Gruppo Sensori –
Laboratorio di Chimica Analitica
Dipartimento di Chimica,
Università di Pavia

via Taramelli 12, 27100 PAVIA; Italy
maria.pesavento@unipv.it

M. Pesavento,
A. Profumo,
R. Biesuz,
G. Alberti,
M. Sturini,
G. D'Agostino,
D. Merli,
L. Cucca,
A. Speltini,
B. E. Rivagli

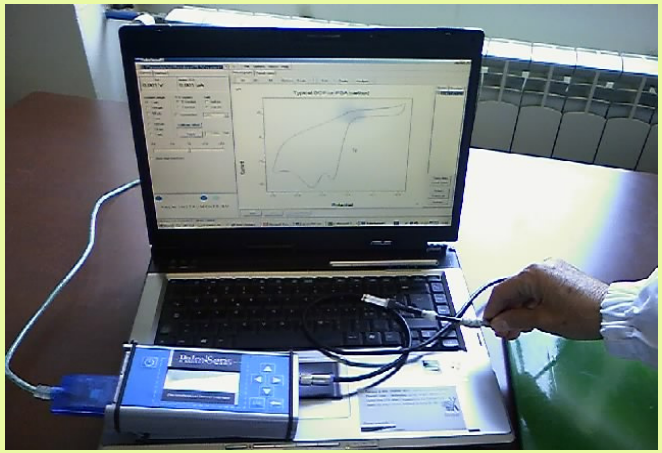
Topics:

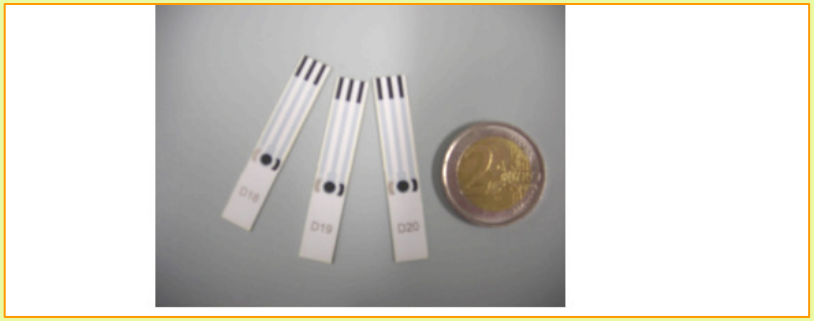
-Molecularly Imprinted Polymeric Membranes for label free electrochemical sensors

