FUNCTIONALIZED SCREEN PRINTED ELECTRODES: EFFECTS OF NANOSTRUCTURATION ON THE DETECTION OF METALLIC POLLUTANTS IN WATER

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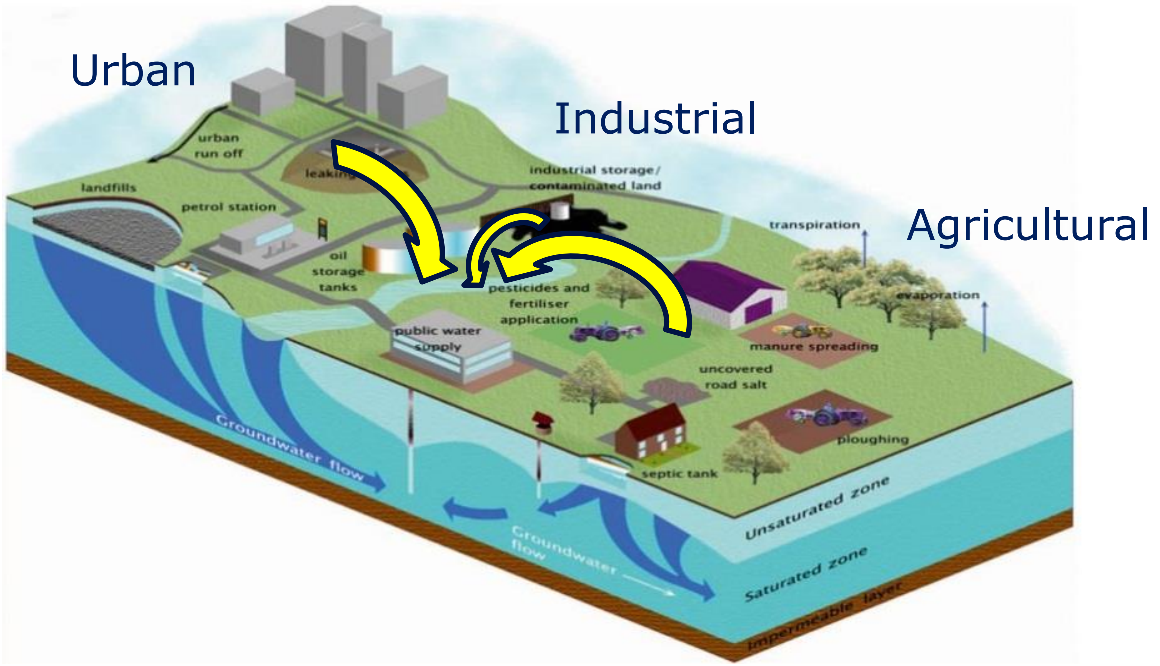
IMPORTANCE OF METALLIC POLLUTANTS DETERMINATION



- ✓ The presence of metallic pollutants in water is of major concern
- ✓ Allowed amounts in waters are regularly lowered

⟹ Necessity to develop reliable and sensitive techniques for on-site analysis

LABORATORY ANALYSIS

Atomic Emission Spectrometry

Atomic Absorption Spectrometry

Mass spectrometry

Advantages

- ✓ Good precision
- ✓ Variety of compounds

Drawbacks

- ✕ Heavy and expensive material
- ✕ Analysis takes time
- ✕ Laboratory analysis

ELECTROCHEMICAL TECHNIQUES

- ✓ Smaller and cheaper material
- ✓ Easy to handle
- ✓ Fast analysis
- ✓ Adaptable parameters
- ✓ Sensitive
- ✓ Suitable for on-site analysis

→ Sensors applications

ELECTROCHEMICAL TECHNIQUES

Interest of electrochemical techniques:

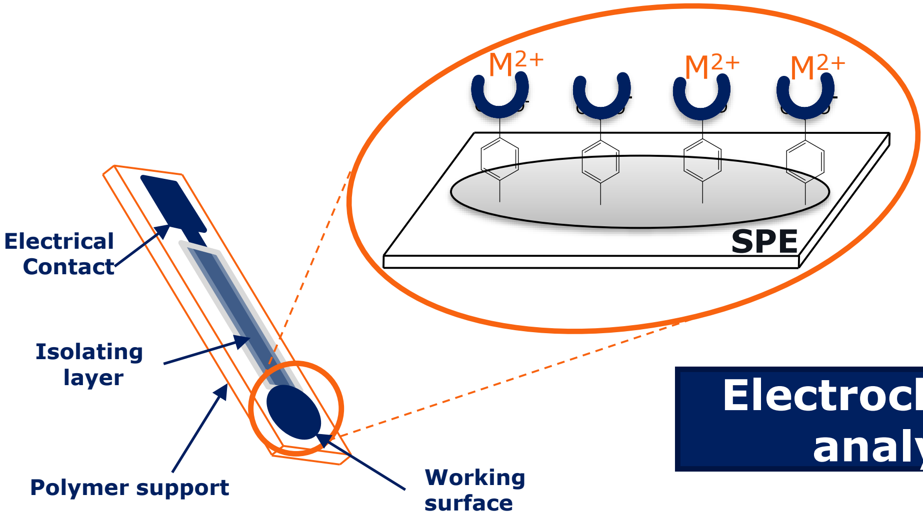
Versatility of techniques and parameters

→ Used in our case for:

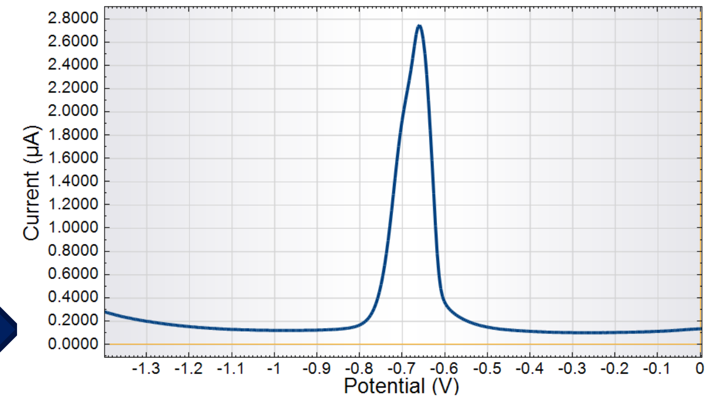
- ✓ The synthesis/**functionalization** of our electrode materials
- ✓ Their **characterization**
- ✓ The electrochemical **analysis**

FUNCTIONALIZED SCREEN PRINTED ELECTRODES AS ELECTROCHEMICAL SENSORS

Screen Printed Electrodes (SPEs)



Electrochemical analysis

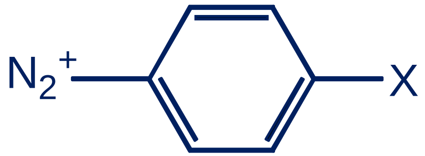


- ✓ Hand-made in the lab
- ✓ Cheap
- ✓ Reliable
- ✓ Suitable for on-site analysis

- ✓ Sensitive technique (LOQ around 10^{-9} M [1])

[1] S. Bouden et al. *Talanta* **2013**, 106, 414.

