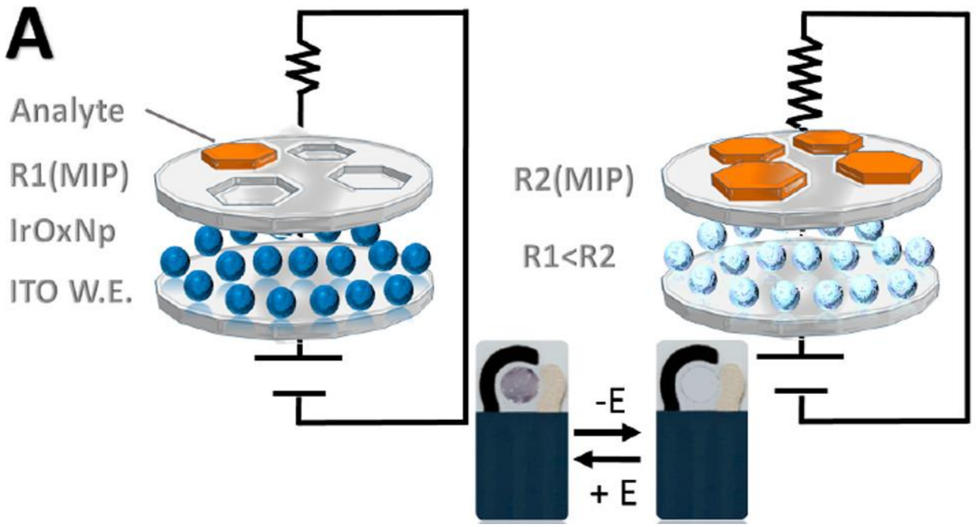
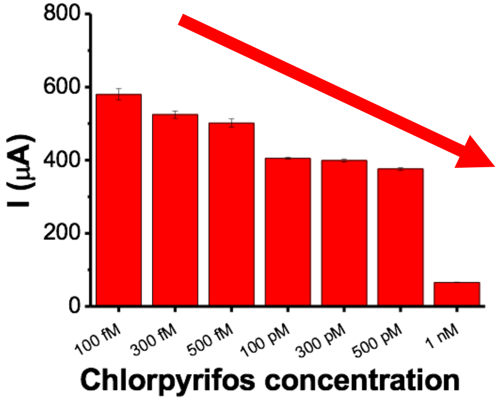
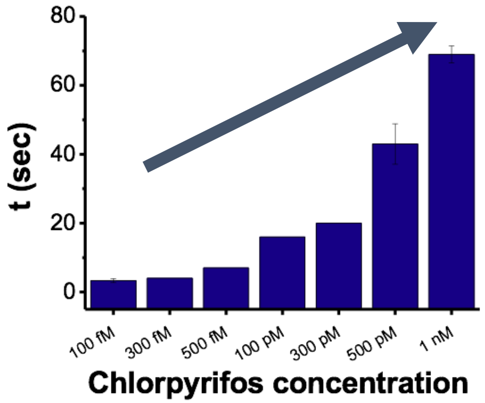
WORKING PRINCIPLE