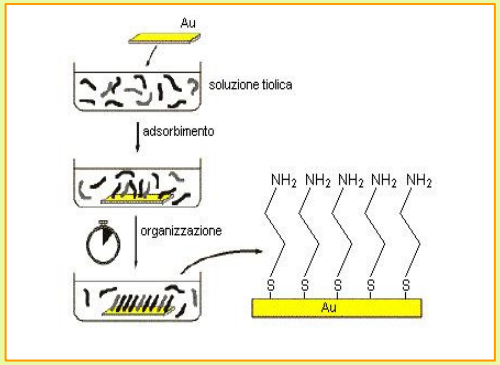
-Surface modified electrodes

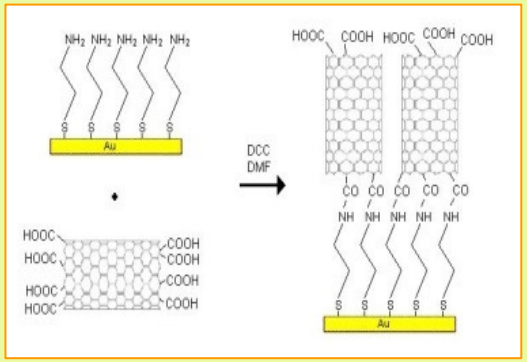
-Miniaturization

- Implementation of screen printed electrodes

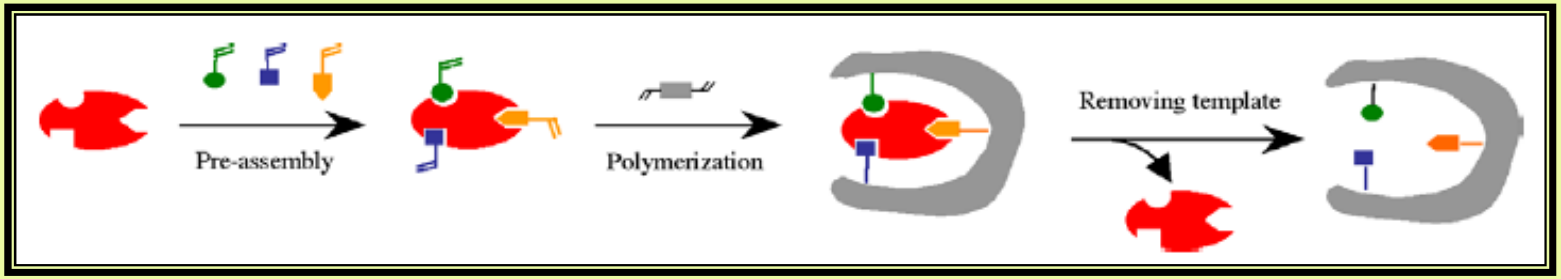




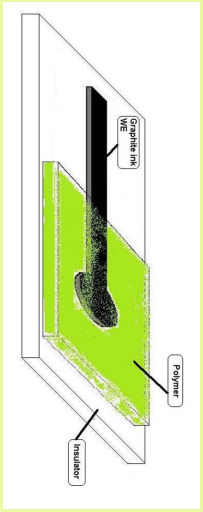


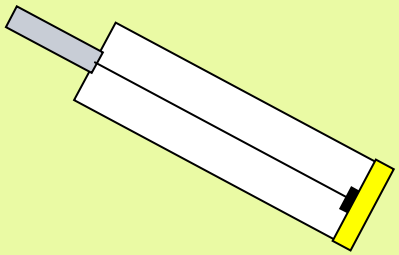


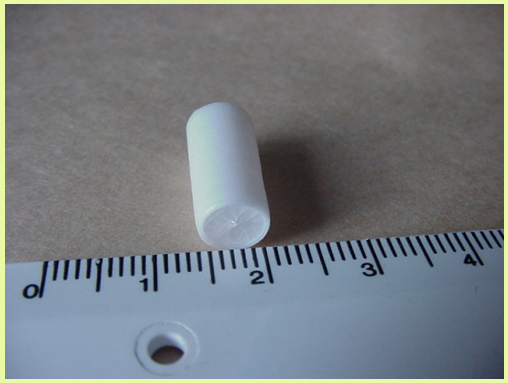
Molecularly imprinted polymers (MIP)



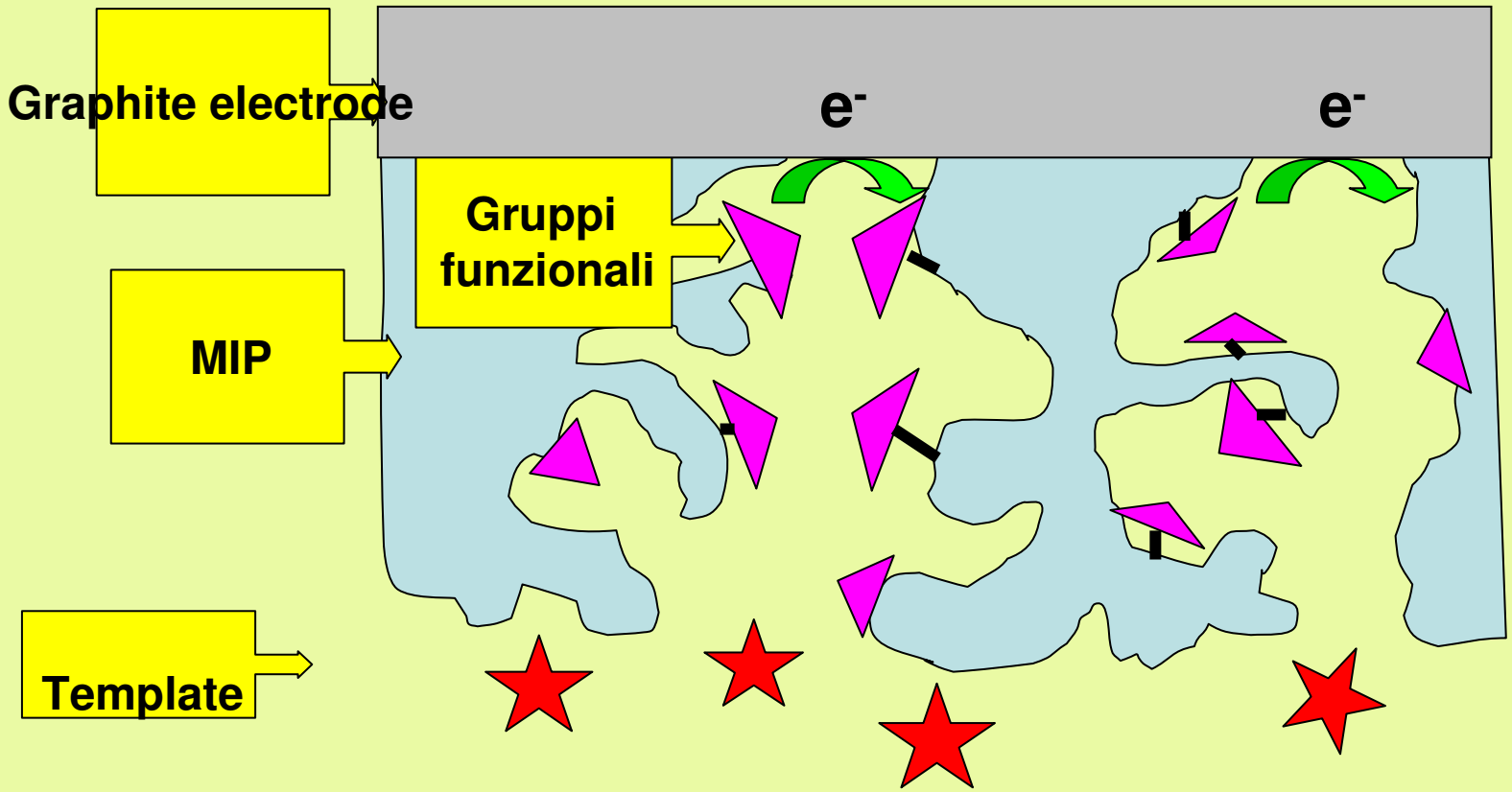
The polymer membrane is directly cast on the conducting surface or is prepared as a monolith at the end of a Teflon tube in a suitable device







