CIN2 CENTRE D'INVESTIGACIÓ EN NANOCIÈNCIA I NANOTECNOLOGIA
CAMPUS UAB. BELLATERRA. BARCELONA

ICN Institut Català de Nanotecnologia

icrea Institució Catalana de Recerca i Estudis Avançats

UAB Universitat Autònoma de Barcelona

Voltammetric screen-printed sensors for heavy metals and phenols.

Achievements and future prospects

Gemma Aragay, Anna Puig, Maria Guix, Arben Merkoçi

nano Bioelectronics & Biosensors Group

ENVIRONMENTAL RISK MANAGEMENT TOOLS FOR WATER QUALITY MONITORING
National Oceanographic Centre, Southampton (UK)
March 30th, 2009

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UAB-ICN WARMER TEAM

ENVIRONMENTAL RISK MANAGEMENT TOOLS FOR WATER QUALITY MONITORING
National Oceanographic Centre, Southampton (UK)
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OUTLINE

- Introduction
- Heavy metals
- Phenols
- Conclusions

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INTRODUCTION

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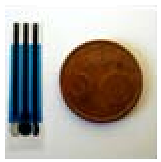
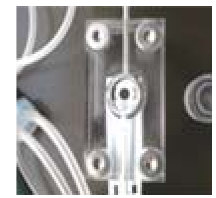
SPE Designs

- Carbon ink
- Mercury modification
- Bismuth modification
- New modifications



Flow Cells Designs

- UAB Designs
- Systea Design
- Optimizations using virtual simulations



Phenol detection

- Phenol detection in the range of 10-200μM
- Stability and shelf lifetime studies
- Optimization of the SPE formulation

Heavy metals detection

In real sea water matrix:

- Stability studies
- Lifetime studies
- Multidetection of heavy metals
- Analytical performance parameters

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OUTLINE

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Heavy metal
Phenols
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- Introduction
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- Conclusions

HEAVY METALS SWASV technique

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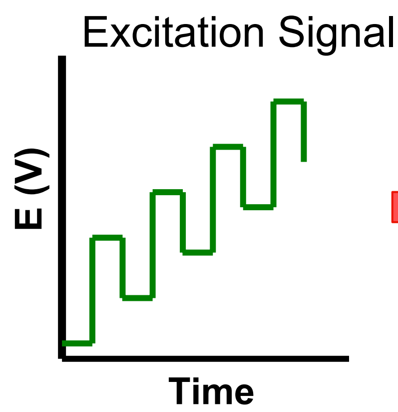
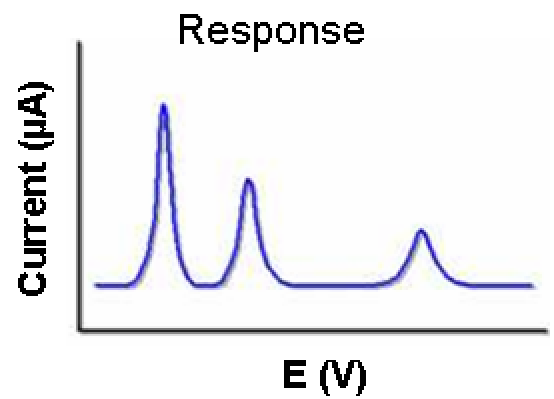
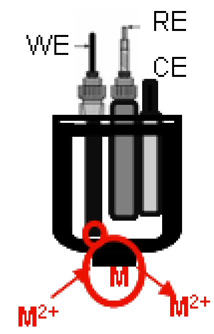
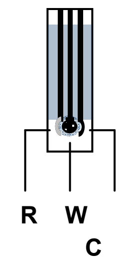
- Introduction
- **Heavy metals**
- Phenols
- Conclusions

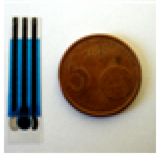
Square Wave Anodic Stripping Voltammetry (SWASV)

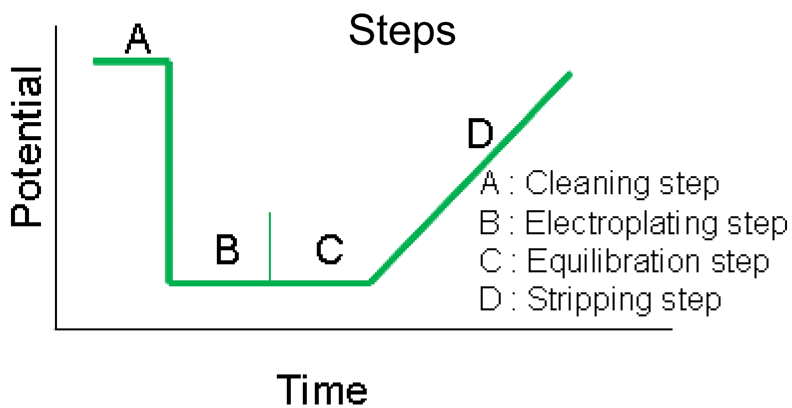






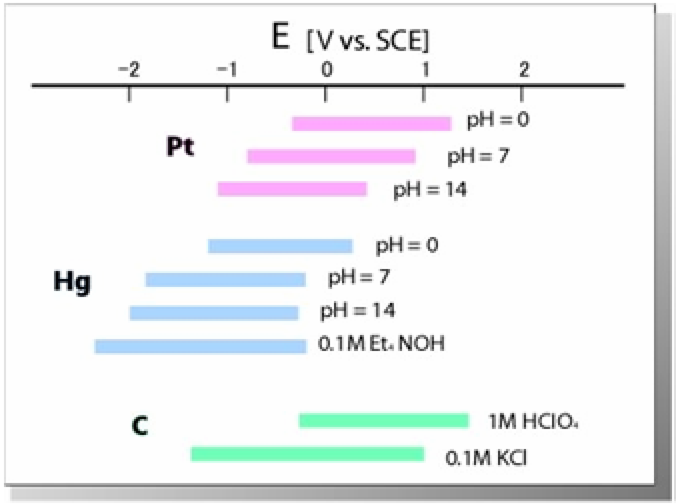






High selectivity and sensitivity
Low cost and user-friendly sensors

Working electrode



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HEAVY METALS SPEEs fabrication

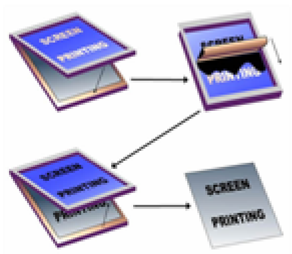
Introduction

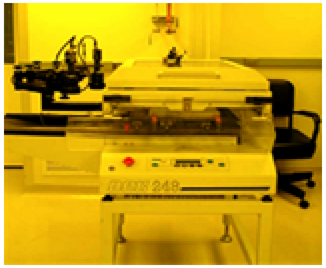
Heavy metals

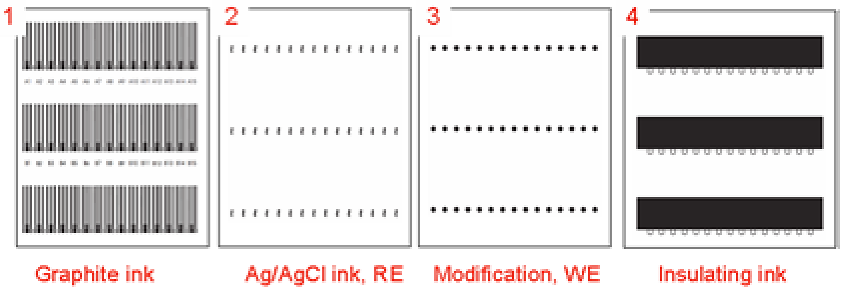
Phenols

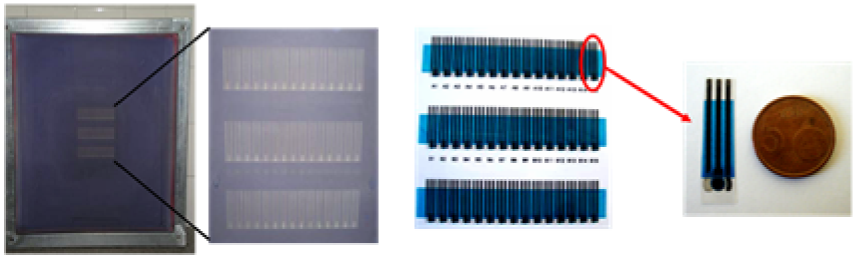
Conclusions

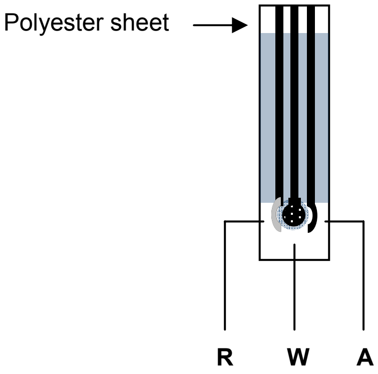
SPE Fabrication process











Modifications of the working electrode

Carbon ink
Mercury modification (commercial SPEs)
Different percentages of Bi powder precursor
Different percentages $Bi(C_2H_3O_2)_3$ powder precursor
Different percentages Bi oxide powder
Modification with CNT
No reproducibility → Bismuth Nanoparticles under study

