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Electroanalysis and speciation of trace inorganic arsenic in natural waters with ensembles of nanoelectrodes

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OUTLINE

1. Introduction:
   preparation and characteristics of
   ensembles of nanoelectrodes (NEEs)

2. Trace electroanalysis of As with NEEs:
   - NEEs vs Conventional Gold Electrodes
   - Speciation of inorganic Arsenic.

3. From 2D to 3D-NEEs

4. Methods and devices for analysis of real samples

5. Conclusions and prospects

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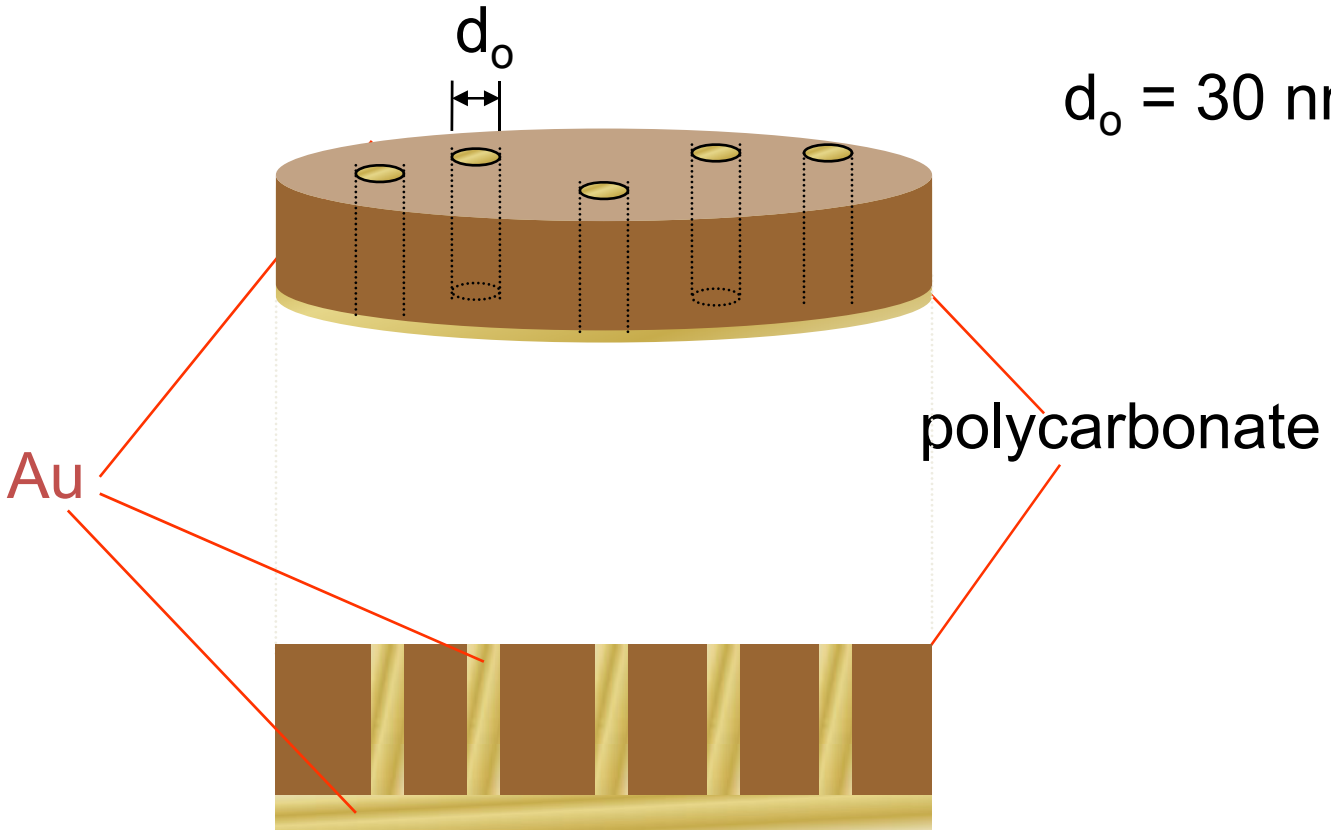
NEE= Nano Electrode Ensemble



Menon & Martin, *Anal.Chem*., 67 (1995) 1920, Ugo et al., *Anal.Chem*., 68(1996) 4160

For reviews see: Ugo & Moretto in *Hanbook of Electrochemistry*, C. Zoski ed., Elsevier 2007 and in *Handbook of Electrochemical Nanotechnology*, 2009

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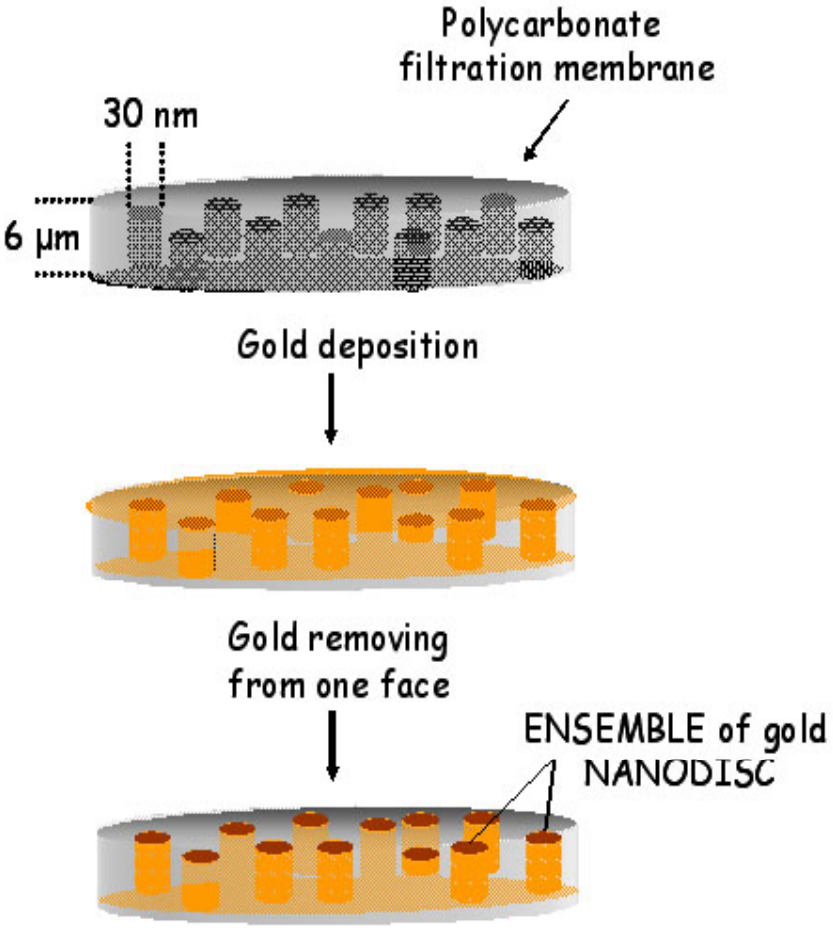
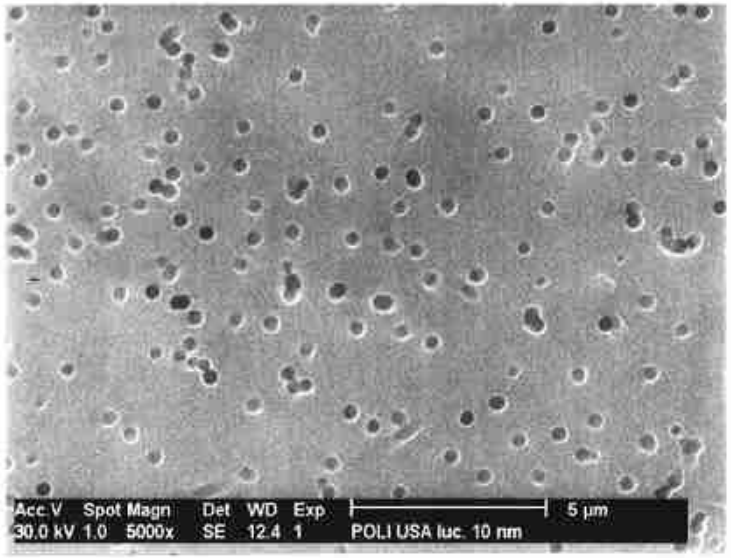
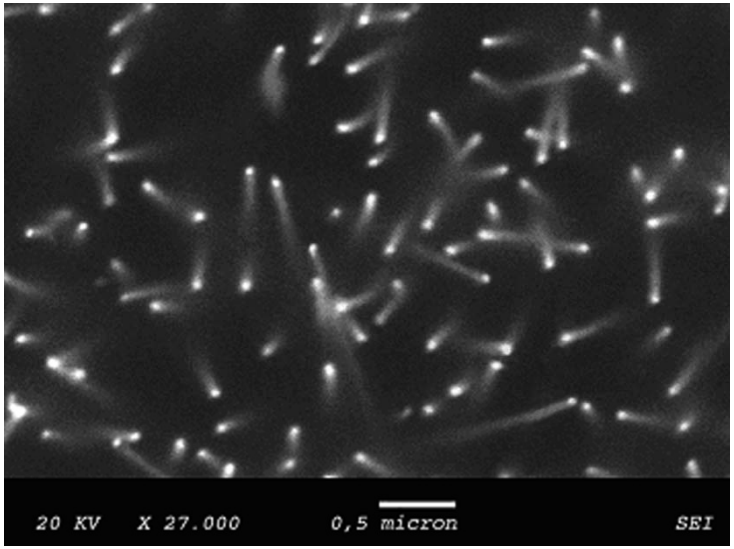
Template deposition of NEE