Amperometric response of electroactive species

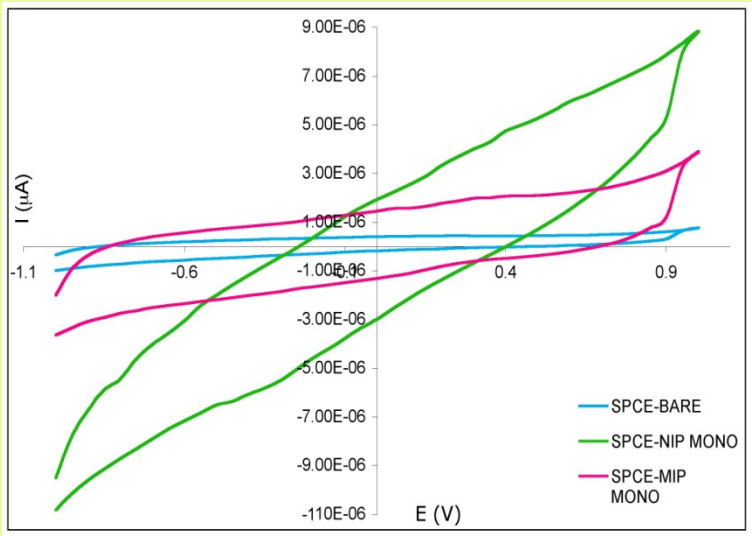


Reducible species: nitroaromatic compounds (M. Pesavento, G.D'Agostino, R. Biesuz, G. Alberti, V. Vacchelli, EUROANALYSIS 2009, Innsbruck, 6-10 September 2009 "*Voltammetric Sensors for Aromatic Nitroderivatives Based on Molecularly Imprinted Polymer Membrane on Conducting Surfaces"***)**

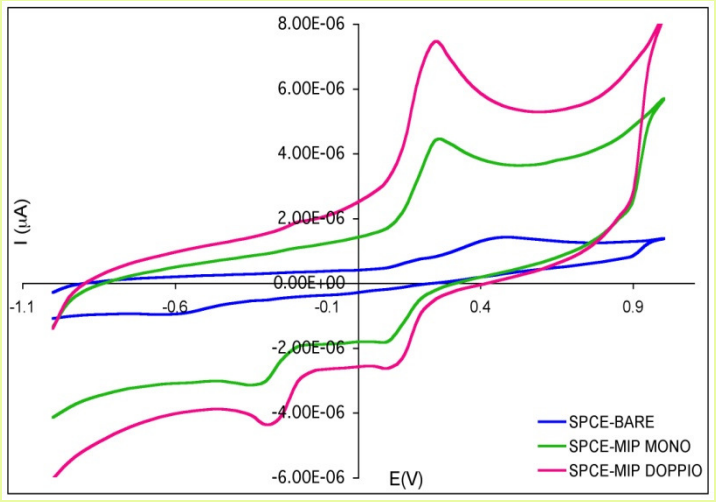
Oxidizable species: dopamine (M. Pesavento, G. D'Agostino, R. Biesuz, G. Alberti 61st Annual Meeting of the International Society of Electrochemistry, Nice 26 Sept-1 Oct 2010, " *MIP-modified Screen Printed Carbon Electrodes as Selective Sensors)*

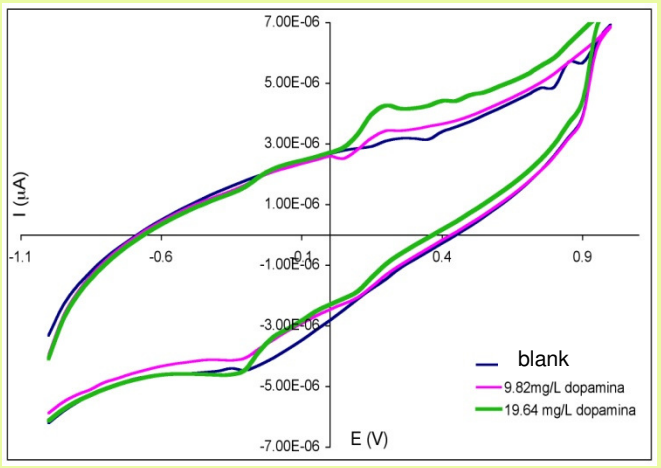
Effectiveness of the imprinting procedure for dopamine by CV

Cyclic voltammetry of a Phosphate buffer 0.05 M, pH=7.3, on SPE and MIP and NIP modified SPEs