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HEAVY METALS Flow cells and potentiostats

Introduction

Heavy metals

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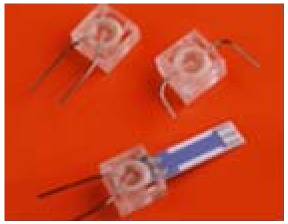
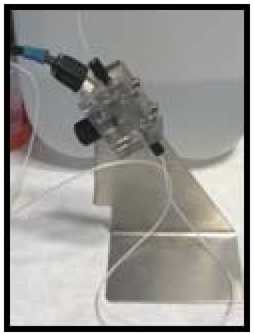
Conclusions

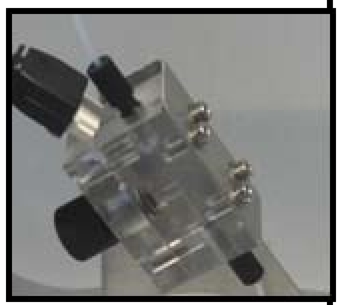
Commercial flow cell



BVT Technologies

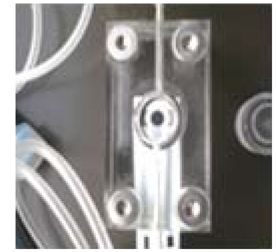
Sysmedia S.r.l. Italy flow cell



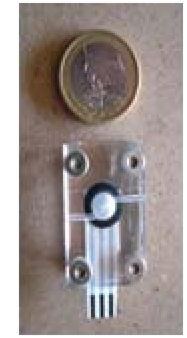


UAB flow cells

HM Flow cell I



HM Flow cell II



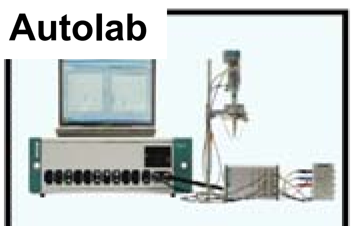
HM Flow cell V

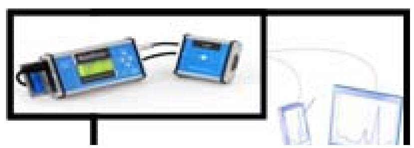
HM Flow cell III

HM Flow cell IV

Potentiostats used

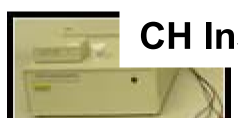
Autolab





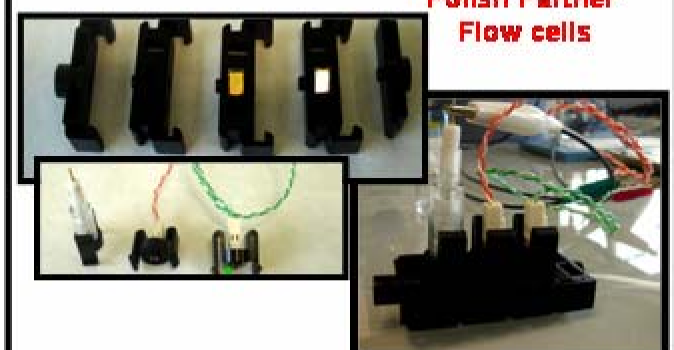
PalmSens Instrument

Emstat



CH Instrument

Polish Partner Flow cells



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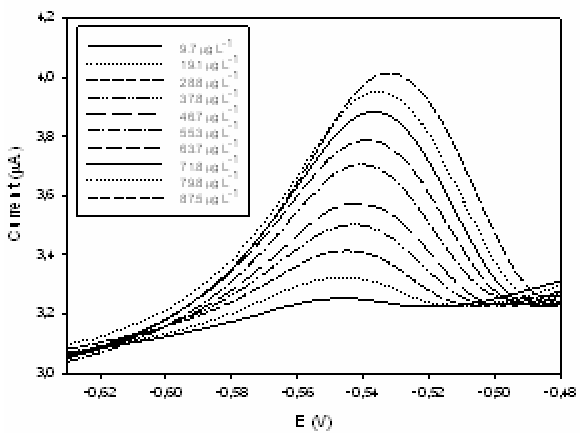
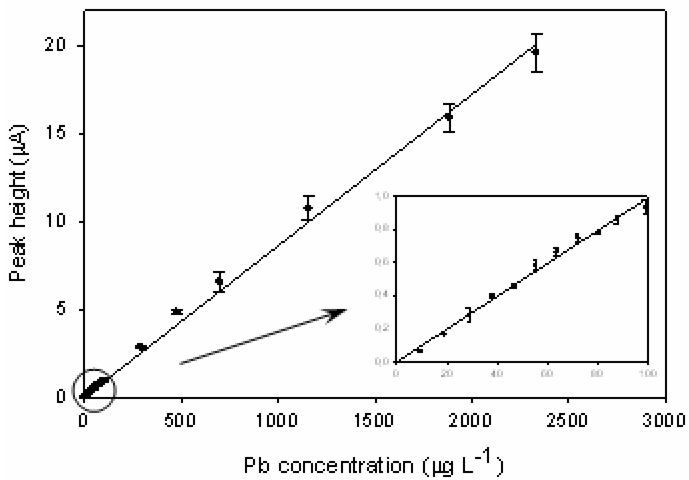
HEAVY METALS Batch system

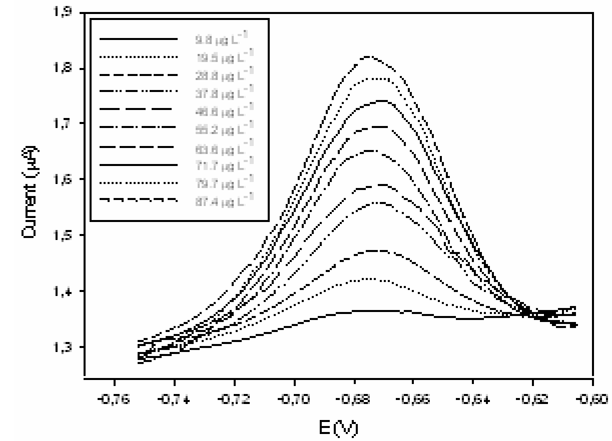
HEAVVY METAL DETECTION WITH MERCURY-COATED SPEs (BATCH)

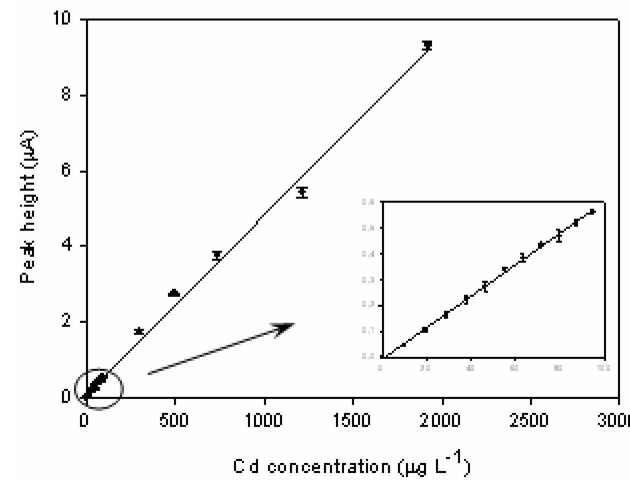
LEAD





CADMIUM





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HEAVY METALS Batch system

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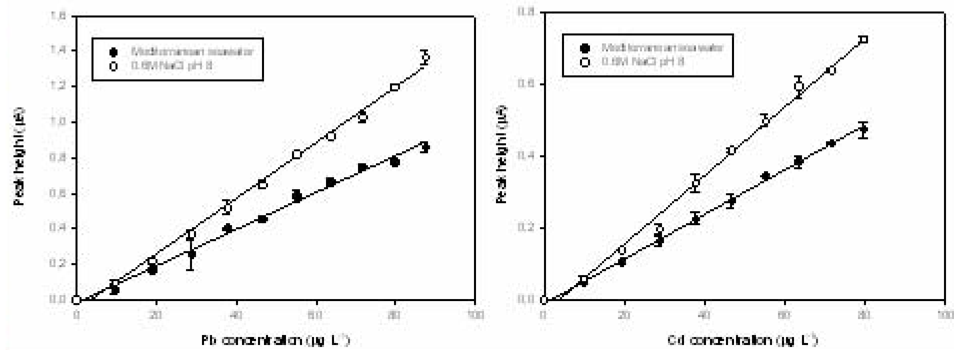
HEAVVY METAL DETECTION WITH MERCURY-COATED SPEs (BATCH)

