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# Carbon-based sensors for industrial applications

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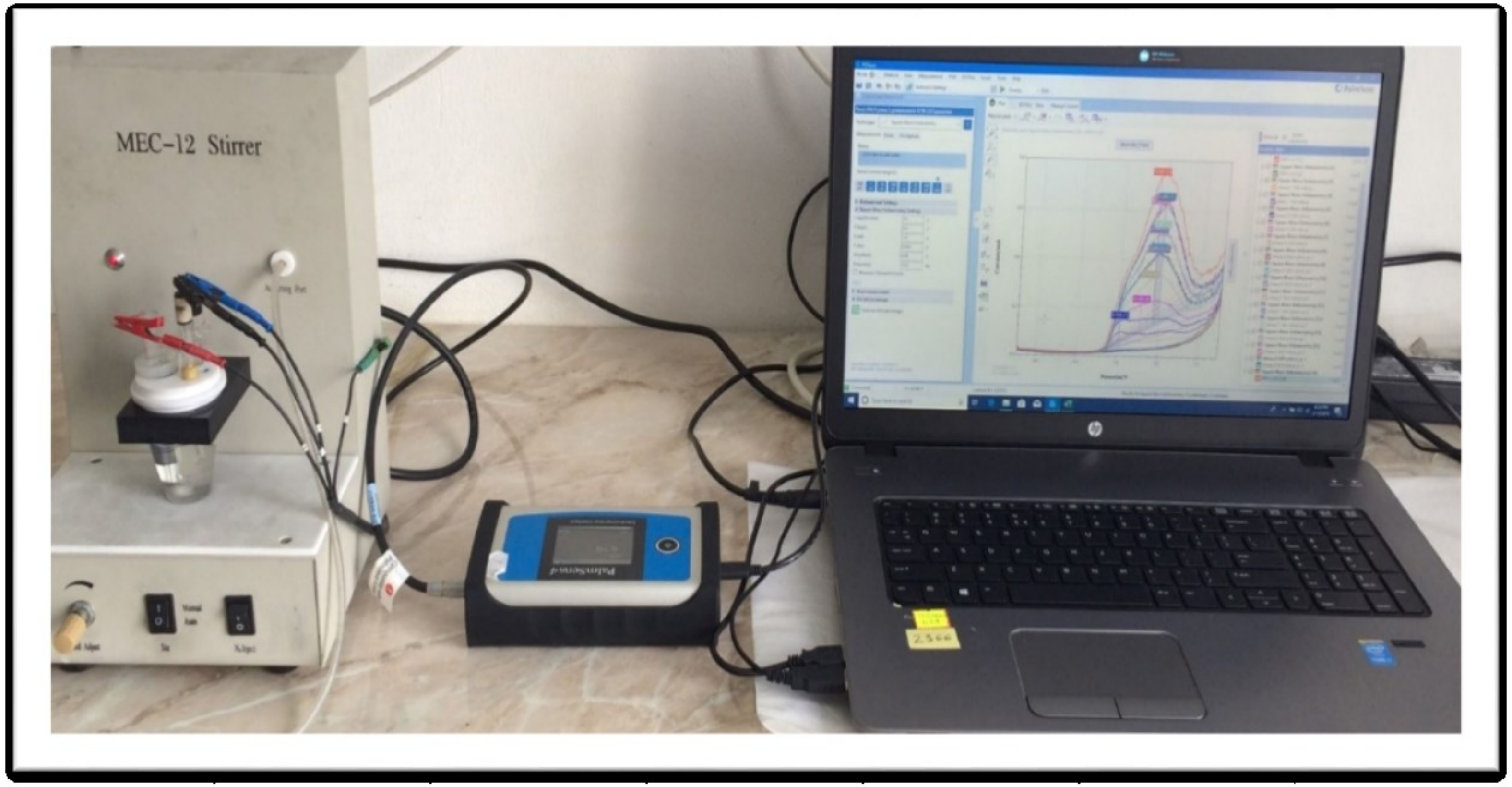
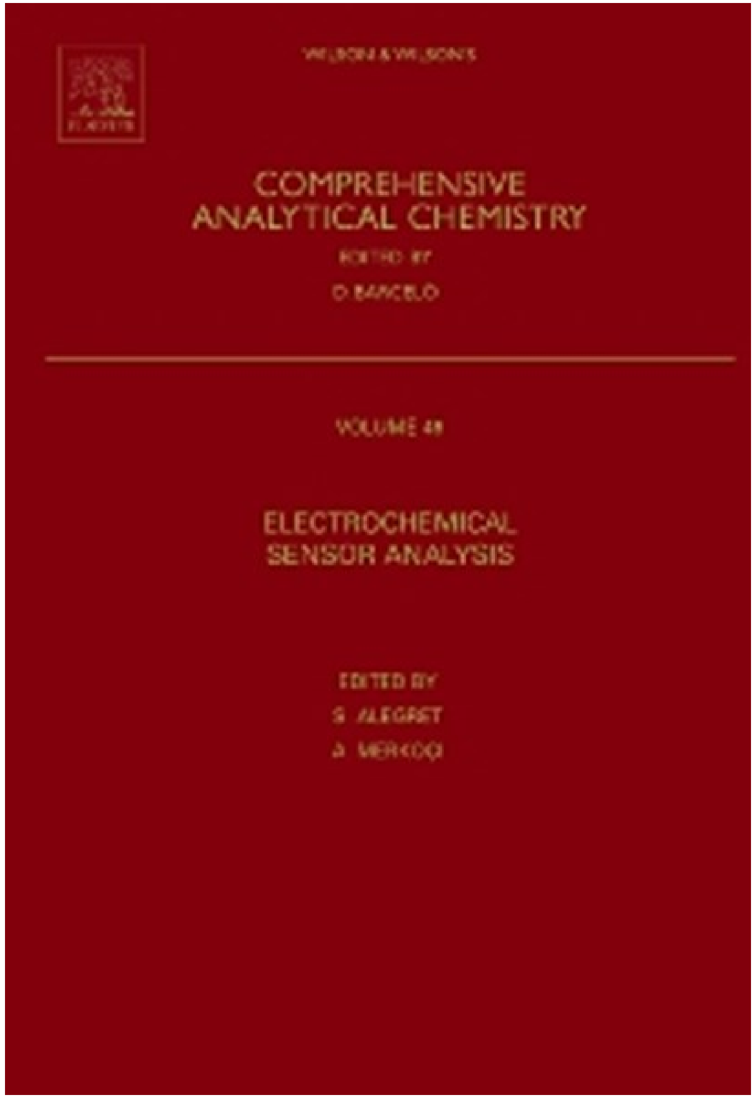


