

I metodi rapidi di analisi consentono di eseguire analisi in campo

1. Campione non trattato o minimamente trattato

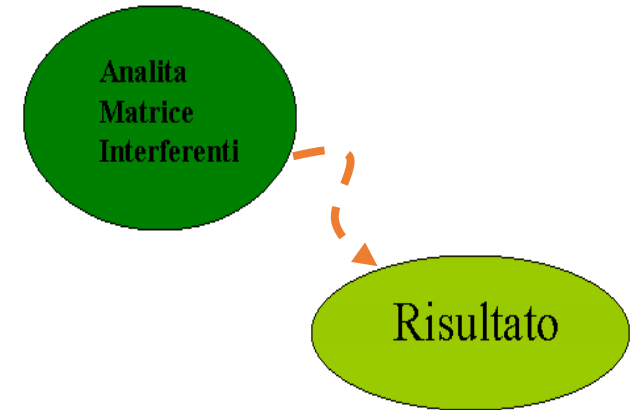
il metodo non soffre interferenze e non è influenzato dall'effetto matrice

Selettività

- Singolo analita
- Classe specifici

Monouso

- Basso costo
- Sostenibili



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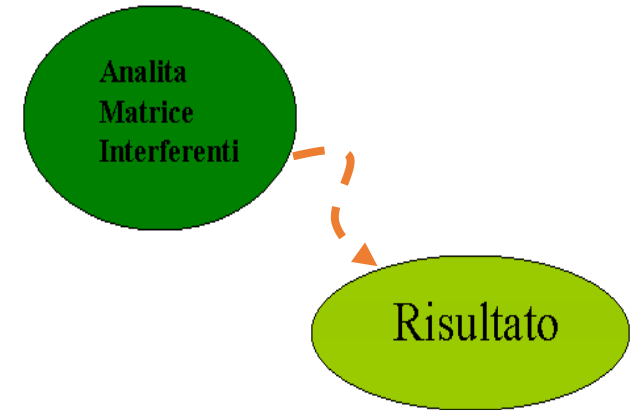
2. Risposta rapida

metodi elettrochimici e metodi ottici

Non subiscono interferenza da colore e materiale in sospensione

correzione del bianco

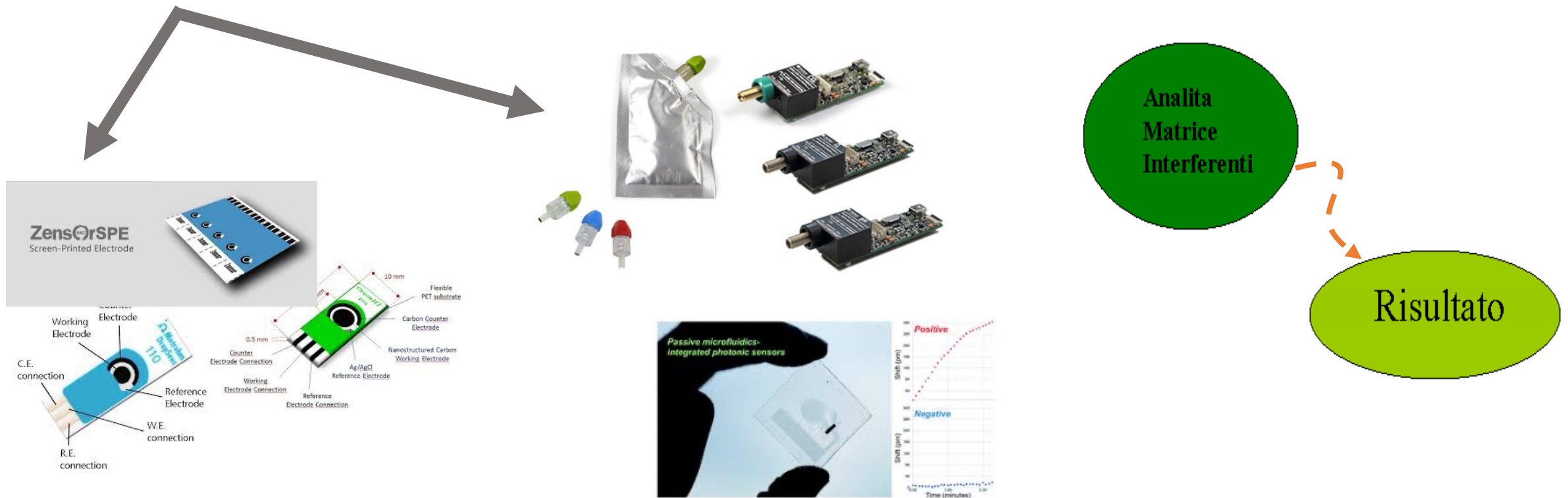
Strumentazione miniaturizzata e a basso costo



I metodi rapidi di analisi consentono di eseguire analisi in campo

3. monouso

interfaccia con il campione viene rinnovata ad ogni misura



I metodi rapidi di analisi come metodi di screening

Per metodo di screening si intende il metodo utilizzato per rilevare la presenza di una sostanza o di una classe di sostanze al livello di interesse.

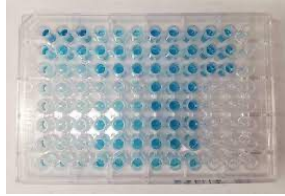
Tali metodi consentono di analizzare un elevato numero di campioni in tempi brevi con l'obiettivo di evitare falsi risultati conformi.

I metodi di conferma sono metodi che forniscono informazioni complete o complementari atte ad identificare la sostanza in modo univoco e, se necessario, quantificarla al livello di interesse.

I metodi rapidi di analisi nel settore alimentare

Soluzioni quantitative e semiquantitative per lo screening degli alimenti, ideali per l'implementazione di piani di autocontrollo al servizio della filiera produttiva alimentare

ELISA;



Kit basati su metodi enzimatici;



Strip test, dipstick/Lateral Flow device;



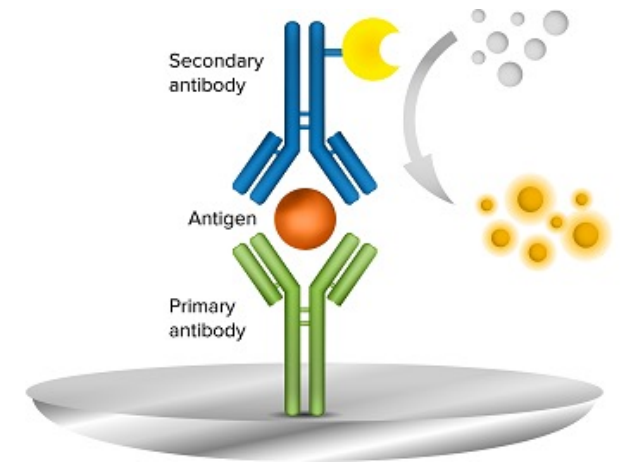
Immunosaggi competitivi



I metodi rapidi di analisi

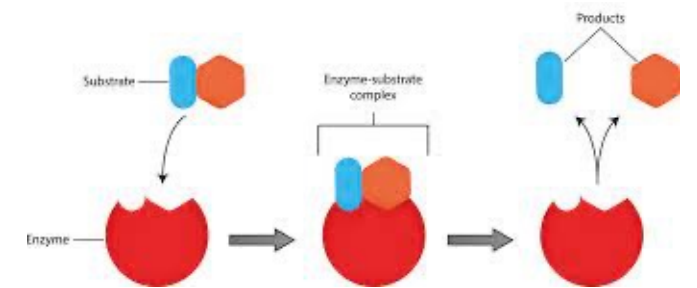
- L'elemento di riconoscimento, il segnale (bio)chimico e la rilevazione sono distinti