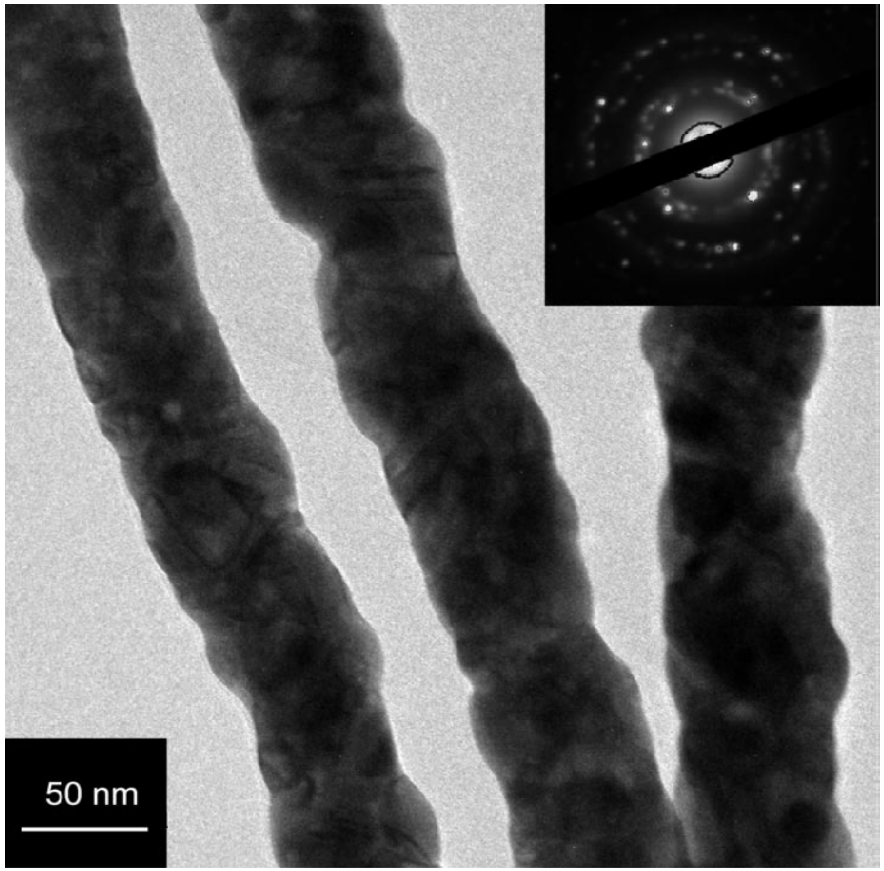


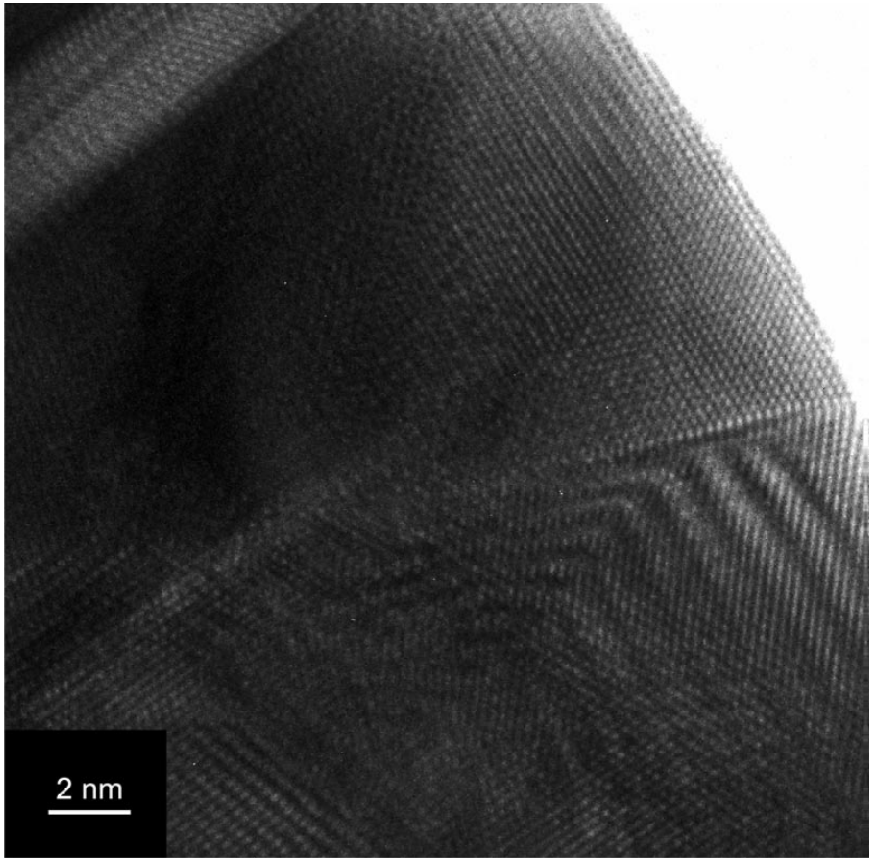




Menon & Martin, *Anal.Chem.*, **67** (1995) 1920

HR-TEM after 24 h Au electroless plating at pH 12





De Leo et al., *Chem. Mater.,* 2007, **19**, 5955

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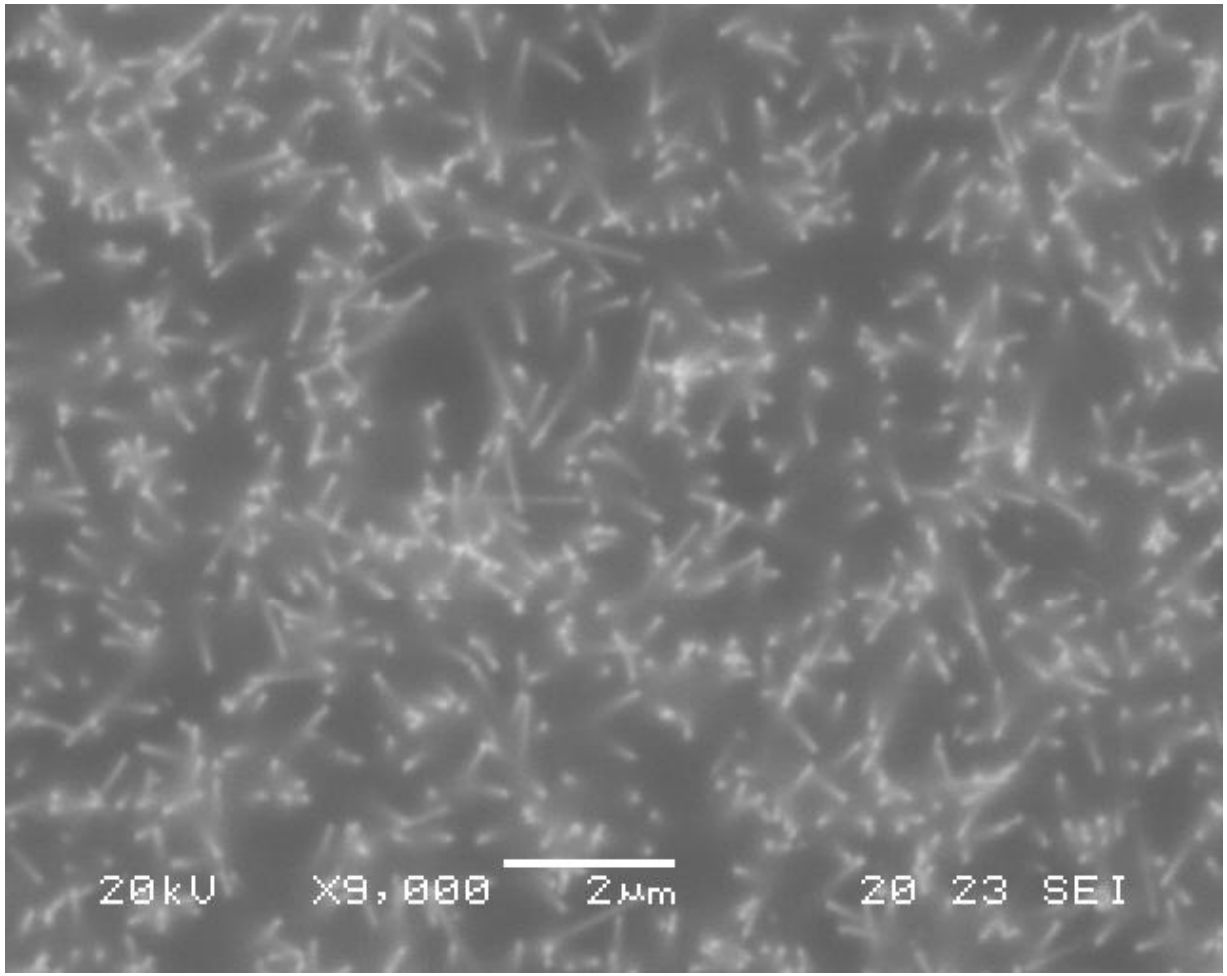
SEM image of NEE (30nm)



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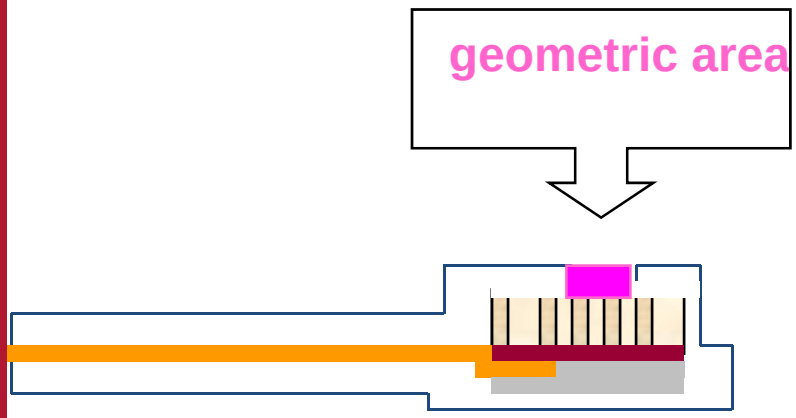
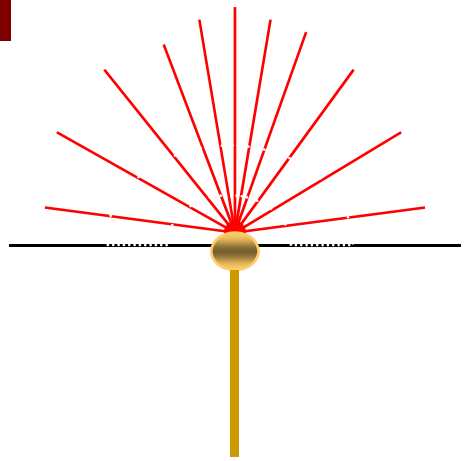
Fabrication of the ensemble

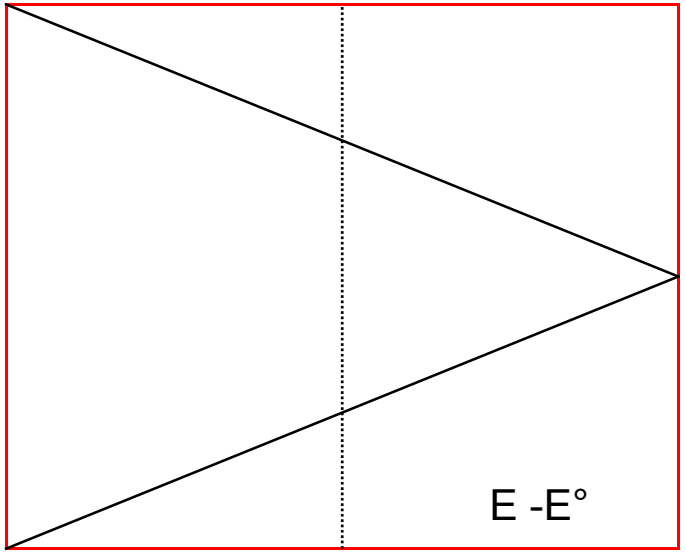


Active area = ΣA_i

Fractional Area = $\frac{A_{active}}{A_{geo}}$

Voltammetry at NEE

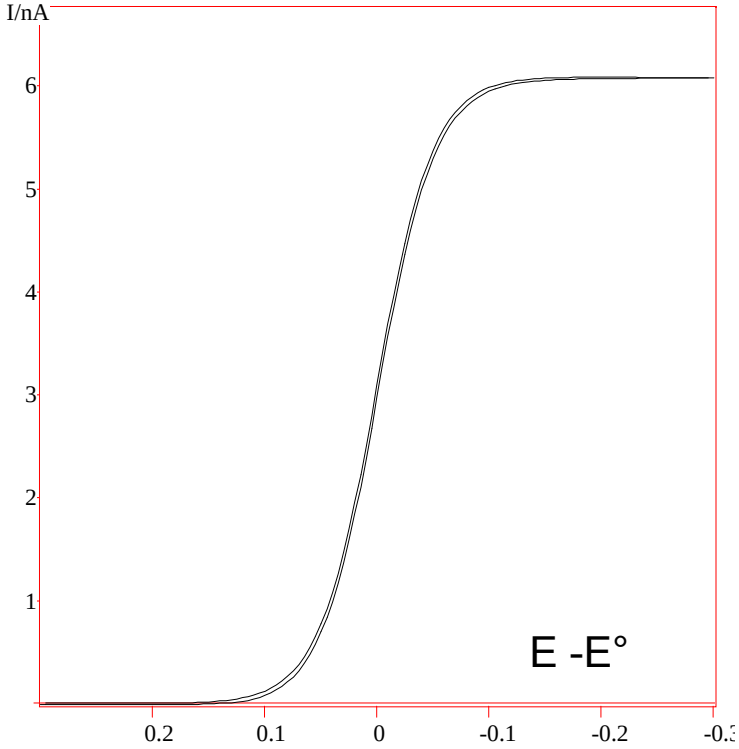




$Ox + n\ e \longrightarrow Red$

Hemi-spherical diffusion at ultramicro-electrodes (steady state)

$I_l = 4nFDCr$ (microdisc)



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Enhanced mass transport at nanoelectrodes

$$1/\delta(t) = [1/(\pi Dt)^{1/2}] + 1/r \qquad (1)$$

where :
- δ is the thickness of the diffusion (depletion) layer,
-*D is the diffusion coefficient of the analyte,*
- *t is the* time scale of the experiment
- *r is the radius of the electrode*

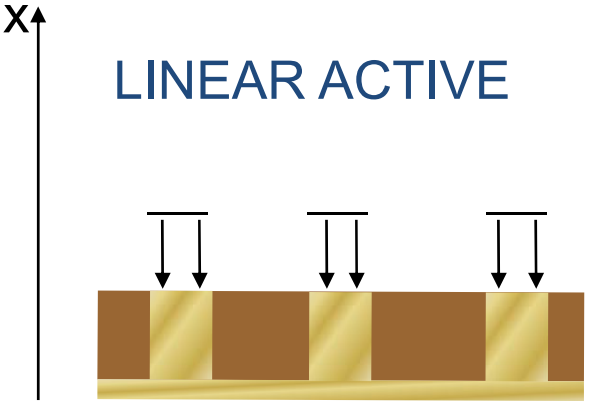
As the electrode decreases in size, the depletion layer thickness approaches the size of the electrode dimension

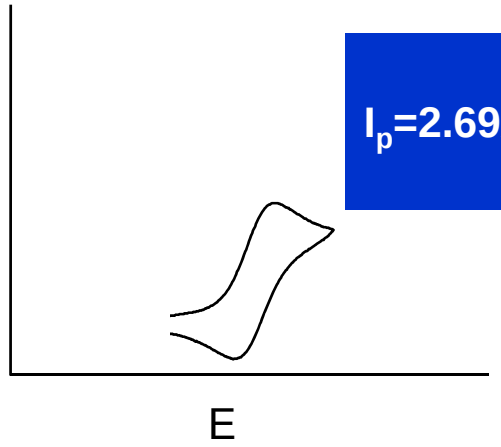
$$I\ (t\rightarrow\infty) = nFAC^* / \delta(t\rightarrow\infty) \qquad (2)$$

Where:
- n is electron stoichiometry;- F is faraday constant;- A is the electrode surface area; - C is the* bulk concentration of the analyte