# Electrochemical (bio)sensor as a powerful analytical device

There is a widespread need for the application of electrochemical sensors with good quality and cost performance

This is a continuing demand which can be noticed in the large number of publications in chemistry, reviews and books.

There are more than 6 volumes in **Comprehensive Analytical Chemistry Series** (44, 49, 66, 74, 77), dedicated to electrochemical (bio)sensor designs, characterisations and their important applications in real clinical, environmental, food, and industry related samples.



*The electrochemical sensor aplications represent important advantages compared with other sophisticated techniques.*

*The most important advantages are:*

*in-situ applications,*

*cost-effective techniques*

*easy-to-use techniques*

*these methods are able to be automated*

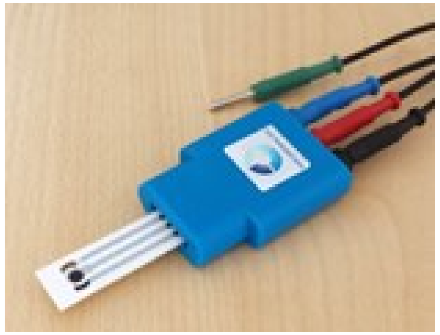
*can provide frequently results*

*can detect short-term pollution sources,*

*can be used from everyone, etc.*

*Recently the studies are focused on:*

- *application of new modifiers*
- easily preparation techniques (printed sensors)



*Sensor-based analysis has attracted considerable interest.*

# Where are (bio)sensors being used?

Farm, garden and
veterinary analysi

Food and drink production and
analysis, fermentation control

Clinical diagnosis
and biomedicine

Pharmaceutical
and drug analysis

Pollution control
and monitoring

**Electrochemical analyses is already a well established research and applied area of analytical chemistry.**

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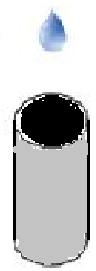
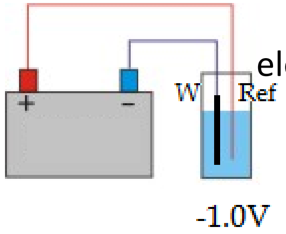
# Different ways to develop carbon-based electrochemical sensors

**Sensors based on surface modifications of GCE**

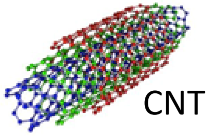


mechanical modification

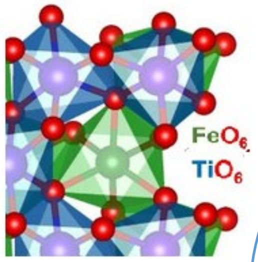



electrochemical modification

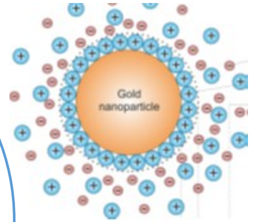
**Composite sensors**
**carbon paste modified**