- Es: ELISA

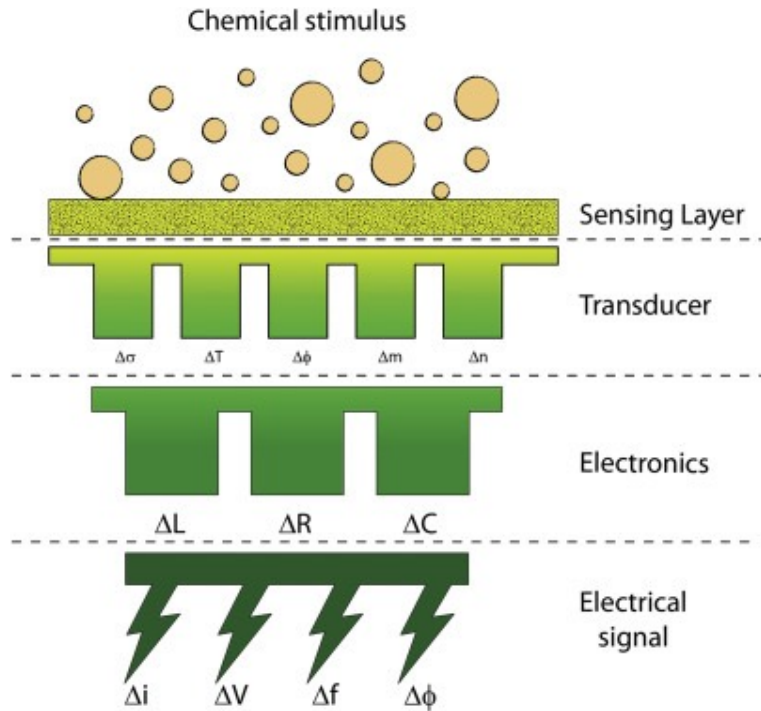


- L'elemento di riconoscimento e la rilevazione sono distinti

- Es: kit enzimatico



I sensori chimici

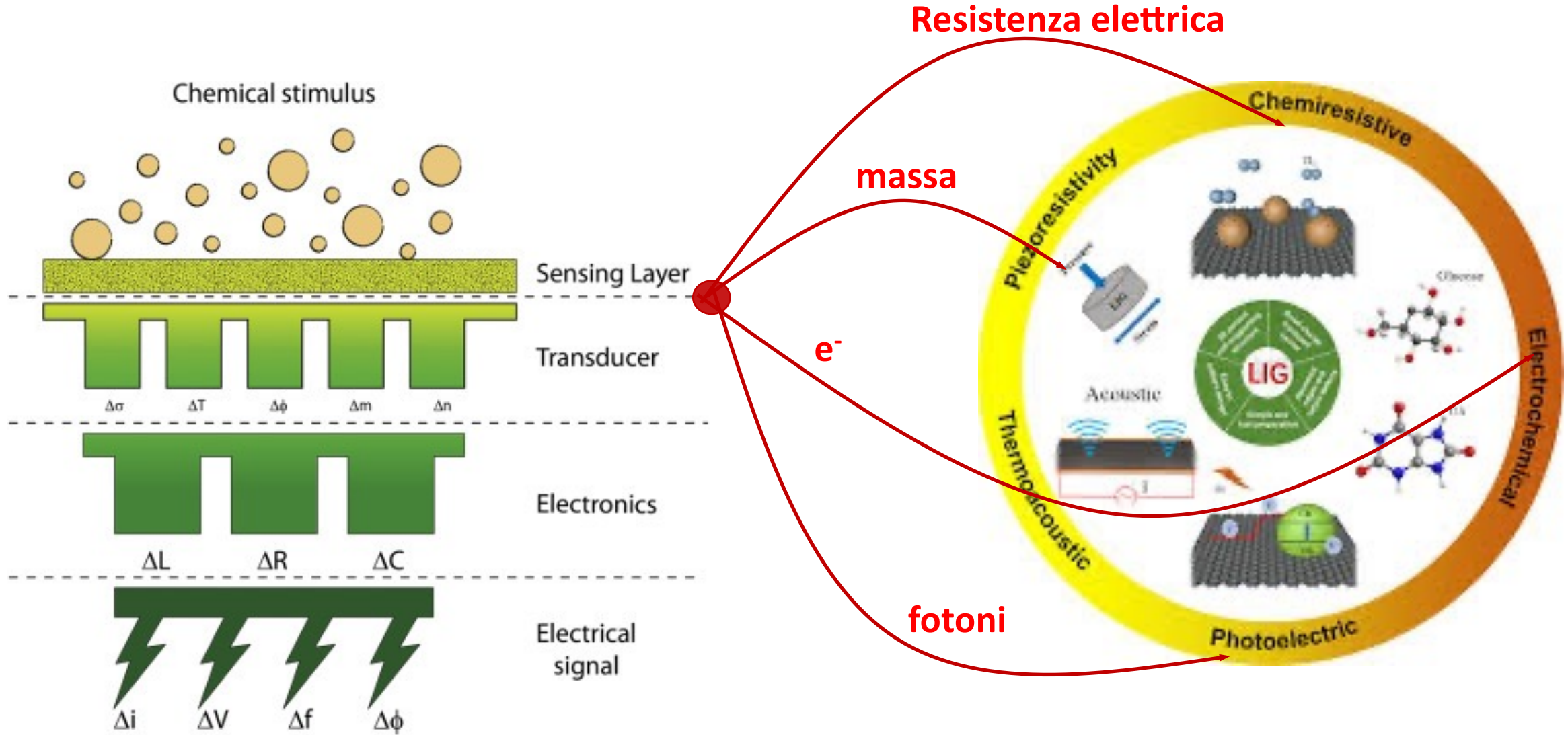


I sensori chimici sono dispositivi di misura che convertono una proprietà **chimica** o **fisica** di un analita specifico in un segnale misurabile, la cui grandezza è normalmente proporzionale alla concentrazione dell'analita.

Proprietà chimica: reattività, carica, acido/base, struttura,

Proprietà fisica: massa

I sensori chimici



I sensori chimici

sensori elettrochimici

voltammetrici

amperometrici

potenziometrici

Table 2.1: Kinds of methods of electroanalytical chemistry based on quantities controlled and measured. I is the symbol for *electric current*, E is the symbol for *electrode potential* and Q is the symbol for *electric charge* [6].

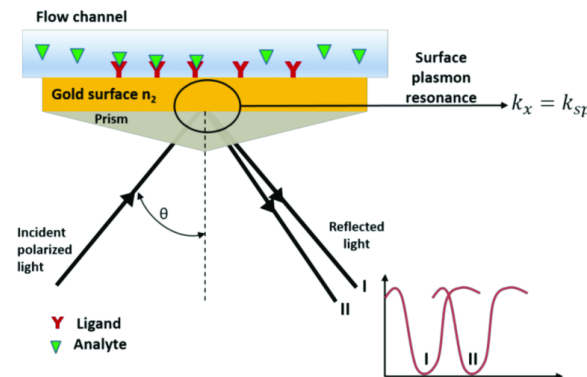
Method	Quantity measured	Quantity controlled
<i>potentiometry</i>	E	$I = 0$
<i>amperometry</i>	I	E
<i>voltammetry</i>	$I = f(t)$	$E = f(t)$
<i>direct coulometry</i>	$Q = \int_{t_1}^{t_2} I(t) dt$	$E = \text{constant}$
<i>conductometry</i>	conductivity (κ)	
<i>impedimetry</i>	electrical impedance (Z)	$E = \text{constant} + f(t)$

sensori ottici

assorbanza

emissione

indice di rifrazione



ELETTROANALITICA

L'elettrochimica è quella branca della chimica che si occupa dei processi che coinvolgono il trasferimento di elettroni: le reazioni di ossido-riduzione (dette comunemente redox).

Quando una specie può essere forzata a cedere o acquistare elettroni tramite l'applicazione di una differenza di potenziale è possibile sfruttare la misura della corrente prodotta per misura la concentrazione della specie stessa (ELETTROANALITICA).

I sensori elettrochimici: amperometrici e voltammetrici

Table 5.1-1: Classification of electrodes by size

Term	Definition	Reference	Note
macroelectrode	<i>Electrode with smallest dimension of order millimetre or greater.</i>	[11] p 45	(1)
microelectrode	<i>Electrode with smallest dimension of less than 1 millimetre and greater than 1 micrometre.</i>		(1), (2), (3), (4), (5)
ultramicroelectrode (UME) (obsolete, not recommended)	<i>Electrode with smallest dimension of less than 25 micrometre.</i>	see [11] p 592, and [11] p 945	(1), (3)
nanoelectrode (NE)	<i>Electrode with smallest dimension less than 1 micrometre</i>	[11] p 608	(5), (6)
not recommended: nanode		See also [22, 23]	

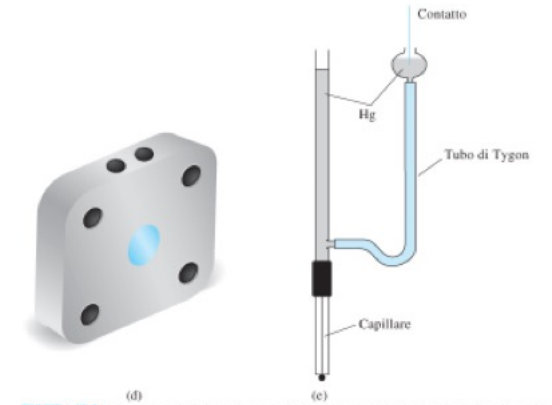
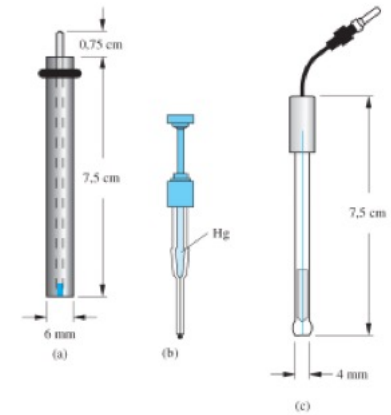


FIGURA 23.3 Alcuni esempi di elettrodi commerciali per la voltammetria. (a) Elettrodo a disco. (b) Elettrodo a goccia pendente di mercurio (HMDE). (c) Microelettrodo. (d) Elettrodo multianalitico a flusso. (e) Elettrodo a gocciolamento di mercurio (DME). (Ristampato con il permesso di Bioanalytical Systems, Inc., West Lafayette, IN.)



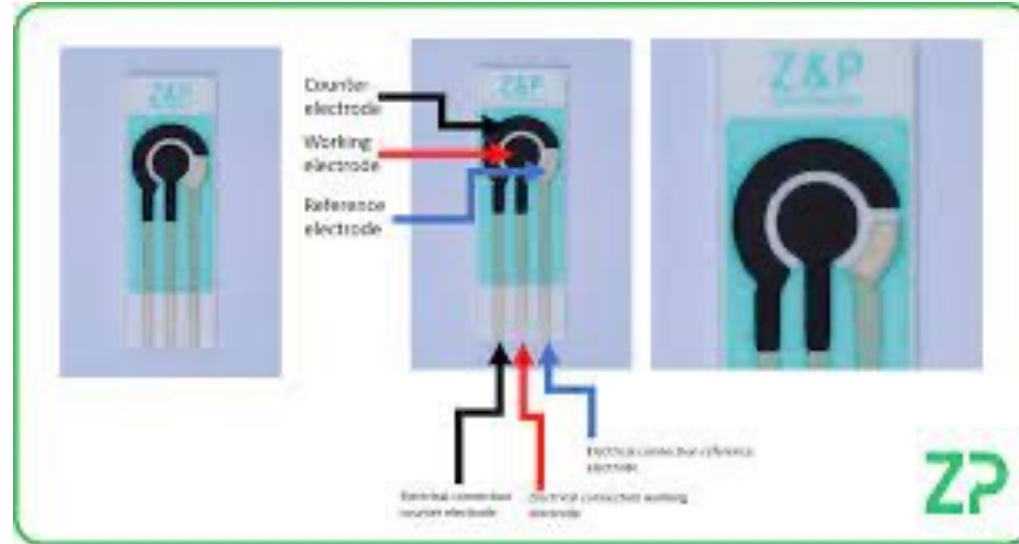
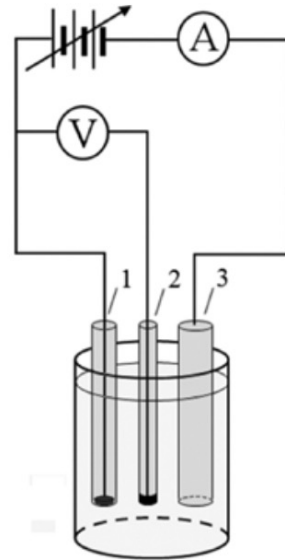
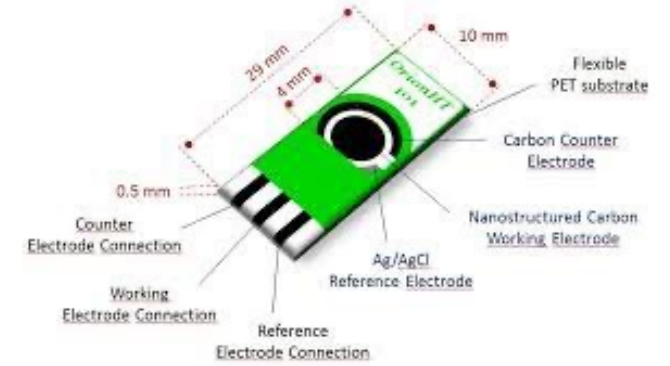
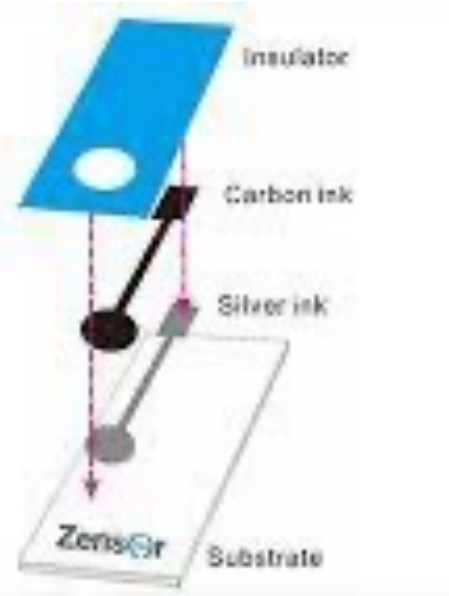
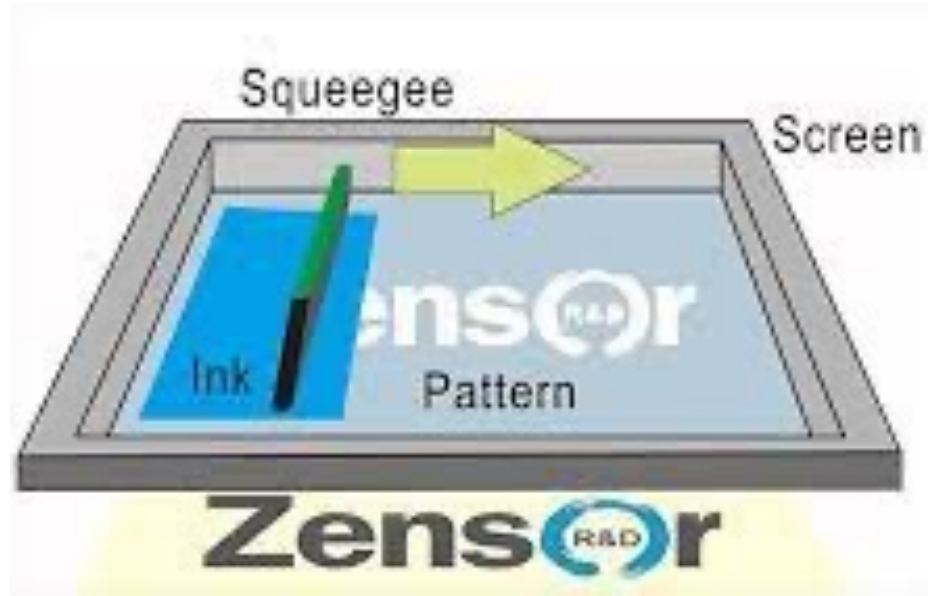
Platino