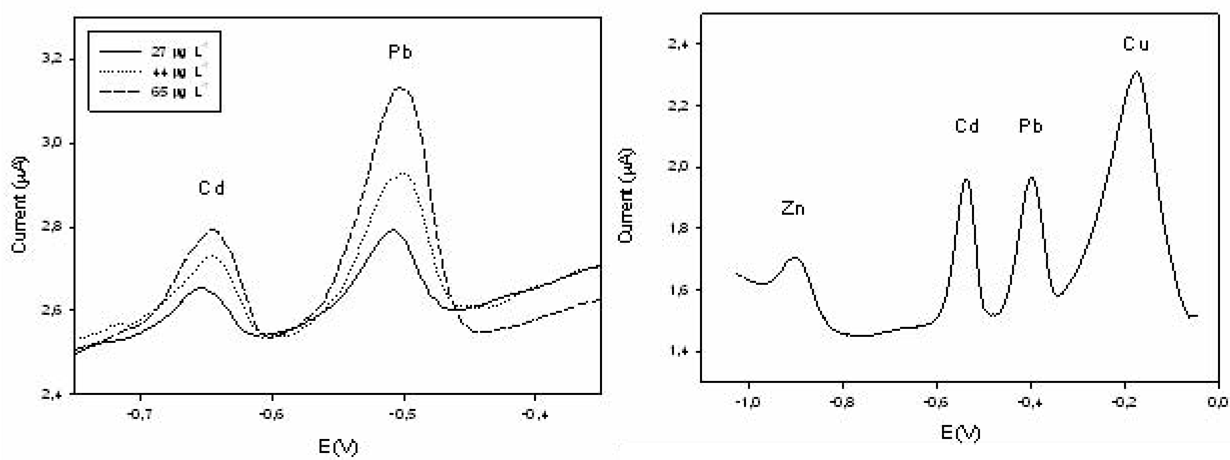
Sea water real samples

Mar menor

Matrix effect for lead and cadmium



MULTIDETECTION



HEAVY METALS Batch system

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HEAVVY METAL DETECTION WITH MERCURY-COATED SPEs (BATCH)

RESULTS

Analytical performance of SWASV measurements

Metal	Determination range	Regression coefficient	a	b	RSD (%)	LOD (μg L^{-1})
Pb	9.7 – 2331 μg L^{-1}	0.9974	0.0085	0.1759	7.1	1.8
	9.7 – 98. 6 μg L^{-1}	0.9934	0.0990	0.0013	2.3	
Cd	9.8 – 1923 μg L^{-1}	0.9956	0.0047	0.0977	-	2.9
	9.8 – 94.9 μg L^{-1}	0.9987	0.0061	0.0071	-	

Results of Pb(II)and Cd(II) ions determination in sea water samples

Sample	Pb SPE (μg L^{-1})	Pb HDME (μg L^{-1})	Pb spiked (μg L^{-1})	Cd SPE (μg L^{-1})	Cd HDME (μg L^{-1})	Cd spiked (μg L^{-1})
Spiked-1	54.8 ± 1.6	54.8 ± 7.6	56.2	-	-	-
Spiked-2	-	-	-	58.9 ± 8.4	56.0 ± 2.0	61.5
Real-1	9.4 ± 3.3	12.8 ± 0.3	-	20,14 ± 3.0	18.3 ± 0.4	-
Real-2	33.8 ± 7.9	34.9 ± 0.9	-	19.41 ± 4.4	24.6 ± 0.5	-

Sensitive and stable monitoring of lead and cadmium in seawater using screen-printed electrode and electrochemical stripping analysis Raquel Güell, Gemma Aragay, Clàudia Fontàs, Enriqueta Anticó, Arben Merkoçi, Analytica Chimica Acta (2008).

HEAVY METALS Flow through system

Introduction

Heavy metals

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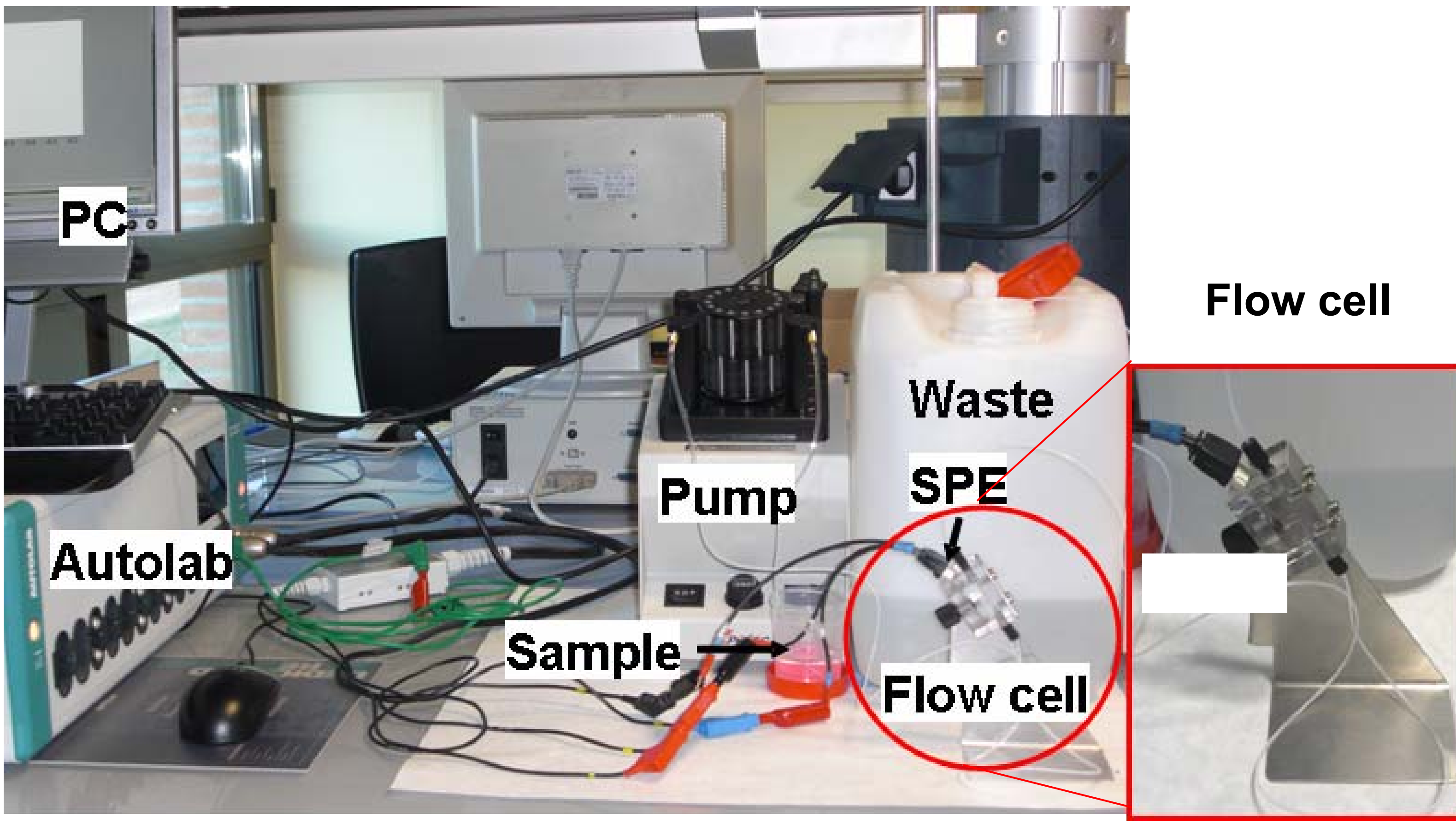
HEAVVY METAL DETECTION IN FLOW THROUGH SYSTEM