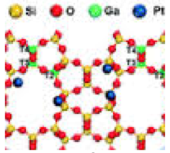
CNT




natural ilmenite



metal-np

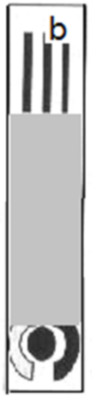


natural zeolite

crude tissue

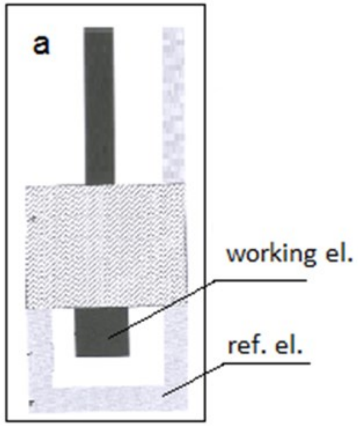
pure enzyme

**Screen-printed electrodes**




Three electrodes in one strip!

ReO2 modifier of C - electrode



# Composite electrodes
# Modified Carbon Paste Electrodes

Widely applicable in electrochemical studies due to:

* their low background current (compared to solid graphite or noble metal electrodes),
* low cost,
* easy preparation,
* feasibility to incorporate different substances during the paste preparation,
* simple renewal of their surface,

# Modified carbon paste electrodes with plant crude tissue and /or Au-np

*pure enzymes*

*crude tissues*

*mushroom*

*banana*

*potato*

*pear*

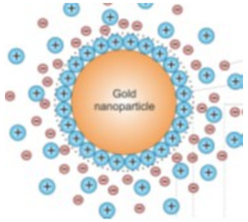
*apple, etc.*

metal nanoparticles

Au–nanoparticles

Ag-nanoparticles,

etc




**double modification**

**crude tissues + Au-nanoparticles**

## Crude tissue as sources of enzyme as modifier of CPE

***Advantages:***

*the enzyme is in its natural environment*

*higher enzyme activity compared with biosensors modified with purified enzyme*

*cofactors may be already present*

*may be used without preparatory work*

*simplicity of the biosensor construction & low cost*

***Disadvantages:***

*the tissue contains more than one enzime*

*(problem with selectivity ? ?*

## Role of Au-np in CPE modified with enzyme

*The structure of PPO enzyme consists in a dense protein layer around its active sites, like a barrier for the electron transfer.*

*Introducing Au-np into the carbon paste electrode a more efficient electron transfer between the active sites of the enzyme and the electrode is obtained.*

Modified sensors using the enzyme and the Au-np are developed for phenolic compounds determinations (Very toxic, Persistence in the environment, highly soluble in water).

**Broli N, Vasjari M. 2013.** *Journal of International Environmental Application $ Science*, Vol 8, Issue 3, pp 412-418.

# Preparation procedure of modified CPE

The graphite powder, paraffin and modifiers (mushroom tissue and/or Au-np solution, zeolite, ilmenite, etc), were mix gently for several minutes, together until a uniform paste was obtained.

The (un)modified paste was kept in a refrigerator at 4°C for 24 hours before measurement.

The carbon paste was packed into the plastic syringe with internal diameter 8 mm and outer 9.5 mm containing a copper wire as the external electric contact.

A glass surface was used to smooth the surface of the electrode before the measurements.

## Objectives:

- Construction of home made (bio)sensor for phenolic compounds, HM,
- Optimization of carbon paste komponents
- Analytical performance  of the bio)sensors

**Broli N, Vasjari M. 2013.** Hacettepe Journal of Biology and Chemistry, Vol 41, Issue 3, pp 187-193.
**Vasjari M, Broli N. 2014,**International Conference: New frontiers of nanomaterial technologies for applications in biology and medicine, 10 – 11 July 2014, Tirana, Albania.