SURFACE FUNCTIONALIZATION *VIA* DIAZONIUM SALTS

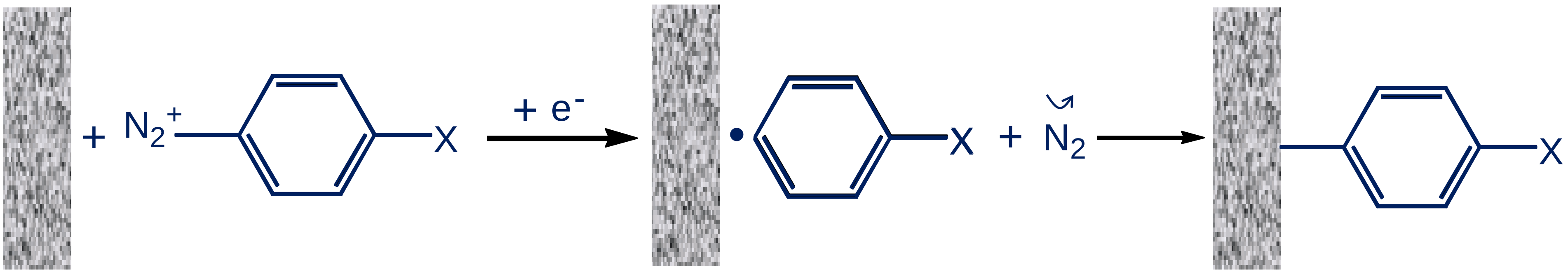


- ✓ Covalent grafting on various substrates [1] : C, Si, Au, Pt, Fe..
- ✓ Compatible with several organic functions
  X = NO_2, COOH, CF_3...
- ✓ Easy processing

[1] J. Pinson et al. *Chem. Soc. Rev.* **2005**, 34, 429.

SURFACE FUNCTIONALIZATION *VIA* DIAZONIUM SALTS

✓ Electroreduction of diazonium salts [1]



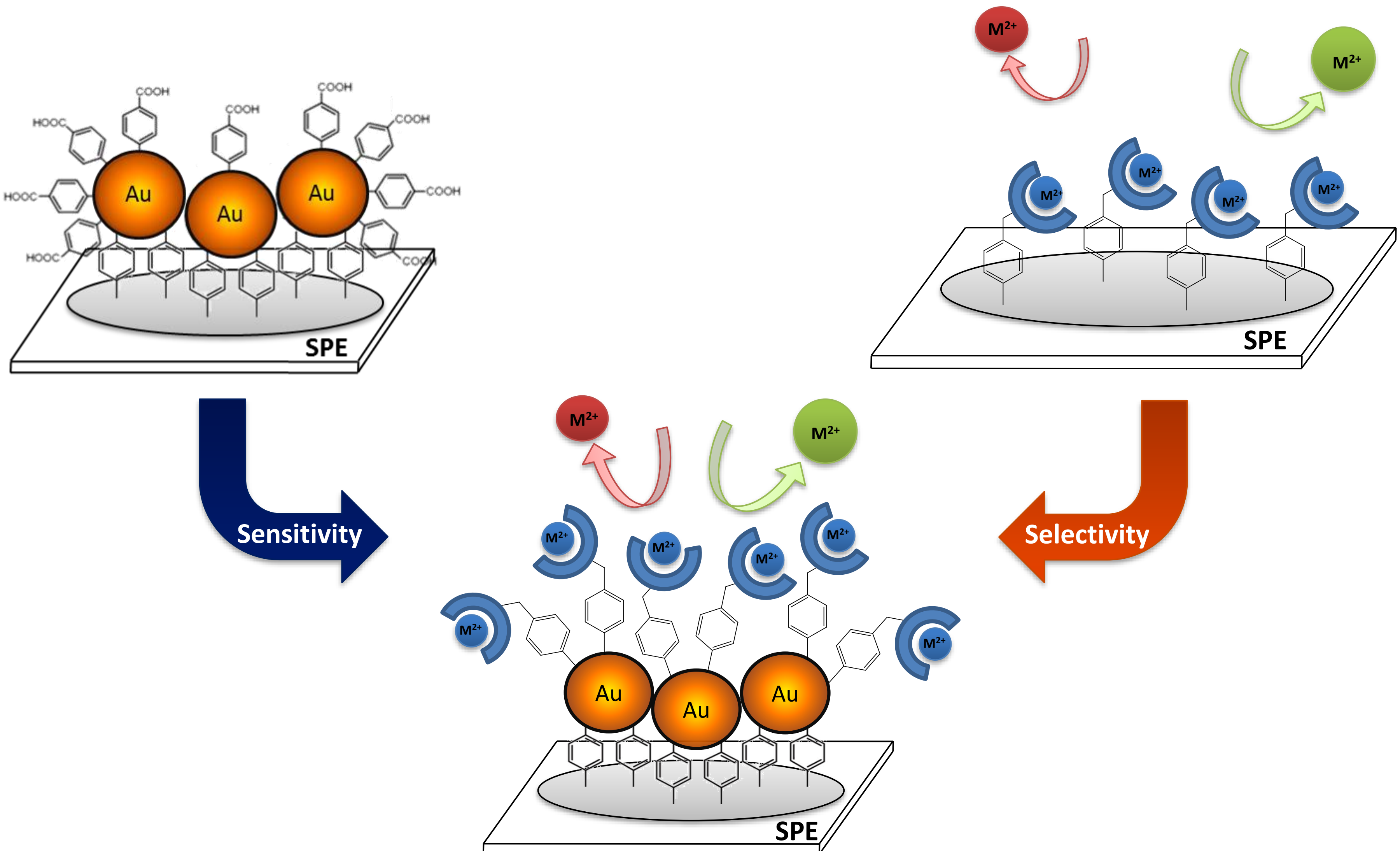
But also :

✓ Chemical reduction [2]

✓ Spontaneous reduction [3]