Smaller electrode provides higher current density

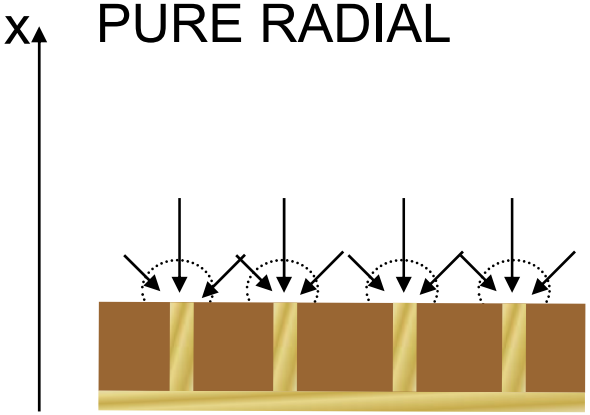
LINEAR ACTIVE

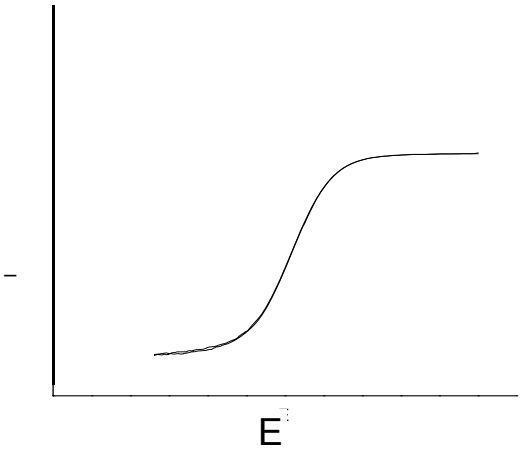




$$I_p = 2.69 \times 10^5 n^{3/2} A_{act} v^{1/2} D^{1/2} C$$

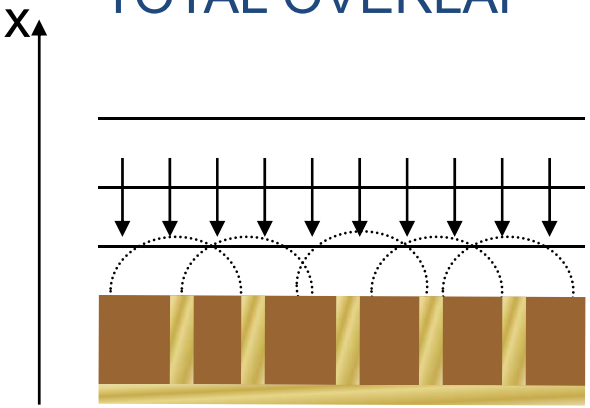
PURE RADIAL

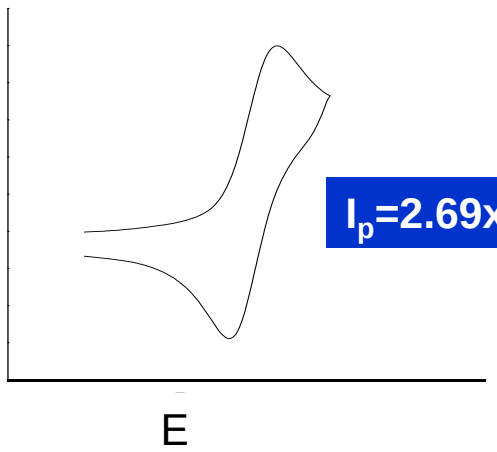




$$I_{lim} = 4nFDCrA_{geom}q$$

TOTAL OVERLAP





$$I_p = 2.69 \times 10^5 n^{3/2} A_{geom} v^{1/2} D^{1/2} C$$

SIGNAL TO BACKGROUND RATIO

At NEE (total overlap regime):

Faradaic current: $I_p = 2.69 \times 10^5 \, n^{3/2} \, \mathbf{A_{geom}} \, v^{1/2} \, D^{1/2} \, c_b$

Background (charging) current : $I_c = \mathbf{A_{active}} \, v \, C_d$

At conventional electrodes:

Faradaic current: $I_p = 2.69 \times 10^5 \, n^{3/2} \, \mathbf{A_{geom}} \, v^{1/2} \, D^{1/2} \, c_b$

Background (charging) current: $I_c = \mathbf{A_{geom}} \, v \, C_d$

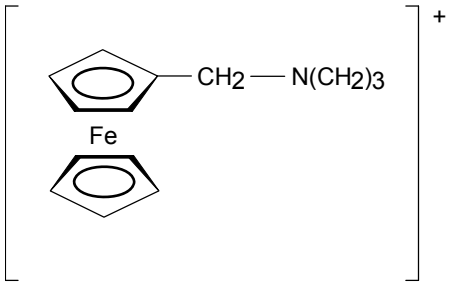
$$(I_p/I_c)_{NEE} = (I_p/I_c)_{conv} \times \mathbf{(A_{geom}/A_{active})} = \frac{(I_p/I_c)_{conv}}{\mathbf{A_{active}/A_{geom}}}$$

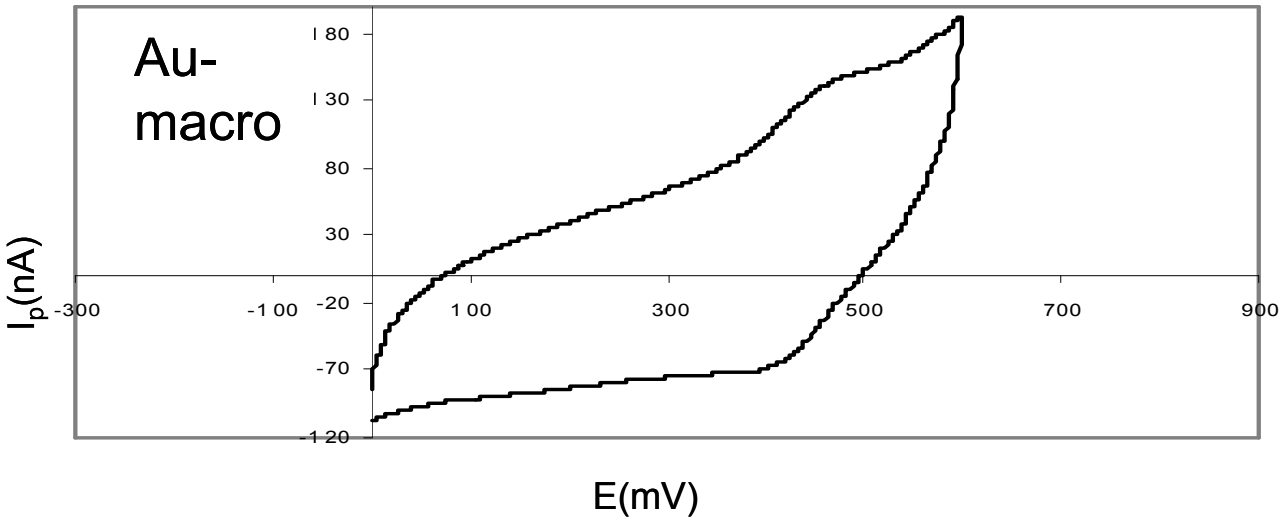
$F = 0.1\text{-}2.5 \times 10^{-2}$

Fractional electrode area

LOWERING OF CAPACITIVE CURRENT AT NEE

5 μM FA^+, 1 mM $NaNO_3$, A_{geom} 0.07 cm^2, 20 mV/s

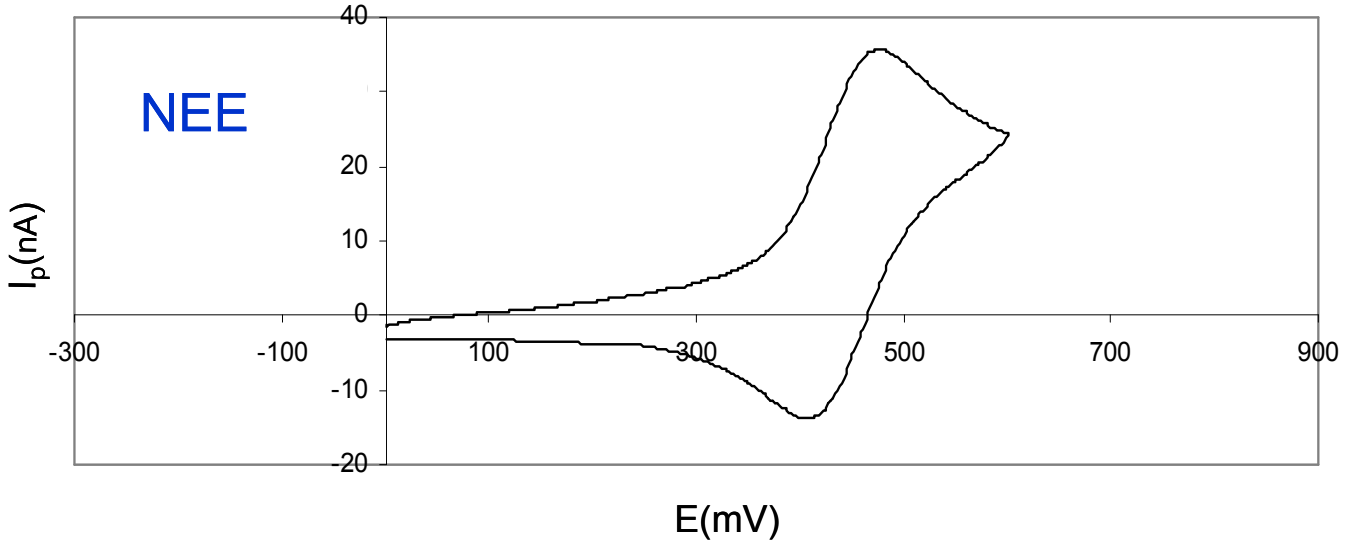




DL at NEE:

Ugo et al.
Anal.Chem.
68 (1996) 4160

Brunetti et al.
J.Electroanal.Chem.
2000, 491(2000)
166



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IMPROVING DETECTION LIMITS WITH NEE

	DETECTION LIMITS	
Analyte	**Macro Au**	**NEE**
FA^{+}	2×10^{-5} M	5×10^{-8} M
$[Ru(NH_3)_6]^{3+}$	2×10^{-5} M	7×10^{-8} M
Azure A	2.4×10^{-6} M	1.2×10^{-7}
MV^{2+}	1×10^{-5} M	2×10^{-6} M
Cytochrome c	2.4×10^{-5} M	1.2×10^{-6} M
Iodide	4×10^{-6} M	3×10^{-7} M

Brunetti et al. *J.Electronal.Chem.*, 491 (2000) 166

Ugo et al. *Talanta*, 62 (2004) 1055

F.C.Pereira et al. *Anal. Chim. Acta* 575 (2006) 16-24

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Arsenic analysis: goals

The development of sensitive and disposable devices for the decentralized analysis of inorganic As(III) and As(V) in water samples, achieving DL < 10 μg/L (WHO recommended limit)

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Steps

- Evaluate the performances of NEEs (vs Macro Gold Electrodes) in anodic stripping voltammetry of As(III).
- Speciation of total inorganic Arsenic
- Etching from 2D to 3D-NEEs
- Analysis of real samples

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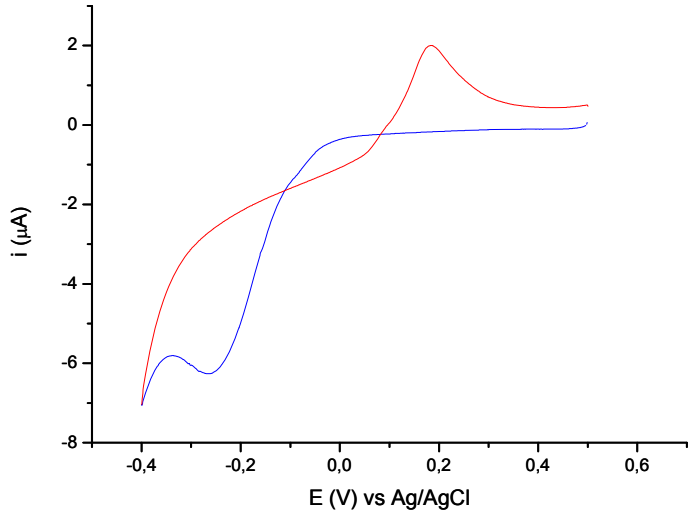
Principles of Anodic Stripping Voltammetry of As on Au electrodes

DEPOSITION STEP: $As^{3+} + 3e^- \longrightarrow As^0$

STRIPPING STEP: $As^0 \longrightarrow As^{3+} + 3e^-$



CV recorded at a Macro Gold Electrode in 1M HCl, 2 g/L hydrazine and 5 μgL^{-1} As(III)