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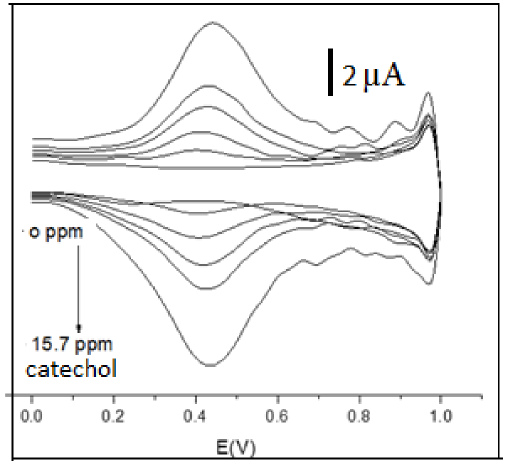
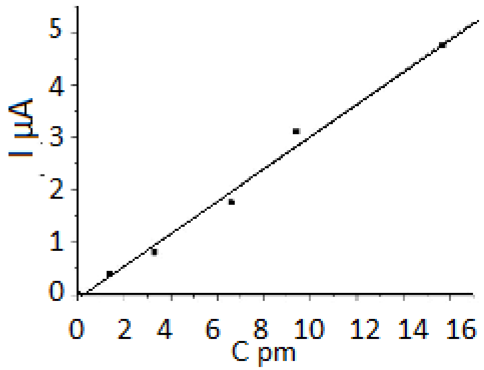
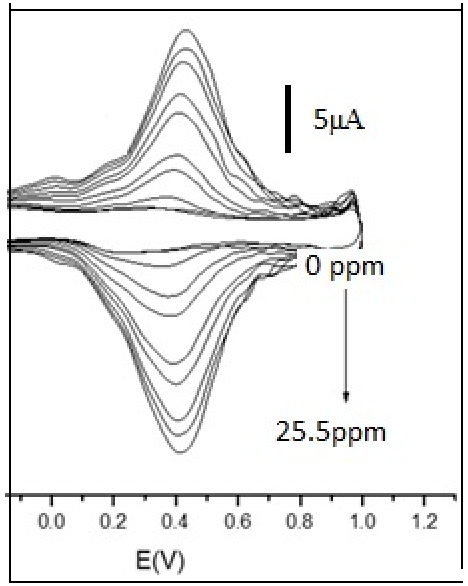
# Carbon paste electrode modified with banana.

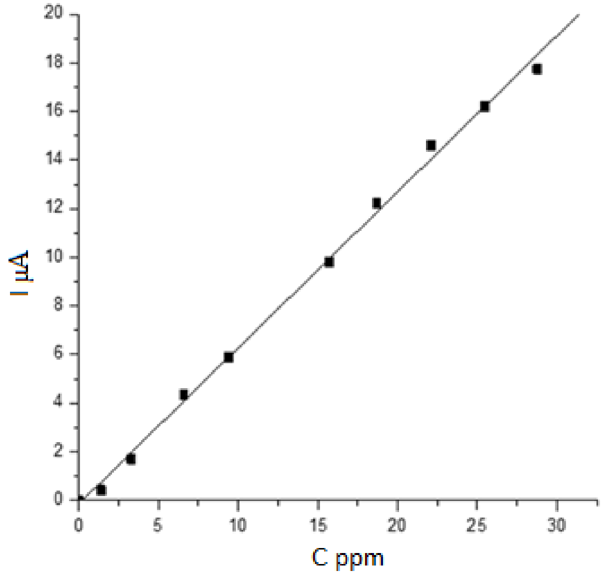
## Unmodified CPE




## Modified CPE with crude tissue and Au-np




| | Sensitivity (μA/ppm) | Linear range (ppm) | (R) | L. D. (ppm) | $S_D$ (ppm) |
|---|---|---|---|---|---|
| CPE | 0.3014 | 1.4-15.7 | 0.99558 | 1.24 | 0.6324 |
| CPE-Enzyme | 0.4218 | 1.4-15.7 | 0.99743 | 0.73 | 0.5517 |
| CPE-Au.np | 0.5556 | 1.4-25.5 | 0.99663 | 0.18 | 0.1977 |
| CPE-Enzym-Au.np | 0.6443 | 1.4-25.5 | 0.99867 | 0.11 | 0.4134 |

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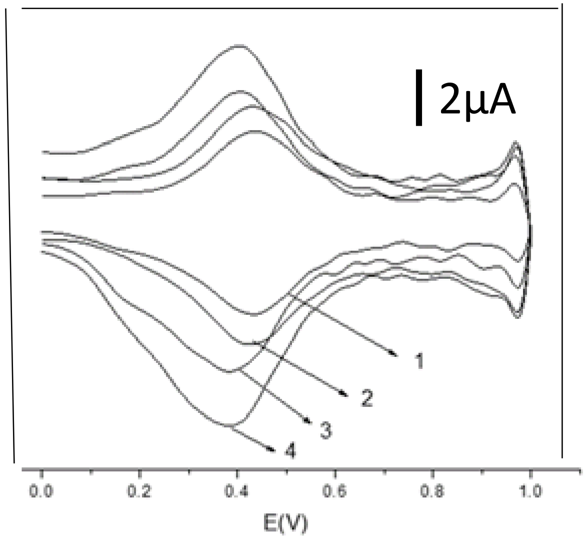
# Voltamogrames recorded in 9.4ppm catechol