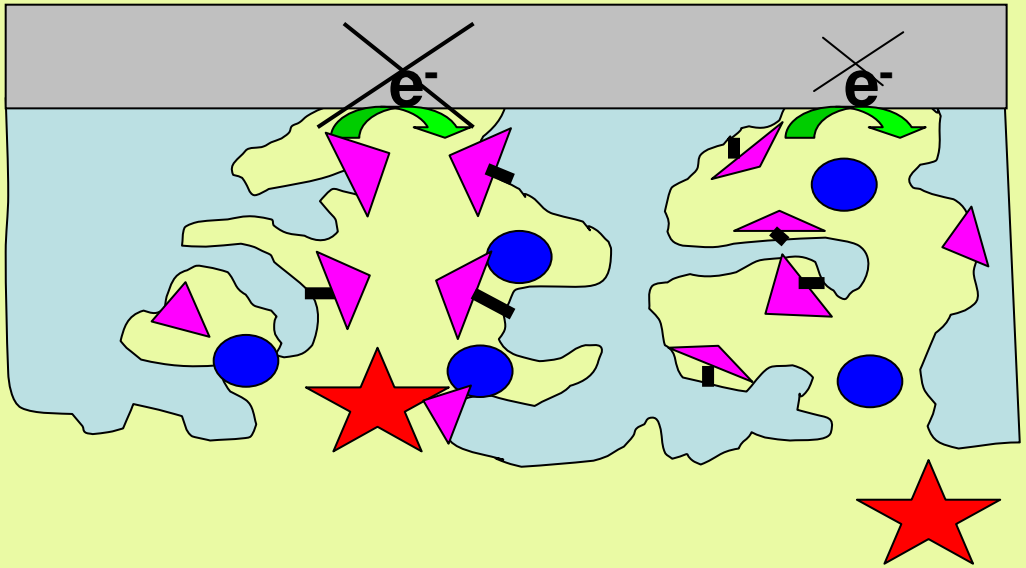


Cyclic voltammetry of DA in Phosphate buffer 0.05 M pH=7.3 on SPE and MIP and NIP modified SPEs

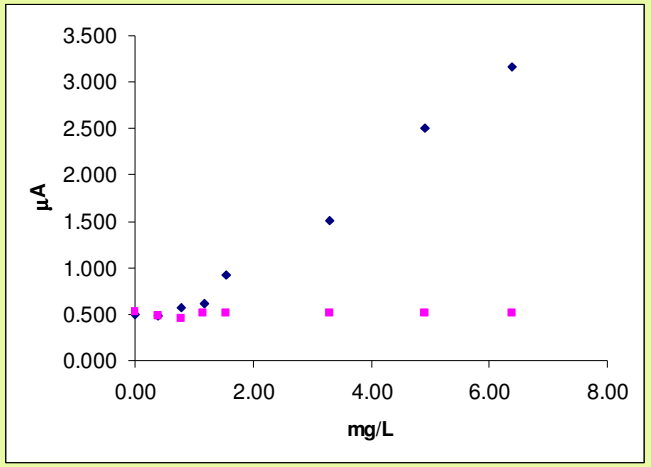




Nonelectroactive analite: response based on polymer conductivity modulation by recombination of the template. Chronoamperometric detection.



Calibration curve of atrazine at different acidities, by amperometric detection.



- M. Pesavento, G.D'Agostino, R. Biesuz, G.Alberti, M. Sturini
EuranalysisXIV, Antwerp (Belgium), 9-14 September 2007, Session S9: Food Analysis, p. 512
A MIP based sensor with amperometric detection for isopropyl-thioxanthene (ITX)

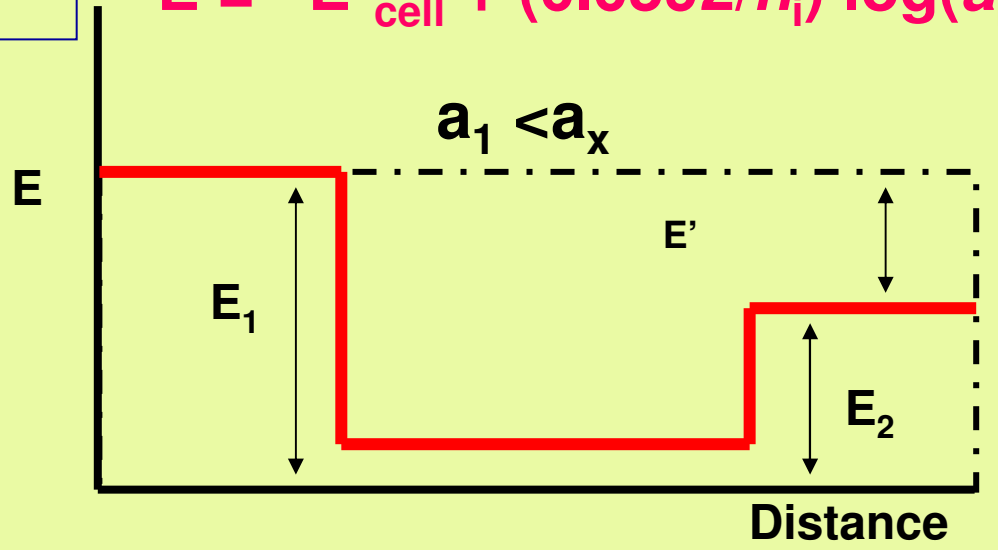
-M. Pesavento, G. D'Agostino, M. Sturini,
12th International Conference on Electroanalysis -Prague,16-19 June 2008 ESEAC 2008
Gate effect of molecular imprinted polymeric membrane for specific sensors