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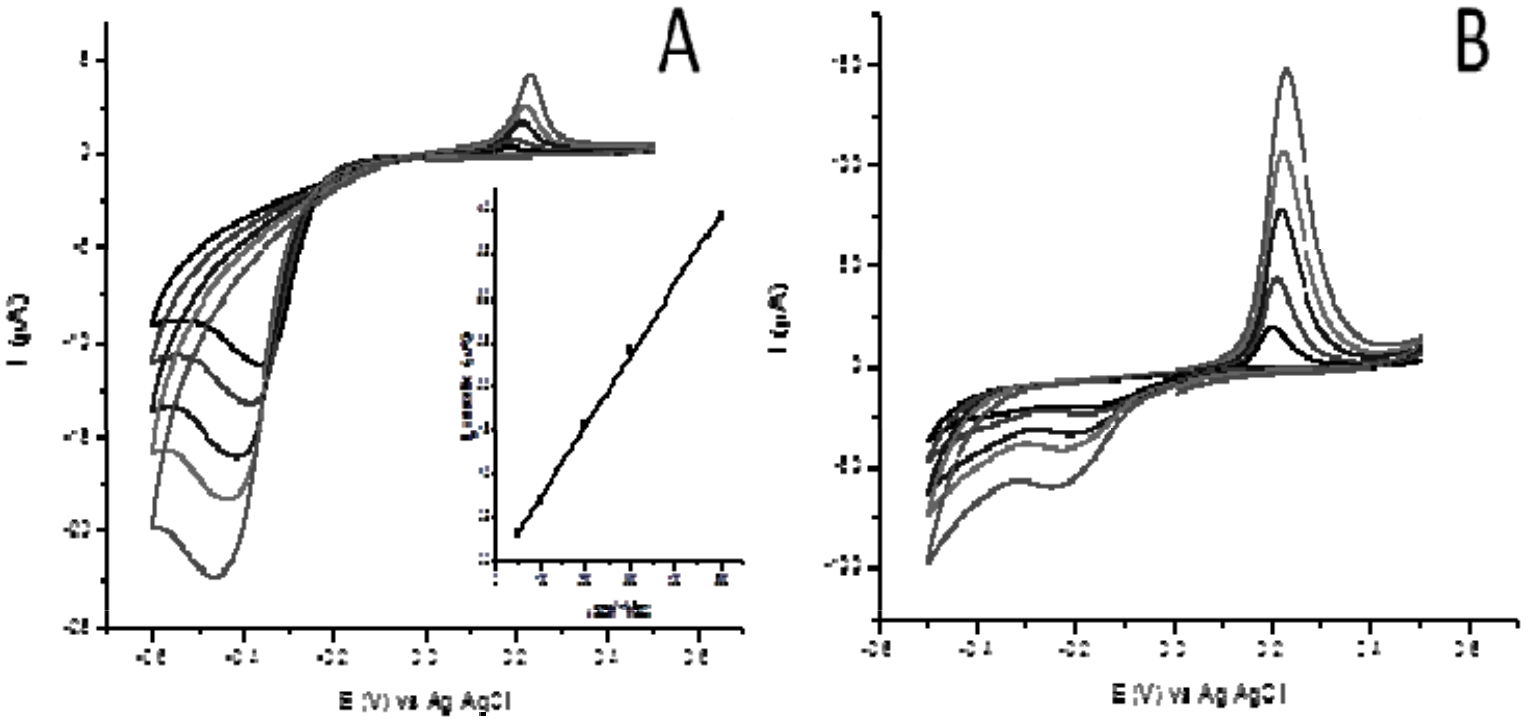
NEE

Au-macro



Cyclic voltammograms recorded at different scan rates (from 0.05 to 0.5 V/sec) at a NEE (A) and at a flat gold electrode (B) in solution of 40 μgL^{-1} As(III) in HCl 0.2M.
Inset: ip vs scan rate.

A. Mardegan et al., Electroanalysis 2012, 24, No. 4, 798 – 806

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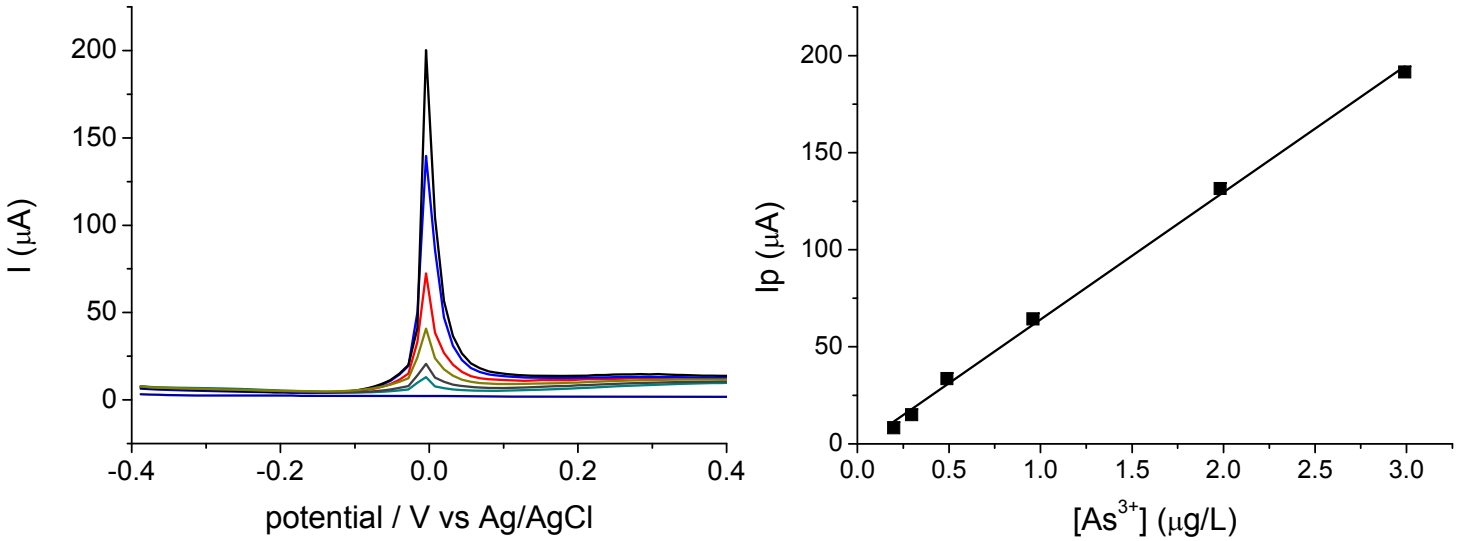
AS-SWV of As(III) at NEE



SW-ASV parameters: incr 12mV; amplitude 75mV; frequency 250Hz.

Analytical procedure:

- Deposition at -0.4 V for 180s
- Stripping between -0.4 and 0.4V
- Cleaning step: 0.5 V for 60 s

Electrolyte concentration:

- HCl 0.2 M
- Hydrazine 62 mM (2 g/L)

Mardegan *et al. Electroanalysis*, 24 (2012) 798

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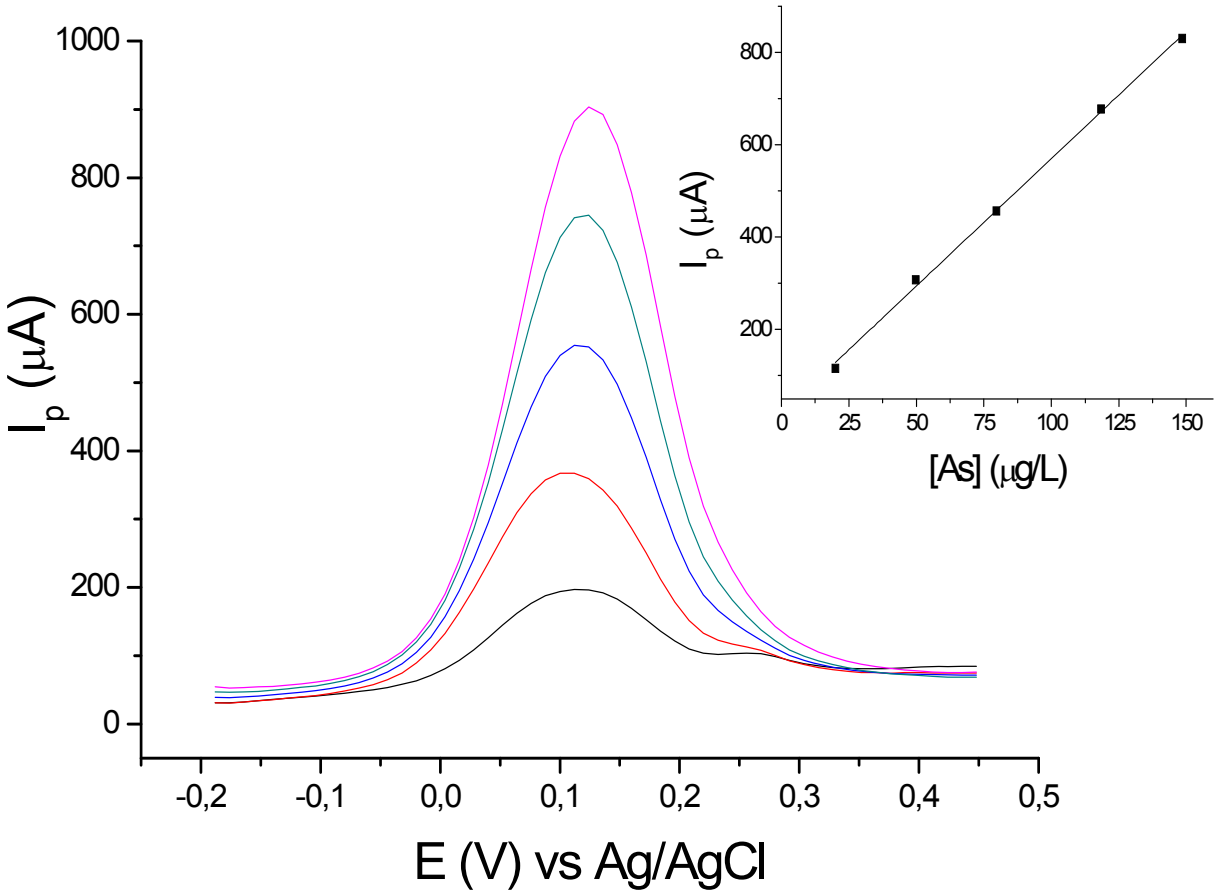
Anodic stripping SWV at Au-macro



Deposition at -0.4 V for 120 s

A. Mardegan et al., Electroanalysis 2012, 24, No. 4, 798 – 806

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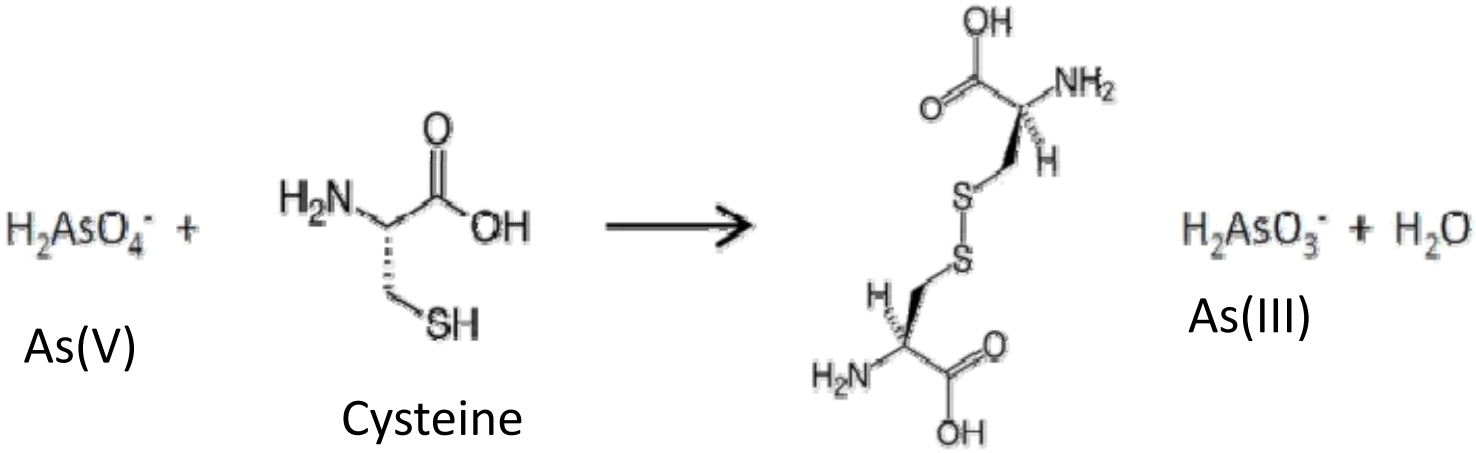
INORGANIC As SPECIATION



Analytical procedure:

- Reduction in not acidified solution with 4.9 mM cysteine
- 80°C for 30 min.