(other experimental conditions are the same),

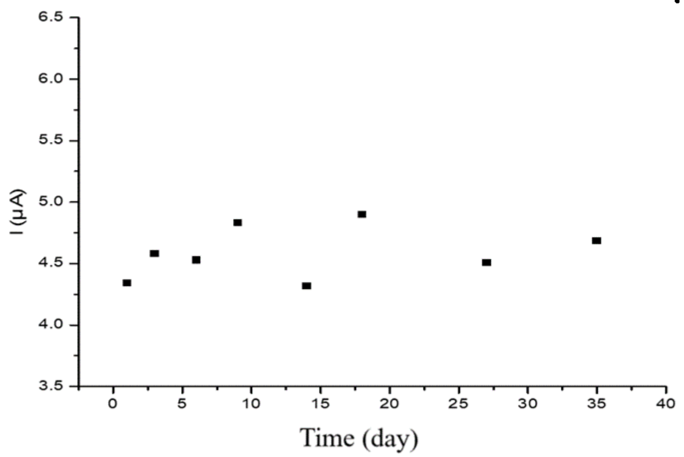
**The current (I µA),** is increased in the following order:

**ICPE < ICPE+CT <ICPE+Au np < ICPE+CT+Au np,**

**Redox potential** is shifted to lower values due to the activity of Au np from 0.42V to 0.38V




1 - unmodified CPE;
2 - modified CPE with crude tissue;
3 - modified CPE with Au np;
4 - modified CPE with crude tissue and Au np.




The modified biosensor with Au np retained successively 85% and 75% of its initial response after 24 and 36 days.

*Determination of catechol in green tea*
** water extraction 141 ± 8.3 mg/L*
** phosphate buffer solution extraction 478.5±6.8 mg/L*
*The calculated recovery was between 89% and 92%*

Broli, N. Vasjari, M. (2017). Journal of Natural and Technical Sciences. JNTS No 43 / 2017, pp 57-72

# Behavior of the modified sensor towards other phenolic compounds

| | Sensitivity (µA/ppm) | Linear range (ppm) | (R) | Limit of detection (ppm) | $S_D$ (ppm) | Relative response % |
|---|---|---|---|---|---|---|
| catechol | 0.64436 | 1.4-24.45 | 0.99867 | 0.11 | 0.41 | 100.0 |
| hydroquinone | 0.52184 | 1.4-25.45 | 0.99316 | 0.14 | 0.39 | 81.0 |
| m-cresol | 0.46744 | 1.4-6.6 | 0.94914 | 1.13 | 0.73 | 72.6 |
| o-cresol | 0.44828 | 3.3-9.4 | 0.98021 | 2.43 | 1.83 | 69.6 |
| nitro-4-phenol | 0.45352 | 0.7-9.4 | 0.97121 | 0.57 | 0.50 | 70.4 |
| nitro-3-phenol | 0.49641 | 0.7-6.6 | 0.97593 | 0.34 | 0.47 | 77.1 |
| chloro -4-phenol | 0.51712 | 1.4-15.7 | 0.95042 | 0.23 | 1.19 | 80.3 |

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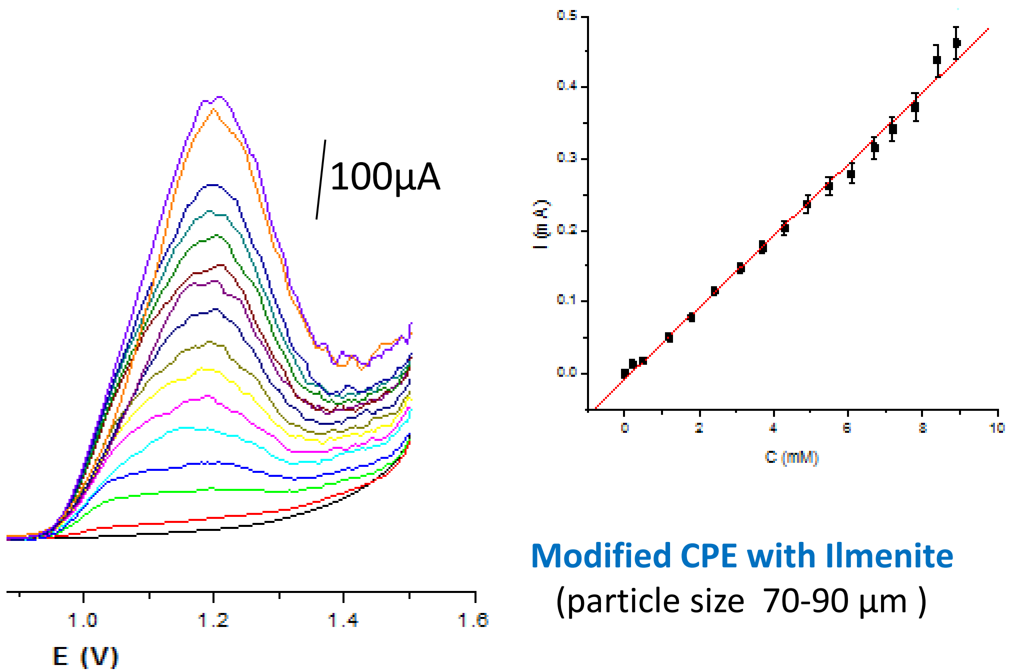
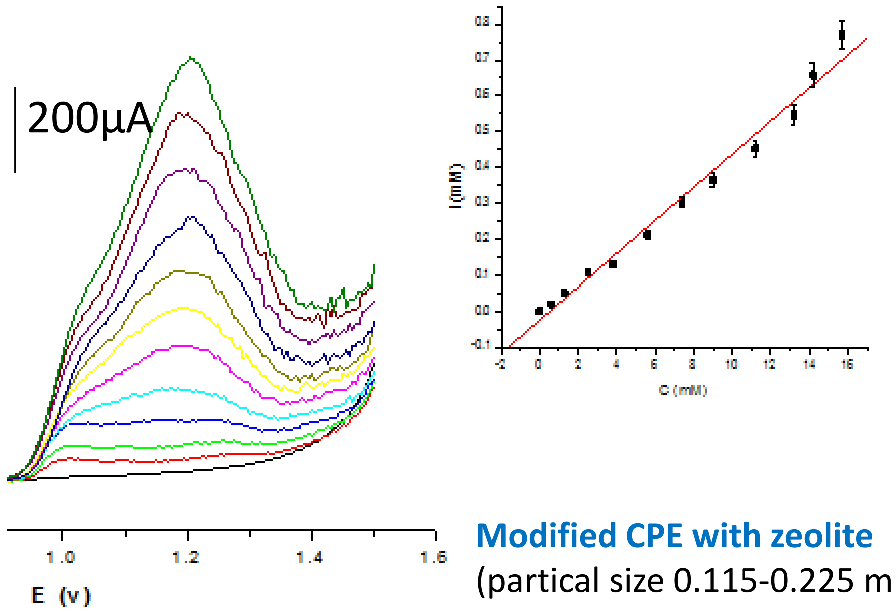
# Modified CPE for determination of propranolol