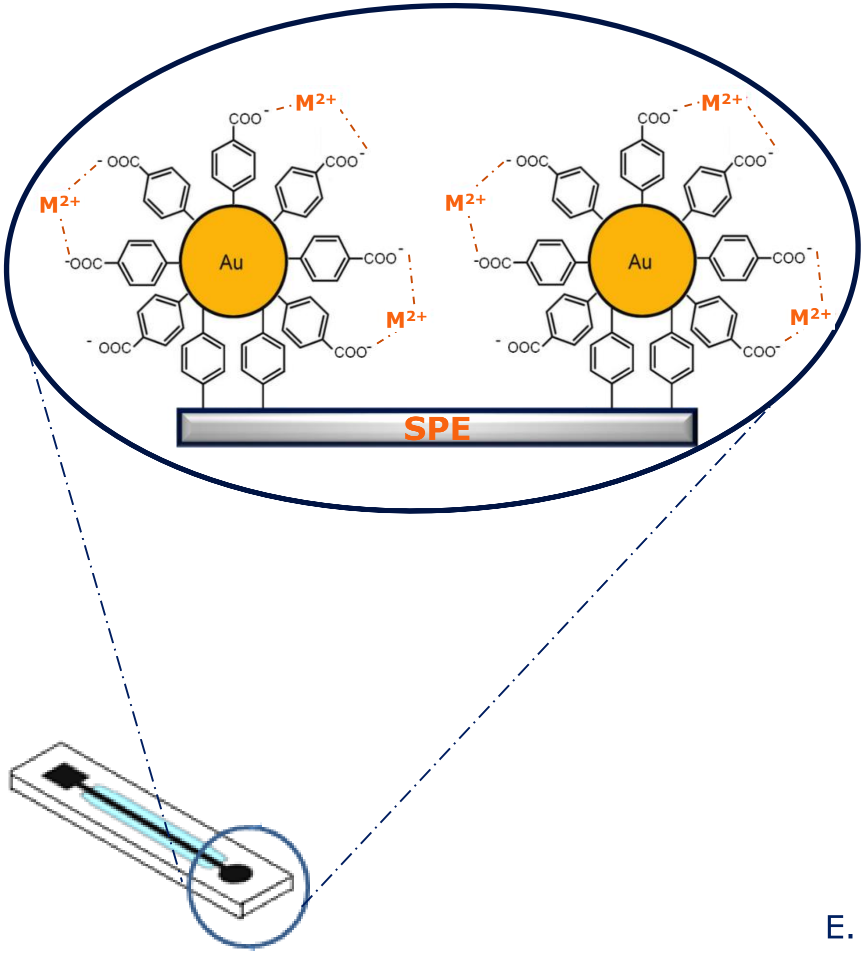
[1] D. Bélanger et al. *Chem. Soc. Rev.* **2011**, 40, 3995.
[2] V. Mevellec et al. patent 2007, US 20080193668 A1
[3] L. Laurentius et al. *ACS Nano* **2011**, 5, 4219.

TOWARDS SELECTIVE AND NANOSTRUCTURED SPEs



TOWARDS NANOSTRUCTURED SPEs

Nanostructuration of SPE surface : grafting of gold nanoparticles (AuNPs)



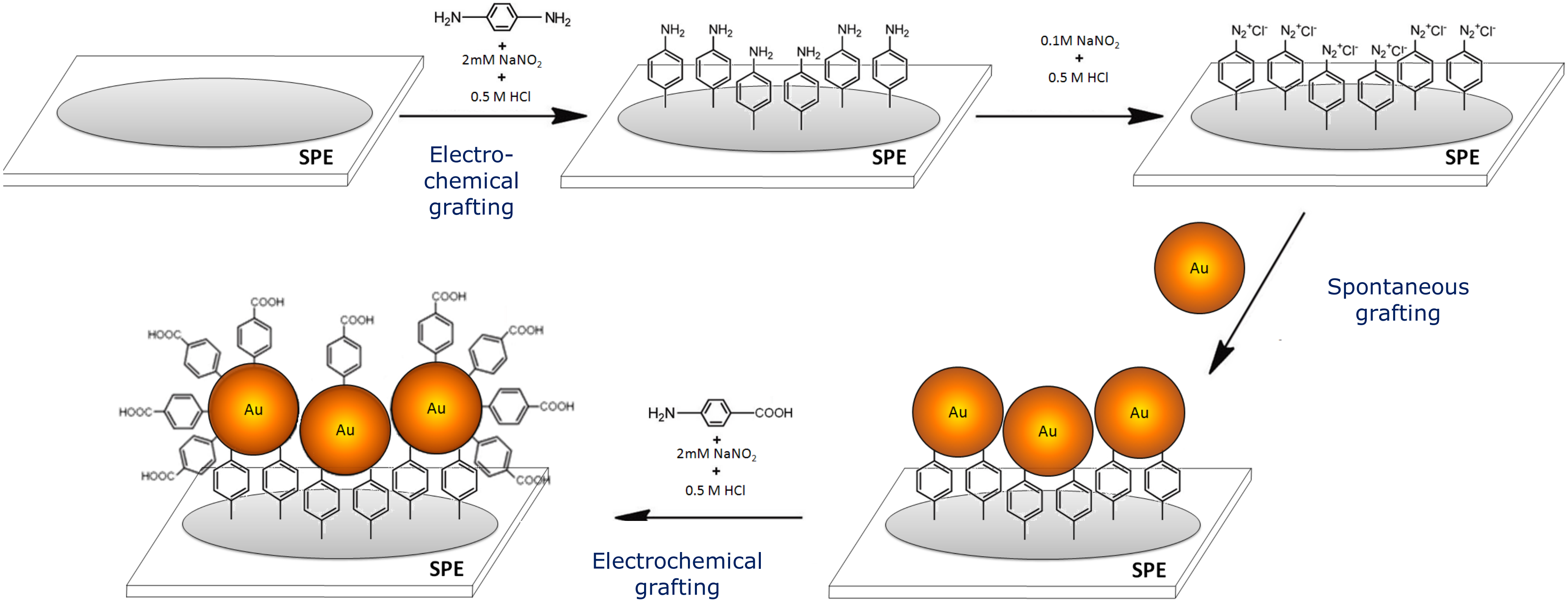
Main interests:

- ✓ Enhancement of specific surface
- ✓ Better electronic transfers
- ✓ Better electrochemical resolution

E. Jubete et al. *Journal of Sensors* **2009**, ID 842575, 1-13

ELABORATION OF NANOSTRUCTURED SPEs

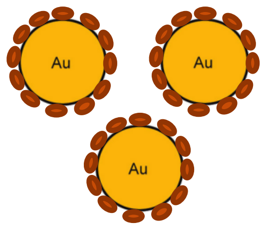
Principle: all-covalent method based on diazonium salts chemistry [1]



J.P. Jasmin et al. *Electrochimica Acta* **2014**, 133, 467.