M.Pesavento, G.D'Agostino, R. Biesuz, G.Alberti, Electroanalysis 2009, 21, No. 3-5, 604 – 611
Molecularly Imprinted Polymer-Based Sensors for Amperometric Determination of Nonelectroactive Substances

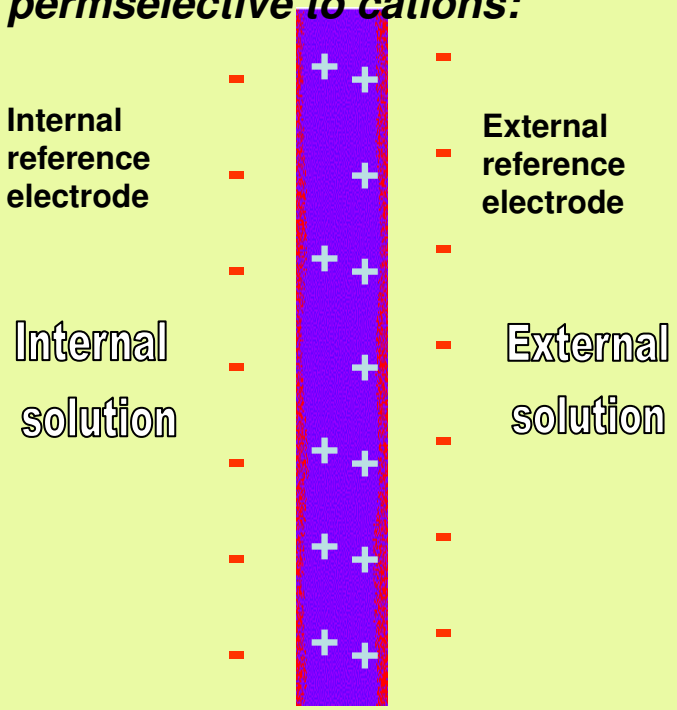
Charged analytes: potentiometric detection

$$E = E^0_{cell} + (0.0592/n_i)\log(a_i)$$

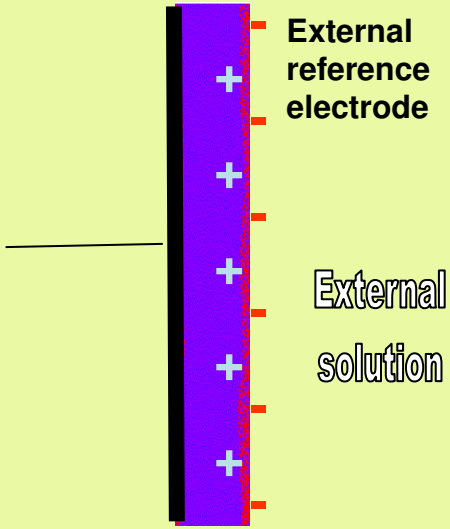
(G.D'Agostino, G.Alberti, R.Biesuz, M.Pesavento, Biosensors and Bioelectronics 22 (2006) 145-152)



Charge separation at a membrane permselective to cations:



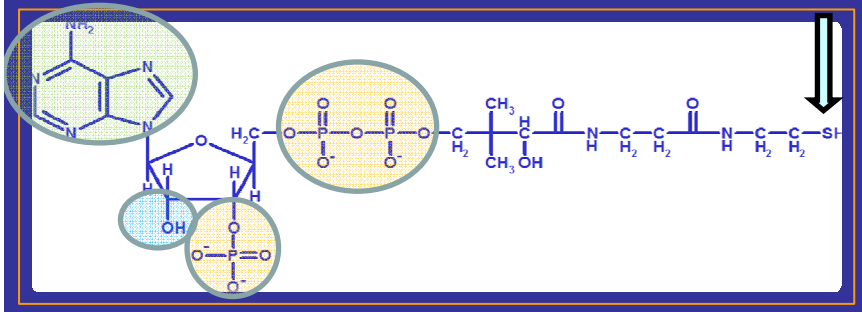
All solid state ISE based on MIP are under investigation:
-screen printed graphite
-screen printed graphite modified with CNT.