**Objectives:**

- Construction of home made sensor for propanolol
- Optimization of ration between carbon - modifier (Ilmenit/zeolit)
- Analytical performance  of the sensors
- Determination of propanolol in **pharmaceutics tablets**




**Modified CPE with Ilmenite**
(particle size  70-90 µm )




**Modified CPE with zeolite**
(partical size 0.115-0.225 mm)

# Analytical performance of sensors:
# unmodified CPE, modified CPE with Ilmenite (CPE-I), modified CPE with zeolite (CPE-Z)

| | Sensitivity (μA/mM) | Linear range (mM) | (R) | L. D. (mM) | $S_D$ (mM) |
|---|---|---|---|---|---|
| CPE-I | 50 | 0.2-8.9 | 0.9969 | 0.08 | 0.008 |
| CPE-Z | 46 | 0.6-15.7 | 0.9919 | 0.45 | 0.035 |
| CPE | 43 | 0.5-4.9 | 0.9983 | 0.5 | 0.008 |

- Determination of propanolol in pharmaceutics tablets (40mg propanolol/tablet)

| | mg/tablet | Spiked propranolol (mM) | Detected (mM) | Recovery % |
|---|---|---|---|---|
| CPE-I | 36.5±1.4 | 1.8<br>3.6 | 1.82±0.2<br>3.54 ±0.4 | 101<br>98 |
| CPE-Z | 37.3±1.9 | 1.8<br>3.6 | 1.65± 0.22<br>3.61 ±0.33 | 92<br>100.2 |