Svancara *et al. Talanta*, 58 (2002) 45

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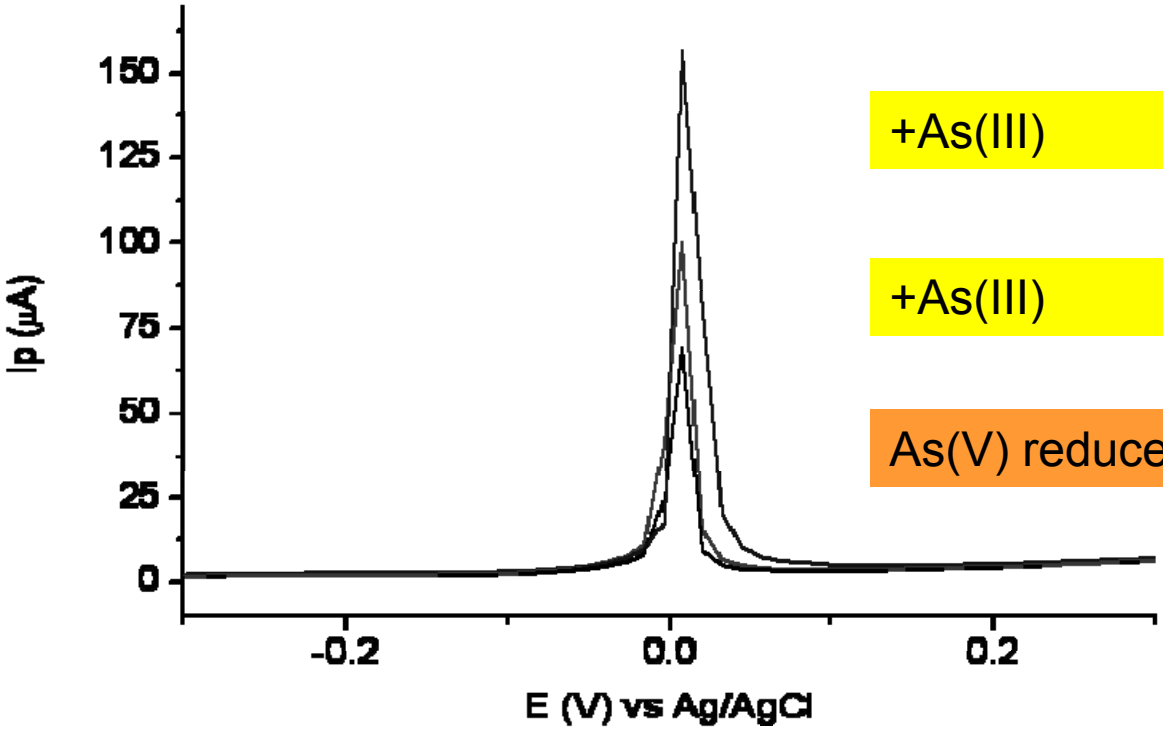
Reductive determination of As (V)



1) As(V) +2cysteine → As(III) + cystine + H_2O
2) As(III) + $3e^-$ → As(0)
3) As(0) → As(III) + $3e^-$

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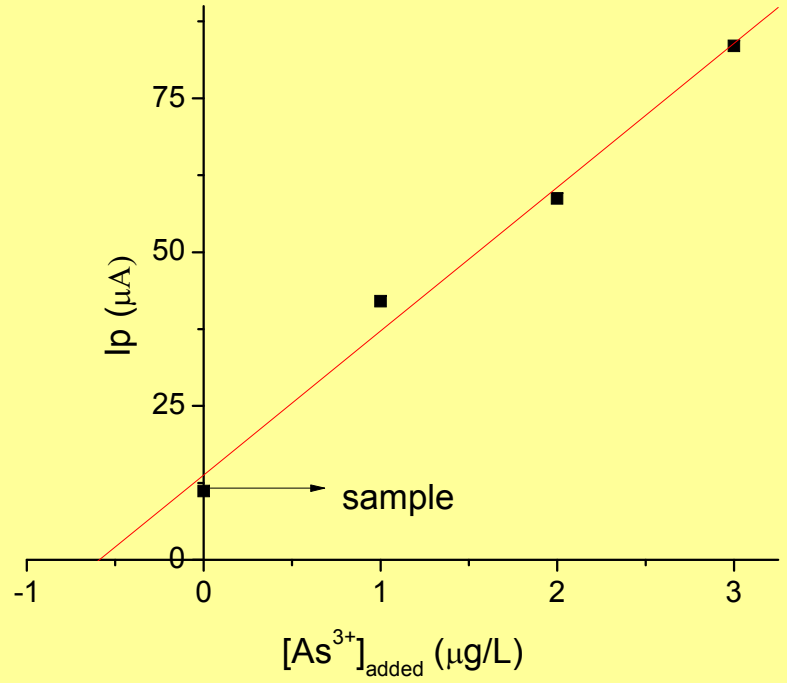
Analytical performances: accuracy

CASS-4
(near shore seawater) diluted 1:1
As certified 1.11 ± 0.16 μgL^{-1}
As found: 1.18 ± 0.06 μgL^{-1}



A. Mardegan et al., Electroanalysis 2012, 24, No. 4, 798 – 806

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Analytical performances: comparison between NEE and Au-macro (deposition time 180 s)

	NEE	Au-macro
Detection limit ($3\sigma_b$ /m)	0.005 µg/L	0.75 µg/L
Linearity range	0.2 - 6 µg/L	20 – 150 µg/L
Sensitivity (m)	65. 6 µA L / µg	5.5 µA L / µg
Background noise (σ_b)	0.11 µA	1.38 µA

Problem

NEEs are easily saturated (very small active area).
It is required to extend their linearity range.

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2° part OUTLINE

3. From 2D to 3D-NEEs
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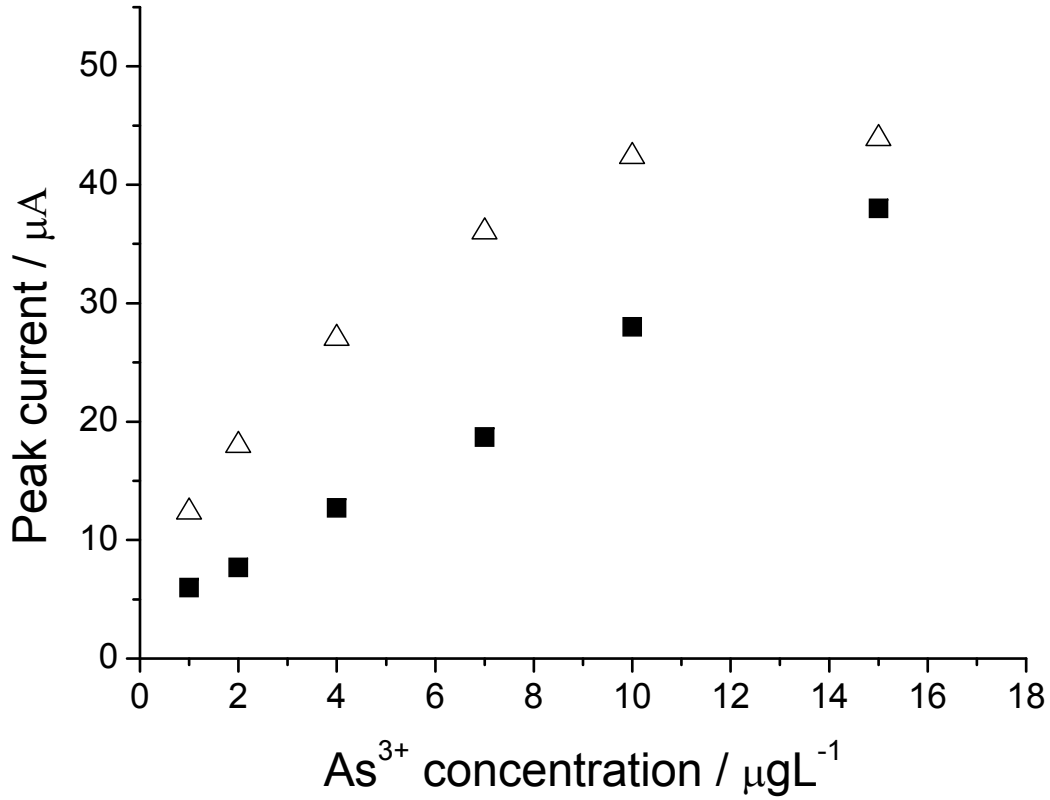
Analytical performances: effect of the deposition time on the linearity range



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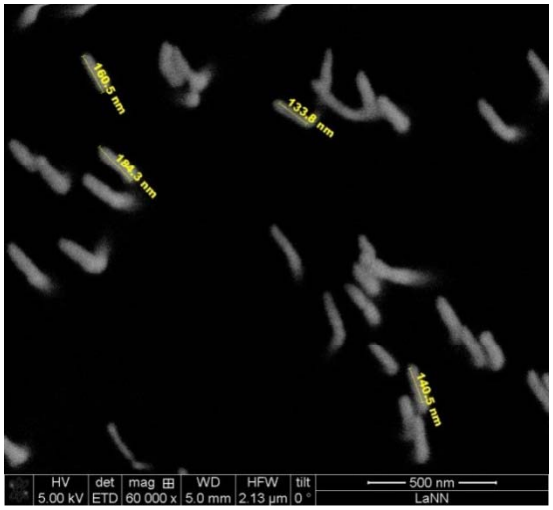
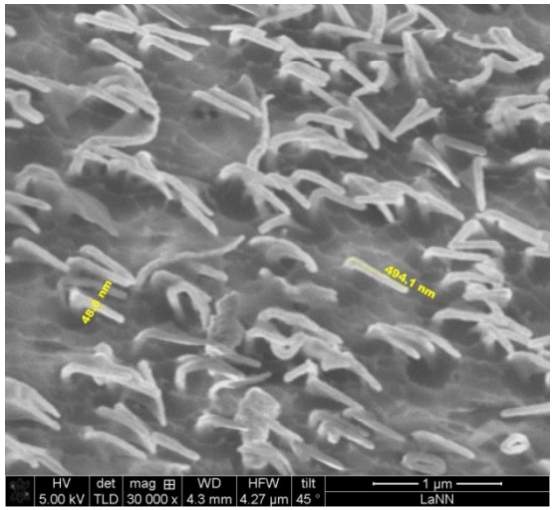
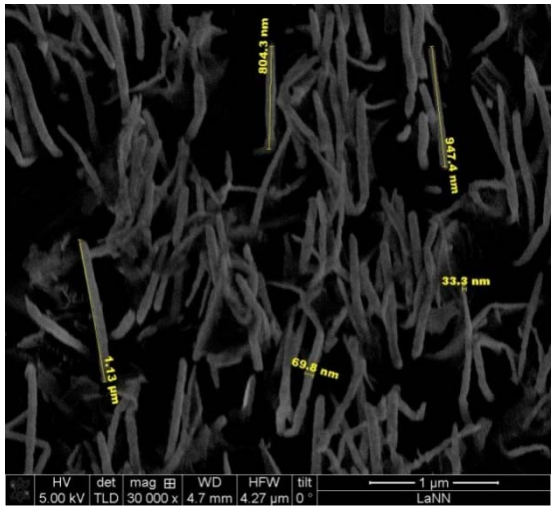
PROBLEM: easy saturation of the NEE surface
SOLUTION: OXYGEN PLASMA ETCHING



1 minute



5 minutes



10 minutes

De Leo et al. *Electroanalysis*., 19 (2007) 227

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Increase of active area with O_2-plasma etching

Treatment duration (min)	Nanofiber lenght (µm)	$A_{(3D\text{-}NEE)} / A_{(2D\text{-}NEE)}$	$A_{(ACTIVE)} / A_{(GEOMETRIC)}$
0	0	1	0.004
1	0.15	20	0.089
5	0.5	67	0.287
10	1	133	0.569

By a controlled increase of the A_{act}/A_{geom} the S/N decreases therefore a compromise between these aspects is required.

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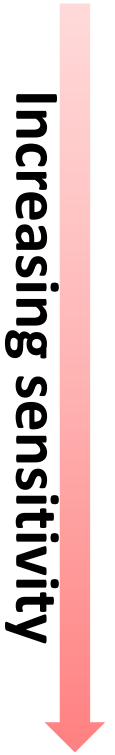
O_2-plasma etching
As(III) response at 3D-NEEs

NEE	$t_{etching}$ (min)	t_{dep} (sec)	LR (µg/L)	m (µA·L/µg)	DL (µg/L)
NEE 528	1	180	2-15	1.54	0.060
NEE 529	1	180	1-20	1.32	0.082
NEE 534	5	180	5-40	3.22	0.079
NEE 535	5	180	2-30	3.40	0.050
NEE 507	10	180	5-40	5.73	0.073
NEE 506	10	180	5-40	5.98	0.064



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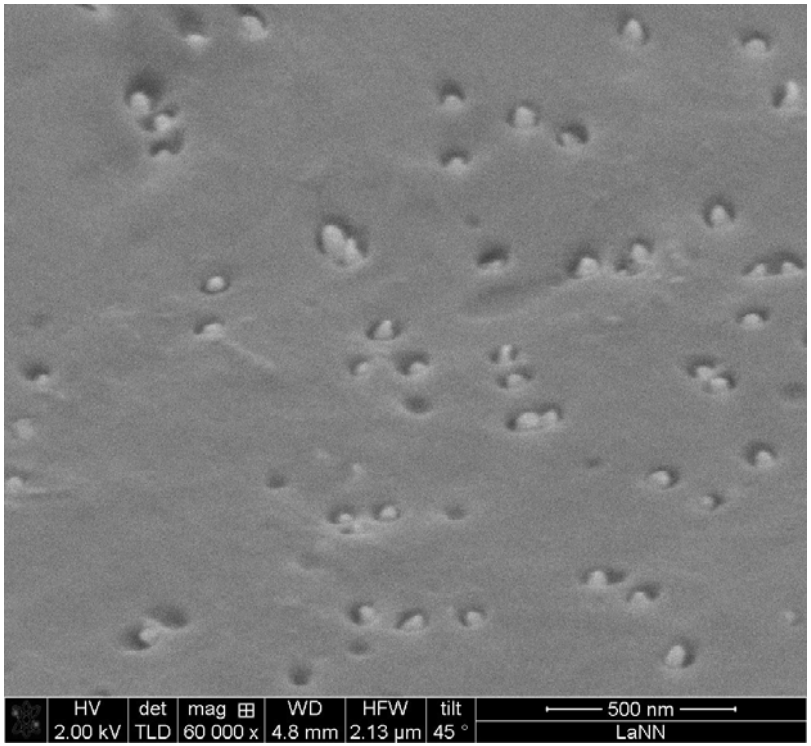
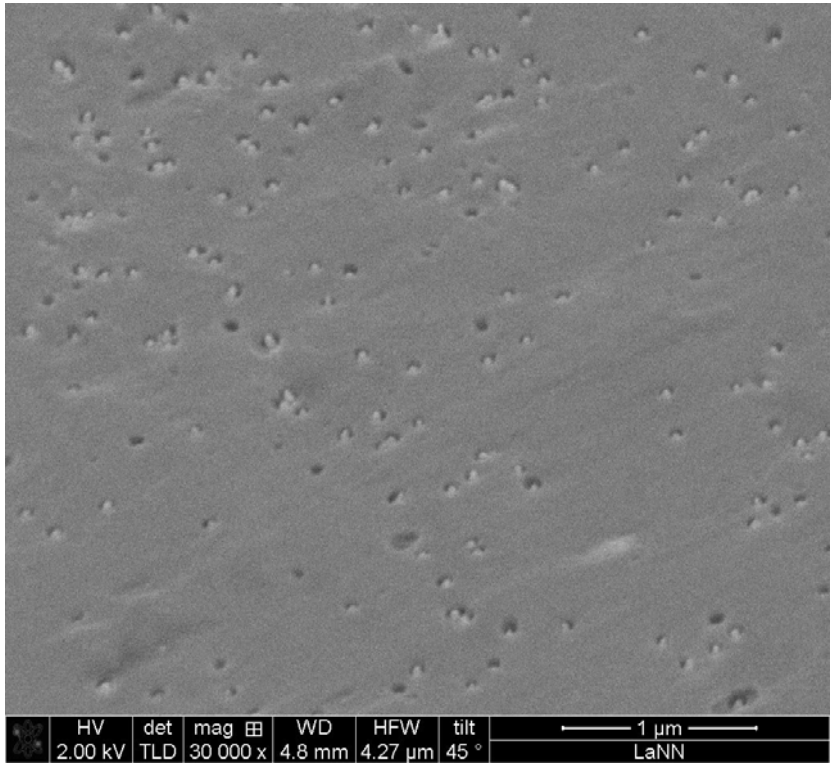
Chemical etching
CH_2Cl_2 : EtOH
1 : 9