Screen printed electrode

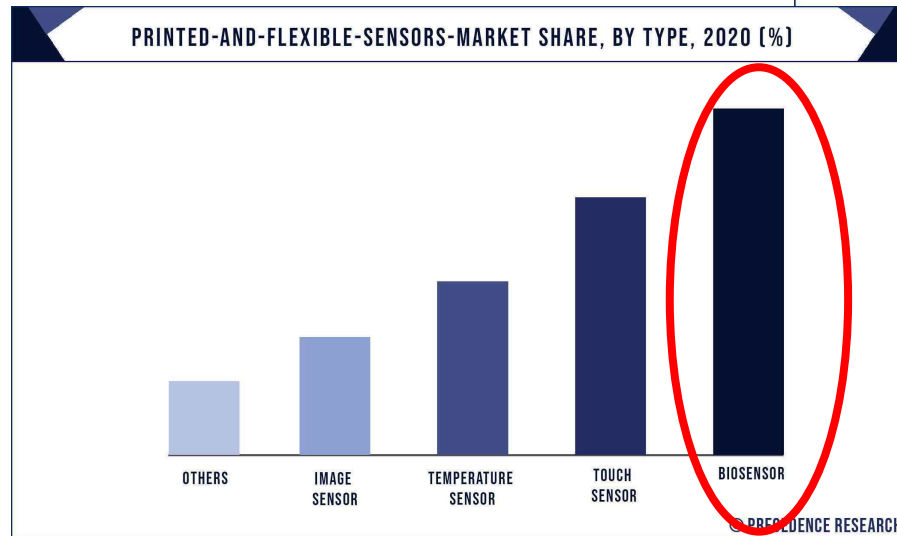
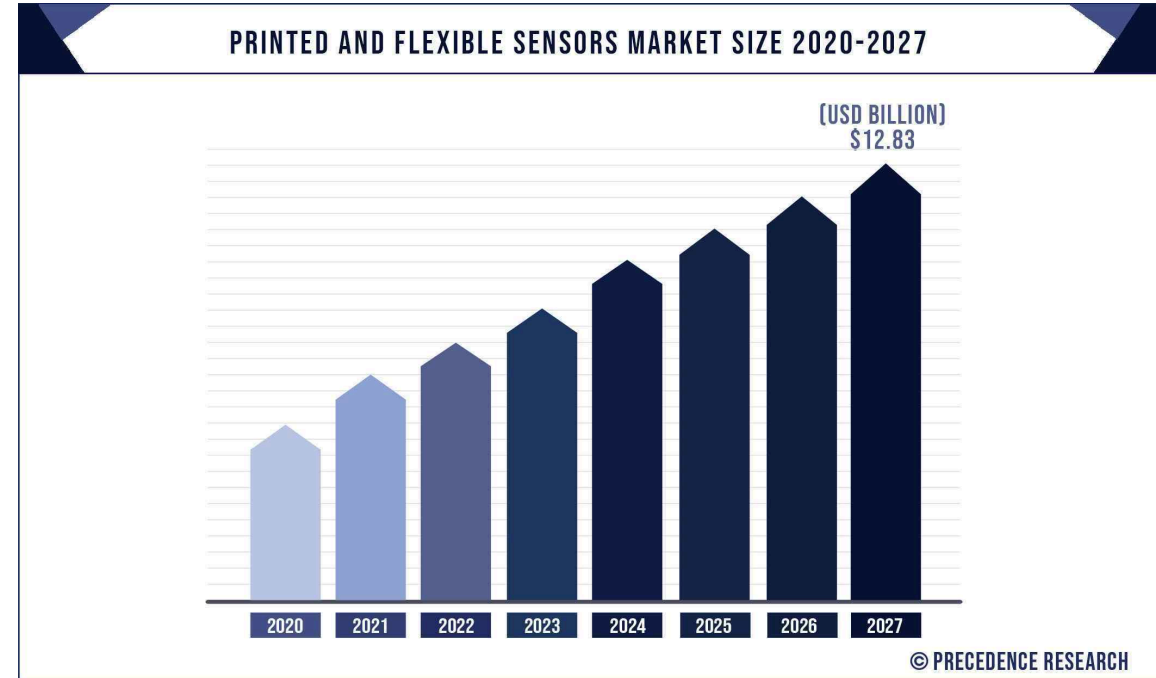


Screen printed electrode



Principali Compagnie del Mercato degli elettrodi screen printed

- Metrohm DropSens
- Boyd GMN
- Eastprint Incorporated
- Bioanalytical Systems
- PalmSens
- Quasense
- Gamry Instruments



APPLICAZIONI DEI SENSORI ELETTROCHIMICI ALLE ANALISI DI ALIMENTI

Sensori elettrochimici

Elettrochimica diretta

Piattaforma per lo sviluppo di Biosensori

CME

Chemically modified electrode

bare electrode

ES1: MISURA DI CONCENTRAZIONE

ES2: MISURA DI UN'ATTIVITA'

ES3: MISURA DI CONTAMINANTI

ELECTROANALYSIS

An International Journal Devoted to Electroanalysis, Sensors and Bioelectronic Devices

Full Paper

Gold Nanoparticles in Nonenzymatic Electrochemical Detection of Sugars

Fredy Kurniawan, Vessela Tsakova, Vladimir M. Mirsky ✉

First published: 19 October 2006 | <https://doi.org/10.1002/elan.200603607> | Citations: 111

Detection of Sugars

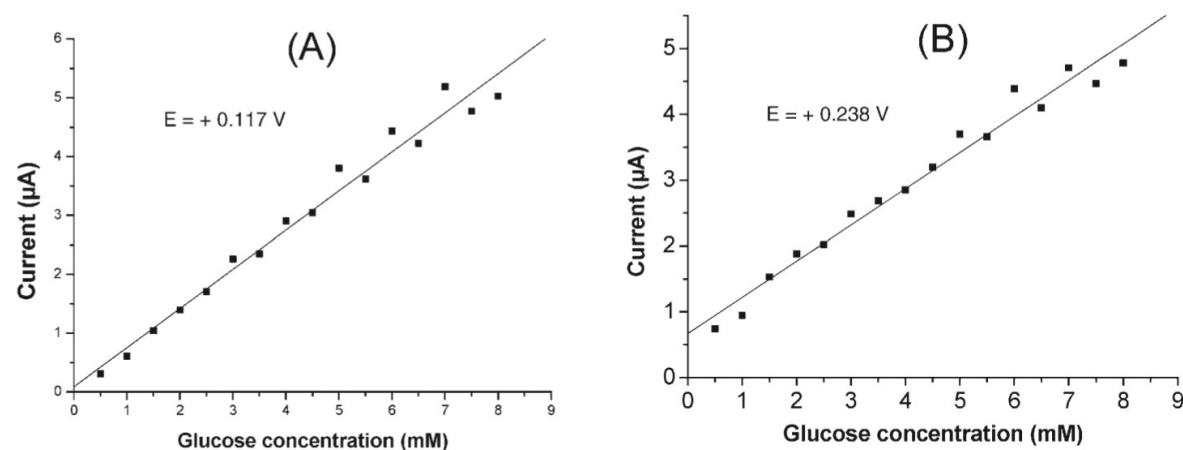


Fig. 6. Dependence of the currents measured at cathodic direction of the potential sweep at the potential +0.117 V (A) and at the anodic direction of the potential sweep at the potential +0.238 V (B). The measurement conditions are indicated in Figure 5.

Bare gold electrode e gold electrode modificato con nanoparticelle d'oro

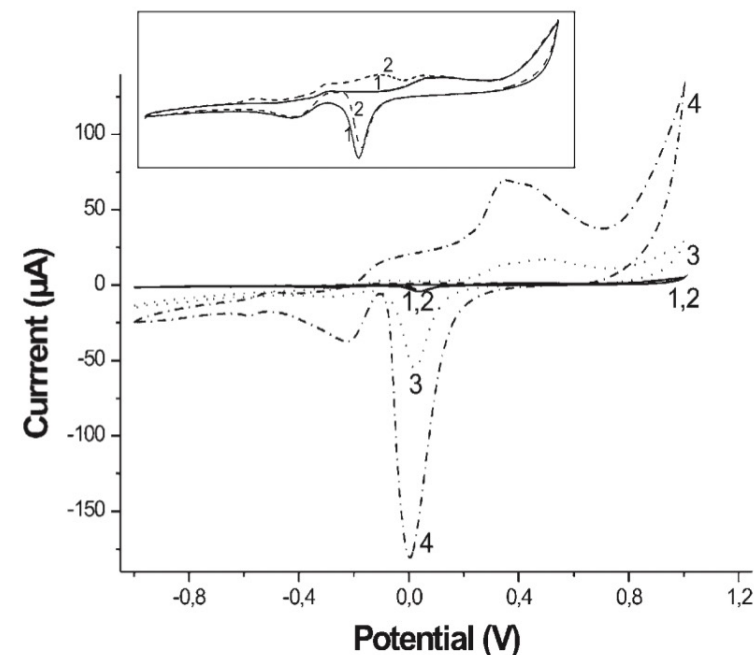


Fig. 4. Voltammograms of uncoated gold electrodes (curves 1, 3) and gold electrodes coated by a layer consisting from polyacrylic acid and gold nanoparticles (curves 2, 4) in 0.1 M NaOH in the absence (curves 1, 2) and in the presence (curves 3, 4) of 0.5 mM glucose. Sweep rate: 20 mV/s. Inset: curves 1 and 2 with magnification of the current scale.