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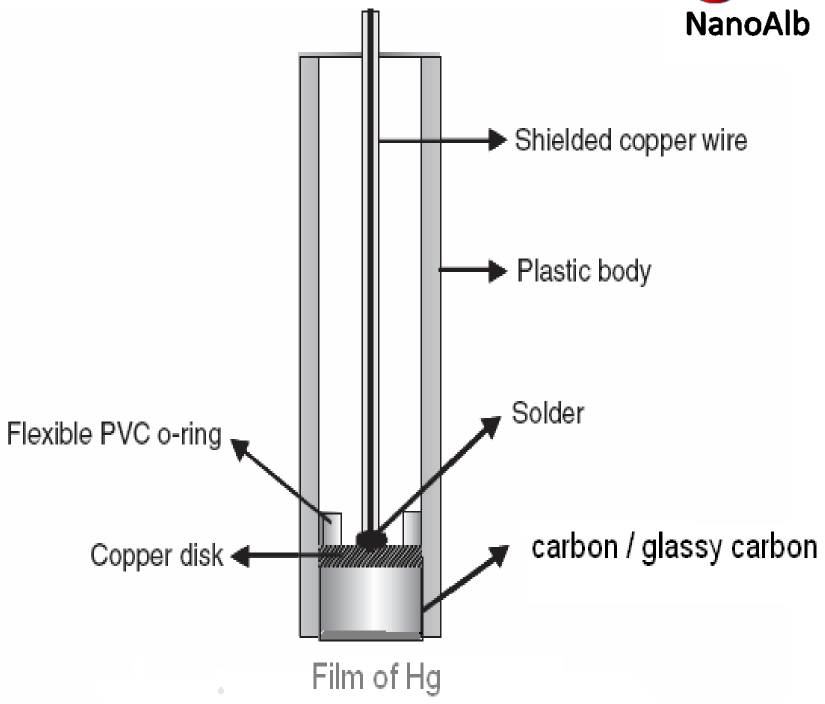
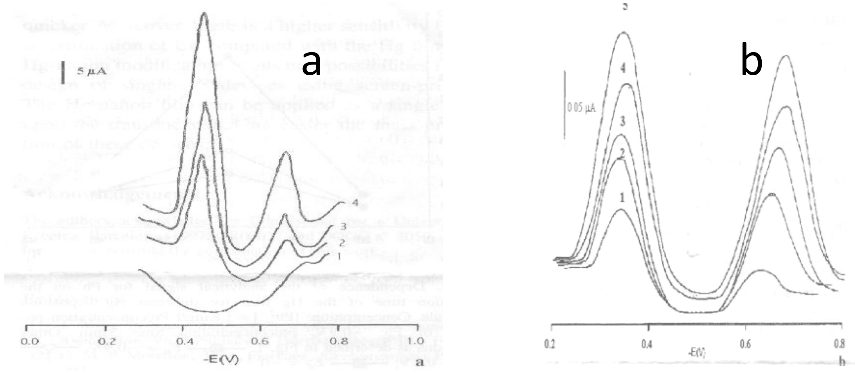
# Sensors based on surface modifications of GCE for determination of HM




Objectives:
Determination of heavy metals (Pb & Cu) by ASV using GCE modified with :
a) electrodeposition of the Hg film
b) GCE was coated mechanically by modifying solution Hg:Naffion




Typical stripping curves for Pb and Cu at different pH
a) electrochemical formation of the Hg film
b) electrode modified with Hg-naffion film

**Results:**
✓Nafion stabilises the Hg mecanically and facilitates the modification procedures.
✓Hg-nafion films gives better sensitivity
✓The procedure based on Hg-naffion film is simpler and quicker
✓This kind of applications opens the new possibilities for the design of single-use devices using screen-printing procedures

Merkoci A. Vasjari M., Fabregas E., Alegret S., ***"Microchimica Acta"*** 135 (2000),29-33

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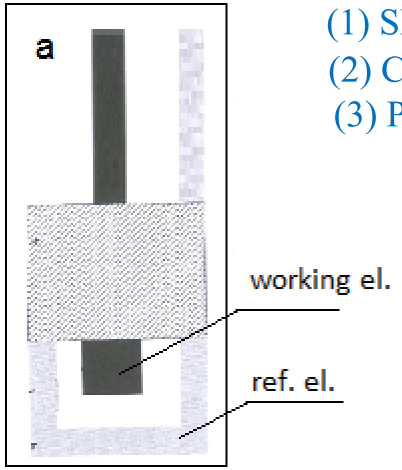
# Screen-printed electrodes for determination of amino acids