CHARACTERISTICS OF THE AUNPs SUSPENSIONS

Turkevich AuNPs

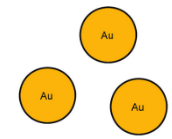


- Diameter 15-20 nm [1]
- Citrate-capped

Advantages :
- Well known synthesis (1951)
- Good stability

Inconvenient:
Presence of citrates at the surface

Eah AuNPs



- Diameter 3-5 nm [2]
- No stabilizing agent

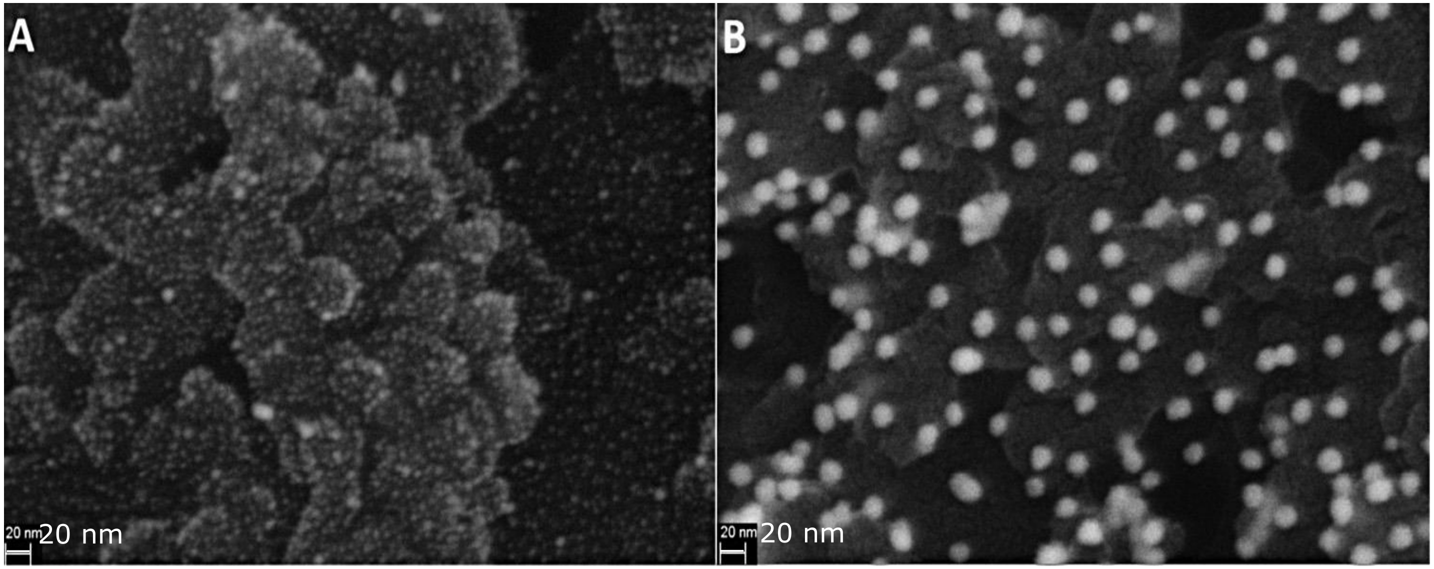
Advantages:
- Small size of the AuNPs
- « Naked » surface

Inconvenient:
Easily destabilized

[1] J. Turkevich et al. *Discuss. Faraday. Soc.* **1951**, 11, 55.

[2] M.N. Martin et al. *Langmuir*, **2010**, 26, 7410.

Scanning electron microscopy (SEM), chimical contrast



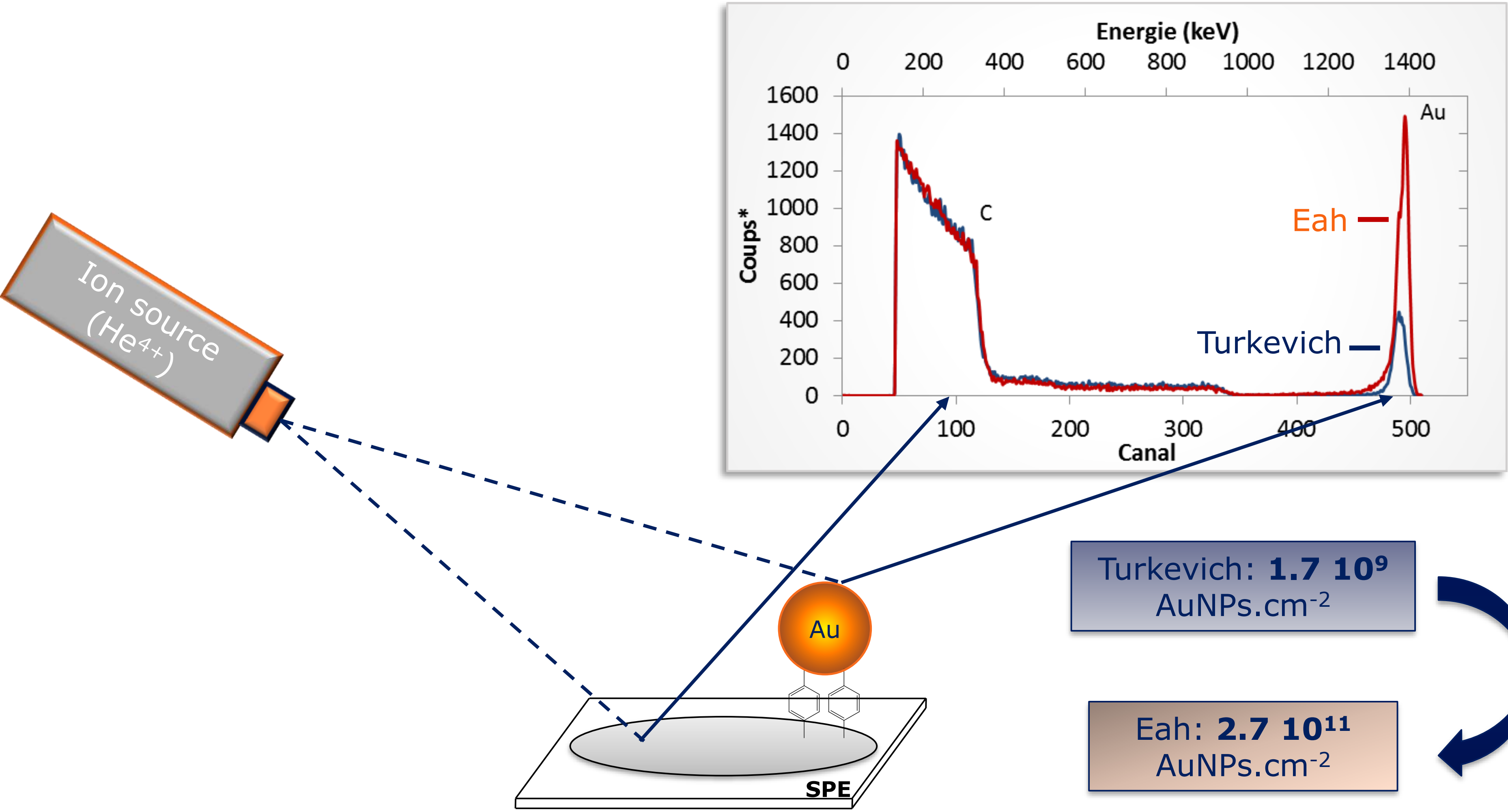
Eah AuNPs

Turkevich AuNPs

→ Homogeneous grafting in both cases, more Eah AuNPs grafted ?

