In-situ voltammetric probe for heavy metal detection

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INTRODUCTION

The successful integration of heavy metal screen-printed sensors (SPE) into the *in situ* voltammetric probe so as to achieve the required analytical performance is strongly dependent to the flow electrochemical cell and the whole flow through and electronic set-up of the system. A new flow through cell that better fits to the developed SPEs ensuring a tight close as well as an easy electrode replacement system has been designed and all the corresponding electrochemical parameters including those of the liquid flow are accordingly optimized. The whole system probe that will ensure the smooth running of all the analytical steps including its hardware is shown. The application of the developed SPEs using the developed in situ probe system represents the final step so as to achieve the objective of WARMER project for voltammetric detection of heavy metals. The hydraulic circuit, the voltammetric flow cell and the hardware (voltammetric measuring unit) have been integrated into a single system.
Some preliminary studies related to the theoretical models of the designed flow cells including some simulations regarding the effect of the liquid flow rate upon the pressure homogeneity/distribution inside the bulk of the electrolytic cell are shown. The whole analytical parameters optimizations (deposition time, conditioning time, conditioning potential, frequency and step potential) are presented in detail. The standard addition method has been studied and the number of heavy metal standard additions (including the concentrations) has been accordingly selected.
The analytical performance of the final voltammetric measuring system (automatic analyzer) based on the use of SPE as detectors and the flow cell is still in process at our laboratories and the final results will be shown later.

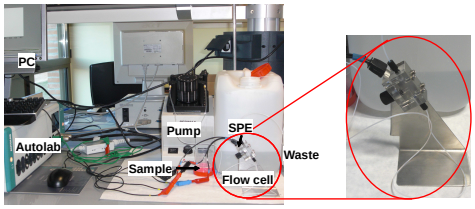
RESULTS AND DISCUSSION

VOLTAMMETRIC FIELD DEPLOYABLE PROTOTYPE

The flow cell used for the voltammetric SPE has been first tested in a laboratory set-up system. Based on these results (shown previously) a prototype voltammetric unit has been designed and fabricated. The developed system will be used for heavy metals detection in the field with SPEs as sensors. The micro Loop Flow Analysis (µLFA) hydraulic circuit, the voltammetric flow cell and the hardware (voltammetric measuring unit) have been integrated.

FLOW THROUGH SYSTEM IN THE LABORATORY

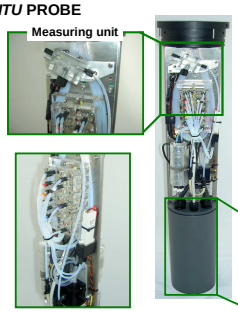
The analytical voltammetric responses for heavy metals have been performed in the laboratory using a flow through system. The system consists of a peristaltic pump, a flow cell (with a SPE integrated), a potentiostat (Autolab PGstat) and a PC.



VOLTAMMETRIC *IN SITU* PROBE

The measuring system includes among others the analytical reactor, the pump and a flow-cell specifically designed to use and easily exchange a SPE. A specific hardware OEM board made by PalmSens is used to acquire and process the current signals from the SPE.

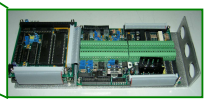
Separated compartments for reagents calibration solutions, water sample and waste have been previewed.
The voltammetric probe prototype will be used to detect low concentrations levels of heavy metals (Pb, Cd, Zn & Cu).



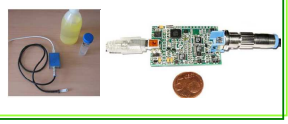
HARDWARE DESCRIPTION

The voltammetric probe integrates different boards (PC-104, SPE data acquisition board etc.) specifically selected for this prototype. A very compact electronic assembly, as shown in the picture, contained in a separate cylindrical compartment inside the external PVC cylinder of the analytical unit, has been developed.
The software periodically executes a self-check of the system, tracing malfunctions or error conditions.

Electronic assembly for the voltammetric *in situ* probe



EmStat potentiostat with USB and sensor connectors with and without housing



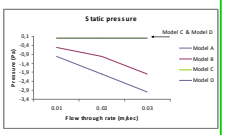
SIMULATIONS WITH DIFFERENT THEORETICAL FLOW THROUGH CELLS MODELS

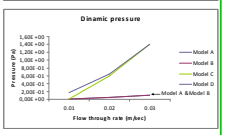
Different theoretical models for the flow cells have been designed using *Solid Edge* software. *Fluent* software is used to study the effect of the flow through rate upon the pressure homogeneity / distribution within the electrolytic cell in order to see later on its effect upon the reproducibility of the electrochemical measurements. Four models that show the effect of the flow through rate upon the pressure homogeneity are shown. The corresponding curves of the dynamic and static pressures vs. flow through rates are also calculated.