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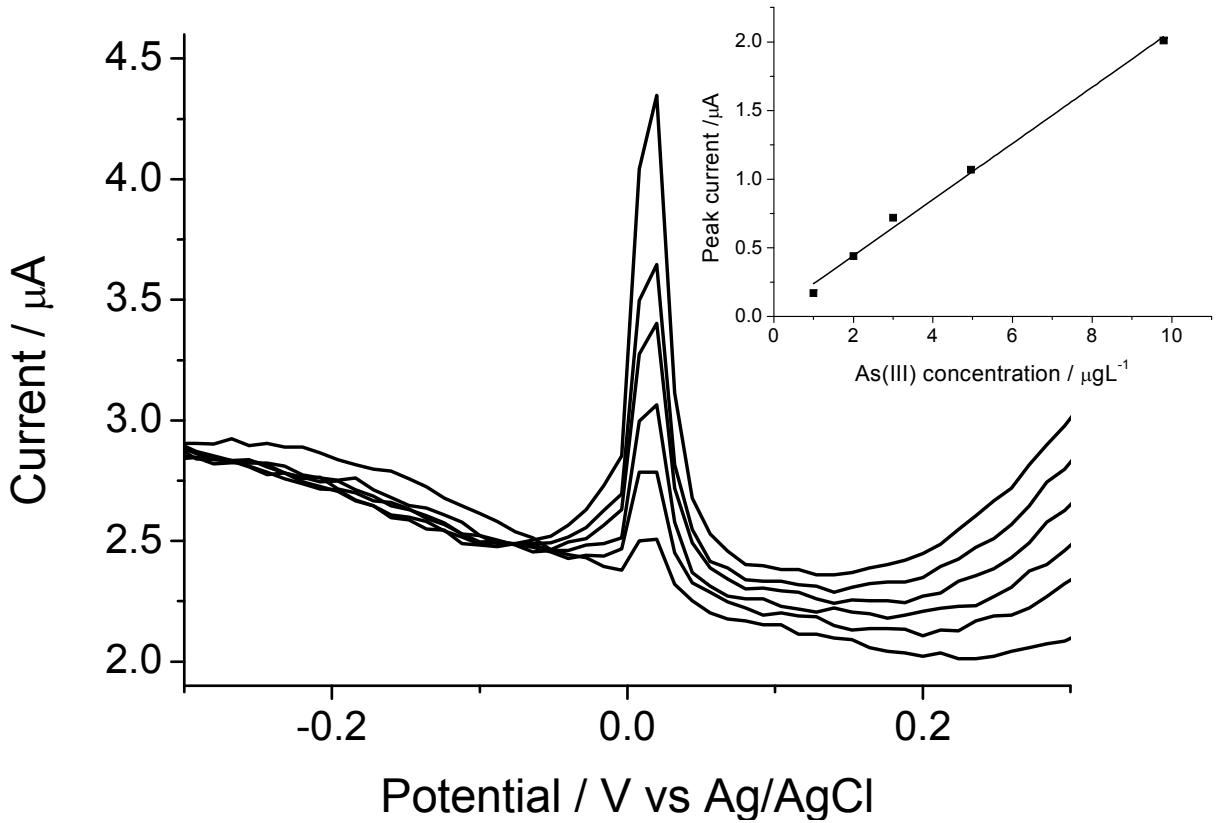
Chemical Etching time: 5s
As(III) response at 3D-NEEs



NEE	$t_{etching}$ (sec)	t_{dep} (sec)	LR (µg/L)	m (µA·L/µg)	DL (µg/L)
NEE 601	5	180	1-5	0.102	0.14

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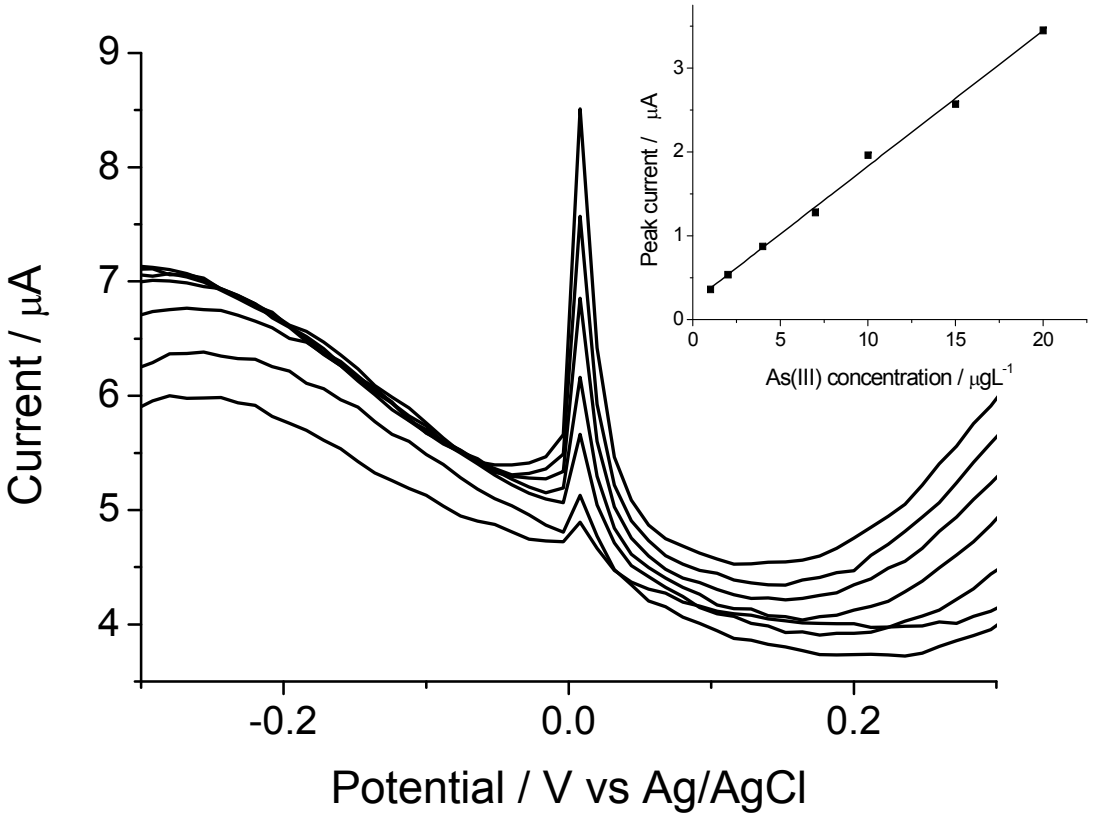
Chemical Etching time: 20s
As(III) response at 3D-NEEs



NEE	$t_{etching}$ (sec)	t_{dep} (sec)	LR (µg/L)	m (µA·L/µg)	DL (µg/L)
NEE 601	5	180	1-5	0.102	0.14
NEE 606	20	180	1-20	0.161	0.08

Increasing sensitivity

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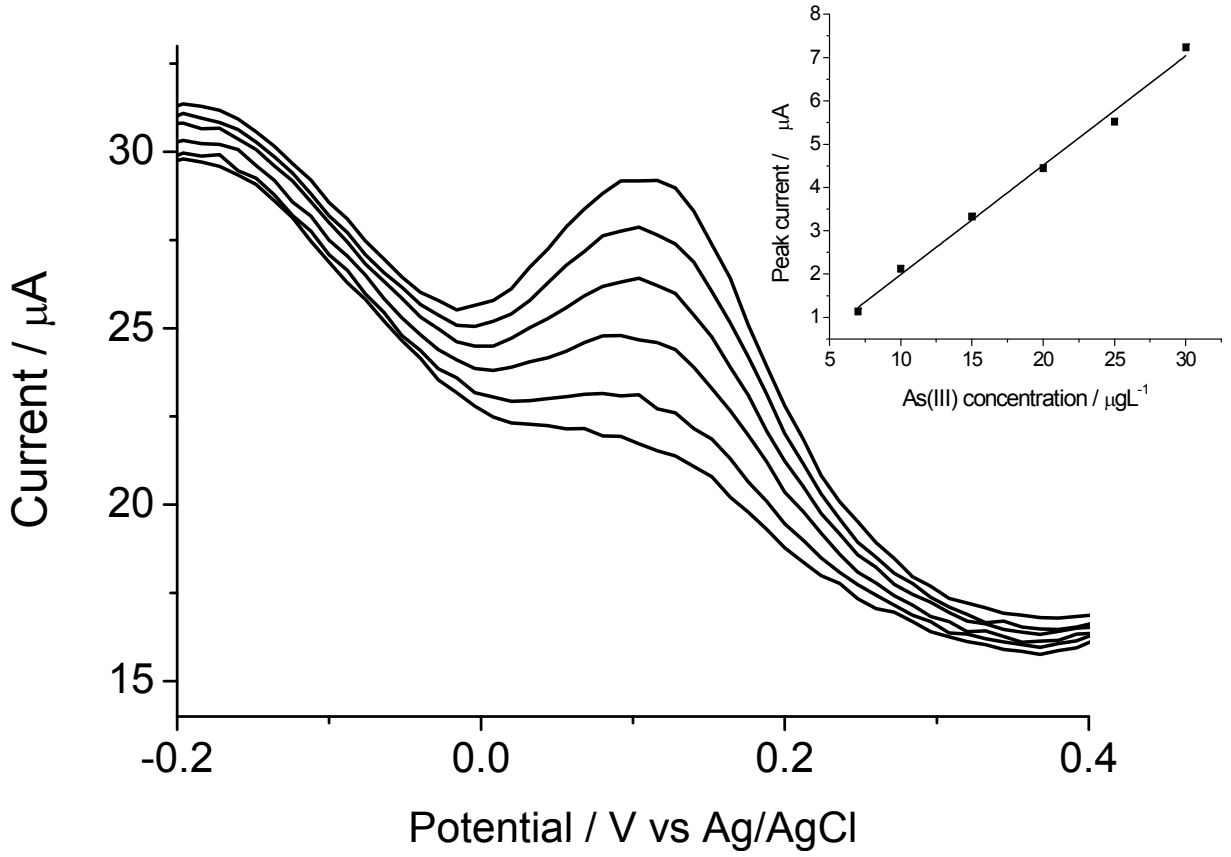
Chemical etching
Etching time: 30s



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Chemical etching
As(III) response at 3D-NEEs

NEE	$t_{etching}$ (sec)	t_{dep} (sec)	LR (µg/L)	m (µA·L/µg)	DL (µg/L)
NEE 601	5	180	1-5	0.102	0.14
NEE 606	20	180	1-20	0.161	0.08
NEE 602	30	180	5-30	0.292	0.11