Evaluation of the Antioxidant Capacity of Individual Phenolic Compounds in Virgin Olive Oil

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D. COMPAGNONE,[§] AND A. FERNÁNDEZ-GUTIÉRREZ[†]

HPLC SEMIPREPARATIVA

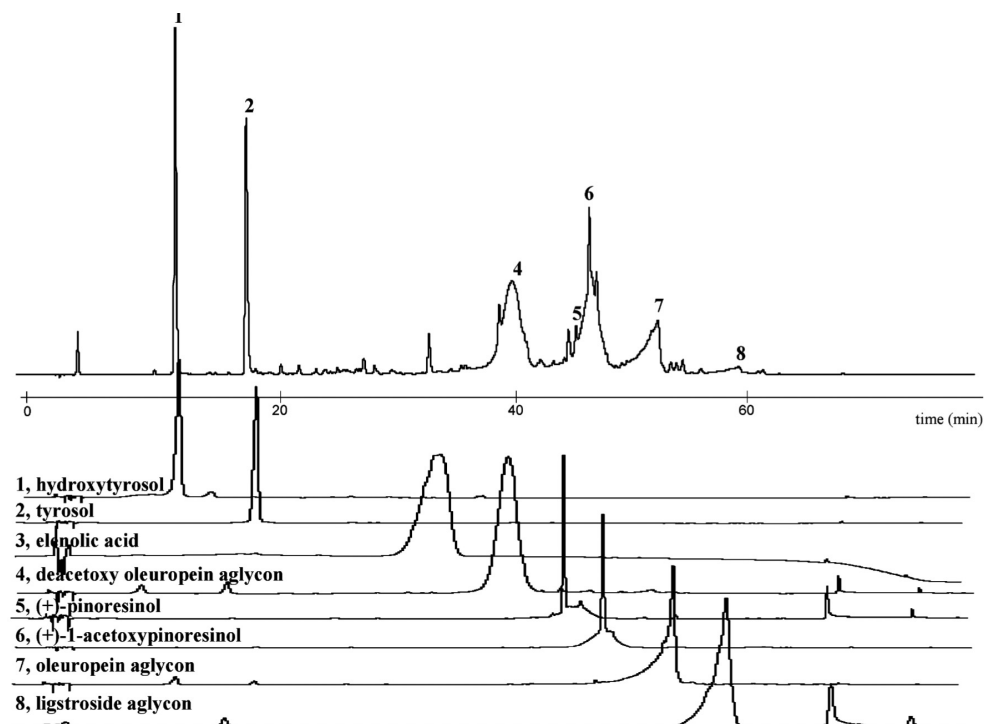


Figure 2. Chromatograms of extra VOO sample and the isolated phenolic compounds under optimized conditions using analytical HPLC. Detection was performed at 280 nm (only in the analysis of elenolic acid, number 3, the detection was performed at 240 nm).

POTERE ANTIRADICALICO

Table 3. Values of DPPH Test for the Isolated Phenolic Compounds at Two Different Concentrations and Order of Classification in Terms of Antiradical Power [Mean Values \pm SD ($n = 6$)]^a

	ARP (218 ppm)	classification	ARP (50 ppm)	classification
hydroxytyrosol	26.23 \pm 0.56	1	5.03 \pm 0.10	1
tyrosol	0.76 \pm 0.05	6	0.18 \pm 0.01	8
elenolic acid	0.69 \pm 0.04	7	0.29 \pm 0.01	7
deacetoxy	7.61 \pm 0.29	2	2.42 \pm 0.14	2
oleuropein aglycon				
(+)-pinoresinol	1.35 \pm 0.08	4	1.08 \pm 0.03	4
(+)-1-acetoxy- pinoresinol	0.60 \pm 0.03	8	0.30 \pm 0.01	6
oleuropein aglycon	6.11 \pm 0.12	3	1.54 \pm 0.03	3
ligstroside aglycon	0.79 \pm 0.04	5	0.38 \pm 0.03	5

^a ARP, antiradical power (in $\mu\text{mol/g}$).

OBIETTIVO: DIMOSTRARE CHE CON UN BARE ELETTRODO DI GLASSY CARBON E' POSSIBILE AVERE INFORMAZIONI SULL'ATTIVITA' ANTIOSSIDANTE DELLE MOLECOLE CON STRUTTURA FENOLICA

IPOSTESI: MAGGIORE E' LA SUSCETTIBILITA' ALL'OSSIDAZIONE ELETTROCHIMICA MAGGIORE E' LA ATTIVITA' ANTIOSSIDANTE DELLA MOLECOLA

APPARATO: CELLA A FLUSSO CON SENSORE IN GLASSY CARBON, POTENZIOSTATO PORTATILE

TECNICHE: VOLTAMMETRIA IDRODINAMICA E VOLTAMMETRIA CICLICA

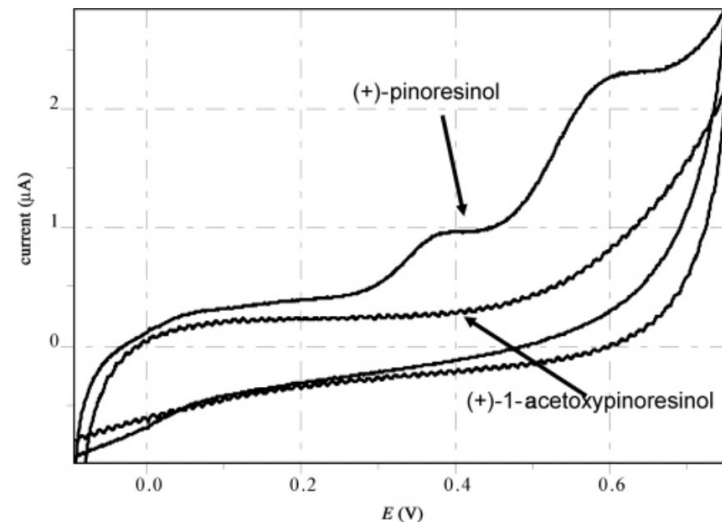
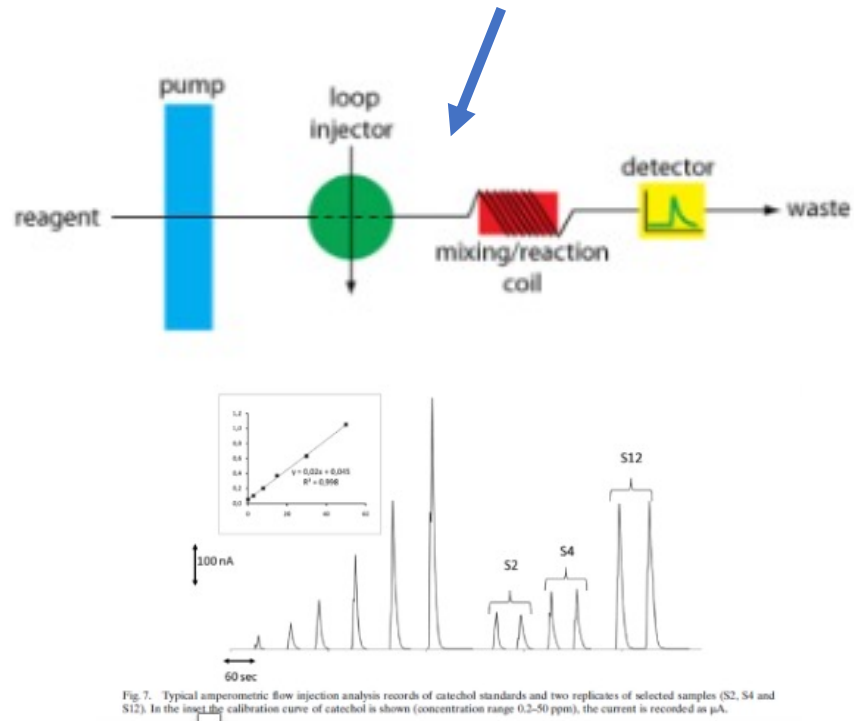


Figure 3. Cyclic voltammograms of (+)-pinoresinol and 1-(+)-acetoxypinoresinol.

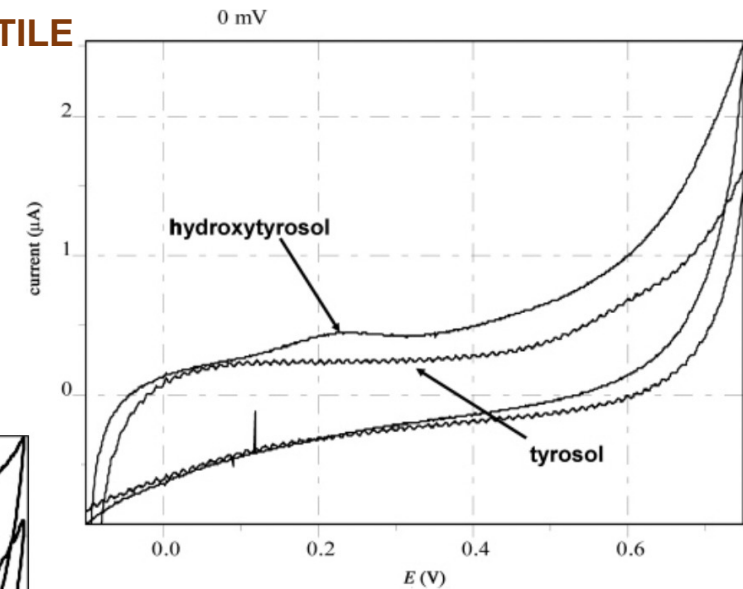
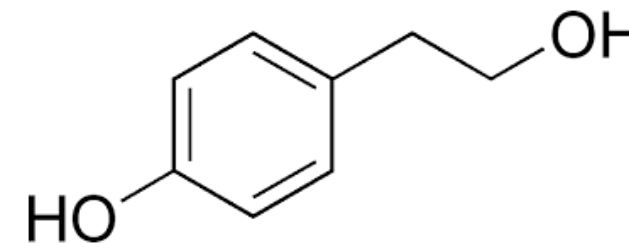
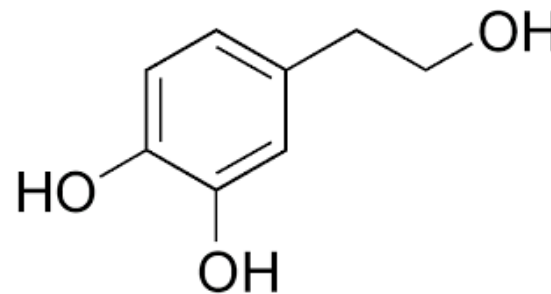


Fig. 4. Cyclic voltammograms of hydroxytyrosol and tyrosol.

Table 5. Plateau Potential Regions (E_{ox}) Evaluated by Hydrodynamic Voltammetry (HV)^a

	E_{ox} (HV) mV vs Ag/AgCl	AOP classification
hydroxytyrosol	0.12–0.17	1
tyrosol	0.35	6
elenolic acid	inactive	7
deacetoxy oleuropein aglycon	0.15–0.30	4
(+)-pinoresinol	0.15–0.22–0.30	3
(+)-1-acetoxypinoresinol	0.22	5
oleuropein aglycon	0.15–0.20–0.30–0.40	2
ligstroside aglycon	inactive	7

^a The AOP classification is based on the lower oxidation potential.