CHARACTERIZATION OF THE NANOSTRUCTURED SPES

Rutterford Backscattering Spectrometry (RBS)



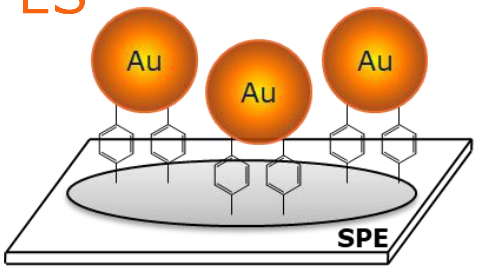
Turkevich: **1.7 10^9** AuNPs.cm^{-2}

Eah: **2.7 10^{11}** AuNPs.cm^{-2}

→ more Eah AuNPs grafted

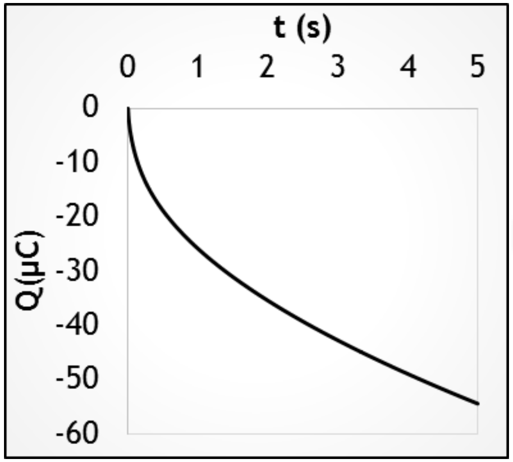
J.P. Jasmin et al. *Applied Surf. Sci.* **2017**, 397, 159-166.

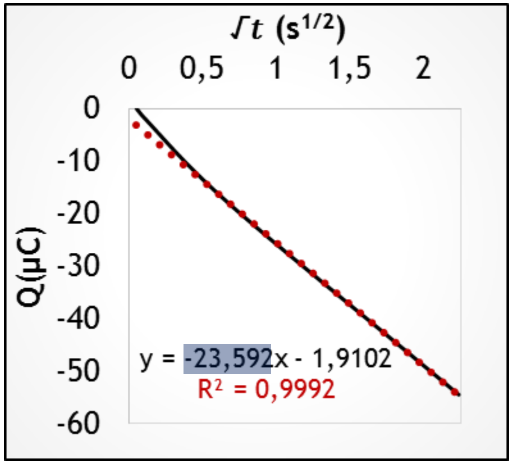
CHARACTERIZATION OF THE NANOSTRUCTURED SPES



Chronocoulommetry – Cottrell Relation

In the presence of an electroactive dye (Ru(III))





Active area	Electrode
7,3±0,1 mm^2	Naked SPE
10,2± 0,5 mm^2	SPE-AuNPs (Turkevich)
17,0±0,2 mm^2	SPE-AuNPs (Eah)

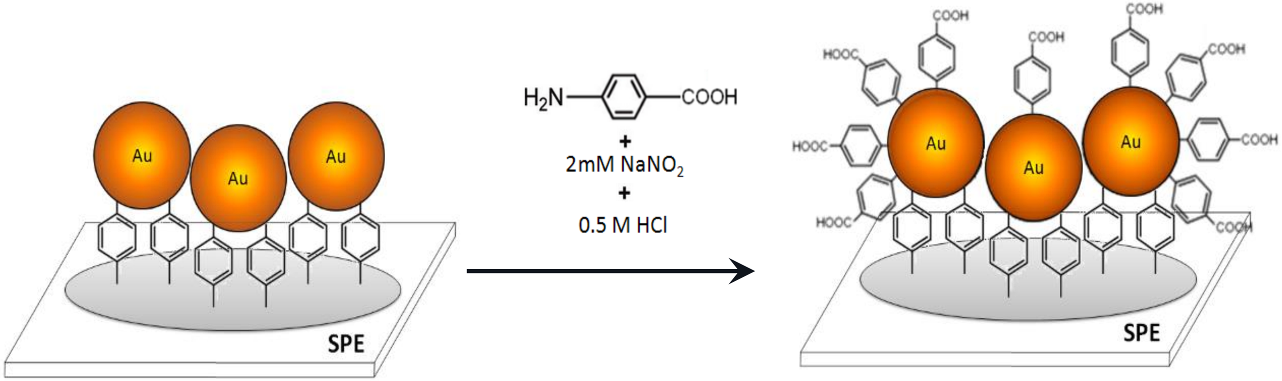
$$Q = \frac{2nFAC\sqrt{D}}{\sqrt{\pi}}\sqrt{t}$$

A: Active area
n: number of electrons involved in the reaction
F: Faraday Constant
C: Dye Concentration
D: Diffusion coefficient of the dye

→ Enhancement of the specific surface with Eah AuNPs by a **factor 2,4**

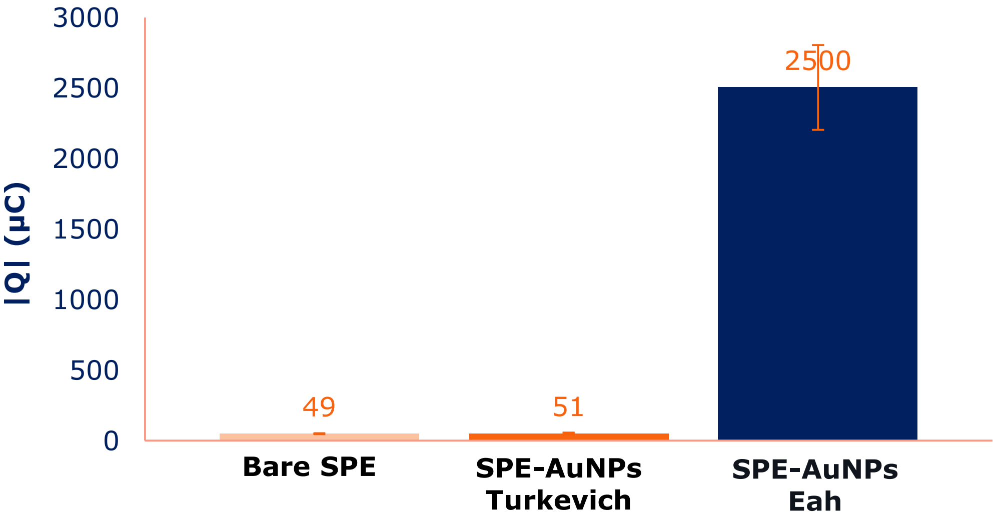
FUNCTIONALIZATION OF NANOSTRUCTURED SPEs