Flow through system in the UAB laboratories



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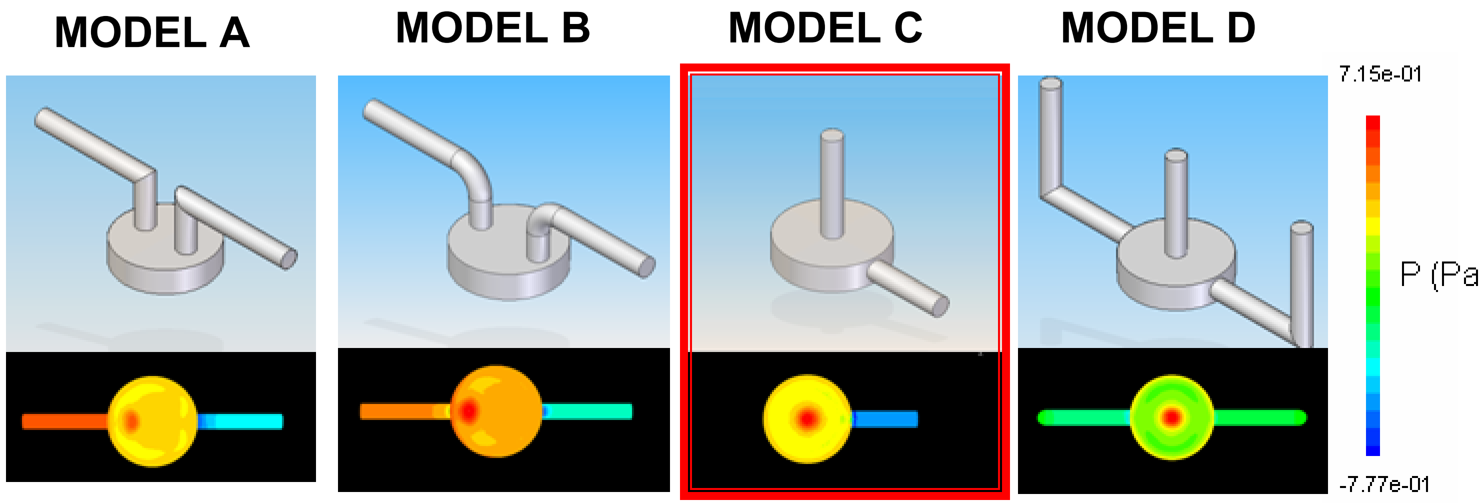
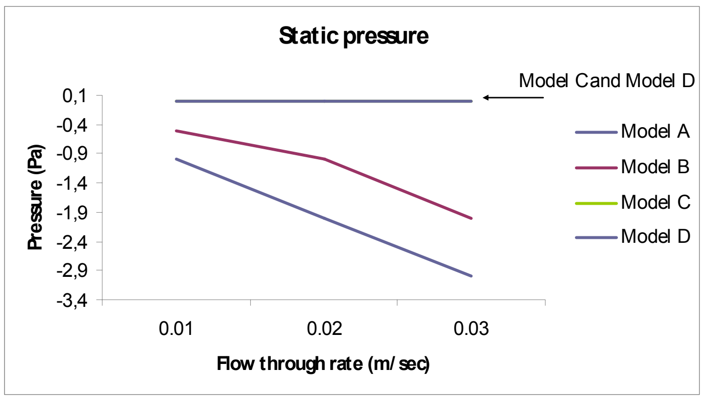
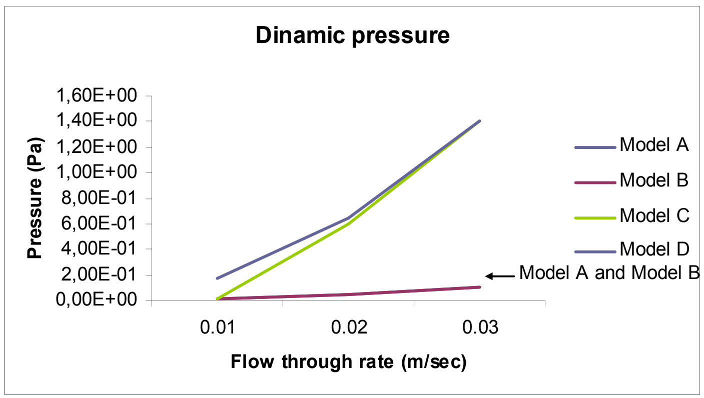
HEAVY METALS Theoretical models

THEORETICAL FLOW THROUGH CELL MODELS







In model A and B - right angle (entering tubes inside the cell) is present the decrease of the pressure is more drastic comparing to the 'soft' angle. However, both models (A&B) present worse distributions of the internal pressures compared to models C&D. By changing the flow rate the static pressures inside these model cells (C&D) remain constant.

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HEAVY METALS Mercury-coated SPEs

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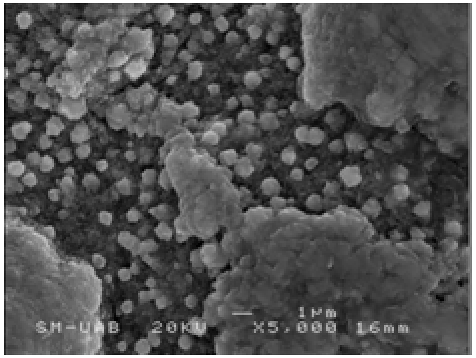
HEAVY METAL DETECTION WITH MERCURY-COATED SPEs (FLOW)

ANALYTICAL PARAMETERS

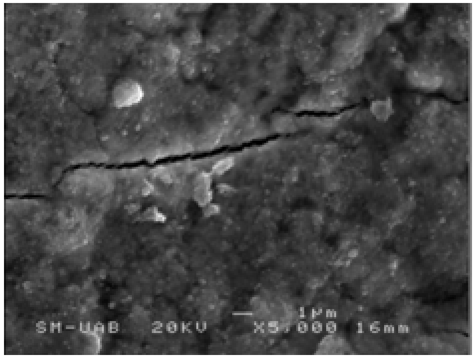
Parameter	*Value*
Regression equation / Correlation coeficient (r^2)	y = 0.004x – 0.022 / 0.9918
Coefficient of variation (CV) / %	11.89
Limit of detection (LOD) / μgL^{-1}	6.9
Limit of quantification (LOQ) / μgL^{-1}	8.8
Repeatibility (σ_2 and σ_6)	For 20 ppb : 6.91 · 10^{-3} / For 80 ppb : 3.19 · 10^{-3}
Lowest detectable change (σ_2 and σ_6)	For 20 ppb : 2.07 · 10^{-2} / For 80 ppb: 9.56 · 10^{-3}

MORFOLOGICAL CHARACTERIZATION

SEM images for mercury-coated SPE WE before activation



SEM images for mercury-coated SPE WE after activation (300 s under -1.1 V)



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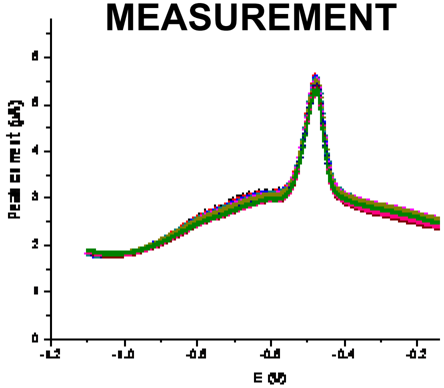
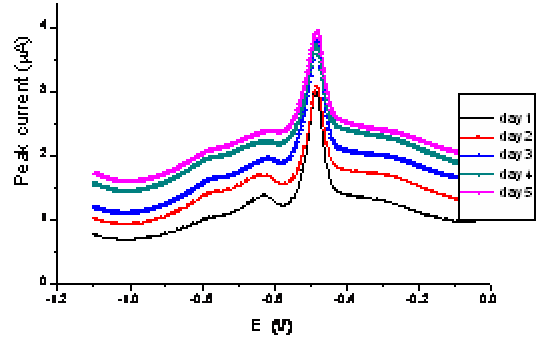
HEAVVY METAL DETECTION WITH MERCURY-COATED SPEs (FLOW)

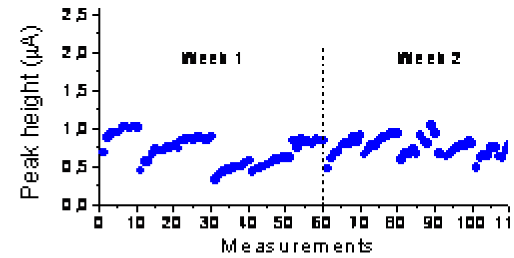
STABILITY IN ONE DAY MEASUREMENT



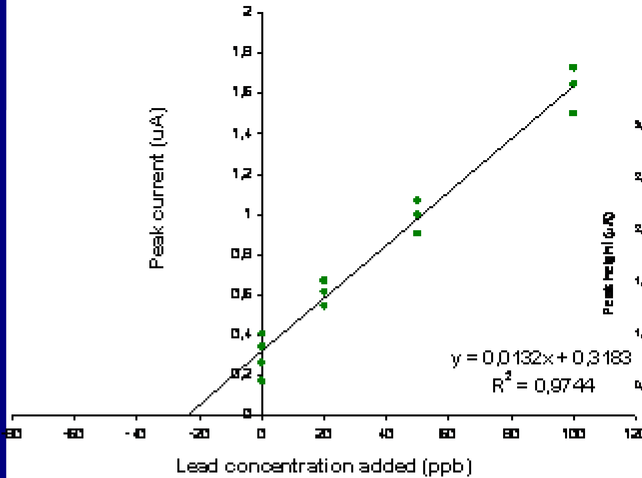
STABILITY BETWEEN DIFFERENT DAYS

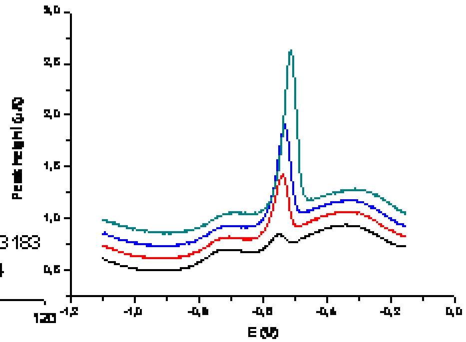


LIFETIME DURING TWO WEEKS

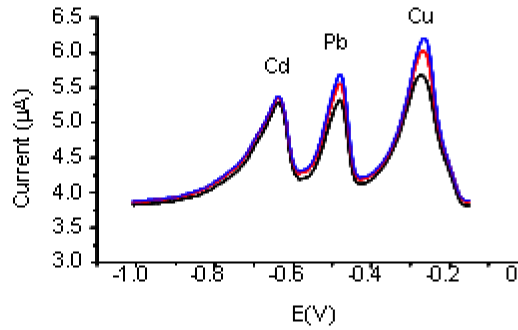


STANDARD ADDITION METHOD FOR A 20 ppb SAMPLE IN SEA WATER





MULTIDETECTION



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HEAVY METALS Mercury-free SPEs