Electron-donating substituents in the ortho position of phenolic molecules tend to weaken the O-H bond of phenol and provide extra stability to the phenoxyl radical. It is important to stress that the electrochemical oxidation of the phenolic moiety goes through the formation of a phenoxyl radical. Therefore, it can be assumed that the AOP, measured on the basis of electrochemical features (oxidation potential and current) of the phenolic molecules, may better describe the radical scavenging activity as previously hypothesized and experimentally shown (....) We verified that, as is generally assumed, the presence of a **single hydroxyl group confers a limited amount of antioxidant activity**. On the other hand, the **presence of an o-diphenol enhances the ability of the phenolic compounds to act as antioxidants**.

IONIX POTENTIOMETRIC STRIPPING ANALYZER

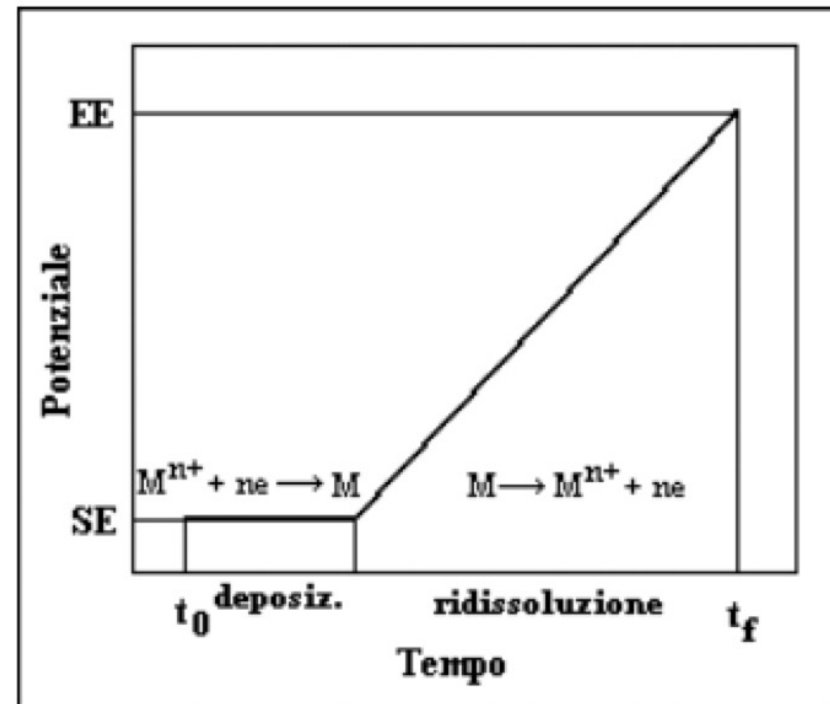
STEROGLASS - Italia

ALCUNI METALLI ANALIZZABILI

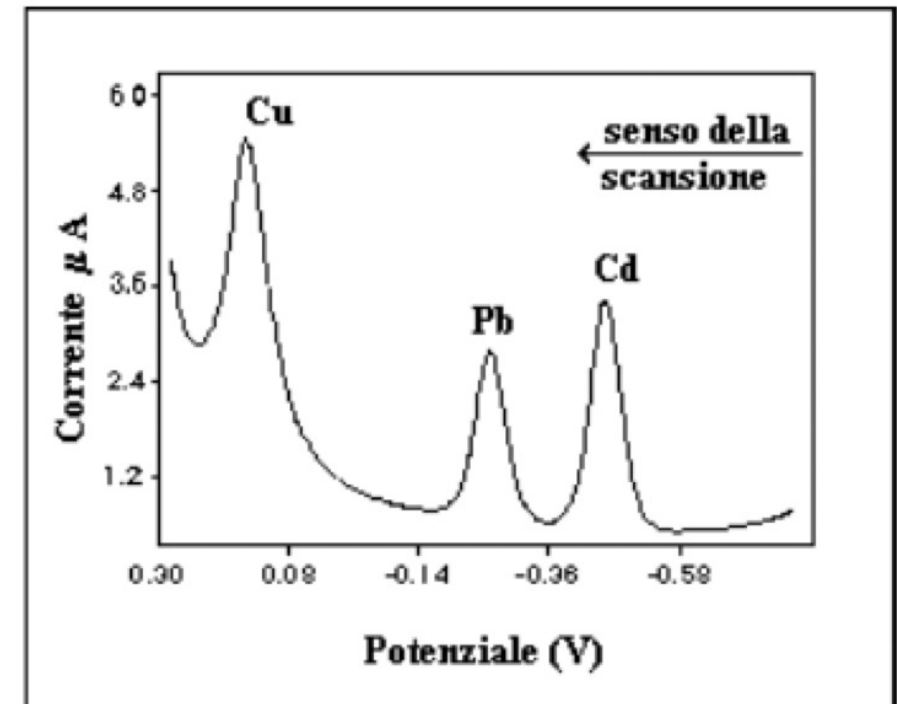
RAME - PIOMBO - CADMIO - ZINCO

CAMPI DI APPLICAZIONE

- Vino, birra, aceto, aceto balsamico, distillati, liquori



a



b

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Chemically Modified Electrodes

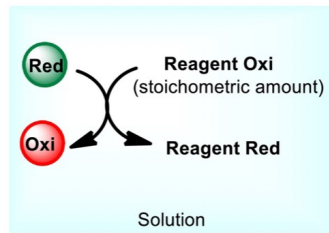
Chemically modified electrode can be defined as a conducting or semiconducting material that has been coated with a monomolecular, multi-molecular, ionic, or polymeric film.

From: [Handbook of Electrochemistry, 2007](#)

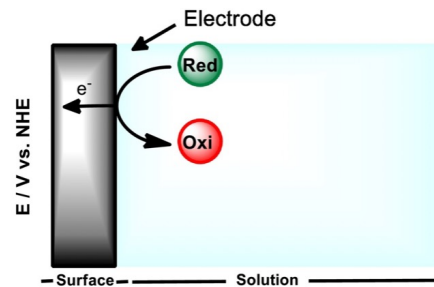
Le principali ragioni per costruire un CME sono maggiore selettività e sensibilità, stabilità chimica ed elettrochimica, maggiori finestre potenziali utilizzabili e resistenza alla passivazione.

Mediatore elettrochimico...maggiore selettività

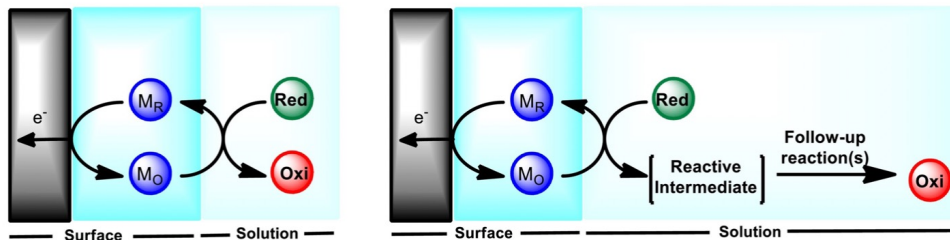
(A) Homogeneous phase



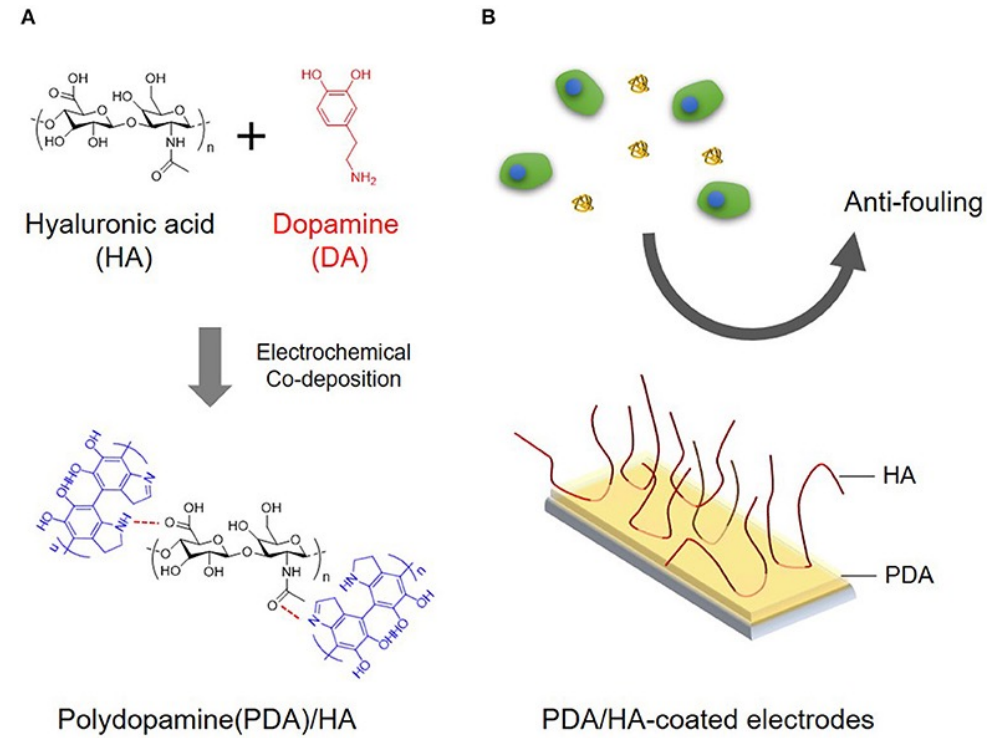
(B) Heterogeneous phase



(C) Heterogeneous and homogeneous phase



Membrane anti-fouling



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

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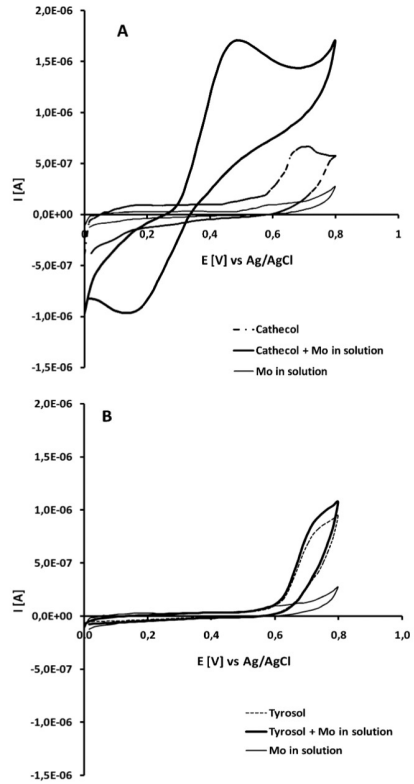


Fig. 2. Cyclic voltammograms of 50 μM catechol (A) and 50 μM tyrosol (B) with carbon paste electrode, the scan rate was 50 mV/s.