In situ electrochemical reduction of 4-carboxyphenyl diazonium salt (4-CPD)



Chronocoulommetry

Total charges recorded during the grafting

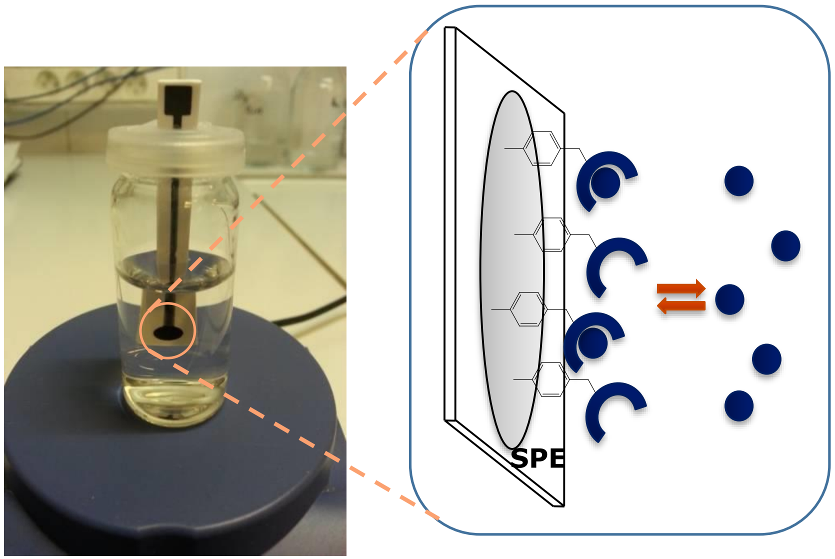


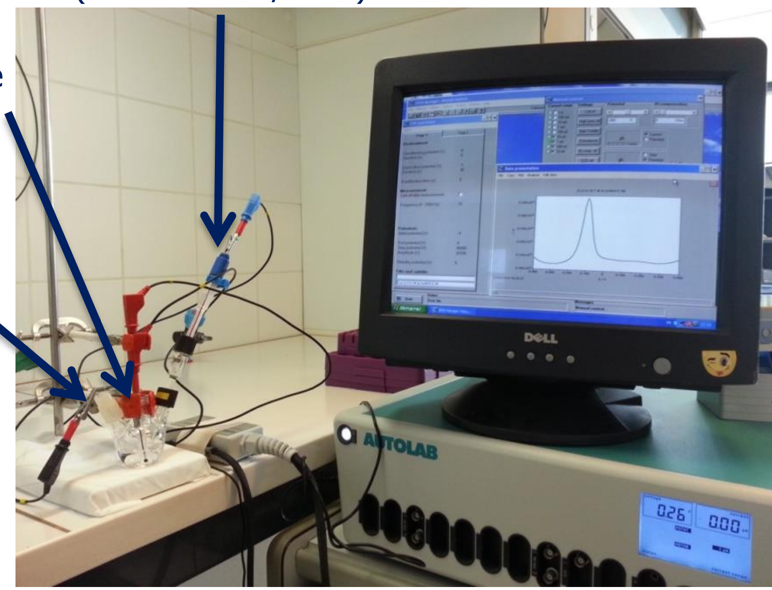
4-CPD grafting: -0.6 V/SCE during 300s
2 mM 4-CPD in 0.1 M H_2SO_4

Enhancement of the total charges by a **factor 50**:

→ **Catalytic effect** of the Eah NPs

PRINCIPLE OF METALLIC POLLUTANTS DETECTION





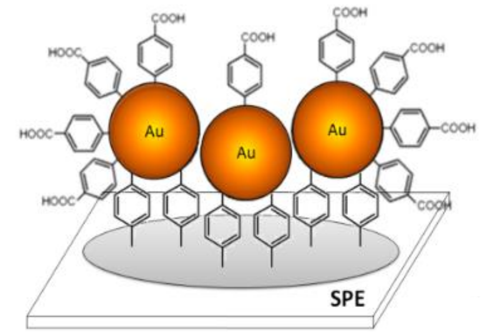
1- Accumulation step

In a buffered solution containing M^{2+}

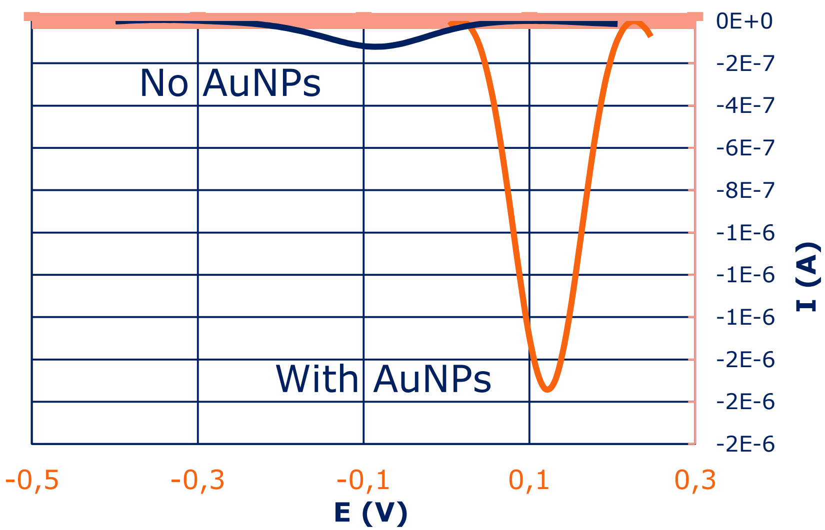
2- Electroanalysis

in a buffered solution free from metal

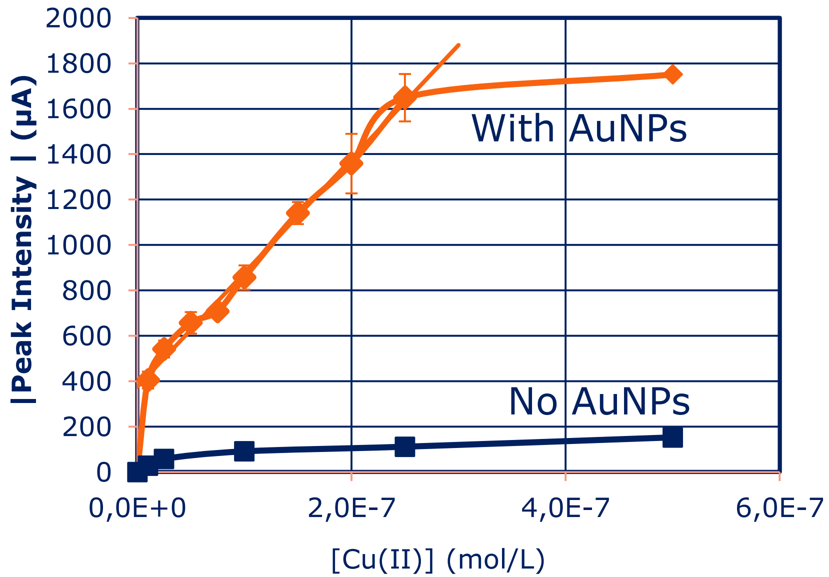
DETECTION OF CU(II) WITH NANOSTRUCTURED ELECTRODES



Detection of Cu(II) by Square Wave Voltammetry:



Calibration plot



[Cu(II)]=2.5 10^{-7}M

Accumulation time: 10mn
Ammonium acetate 0.1 M, pH 7.