CME

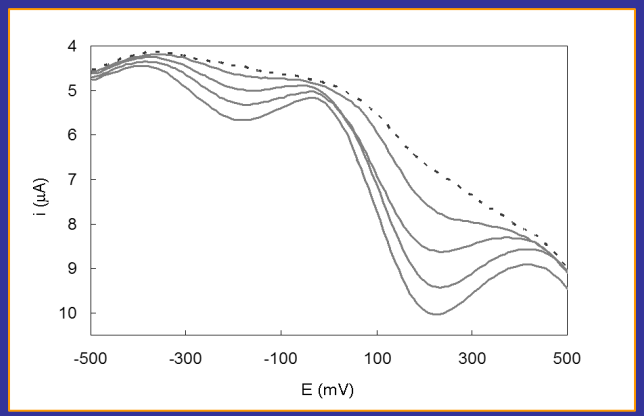
ELETTRODI CHIMICAMENTE MODIFICATI:SAM (*Self Assembled Monolayer*)

Vantaggi: possibilità di aumentare la selettività delle reazioni all'elettrodo, introducendo un gruppo funzionale selettivo in grado di interagire in modo specifico con l'analita di interesse. Tra gli elettrodi SAM, particolarmente interessanti sono quelli su elettrodo d'Au, preparati impiegando gruppi SH che sono facilmente chemiadsorbiti sulla superficie dell'elettrodo dando origine a monostrati altamente ordinati.

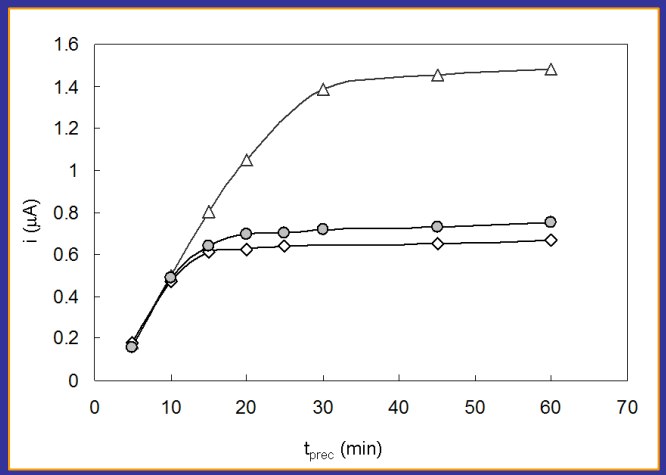


CoA-SAM

Interazione con metalli pesanti (Pb,Cu,Cd)



DPV preceduta da preconcentrazione in KCl 10^{-2}M a circuito aperto, di Pb (E_p = -170 mV) e Cu (E_p = +180 mV) in Na citrato (0.1M, pH = 9.0). Cu da 2 a 8µgL^{-1} ; Pb da 5 a 20mgL^{-1}



corrente di picco vs. tempi di preconcentrazione: Δ Cu10 µgL^{-1}; **O** Cd 10 µgL^{-1}; □ Pb 10 µgL^{-1}.

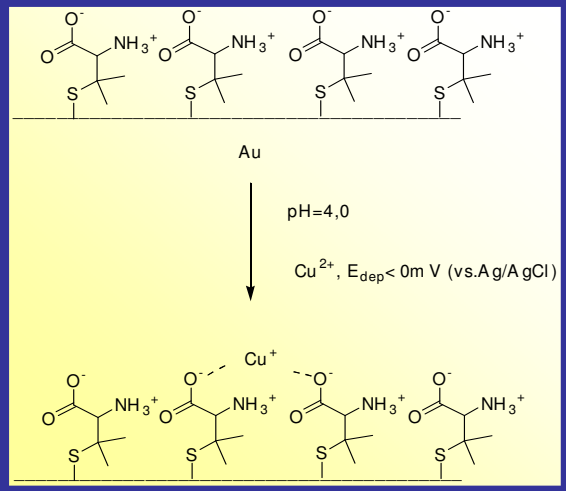
CME

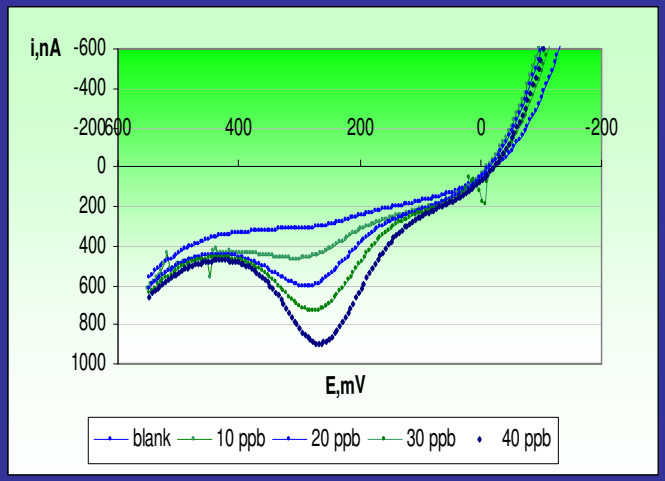
DL PENICILLAMINA SAM PER LA DETERMINAZIONE DI Cu(II)

DL penicillamina (RSH) $RS^{\cdot}_{(ads)} + H^{+} + e^{-}$, dove R è il gruppo aminoacidico. Questo composto è adsorbito sulla superficie dell'elettrodo d'Au attraverso i gruppi SH.
Il SAM è preparato immergendo l'elettrodo in una soluzione etilica 5 mM di DL penicillamina per 12 ore, quindi risciacquato con acqua ed etanolo prima dell'uso.

ipotesi per il processo all'elettrodo:

il Cu(II) viene complessato sulla superficie modificata dell'elettrodo e si riduce a Cu(I) al potenziale applicato. Successivamente viene riossidato nella fase di scansione anodica. Il processo è reversibile e controllato dalla diffusione.