+ MEDIATORE

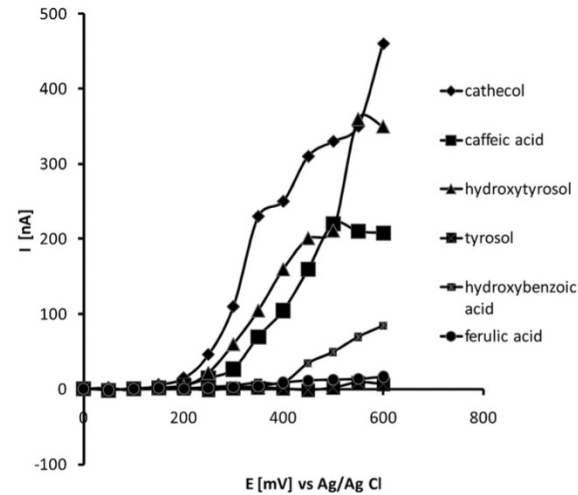
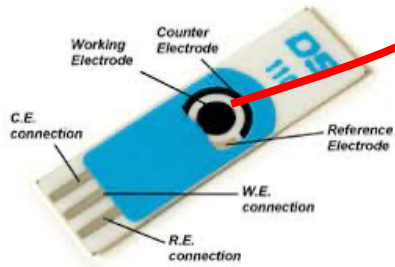


Fig. 5. Hydrodynamic voltammogram of catechol, caffeic acid, hydroxytyrosol, tyrosol, hydroxybenzoic acid, ferulic acid. Comparison of the electrochemical behavior in presence of Na_2MoO_4 .

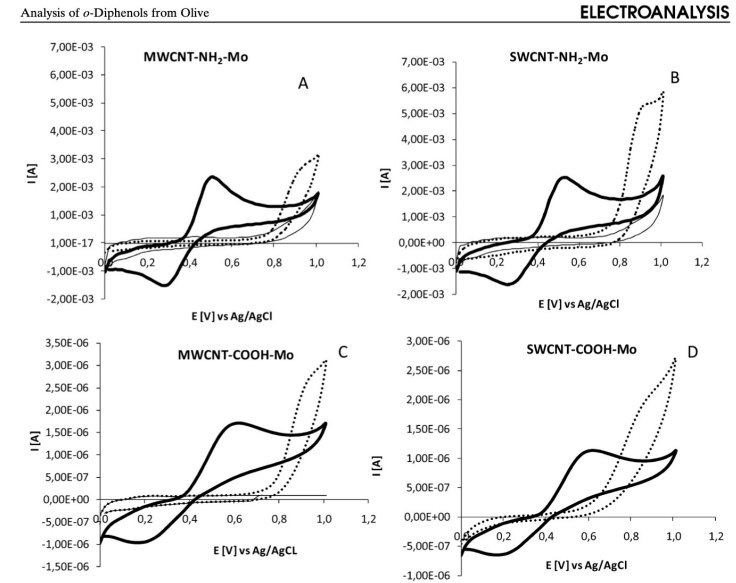


Fig. 4. Comparison of the mediated electrochemical response of the four CNTs chemically modified nanosensor to catechol and tyrosol.

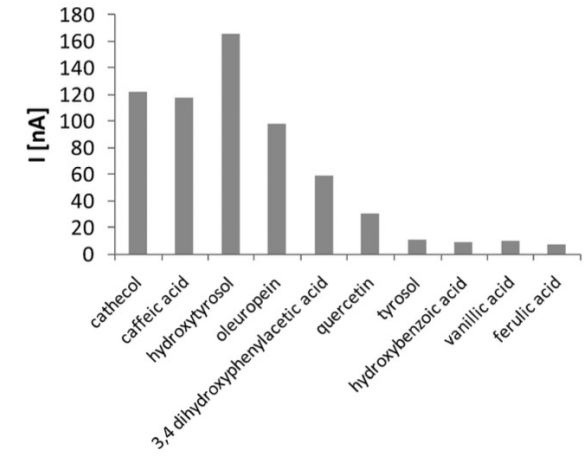


Fig. 6. Selectivity of the FIA amperometry method using a potential of +380 mV; standard concentration was 20 $\mu\text{mol L}^{-1}$.

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Microchimica Acta (2019) 186: 363
https://doi.org/10.1007/s00604-019-3418-5

ORIGINAL PAPER

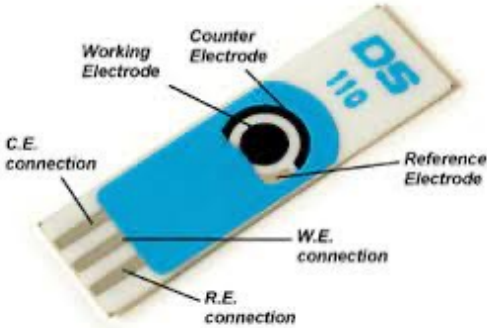
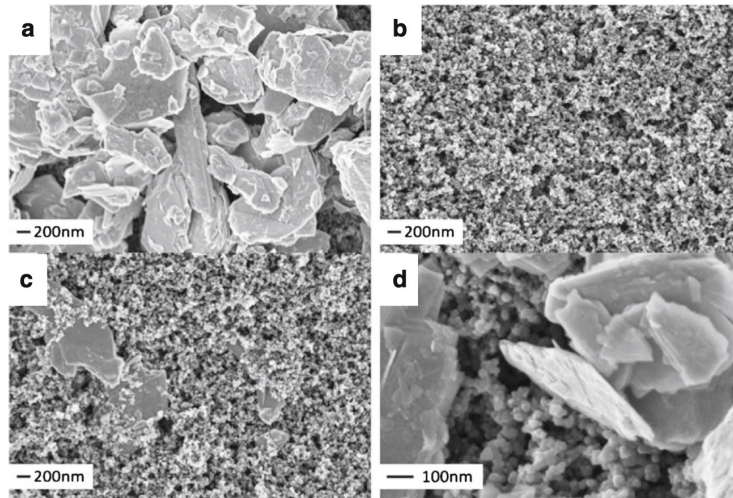


Nanohybrid carbon black-molybdenum disulfide transducers for preconcentration-free voltammetric detection of the olive oil o-diphenols hydroxytyrosol and oleuropein

Daniel Rojas^{1,2} · Flavio Della Pelle¹ · Michele Del Carlo¹ · Emiliano Fratini³ · Alberto Escarpa^{2,4} · Dario Compagnone¹

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Fig. 2 SEM micrographs of a) exfoliated MoS₂, b) CB, c) and d) CB-MoS₂ hybrid at 75:25 ratio with magnification of 50 kX and 200 kX, respectively



Dispersioni di CB e MoS₂ sono state preparate in DMF-H₂O sonicando per 6 ore mantenendo il temperatura inferiore a 25 °C. la superficie dello SPE è stata modificata per drop-casting

Obiettivo: migliorare le prestazioni analitiche della grafite combinando a materiale nanostrutturato un mediatore elettrochimico anch'esso nano strutturato

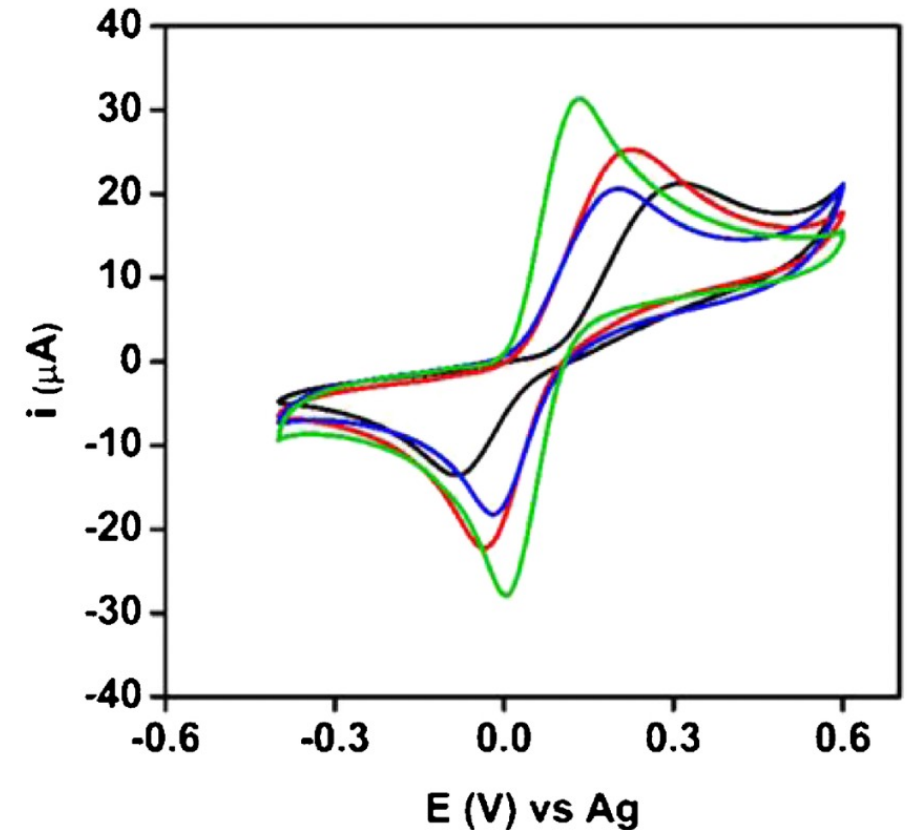


Fig. 3 CV of 1 mM Catechol in Phosphate Buffer (50 mM, 0.1 M KCl, pH=7) at SPE (black), CB (red), MoS₂ (blue) and MoS₂-CB (green). Scan rate of 50 mV s⁻¹



Nanohybrid carbon black-molybdenum disulfide transducers for preconcentration-free voltammetric detection of the olive oil o-diphenols hydroxytyrosol and oleuropein

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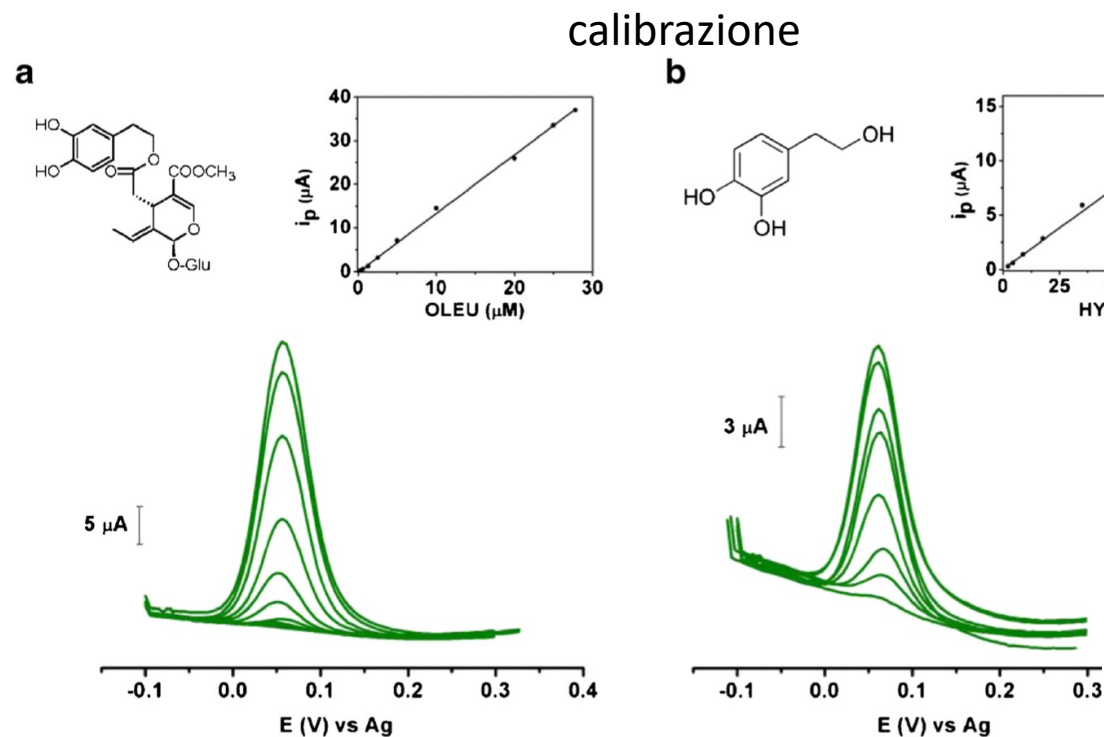