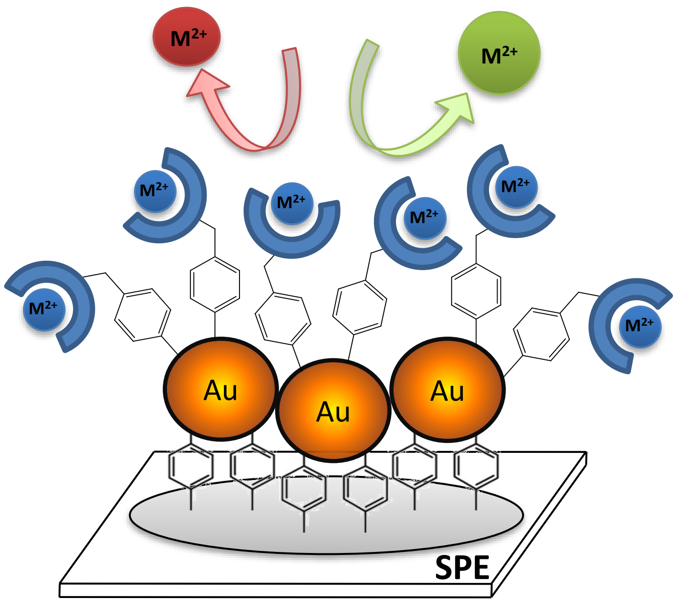
SWV: Pulse amplitude 25 mV,
ΔV 4 $mV.s^{-1}$, freq. 25 Hz.
Ammonium acetate 0.1 M, pH 7.

→ Enhancement of the signal by a **factor of 15**

Linearity between 10 and 250 nM, i.e. **between 0.6 and 16 µg. L^{-1}**

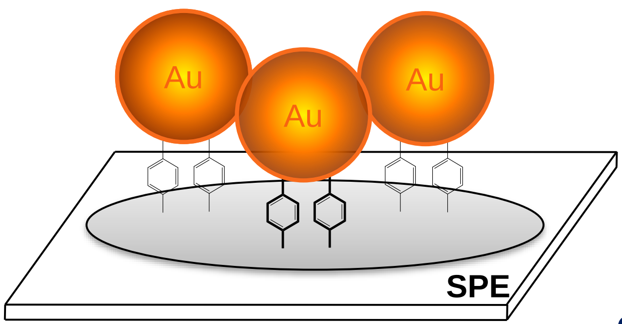
(WHO recommendations for drinkable water sensors
3.1 µM, i.e 0.2 $mg.L^{-1}$)

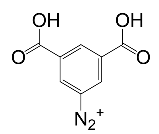
TOWARDS SELECTIVE SPEs



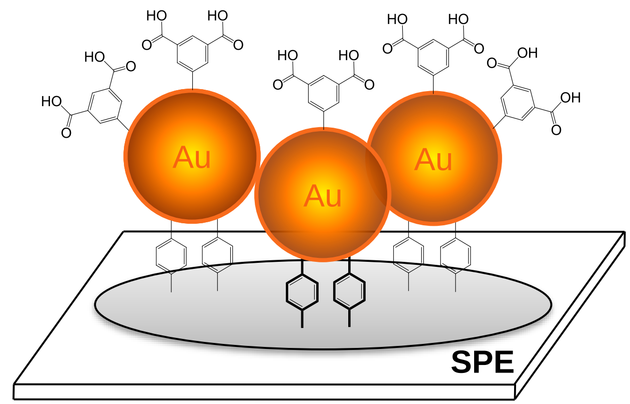
SYNTHESIS OF AZA-FUNCTIONALIZED SPES

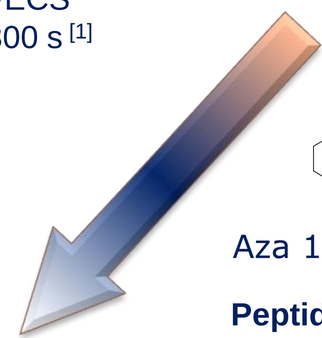
2 steps functonalization by aza 18-crown-6 ether

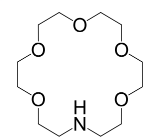




Chronocoulommetry
-0.7 V/ECS
during 300 s [1]

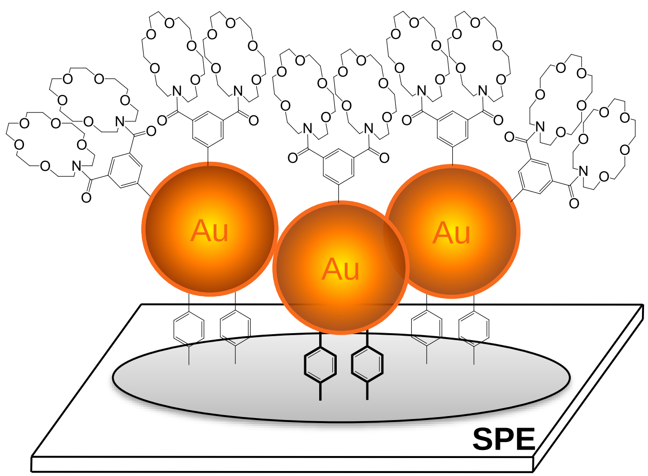






Aza 18-Crown-6 [2]