Increasing sensitivity

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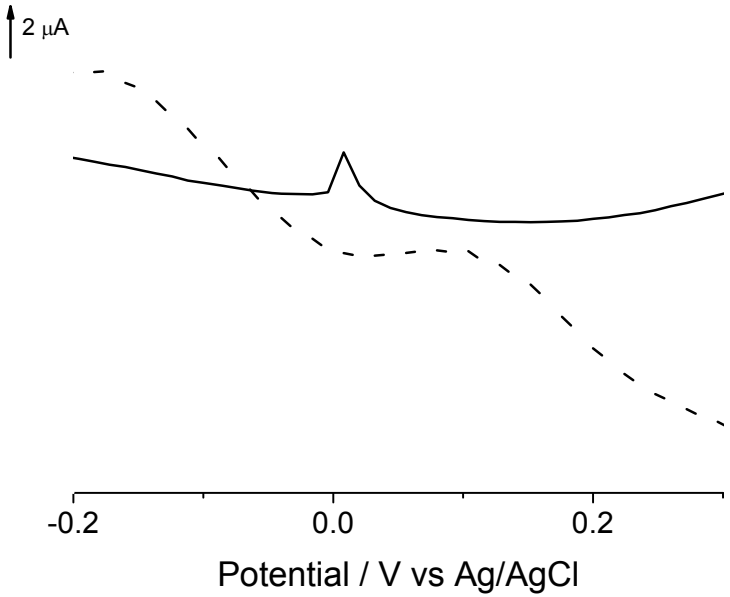
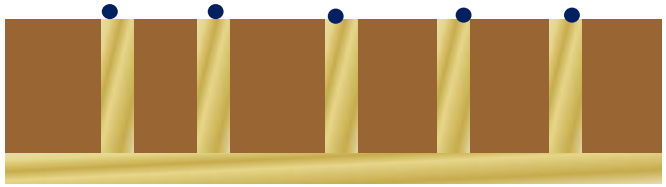
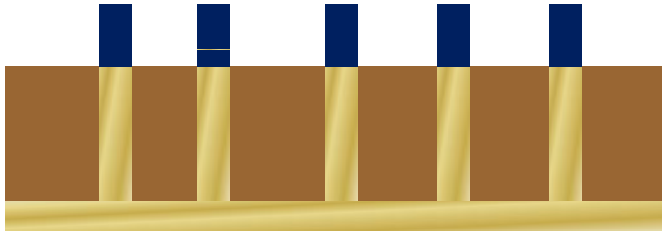
INFLUENCE OF ETCHING ON THE STRIPPING PEAK POTENTIAL





On un-etched NEE, As nuclei are deposited



On 3D-NEE thin As film is deposited

NEE 606-3D at two different etching time in solution of 10 ppb As (III)

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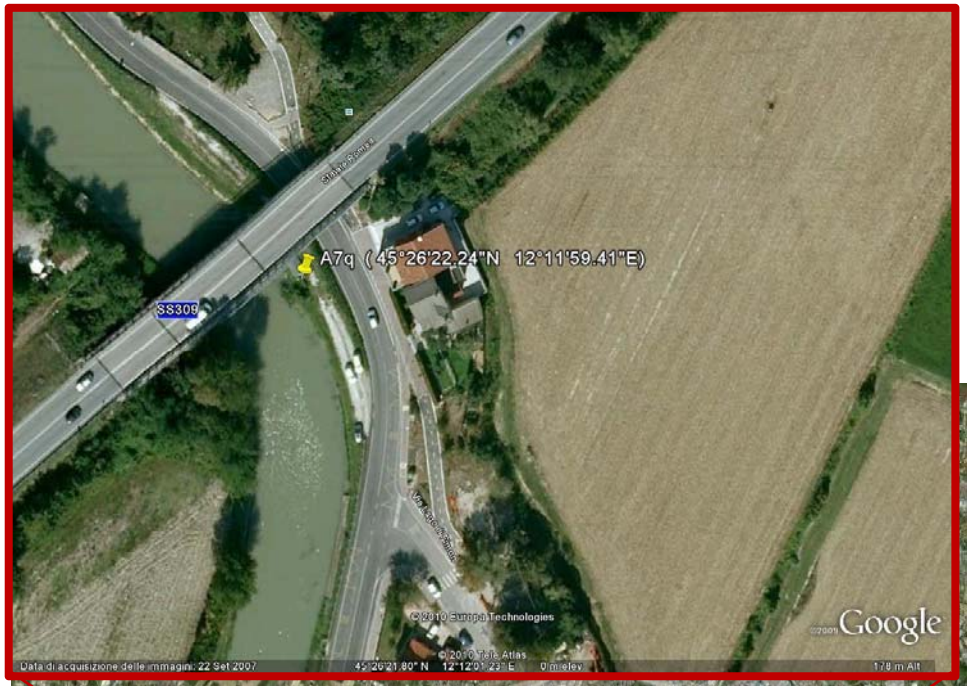
REAL SAMPLES

Sampling



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ANALYTICAL PROCEDURE

SAMPLING AND FILTERING (O.45µm)

~~**REDUCTION WITH SOLID CYSTEINE**~~

DILUTION AND ACIDIFICATION (pH 0.8 in HCl)

ANODIC STRIPPING VOLTAMMETRY AT 60 SEC. DEP. TIME

No peak detected

3 STANDARD ADDITIONS OF As(III)

ANODIC STRIPPING VOLTAMMETRY AT 120 or 180 SEC. DEP. TIME

3 STANDARD ADDITIONS OF As(III)

As(III) CONCENTRATION

TOTAL INORGANIC As CONCENTRATION

(Tot_{inorg} As)

$As(V) = Tot_{inorg} As - As(III)$

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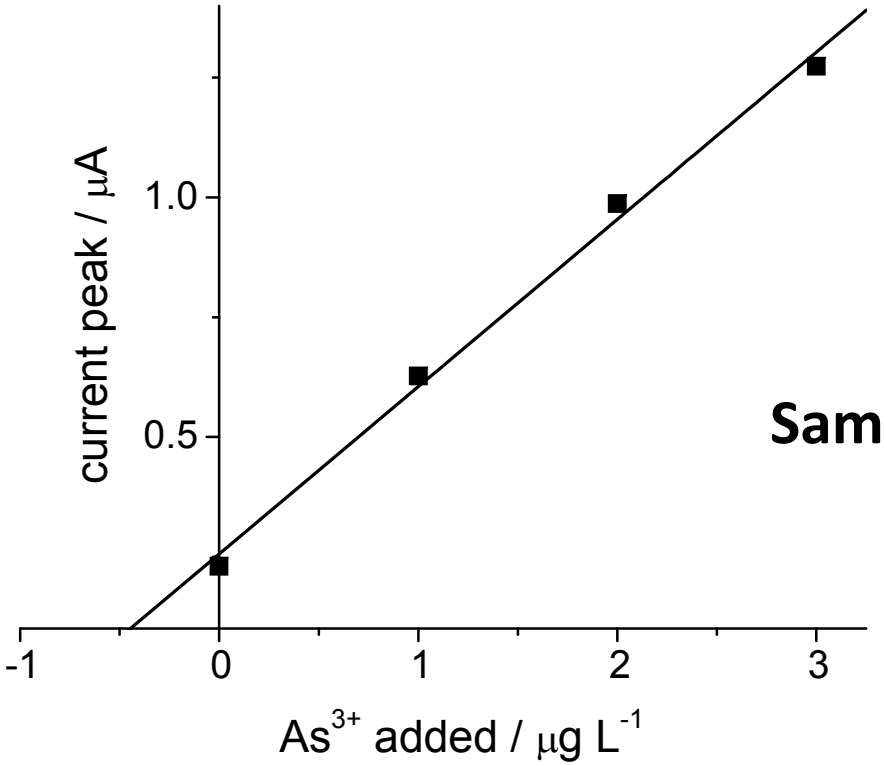
REAL SAMPLES WITH 3D-NEE



Sample diluted 1:3

3D-NEE value = 2.9 µg/L

ICP-MS value* = 2.7 µg/L

*** = ARPAV with ICP-MS following UNI EN ISO 17294-2:2005**

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REAL SAMPLES (river from Venice Lagoon basin) 3D-NEE reproducibility

T dep	Dilution	Inorg As (µg/L)	# NEE	As(III) in diluted samples (µg/L)
180	1:3	3.1	NEE 616 3D	1.1
180	1:3	3.3	NEE 615 3D	1.2
120	1:3	3.1	NEE 614 3D	1.0

3D-NEE value = 3.2 ± 0.2 µg/L

ICP-MS value = 3.2 ± 0.1 µg/L

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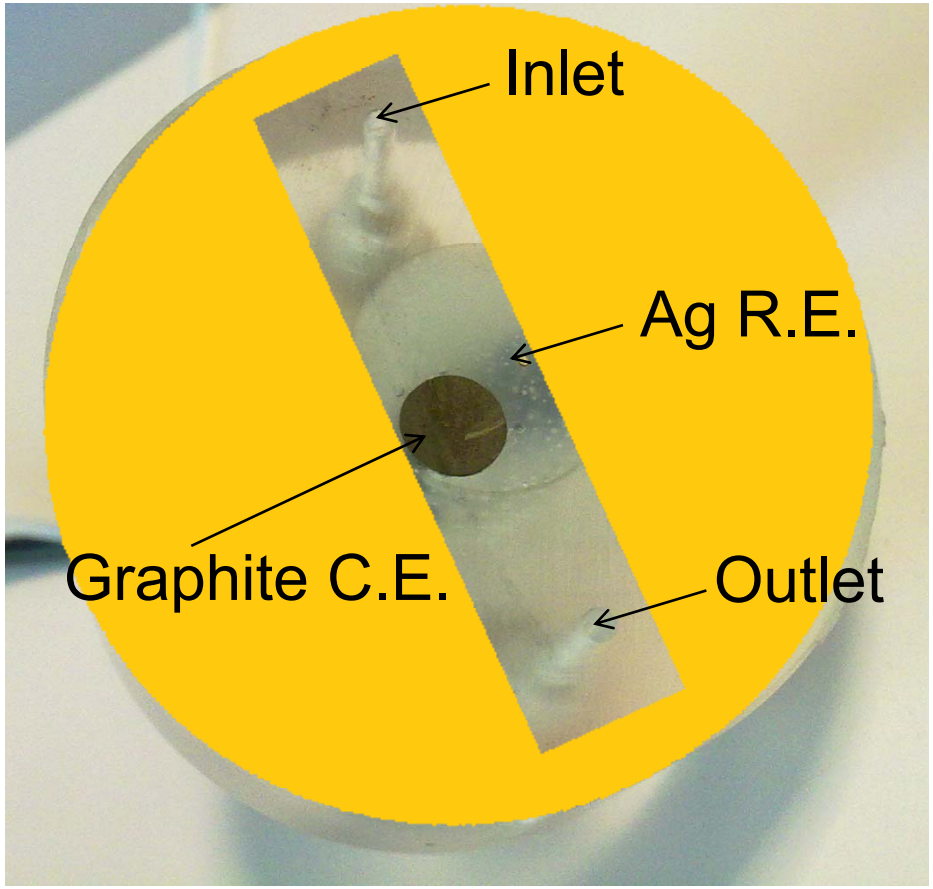
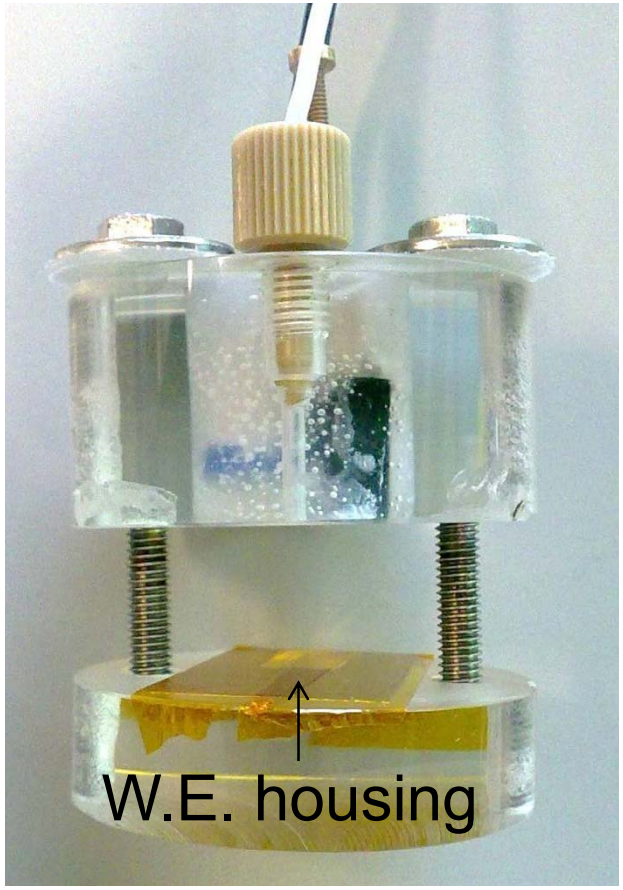
FLOW ANALYSIS
preliminary results