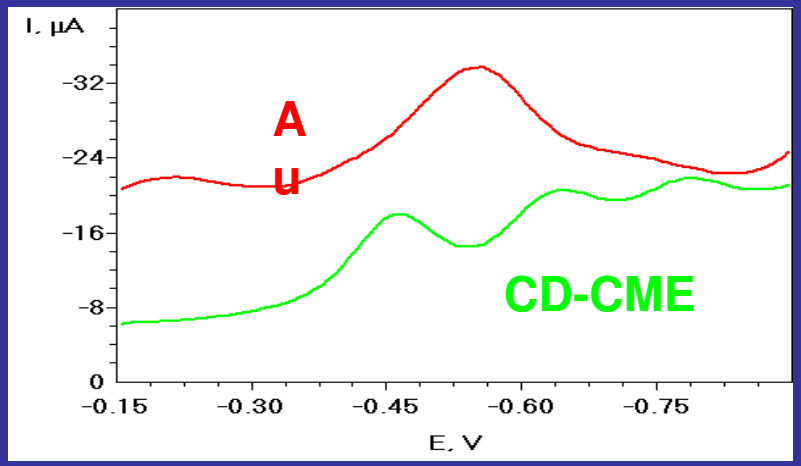


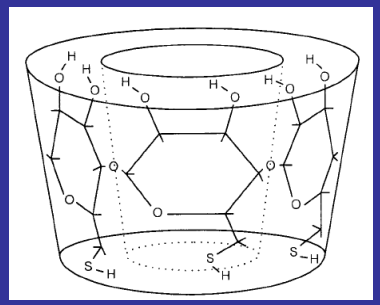
DPV e retta di calibrazione per aggiunte successive di Cu di 10 µg/L a un campione di acqua naturale in tampone acetato.
i (µA) = 8.43 ppb Cu - 1.51

A. Profumo, D. Merli, M. Pesavento , Analytica Chimica Acta 557 (2006) 45–51

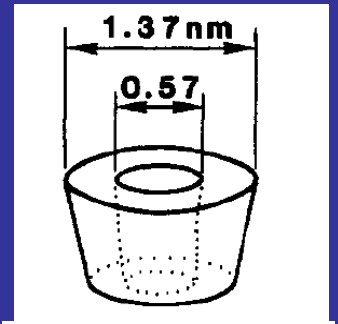
CME

αCD- Au CME per la determinazione del TNT



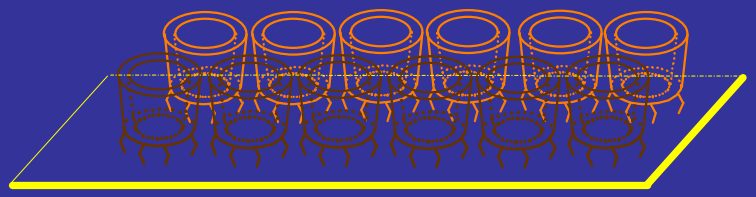


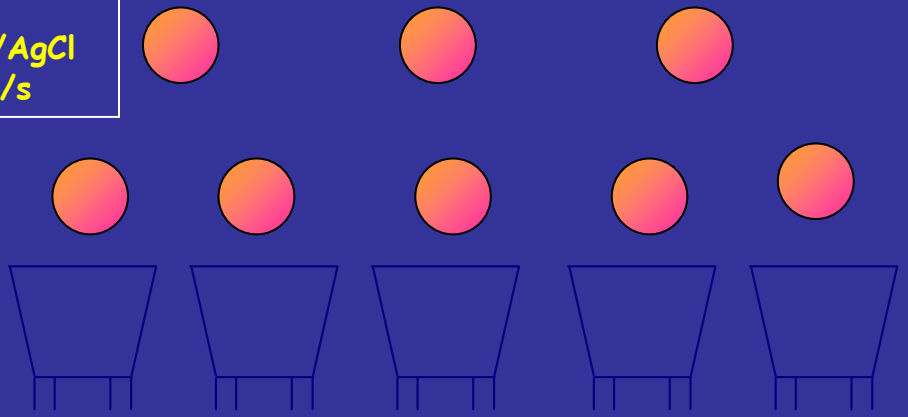
6 unità di glucosio



a-ciclodestrina

fra oro nudo e αCD-CME
[TNT] 10 mg/L; KCl 0.1 M; E_{dep} -300 mV (vs. Ag/AgCl sat.); t_{dep} 60 s, E_i -100 mV, E_f -1000 mV; 100 mV/s