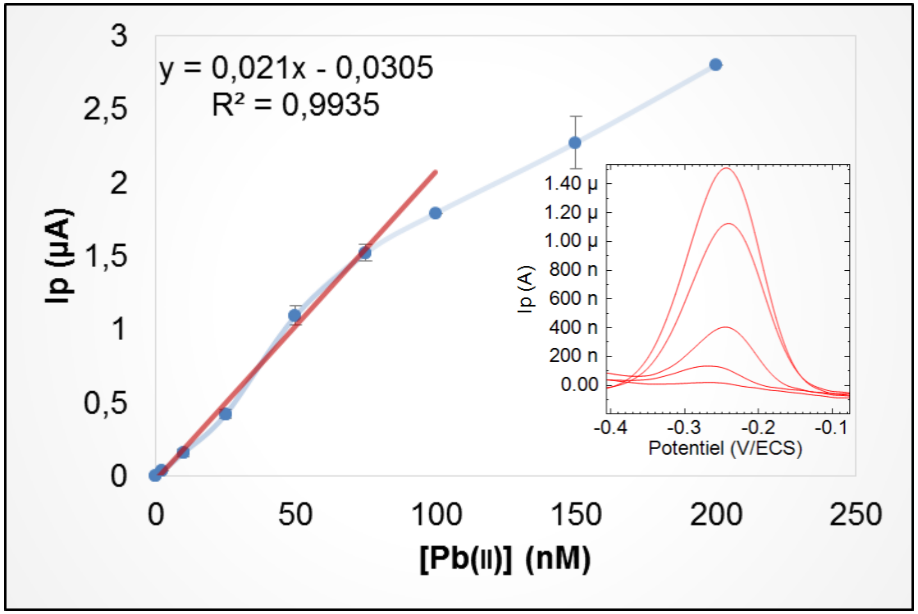
Peptidic coupling
MES Buffer
EDC / NHS

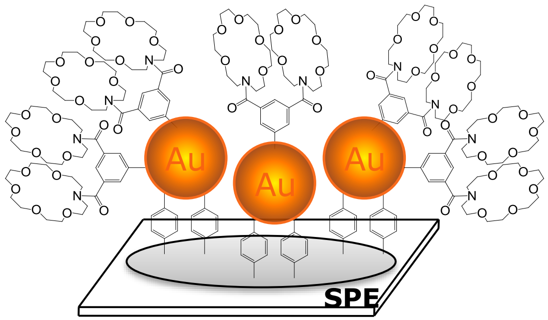


[1] S. Bouden et al. Electrochem. Commun. **2014**, 41, 68.
[2] X. Wang et al. *Sens. Actuators, B* **2014**, 193, 413.

ANALYTICAL PERFORMANCES OF SPES@AZA

Calibration plot





Accumulation time: 10mn
Ammonium acetate 0.1 M, pH 7.

SW-ASV: Deposition Potential -0.75 V for 5 s ; pulse amplitude 25 mV, ΔV 4 mV.s^{-1} , freq. 25 Hz.
Ammonium acetate 0.1 M, pH 7.

✓ **Enhancement** of the signal by a **factor 2** with AuNPs
(i.e. corresponding to the enhancement of the active surface.

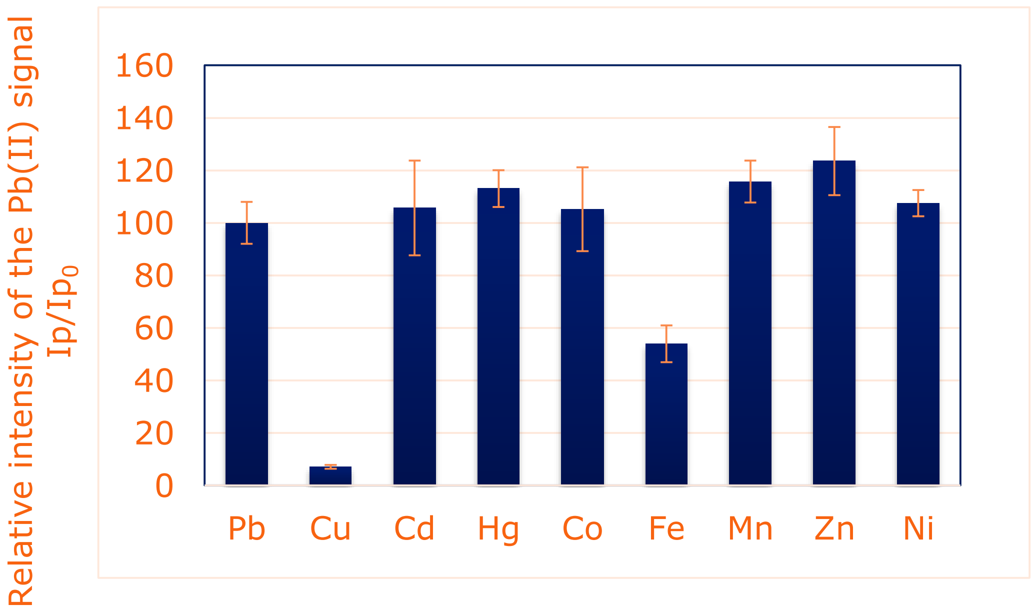
→ H°: **Formation of intermetallic species** during electrodeposition

✓ **Linearity** between 2.5 and 75 nM i.e **between 0.5 and 15 µg.L^{-1}**

→ **Suitable for the determination of natural water samples**
(accepted LOD 4.8 nM i.e **1 µg.L^{-1}**)

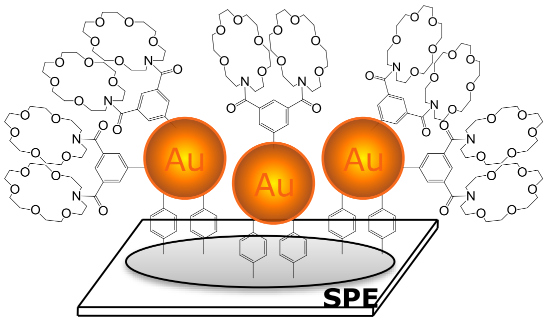
INTERFERENCES STUDY

Detection of Pb(II) in the presence of a 100 fold excess of other metals:



Pb(II) 10^{-7} mol.L^{-1}
Accumulation time: 10mn
Ammonium acetate 0.1 M, pH 7.

SW-ASV: Deposition Potential -0.75 V for 5 s ;
pulse amplitude 25 mV, ΔV 4 mV.s^{-1} , freq. 25 Hz.
Ammonium acetate 0.1 M, pH 7.



➡ Interference of Cu(II), Fe(II)

H°: Formation of a sandwich complex[1] between 2 ligands and a metal ion.

[1] A. Alizadeh et al. *Nanotechnol.* **2010**, 21, 315503

CONCLUSIONS

- ✓ Robust all-covalent nanostructured SPEs *via* diazonium salt chemistry
- ✓ Spontaneous grafting of Eah AuNPs offers the best nanostructuration
- ✓ Enhancement of the electrochemical signal due to the presence of AuNPs

  but dependent on the targeted metallic ion
- ✓ Grafting of macrocyclic ligands at SPEs surface in order to enhance the selectivity

NB: *Necessary to work with <u>electroactive species</u> → Idea: change the strategy,*

using electrochemistry at liquid-liquid microinterfaces

(Cf. Poster)

THANKS !

Colleagues

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