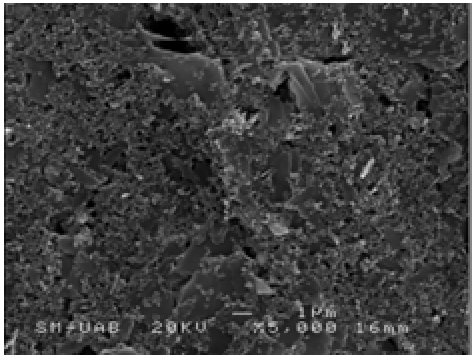
HEAVY METAL DETECTION WITH MERCURY-FREE SPEs (FLOW)

ANALYTICAL PARAMETERS

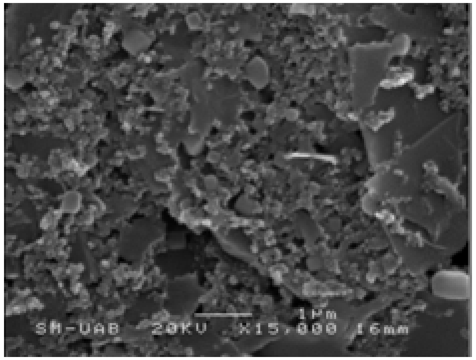
Parameter	*Value*
Regression equation / Correlation coeficient (r^2)	y = 0.0087X – 0.007 / 0.9875
Coefficient of variation (CV) / %	9.9
Limit of detection (LOD) / $\mu g L^{-1}$	3.00
Limit of quantification (LOQ) / $\mu g L^{-1}$	8.14
Repeatibility (σ_2 and σ_6)	For 20 ppb : $8.94 \cdot 10^{-3}$ / For 80 ppb : $1.18 \cdot 10^{-2}$
Lowest detectable change (σ_2 and σ_6)	For 20 ppb : $2.68 \cdot 10^{-2}$ / For 80 ppb: $3.56 \cdot 10^{-2}$

MORFOLOGICAL CHARACTERIZATION

SEM images for mercury-free SPE WE before activation



SEM images for mercury-free SPE WE after activation (overnigth under -0.15 V)



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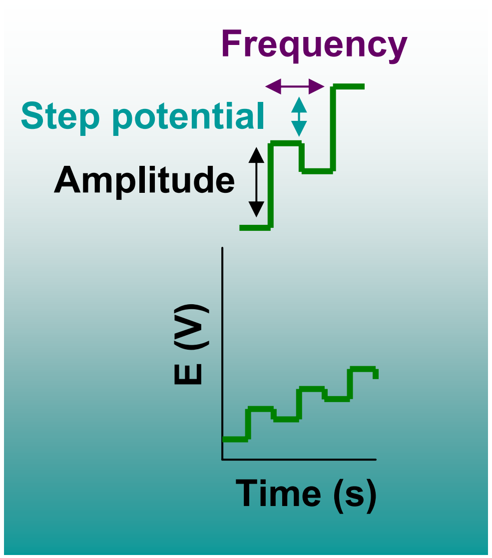
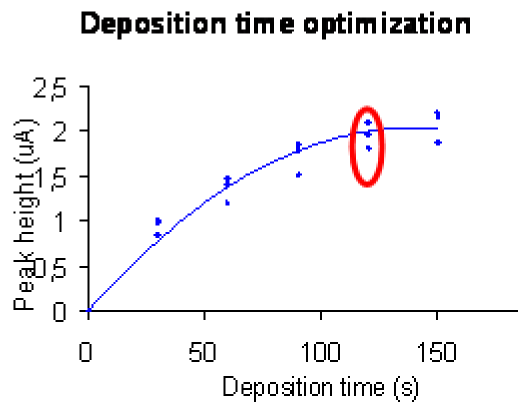
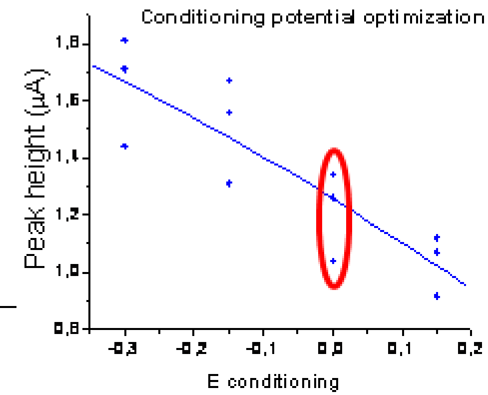
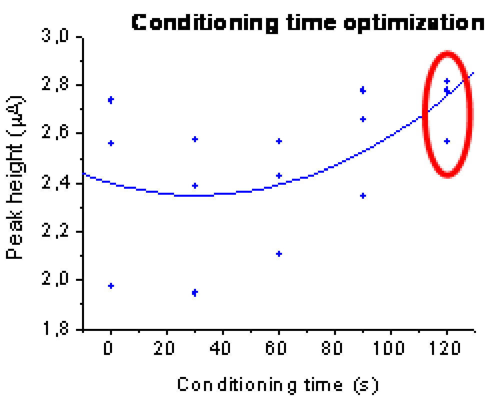
HEAVY METALS Mercury-free SPEs

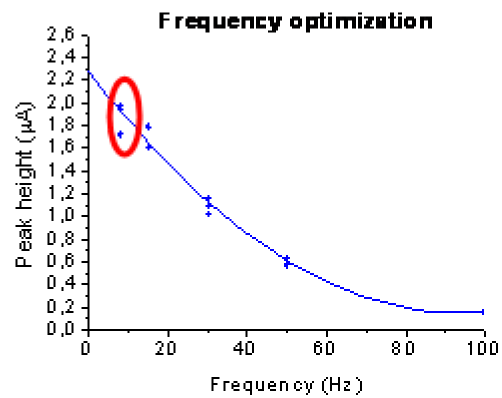
ANALYTICAL PARAMETERS OPTIMIZATIONS FOR MERCURY-FREE SPEs (FLOW)

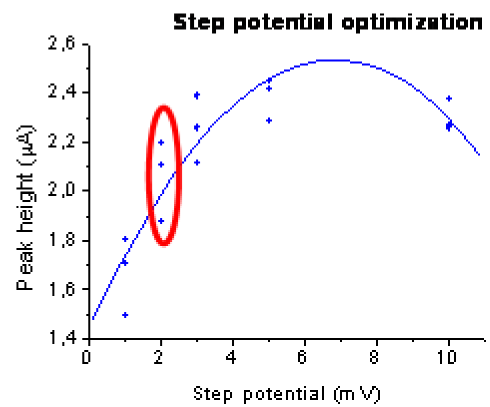












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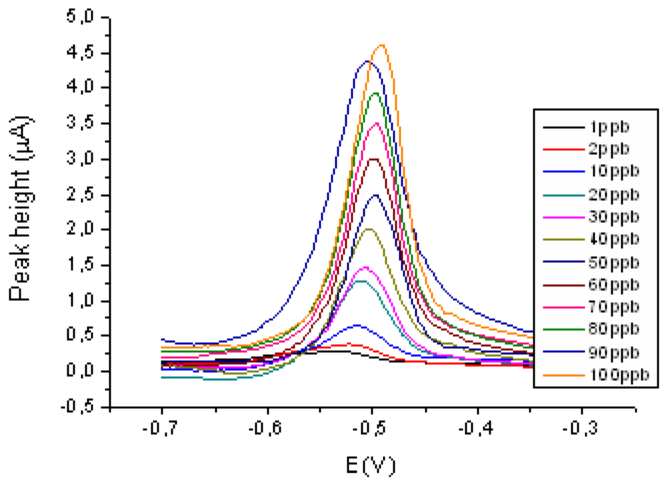
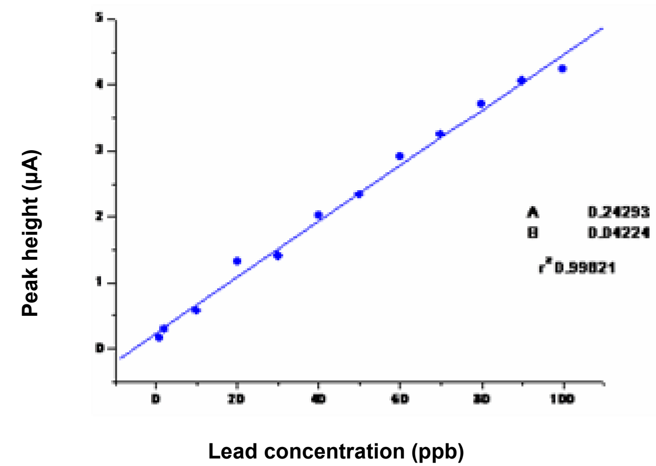
HEAVY METALS Mercury-free SPEs