Fig. 5 DP voltammograms for calibration concentrations of **a**) OLEU and **b**) HYT in Phosphate Buffer (50 mM, 0.1 M KCl, corresponding calibration plot. The DPV parameters were: pulse amplitude of 25 mV and a scan rate of 50 mV s⁻¹

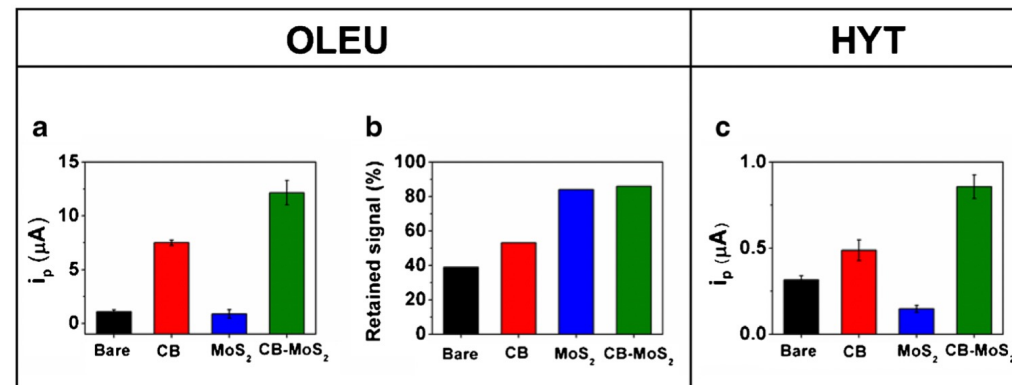


Fig. 4 **a**) DPV peak current intensities for OLEU **b**) fouling resistance of each SPE ($n = 10$ consecutive measurements of OLEU) and **c**) DPV peak current intensities for HYT. Experiments carried out in Phosphate Buffer (50 mM, 0.1 M KCl, pH = 7) containing 10 and 5 μM of OLEU and HYT respectively with pulse amplitude of 25 mV and a scan rate of 50 mV s⁻¹

Campioni reali

Table 2 Quantitative determination of o-diphenols in EVOO and related samples using CB-MoS₂-based electrochemical sensor and HPLC

Sample	CB-MoS ₂ -electrochemical sensor ^a		HPLC-UV ^b	
	OLEU eq. (mg Kg ⁻¹)	RSD (%)	o-diphenols (mg Kg ⁻¹)	RSD (%)
Dietary Supplement	5708 ± 562	10	5534 ± 277	5
Olive Leaf 1	1286 ± 55	4	1302 ± 91	7
Olive Leaf 2	1193 ± 97	8	1007 ± 50	5
EVOO 1	129 ± 16	13	115 ± 2	2
EVOO 2	156 ± 15	12	164 ± 18	11
EVOO 3	45 ± 3	7	36 ± 6	15

Results expressed as mean value ± standard deviation ($n = 3$), RSD = Relative Standard deviation

^a Expressed as OLEU equivalents, ^b Expressed as sum of each individual OLEU and HYT

APPLICAZIONI DEI SENSORI ELETTROCHIMICI ALLE ANALISI DI ALIMENTI

Sensori elettrochimici

Elettrochimica diretta

Piattaforma per lo sviluppo di Biosensori

CME

Chemically modified electrode

bare electrode

ES1: MISURA DI CONCENTRAZIONE

ES2: MISURA DI UN'ATTIVITA'

ES3: MISURA DI CONTAMINANTI

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Talanta 253 (2023) 124010

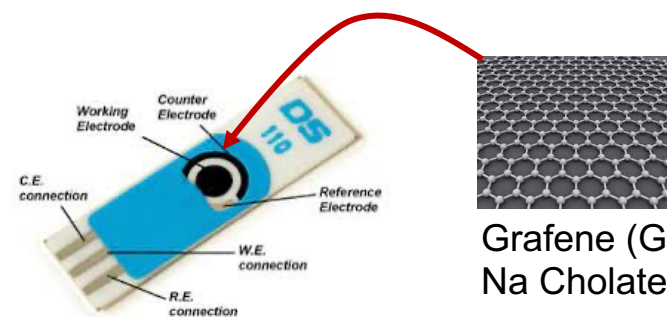
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Liquid-phase exfoliated 2D graphene nanoflakes electrochemical sensor coupled to molecularly imprinted polymers for the determination of citrinin in food

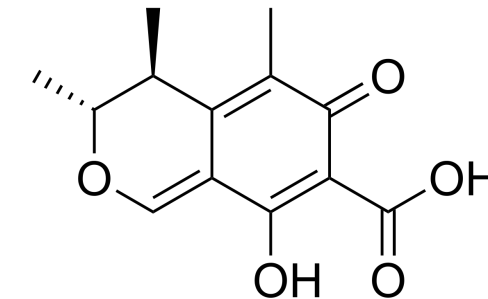
Dounia Elfadil^{a,b,1}, Filippo Silveri^{a,1}, Sara Palmieri^a, Flavio Della Pelle^{a,*}, Manuel Sergi^a, Michele Del Carlo^a, Aziz Amine^{b,**}, Dario Compagnone^a



Grafene (GF)
Na Cholates (SC)

L'esfoliazione della grafite, per ottenere nanoflakes di grafene è stata eseguita disperdendo grossolanamente 50 mg di grafite e 5 mg di SC in 5 ml di acqua; La dispersione è stata sottoposta a sonicazione pulsata per 1,5 ore.

Citrinin (CIT) è una micotossina prodotta come metabolita secondario da diversi tipi di funghi ubiquitari contaminanti, (*Penicillium*, *Aspergillus*) può essere prodotta principalmente durante i trattamenti post-raccolta e lo stoccaggio



(3R,4S)-4,6-dihydro-8-hydroxy-3,4,5-trimethyl-6-oxo-3H-2-benzopyran-7-carboxylic acid

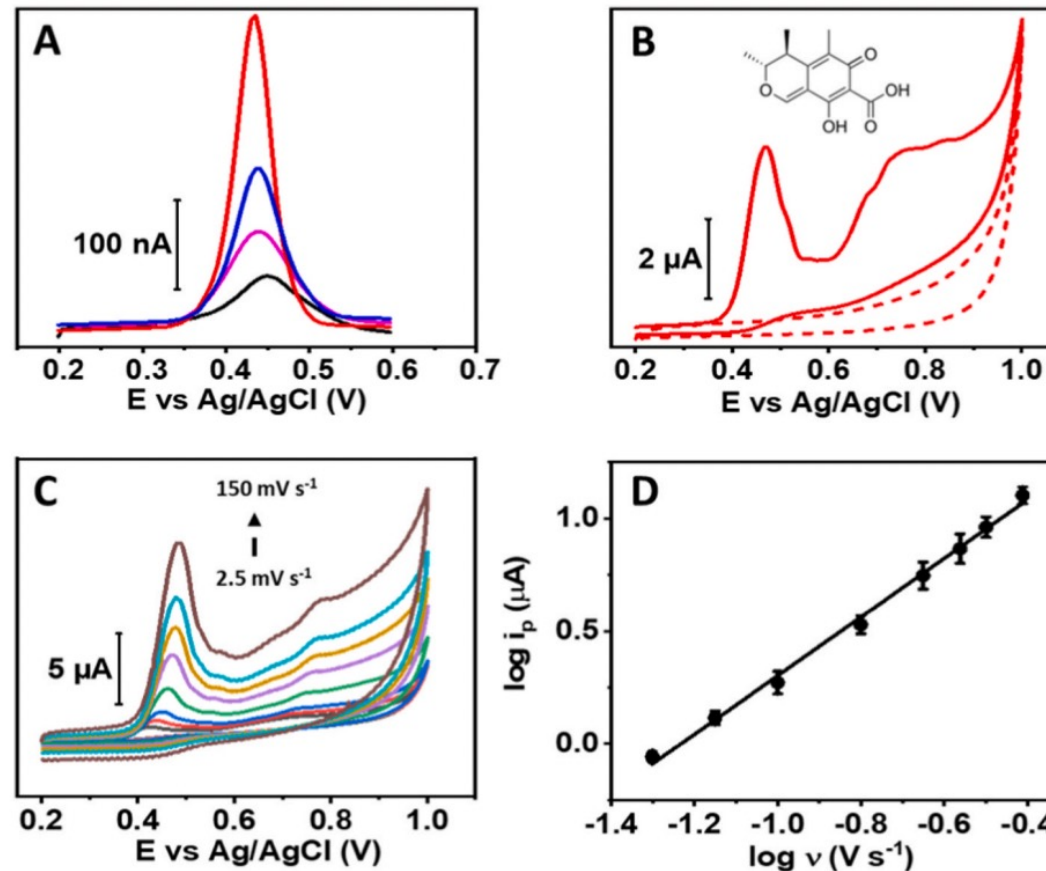


Fig. 1. (A) Differential pulse voltammograms of 2.5 μM CIT in PB obtained at a graphite-SPE (black curve), and at the GF-SC (red curve), CB-SC (blue curve), and CNTs-SC (magenta curve) modified electrodes. (B) Cyclic voltammograms obtained at the GF-SC electrode in the absence (dotted curve) and presence (full curve) of 200 μM CIT; measurements carried out in PB at 25 mV s^{-1} . Inset: chemical structure of citrinin. (C) Cyclic voltammograms of 200 μM CIT at GF-SC electrode performed at increasing scan rate (from 2.5 to 150 mV s^{-1}) in PB. (D) Linear relationship between the logarithm of CIT peak intensity current and the logarithm of the scan rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Ottimizzazione delle condizioni di misura