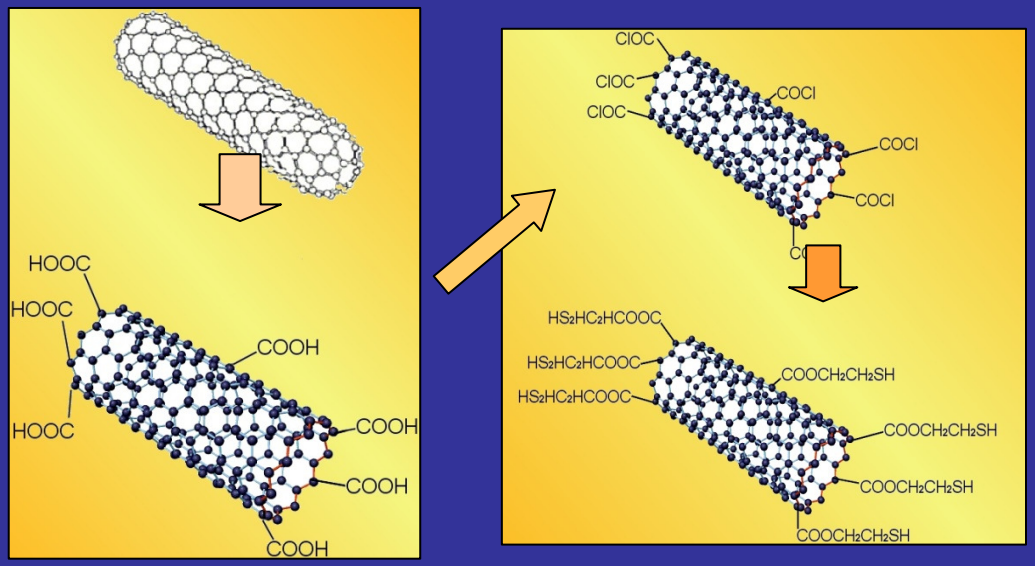
Cavità idrofobiche in una struttura rigoda. La prima onda di riduzione del TNT è spostata a potenziali più alti sul CD-CME

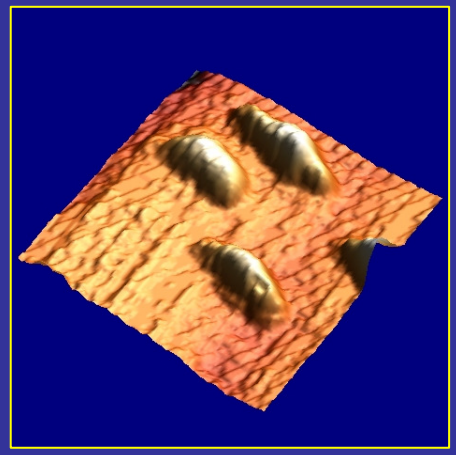
I. Tredici, D. Merli, F. Zavarise, A. Profumo J. Electroanal. Chem. 645 (2010) 22–27

CME

CNT-CME

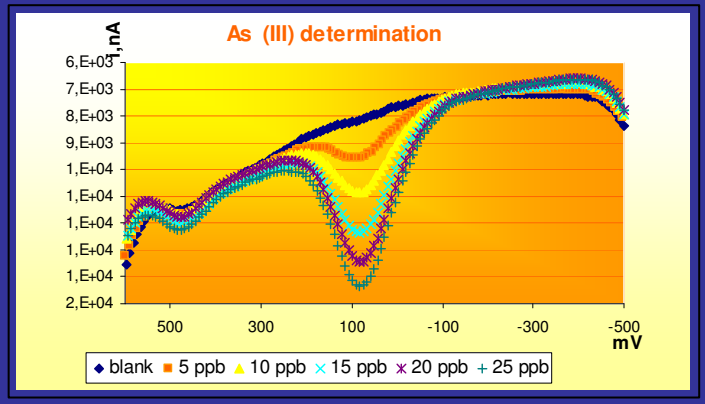
(CNTs) are fullerene-related molecules which can have a single cylindrical wall (SWNTs) or multiple walls (MWNTs).
Electronic and thermal properties of CNTs largely depend on their structural characteristics (defined by their diameter, length, chirality, and twist).
Chemically modified gold electrodes with nanotubes were obtained by β- thioester derivatization of crude material





- CNT-CME have been used for trace determination of Bi and As in water In acetic buffer (pH=4,0).
- At bare gold electrode only poor and irreproducible response is obtained

  At MWCNTs electrode there is a great increase in signal and in reproducibility.



A. Profumo, M. Fagnoni, D. Merli, S. Protti, . Dondi,*A.* Albini , Anal. Chem. 2006, 78, 4194-4199

CME

Elettronica molecolare

- Applicazioni fotoelettrochimiche:

Il trasferimento di elettroni a stati eccitati, promosso dalla luce, favorisce processi redox di sostanze altrimenti difficilmente riducibili.

Nei nanotubi di C, l'irraggiamento con la luce ($E=h\nu$) può portare gli elettroni da una banda di valenza a una banda di conduzione, rendendoli più disponibili per processi elettrochimici.

Sono state eseguite prove su **CME-SWCNT** con acido ascorbico come sonda redox.

L'applicazione della luce a E diversi evidenzia che l'elettrodo si comporta da fotodiodo

L' applicazione della luce on-off a E costante provoca risposta dell'elettrodo on-off (interruttori molecolari).

D.Merli, A. Profumo,D. Dondi, A.Albini, ChemPhysChem 2009, 10, 1 – 8