- Introduction
- **Heavy metals**
- Phenols
- Conclusions

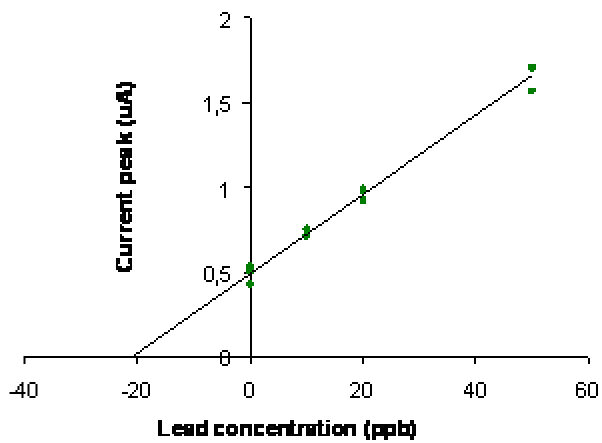
HEAVY METAL DETECTION WITH MERCURY-FREE SPEs (FLOW)

LEAD CALIBRATION WITH MERCURY-FREE SPEs





STANDARD ADDITION FOR LEAD WITH MERCURY-FREE SPEs



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HEAVY METALS Mercury-free SPEs

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STANDARD ADDITION OPTIMIZATION FOR LEAD WITH MERCURY-FREE SPEs

Number of additions of Pb solution	Selected additions of Pb solution	[Pb] (ppb)/RDS (%)/ Sensitivity (μA/ppb)
3	Sample + 10, 20, 50 ppb	21.07/5.4/0.023
2	Sample + 10, 20 ppb	**20.69/3.5/0.024**
2	Sample + 20, 50 ppb	**21.05/5.2/0.023**
1	Sample + 10 ppb	20.68/3.4/0.024
1	Sample + 20 ppb	20.69/3.4/0.024
1	Sample + 50 ppb	20.94/4.7/0.023

From these results can be concluded that using only **two additions** a good result can be achieved with a RDS of 3.5 - 5.2 %.

HEAVY METALS Mercury-free SPEs

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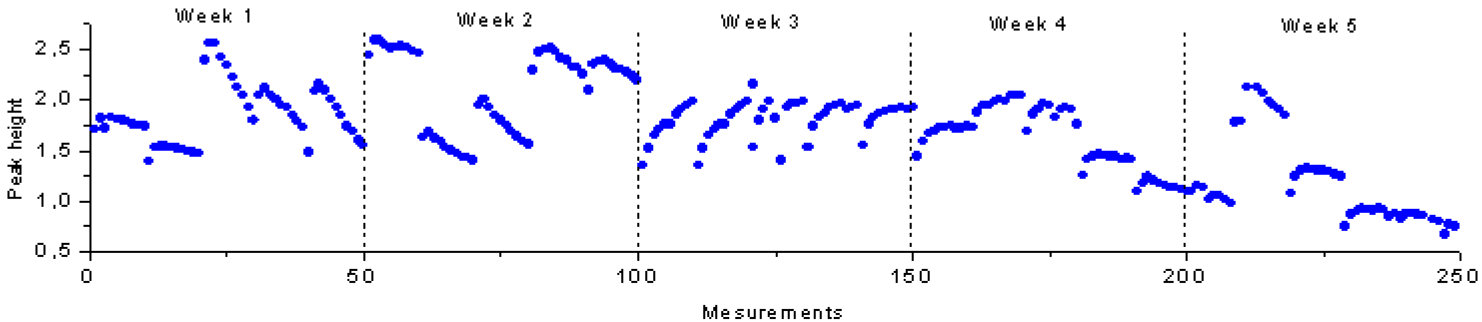
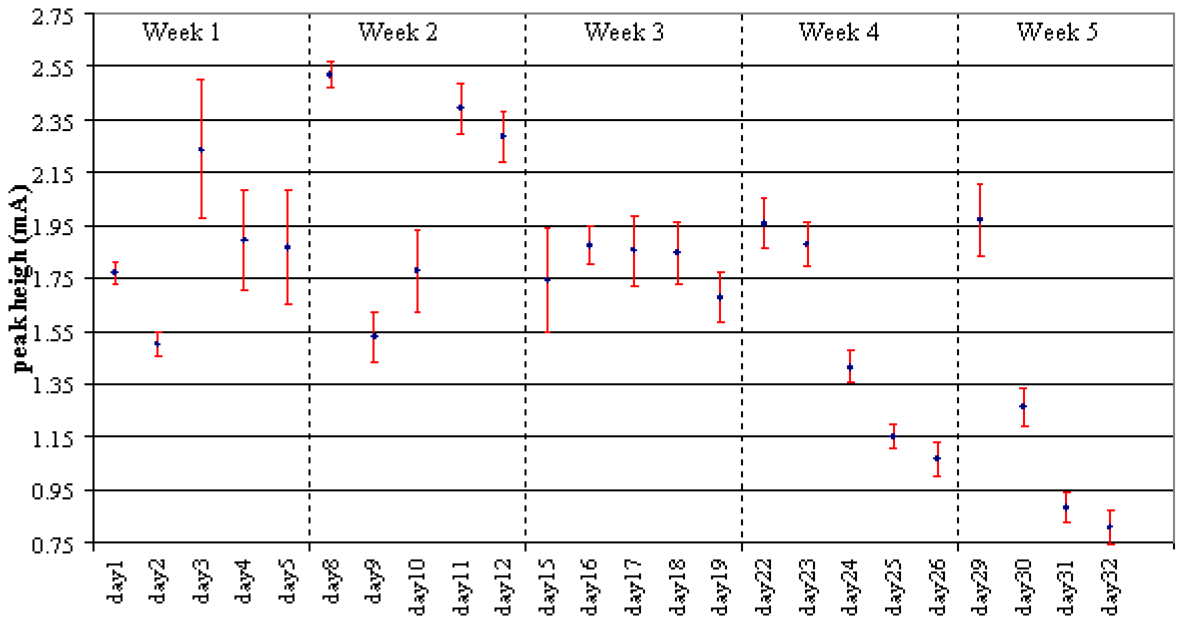
Five weeks stability study for mercury-free SPE for 100 ppb Pb





OUTLINE

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Heavy metal

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- Introduction
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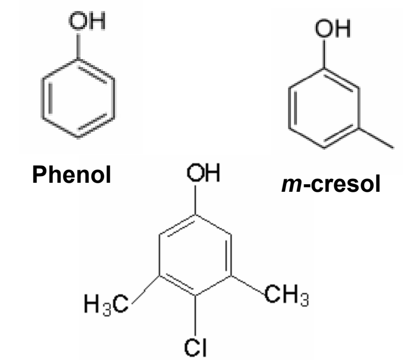
PHENOLS

Introduction

- **Phenols**

Chemical compounds formed by an **hydroxyl group** attached to an **aromatic hydrocarbon group.**

- Considered as **dangerous substances** by the **European Comunity** and the **Environmental Protection Agency of United States** (Non-carciogenic effects in domestic drinking water in concentrations lower than 40µM)



Phenol **m-cresol** **Chloro-3,5-dimethylphenol**

- Phenols determination:
  - o Gas chromatography
  - o Spectrophotometric analysis
  - o Electrochemical techniques

- **Expensive**
- **Time-consuming**
- Difficult **in-situ application** (pretreatment of the sample)

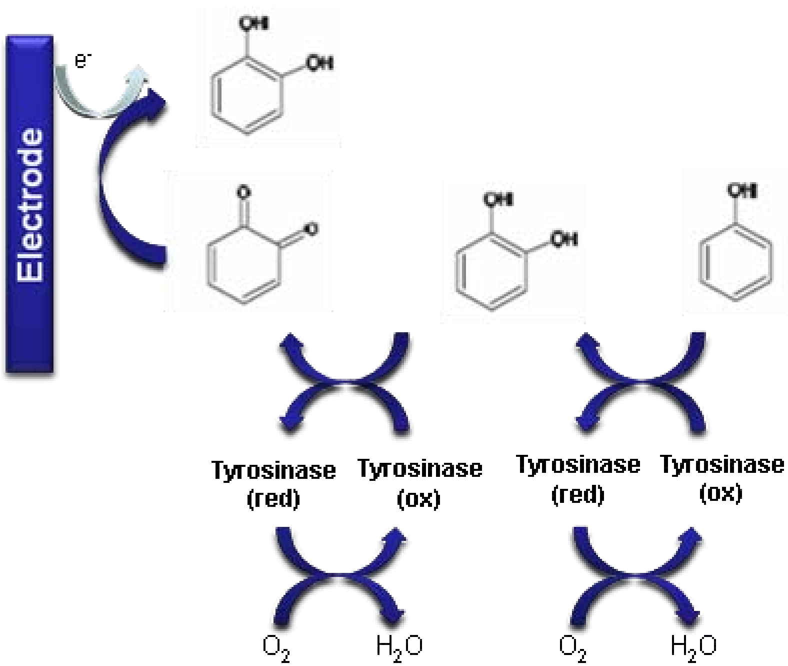
- Concentration of phenols considered in **WARMER project**: 10-200µM

PHENOLS Phenol detection with SPEs

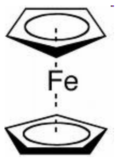
- Introduction
- Heavy metals
- Phenols
- Conclusions

• Phenol detection

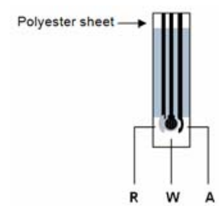
Biosensor principle



- The **reduction** of quinone to cathecol is followed.
- Work at **moderately negative potential** (-0.2V).
- Chronoamperometric measurements with a **potentiostat CH instrument**, model CHI600C in **stirring and batch conditions**.
- Presence of **mediator** (Ferrocene) had been studied in phenol's detection.