(8) MIP based sensing

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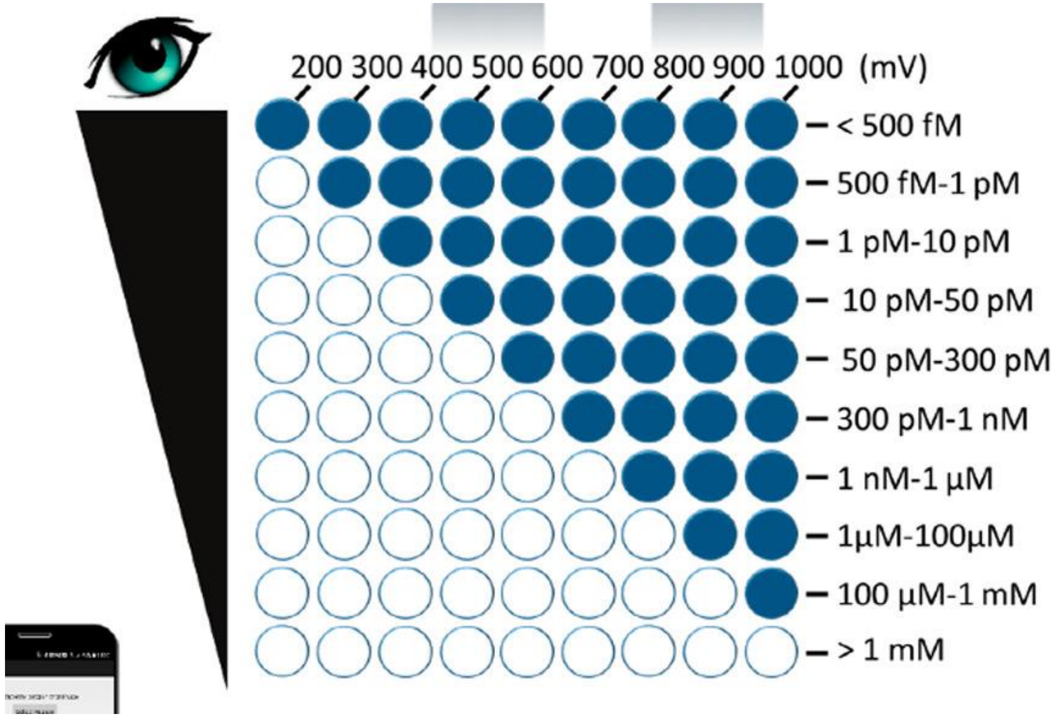
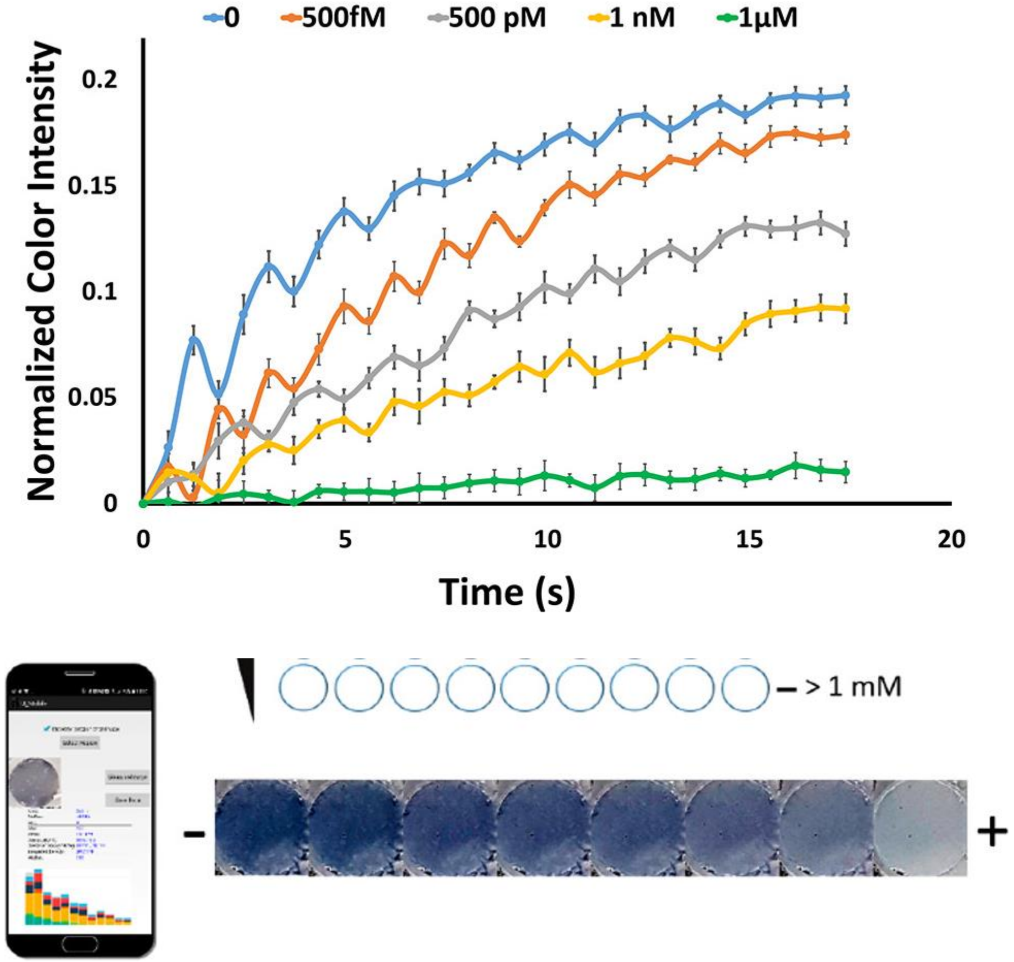
VISUAL APPROACH