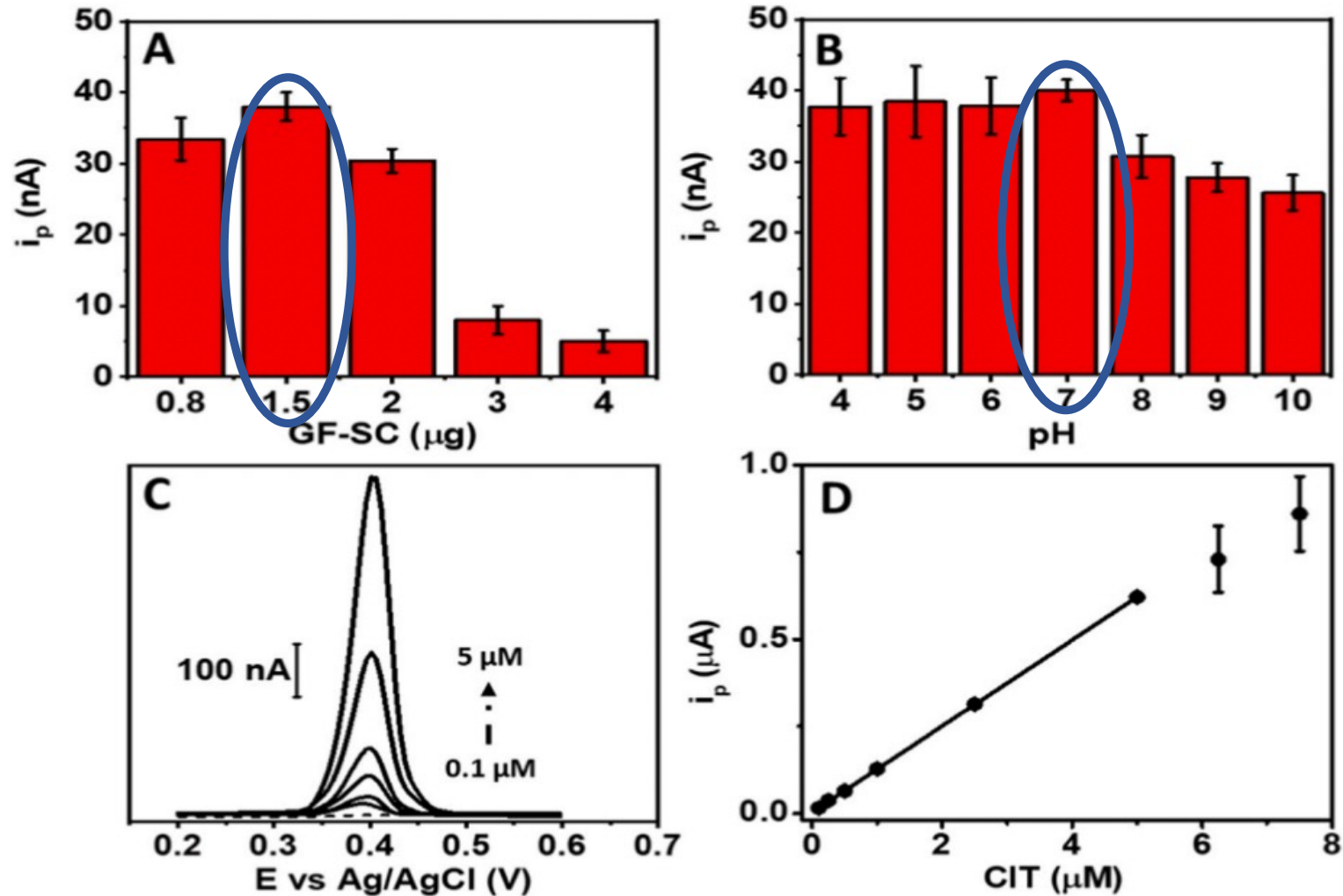


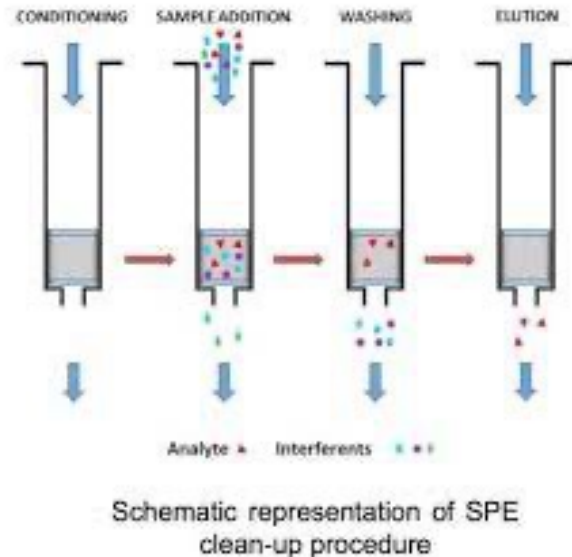
Fig. 3. (A) DPV peak currents obtained for 2.5 μM CIT analyzed at SPE modified with different amounts of GF-SC. (B) DPV peak currents obtained for 2.5 μM CIT at different measurement pH. (C) Different pulse voltammograms obtained for increasing concentrations of CIT (full lines) (0.1–5 μM) and blank measure (dashed line) at the GF-SC electrode. (D) Dose-response curve for increasing concentration of CIT obtained at GF-SC electrode.

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Come superare i problemi legati alla matrice e agli interferenti?

CIT si trova principalmente nelle matrici vegetali, con altri costituenti (ad es. composti fenolici, zuccheri, vitamine, pigmenti, ecc.) che possono influenzare la misura, quindi **l'estrazione/purificazione** selettiva della CIT dalla matrice campione è necessaria.

A questo scopo, usiamo un'un'estrazione in fase solida basata su **MIP** (MIP-SPE).



Cosa sono i MIP?

I polimeri a stampo molecolare (MIP- **Molecularly Imprinted Polymer**) sono strutture con "memoria" di forma e gruppi funzionali affini ad una molecola stampo. Tale materiale riconosce selettivamente la molecola stampo usata nel processo di polimerizzazione, anche in presenza di composti con struttura e funzionalità simili a quelle della molecola stampo.

Come funziona un MIP

I polimeri a stampo molecolare hanno un comportamento simile a quello degli anticorpi. Diverse molecole possono essere utilizzate al fine di ottenere elevato riconoscimento molecolare.

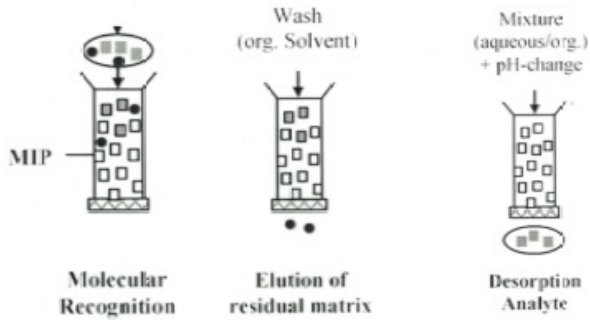
Come si ottiene un MIP

1- Lo stampo molecolare è un processo di polimerizzazione in cui monomeri specifici (scelti in base ai loro gruppi funzionali) vengono fatti auto assemblare intorno ad una molecola stampo in presenza di crosslinker.

2- Successivamente la molecola stampo viene rimossa dal polimero prodotto, si formano così cavità complementari in forma e funzionalizzazione (alla molecola stampo) che successivamente legheranno composti omologhi o strutturalmente simili alla molecola stampo.

Chemically modified electrode (CME): APPLICAZIONI ALL'ANALISI DI ALIMENTI

Come superare i problemi legati alla matrice e agli interferenti?



Estrazione/purificazione su colonna impaccata con MIP-CIT specifico

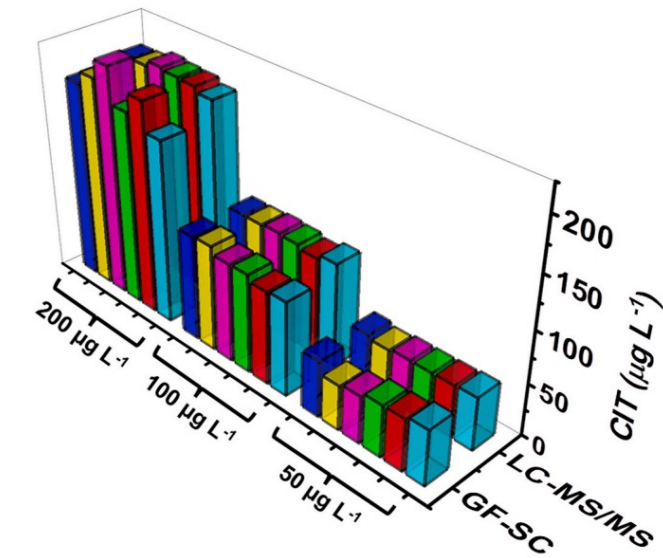


Fig. 5. 3D histogram of CIT spiked samples determined using the GF-SC sensor and the LC-MS/MS reference method. Rice starch (blue bar), wheat germ (yellow bar), turmeric (green bar). Red rice (red bar), blueberry (cyan bar), maize (magenta bar). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

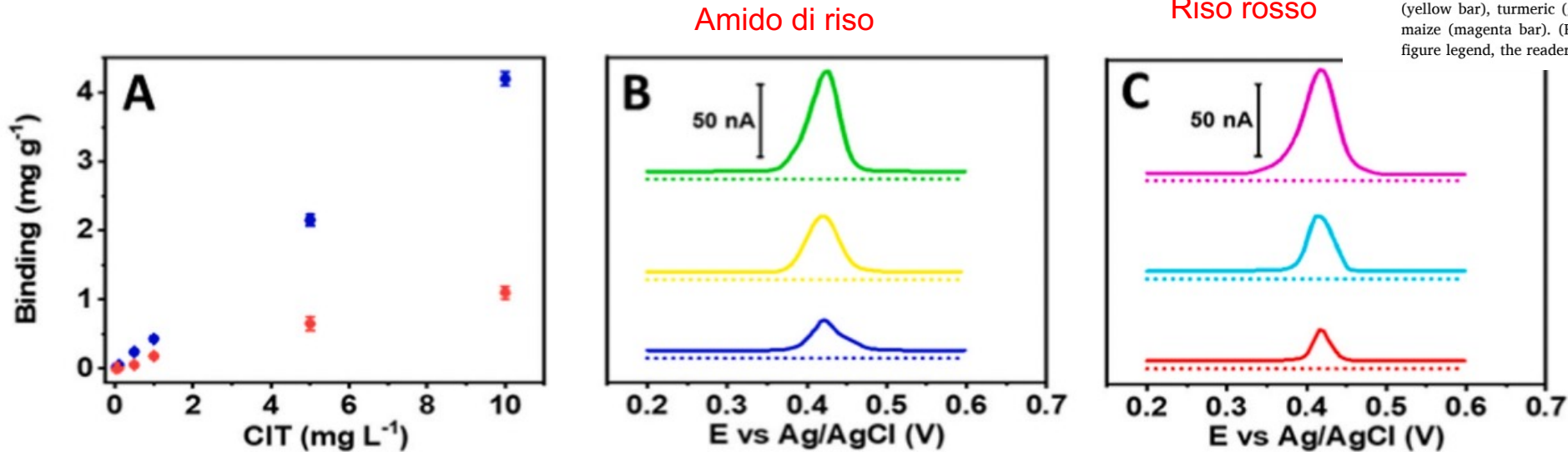


Fig. 4. (A) Absorption isotherm of MIP (blue) and NIP (red) obtained by studying increasing concentrations of CIT (from 0.025 to 10 mg L^{-1}); CIT determination performed using LC-MS/MS. Differential pulse voltammograms of CIT spiked (full curves) and unspiked (dotted curves) samples at GF-SC electrode: (B) rice starch (blue, 50 μM), wheat germ (yellow, 100 μM) and turmeric (green, 200 μM); (C) red rice (red, 50 μM), blueberry (cyan, 100 μM) and maize (magenta, 200 μM). The voltammograms have been staggered for graphic reasons. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)