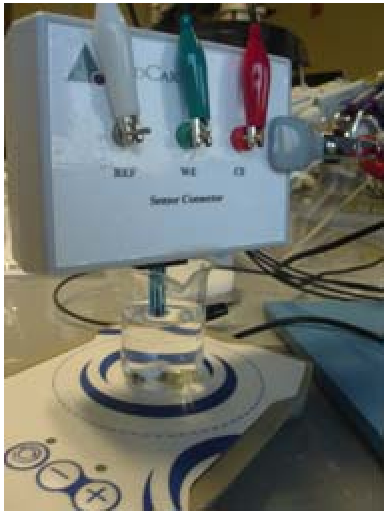
Experimental setup



R: Reference electrode (Ag/AgCl)

W: Working electrode

A: Auxiliar electrode



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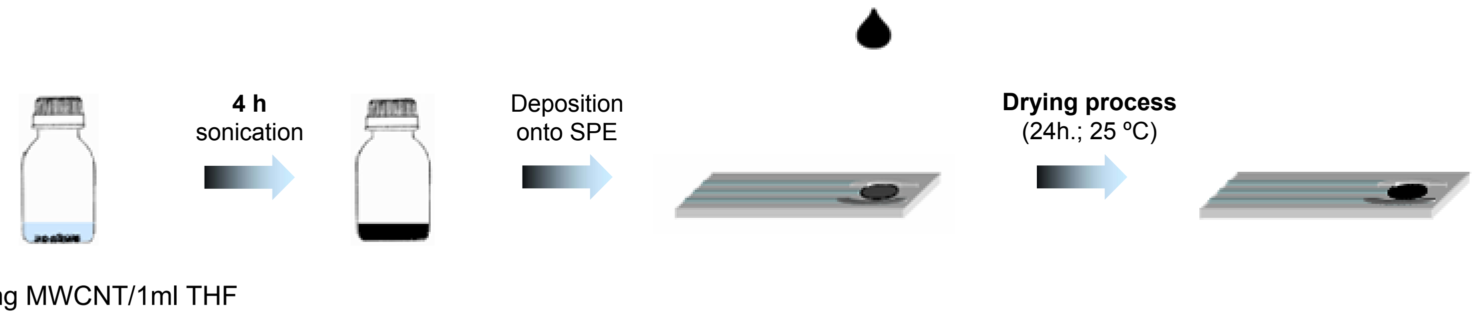
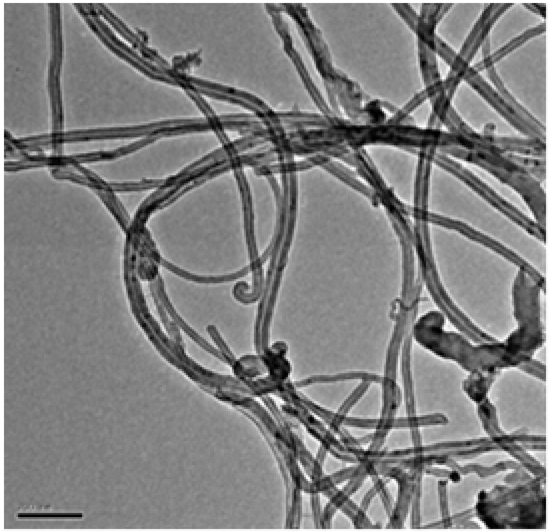
PHENOLS

SPEs characterization

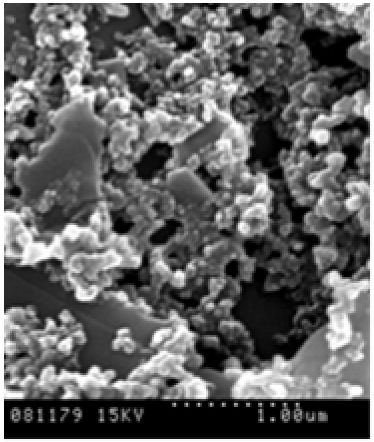
- **SPE modified with Multiwall Carbon Nanotube**



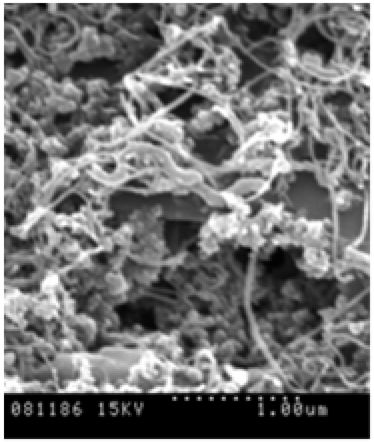
Carbon Nanotube dispersion



Characterization of the Working Electrode surface



Bare SPE



SPE modified with MWCNT

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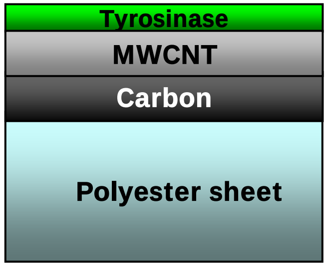
PHENOLS SPEs characterization

• Confocal studies

Held in order to **evaluate**:

- **Real distribution** of Tyrosinase over the working electrode surface.
- **Penetration** of tyrosinase in the material, especially in the case of modifying SPE with CNT.

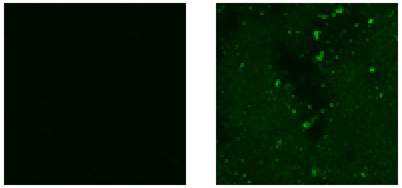
Layers configuration



Control experiment

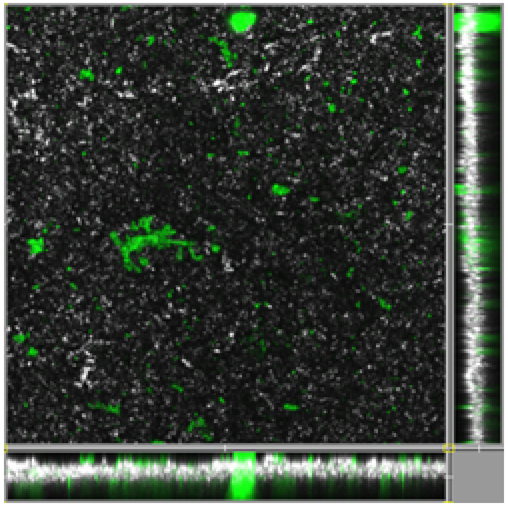
Primary label

Tyr/MWCNT/SPE

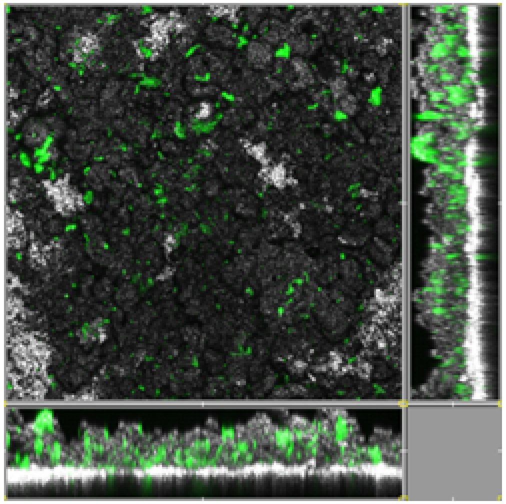


Primary label +
Secondary label
(Alexa488)

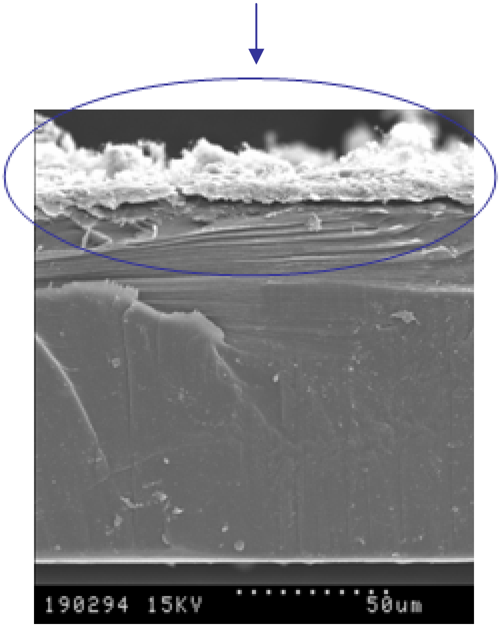
Tyr/MWCNT/SPE



Tyr/SPE



Tyr/MWCNT/SPE



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PHENOLS Electrochemical studies