SMARTPHONE APPROACH



(9) MIP based sensing

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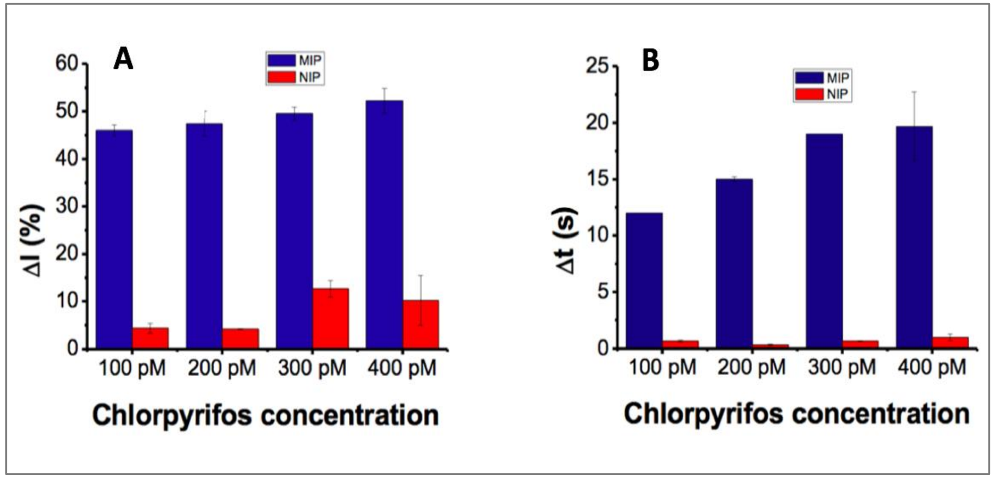
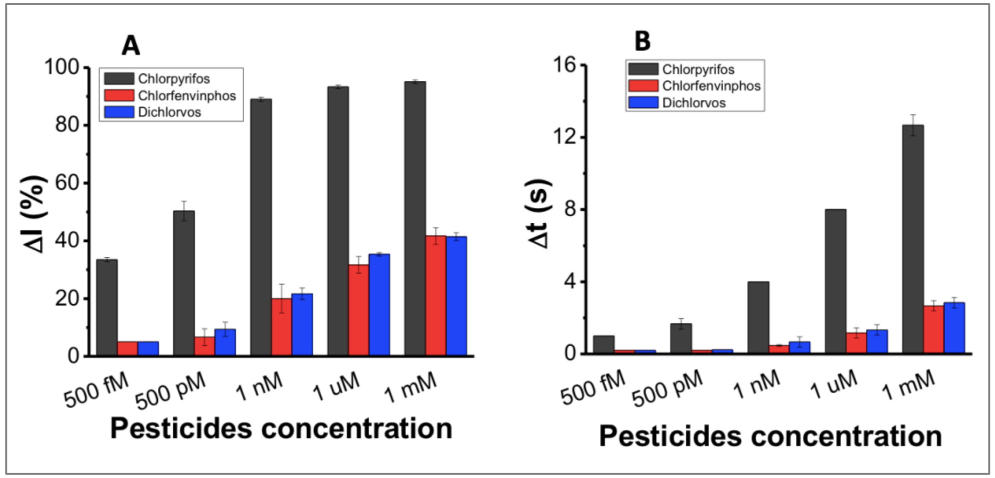
MIP vs NIP



SELECTIVITY (500 mV-1000 mV)



analytical chemistry Article
Cite This: Anal. Chem. XXXX, XXX, XXX−XXX pubs.acs.org/ac

Electrochromic Molecular Imprinting Sensor for Visual and Smartphone-Based Detections

Denise Capoferri,[†,‡,§] Ruslan Álvarez-Diduk,[†,§] Michele Del Carlo,[‡] Dario Compagnone,[‡] and Arben Merkoçi*[,†,∥]

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[‡]Faculty of Biosciences and Technologies for Food, Agriculture and Environment, University of Teramo, via R. Balzarini 1, 64100 Teramo, Italy
[∥]Catalan Institution for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

Recovery values of chlorpyrifos in spiked drinking water samples (n = 3) using the current response

Added (Spiked)	Found	Recovery (%)	RSD (%)
500 fM	517.19 fM	103.44 ± 16.14	15.60
500 pM	471.45 pM	94.29 ± 17.92	19.00
1 nM	0.99 nM	99.50 ± 19.90	20.00
1 µM	0.98 µM	97.55 ± 25.87	26.52
1 mM	1.07 mM	106.57 ± 15.30	14.36