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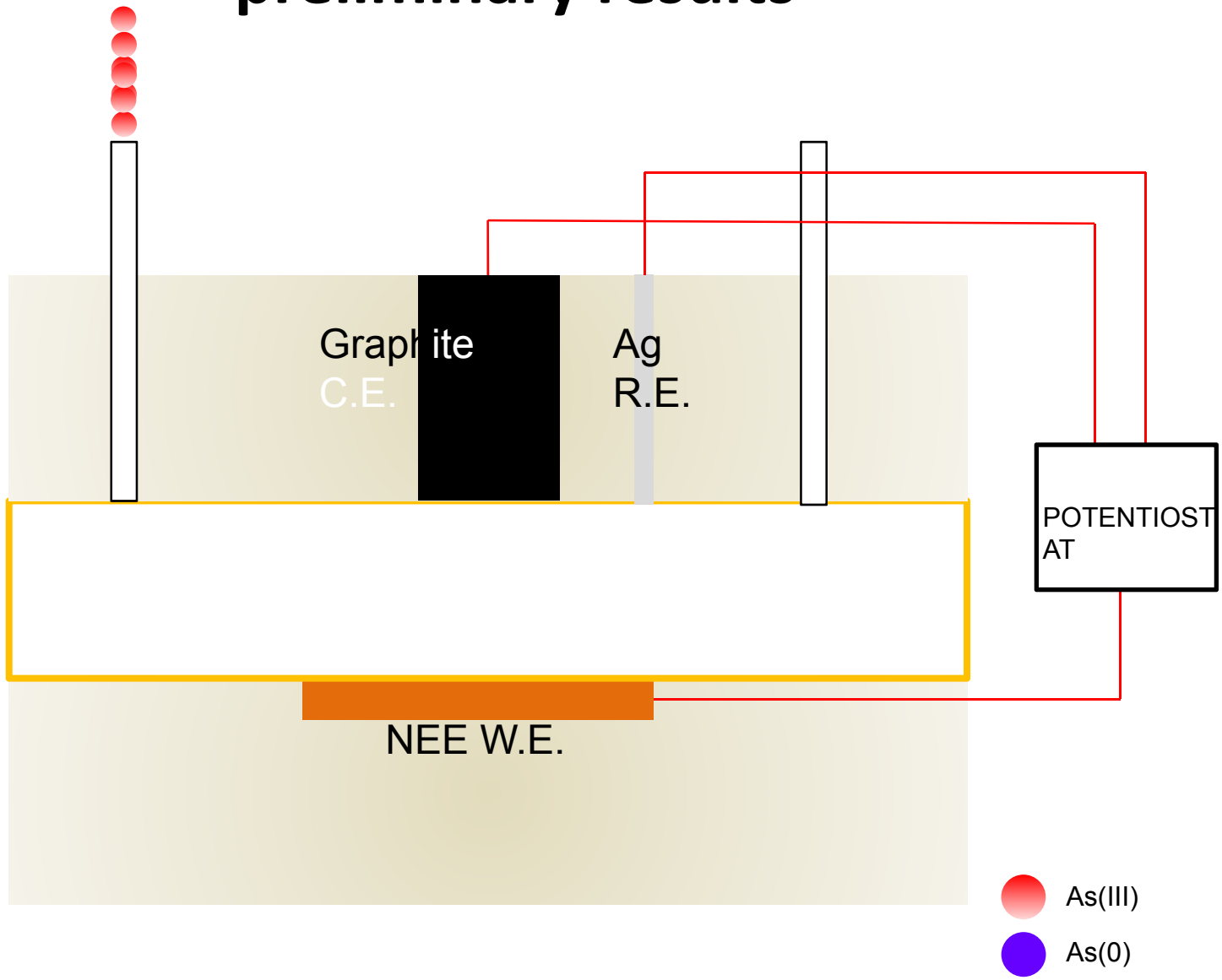
FLOW ANALYSIS
preliminary results



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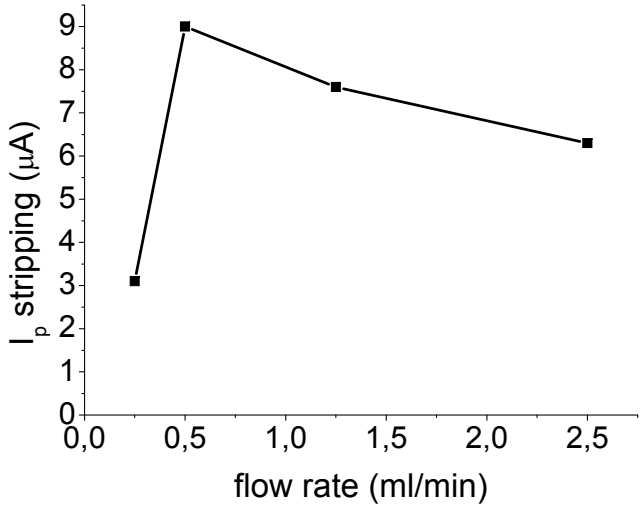
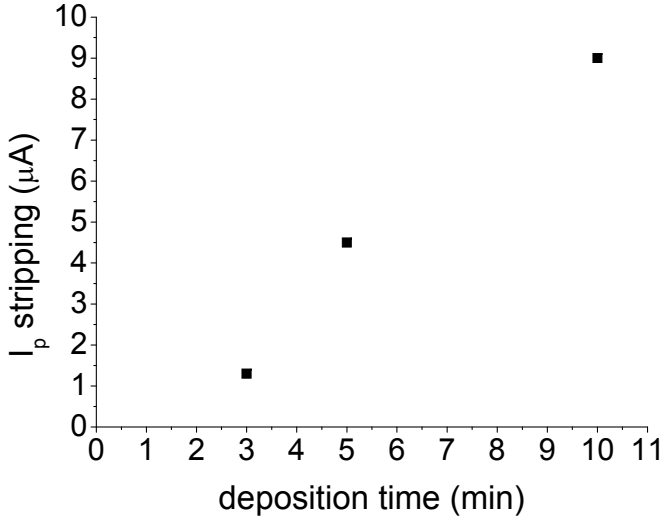
FLOW ANALYSIS
preliminary results

INFLUENCE OF THE FLOW RATE



INFLUENCE OF THE DEPOSITION TIME



First steps towards the optimization of the flow cell:
determination of the optimal flow rate
And
correlation between stripping current and deposition time.

Experiments performed in 1 ppm As solution.

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CONCLUSIONS

- NEEs showed good results in the determination of trace As(III) through SW-ASV.
- Solid cysteine was used as reducing agent for As(V) allowing us to detect total inorganic arsenic.
- Through plasma or chemical etching of NEEs the linearity range of the analytical response was extended.
- 3D-NEEs can be applied for the successfull determination of inorganic arsenic in river water and natural waters.

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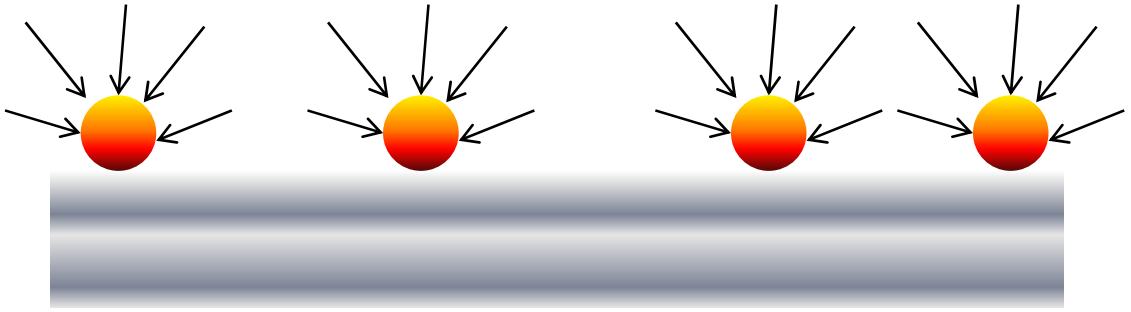
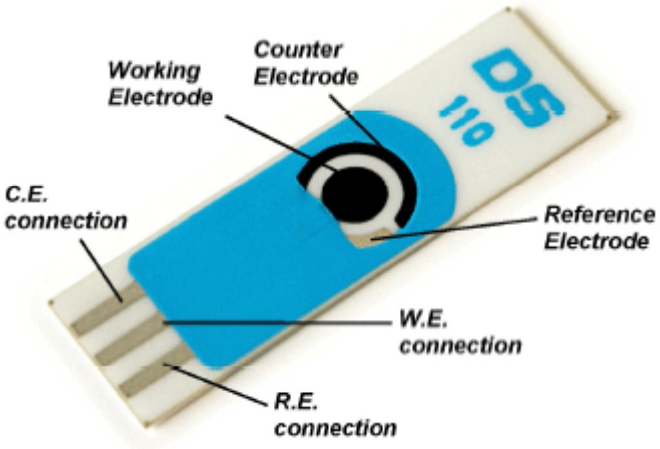
Prospects

develop cheap and disposable electrodes and devices for automatic As determination



Arrays of Nanoparticles ≅ Arrays of Nanoelectrodes

- Screen-printed electrodes modified with Gold NanoParticles
- Developing a batch analyzer employing a flow cell



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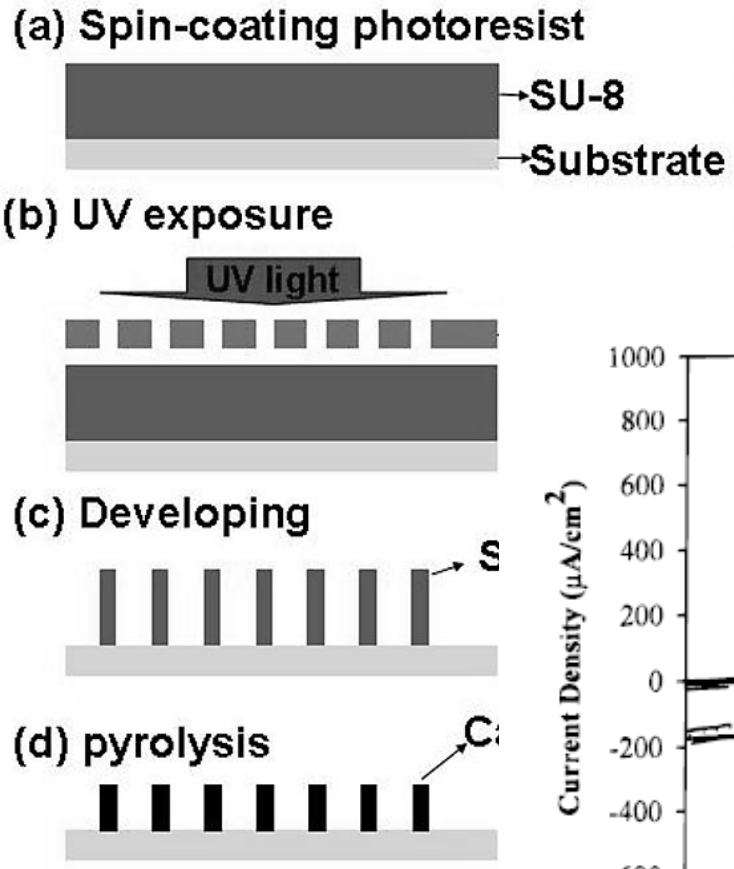
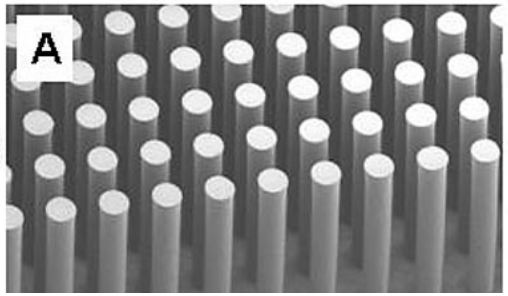
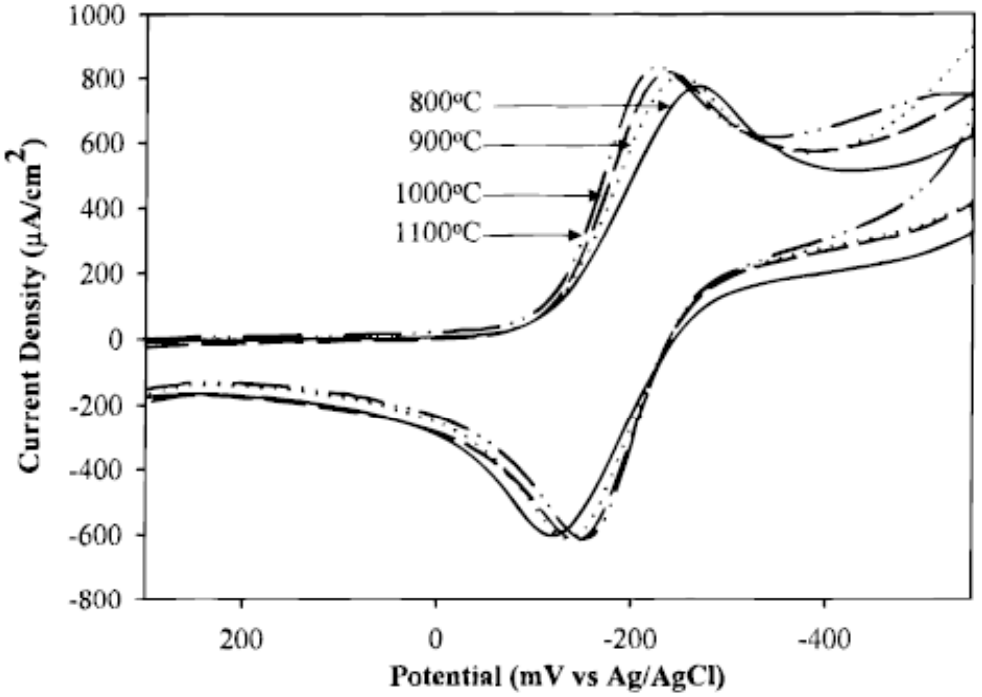
Prospects

Towards pyrolyzed photoresist nanoelectrodes arrays to combine carbon nanostructures with gold modification.







Madou et al. *J Electrochem Soc*, 147 (2000) 277


Thank you !!!!
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