Introduction

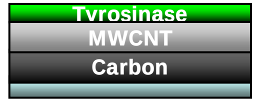
Heavy metals

Phenols

Conclusions

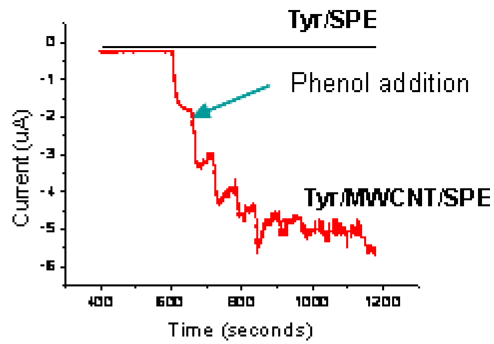
MWCNT effect

Layers configuration



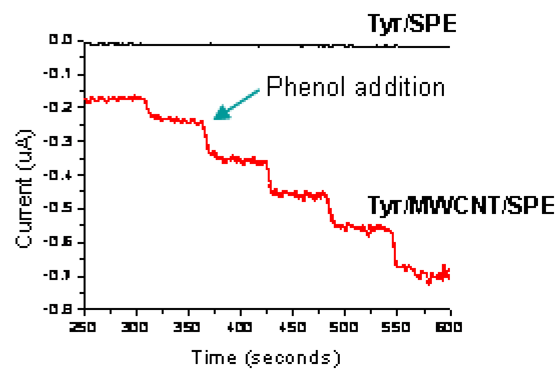
High concentration range

(25µM-250µM)



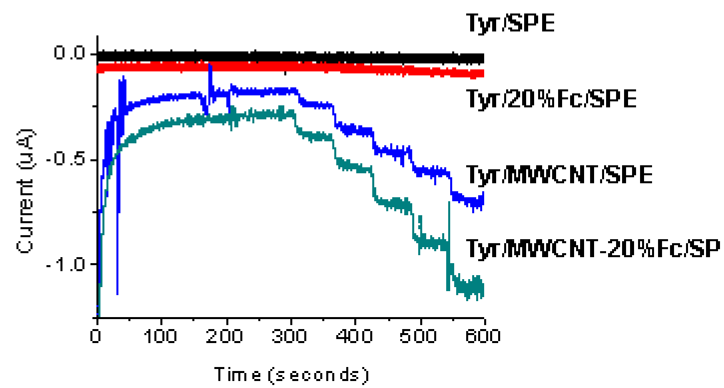
Low concentration range

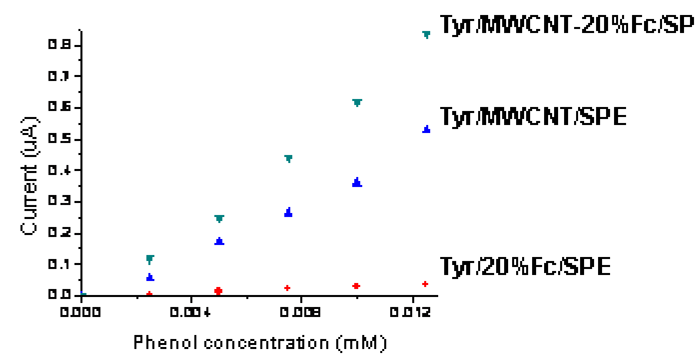
(2.5µM-25µM)



Mediator effect

Layers configuration





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PHENOLS Detection, stability and lifetime study

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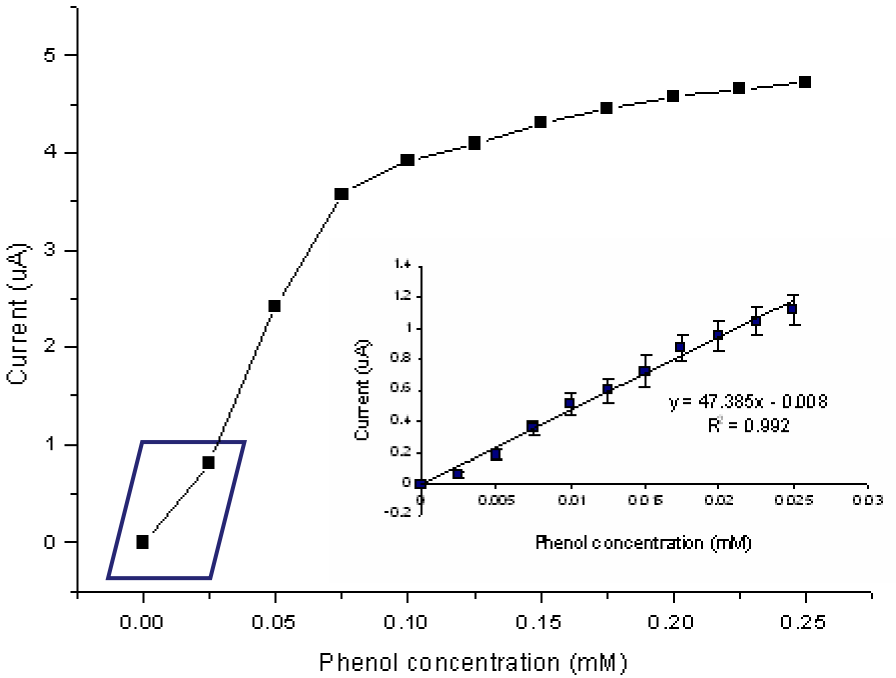
- Introduction
- Heavy metals
- **Phenols**
- Conclusions



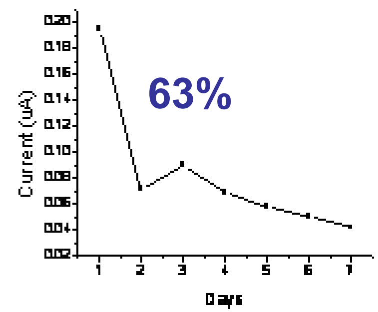
Analytical parameters

Detection limit = 1.35 μM

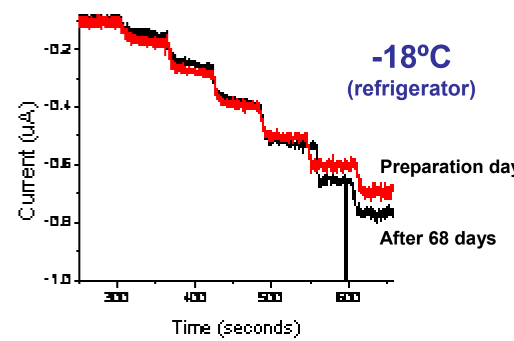
Sensitivity = 47.4 μA·mM-1

Linear range = 2.5-75 μM

Stability study



Shelf lifetime study



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OUTLINE

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CONCLUSIONS

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Introduction

Heavy metals

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Conclusions

Heavy metals

- Screen-printing technology is successfully used for the fabrication of mercury-free screen-printed electrodes (SPEs).
- Mercury-coated and mercury-free SPEs have been checked in a flow through system for lead detection and analytical parameters (linearity, LOD, LOQ, repeatability and lowest detectable change) related to lead detection have been given.
- Cell designs considering including the flow through model effect upon the pressure distribution have been optimized.
- The SWASV parameters for mercury-free SPEs in the flow through system have been optimized.
- Stable response for the mercury-free SPE for up to 5 weeks in continuous measurements in sea water has been obtained.
- The double standard additions method gives good results with a RSD between 3.5 - 5.2 %.

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CONCLUSIONS

Introduction

Heavy metals

Phenols

Conclusions

Phenols

- **CNT homogeneous dispersion at THF is shown.**
- A **simple method**, for **immobilizing the enzyme**, based on its **physical adsorption** onto the working electrode surface has been achieved. This **homogeneous distribution** over all the working electrode is demonstrated by **confocal studies**.
- Formulation of **SPE electrode modified with CNT and tyrosinase** gives **the best electrochemical response**.
- An **appreciable decrease** of the signal (around **63%**) from the first to the second day is observed.
- **Shelf lifetime study** show that the biosensors can be used up to **68 days** (saved at -18Cº)
- The **analytical performance of the phenol biosensor designed fits WARMER Project objectives in relation only to detection limit but not for the satbility**.
- **Future studies:**
  - Achieve lower limit of detection.
  - Study possible interferences.
  - Improve the stability.
  - Biosensors vs. conventional / official methods.

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Thank you!

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ENVIRONMENTAL RISK MANAGEMENT TOOLS FOR WATER QUALITY MONITORING
National Oceanographic Centre, Southampton (UK)
March 30th, 2009