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foods MDPI

Review

Affinity Sensing Strategies for the Detection of Pesticides in Food

Denise Capoferri, Flavio Della Pelle, Michele Del Carlo and Dario Compagnone *

Faculty of Biosciences and Technologies for Food, Agriculture and Environment, University of Teramo, via R. Balzarini 1, 64100 Teramo, Italy; dcapoferri@unite.it (D.C.); fdellapelle@unite.it (F.D.P.); mdelcarlo@unite.it (M.D.C.)
* Correspondence: dcompagnone@unite.it; Tel.: +39-0861-266942

check for updates

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sensors MDPI

Review

Nanomaterial-Based Sensing and Biosensing of Phenolic Compounds and Related Antioxidant Capacity in Food

Flavio Della Pelle and Dario Compagnone *

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64023 Teramo, Italy; fdellapelle@unite.it
* Correspondence: dcompagnone@unite.it; Tel.: +36-0861-266942

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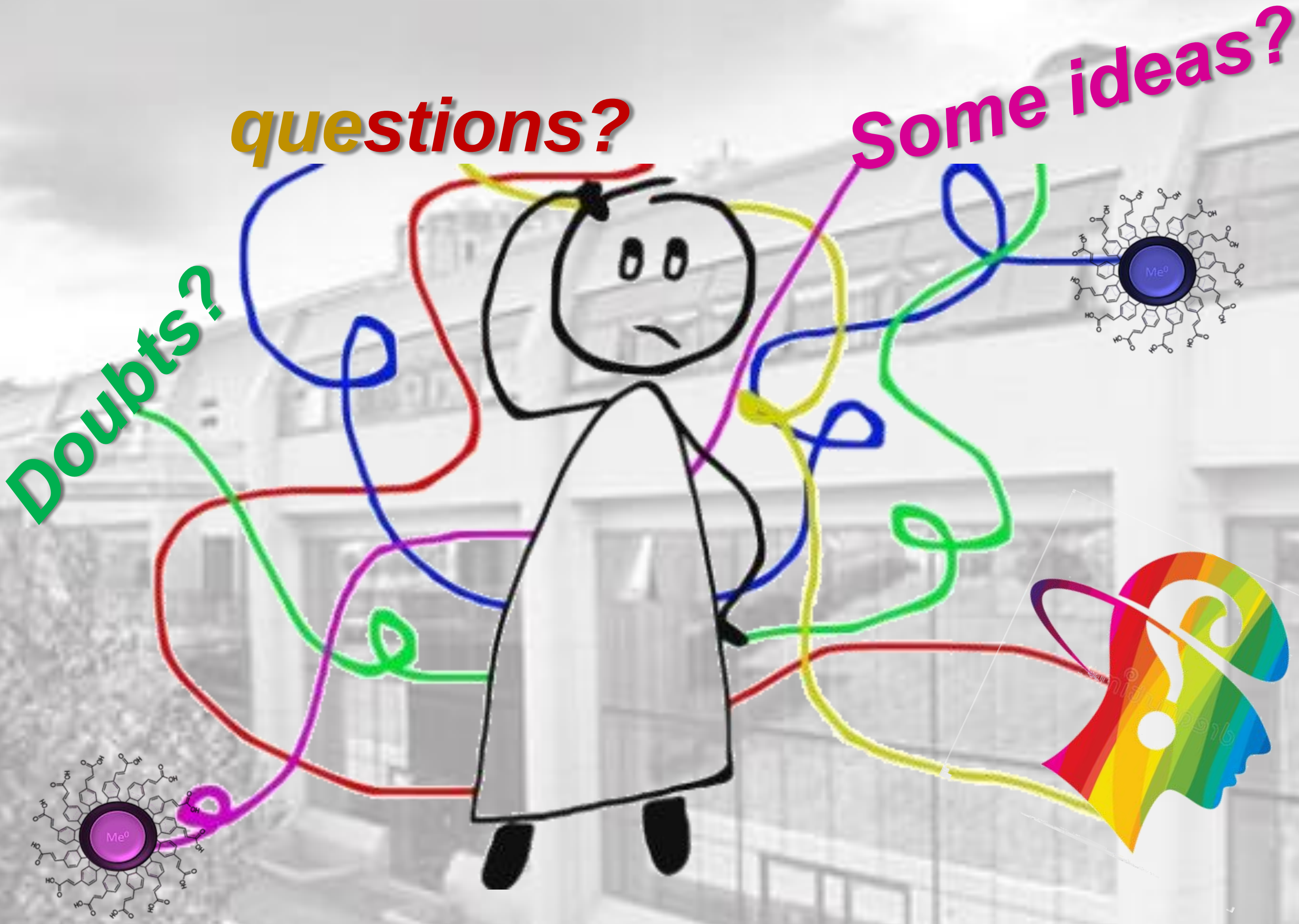

...Thanks for your attention...