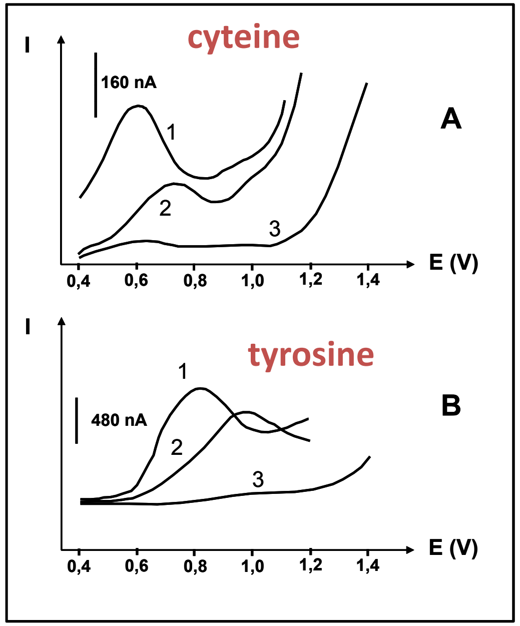
**Cysteine and Thyrosine**

LSV in 0.1M KCl +buff pH =7,0

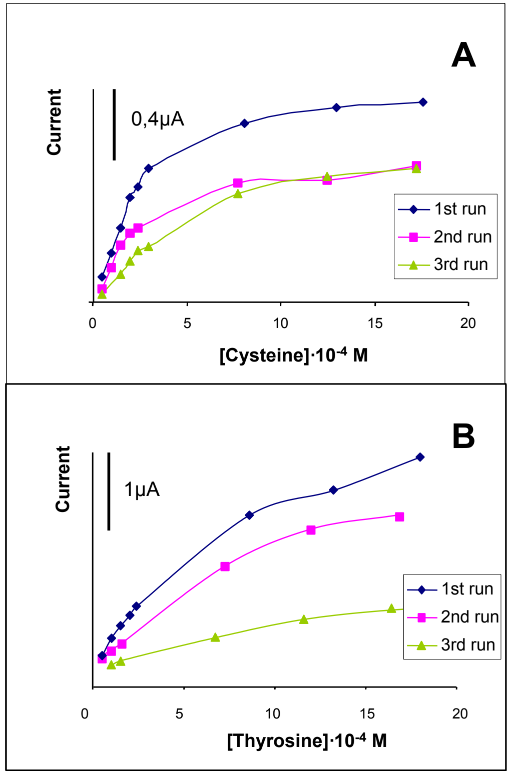
.




(1) SPES
(2) CE
(3) Pt




LS V for A)cysteine and (B) thyrosine concentration 2.4*$10^{-3}$M




Amperometric calibration curves for A)cysteine 0.6V and (B) thyrosine 0.8V

**Results:**

The suitability of SPES for fast analysis of amino acids in commercial pharmaceutical products.


M.Vasjari, A.Merkoci, et al “Amino acid determ. using SPES ***Microchim. Acta*** (2005), DOI 10.10007/s00604-005-0361-4

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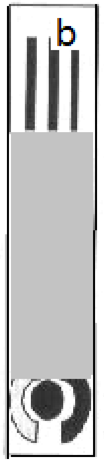
# Screen-printed electrodes for determination of heavy metals;  histamine

**Objective 1:**

- Determination of heavy metals using screen-printed electrodes.

Technique:

- Anodic Stripping Voltametry




Configuration of the SPE:

Three electrodes in one strip!

Collaboration with:

✓Barcelona
✓Florence

**Results**:

✓Optimization
✓Determination of Cd in sea water
✓Quality controll based on recocery of analyte additions

Vasjari, Karai, Merkoci. AKTET –IV 207-213, 2011

**Objective 2:**

- Determination of histamine using rhenium (IV) oxide  as modifier of carbon electrodes:

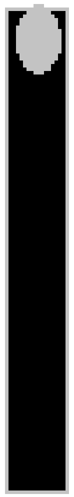
modified  CP E
modified  SP CP E

**Working el. is SPE**

Counter and reference are clasical ones

Experiments :

✓in batch system
✓In  flow system



**Results**:

✓Determination of histamine in real samples (fish sauce)

Veseli, Vasjari, Kalcher, ***Sensors and Actuators B Chemica***, 2016, 228:774-781

# Selected publication

Merkoci A. Vasjari M., Fabregas E., Alegret S., *“Determination of Pb and Cu by anodic stripping voltametry using glassy carbon electrodes modified with mercury or mercury nafion films*”, “**Microchimica Acta**” 135 (2000),29-33

Vasjari M., Mirsky V.M., “*Calibrated nanoinjections of mercury vapor*”, **“Fresenius’Jurnal of Analytical Chemistry"**,(2000) 368 727-729

V.Mirsky, M.Vasjari, I.Novotny, V.Rehacek, V.Tvaroyek and O.Wolfbeis, “*Self-assembled monolayers as selective filter for chemical sensors*”, “**NANOTECHNOLOGY"**, (2002), No.13, f.1-

M.Vasjari, A.Merkoci, J.P.Hart, S.Alegret, “*Amino acid determination using screen-printed electrochemical sensors*”, **Microchim. Acta** (2005), DOI10.10007/s00604-005-0361-4 (Springer-Verlag 2005)

M.Vasjari, Z.M.Shirshov, A.V.Samoylov, V.M.Mirsky; “*SPR investigation of mercury reduction and oxidation on thin gold electrodes*”, **Journal of Electrochemical Chemistry;** 605 (2007)73-76

M. Vasjari, V.M. Mirsky,”*Chemoresistor for determination of mercury vapor*, in: S. Alegret, A. Merkoci (Eds.), **Electrochemical Sensor Analysis;Comprehensive Analytical Chemistry, vol. 49**, Elsevier, 2007, pp.233–249.

N. Broli, M. Vasjari, -" *A modified cabon paste biosensor for phenolic compounds*".-**Journal of International Environmental Application $ Science**. Vol 8, Issue 3, pp 412-418, July 2013.

A. Veseli · **M. Vasjari** · T. Arbneshi · A. Hajrizi ·Ľ. Švorc · A. Samphao · K.Kalcher “ *Electrochemical determination of histamine in fish sauce using heterogeneous carbon electrodes modified with rhenium (IV) oxide*” Feb 2016 · **Sensors and Actuators B Chemical** Volume 228, 2016, Pages 774–781

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# Thank you!

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