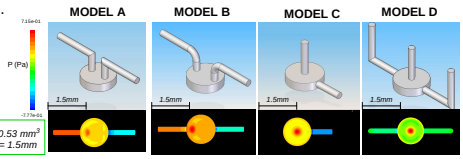
• Comparing all the studied models the best that better fits with our objective is model C due to the uniformity in the pressure distribution inside the flow cell. This model represent the higher pressure value in the middle of the cell which could indicate a good homogeneity of the sample in contact with the surface of the SPE. In addition, the simulations reveal an increase of the internal dynamic pressure (model C & D) while increasing the flow rate being this increment higher for the model C.

• If we focus our attention in model A and B we can observe that when a 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. In addition the by changing the flow rate the static pressures inside these model cells (C&D) remain constant.

• Although model D is a good model it does not bring any advantage considering its complicated design.





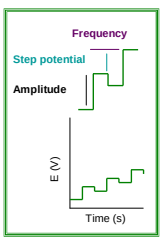


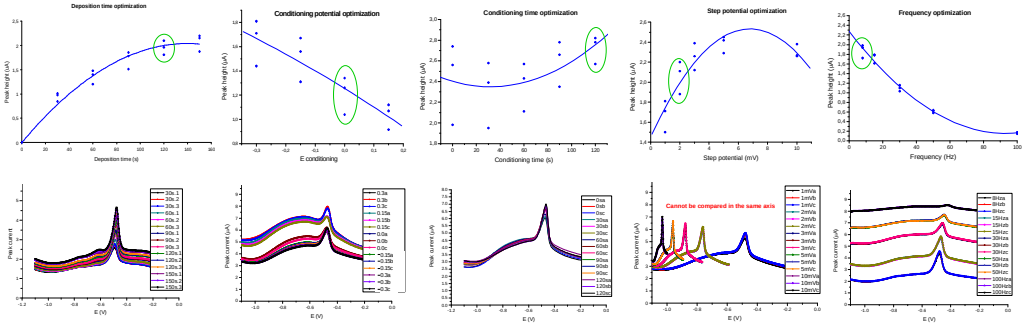
Flow cell vol. (SPE) = 100.53 mm³
Channel diameter = 1.5mm

Color interpretation: Red areas indicate the flow entrance inside the flow cell (higher pressure). Blue areas indicates the outflow (lower pressure).

OPTIMIZATION OF THE ELECTROCHEMICAL PARAMETERS FOR THE MERCURY-FREE SPEs IN THE FLOW THROUGH SYSTEM

The optimization of the electrochemical parameters in the flow through system using sea water and the mercury-free SPEs as detectors was performed. The optimum parameters were defined as the compromise between the highest peak response, the highest reproducibility and the best electrochemical cleaning of the SPE after performing the measurement. The selected parameters are E_{dep}, -1.1 V; t_{dep}, 120 s; E_{cond}, 0.0 V; t_{dep}, 120 s; Step potential, 3 mV; Frequency, 8 Hz.





Standard addition optimization

Number of Pb solution additions into the sample	Pb concentrations added / ppb	[Pb]; RSD; Sensitivity ppb ; % ; µA / ppb Pb
3	10, 20, 50	21.07 ; 5.4 ; 0.023
2	10, 20	**20.69 ; 3.5 ; 0.024**
2	20, 50	**21.05 ; 5.2 ; 0.023**
1	10	20.68 ; 3.4 ; 0.024
1	20	20.69 ; 3.4 ; 0.024
1	50	20.94 ; 4.7 ; 0.023

Using only **two additions** of Pb solution into the sea water sample gives good results with RSDs of 3.5 to 5.2 %.

CONCLUSIONS

The prototype for the SPEs voltammetric unit including the integration of the µLFA hydraulic circuit, the voltammetric flow cell and the hardware has been successfully designed and fabricated based on the results of the laboratory set-up optimization. In addition, the designed flow cells theoretical models reveals that the homogeneity / distribution of the sample (concentration gradients during the operation) inside the electrolytic flow cell depends on the shape and the positioning of the entering flow channels. This effect has been confirmed by the study of the pressure distribution (static and dynamic) inside the flow cell. The optimization of the electrochemical parameters in the laboratory set-up flow through system using sea water and the mercury-free SPEs is presented. The following parameters: E_{dep}, -1.1 V; t_{dep}, 120 s; E_{cond}, 0.0 V; t_{dep}, 120 s; Step potential, 3 mV; Frequency, 8 Hz were found as the best as the compromise between the highest peak response, the highest reproducibility and the best electrochemical cleaning of the SPE after performing the measurement. Standard addition method was the technique used for heavy metal determination. By using two additions of heavy metal standard solution upon the sea water sample a good accuracy and a RSD between 3.5 - 5.2 % have been achieved.
The final characterization and application of the developed voltammetric automatic analyzer is still under study at our laboratories and will be presented soon.

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