

**NAFION-COATED MERCURY FILM ELECTRODES FOR SQUARE WAVE  
STRIPPING VOLTAMMETRIC DETERMINATION OF LEAD AND CADMIUM  
IN CONTINUOUS FLOW**

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**Abstract**

A Nafion-coated wall-jet mercury film electrode was tested to determine cadmium and lead at trace levels in flowing systems by square wave anodic stripping voltammetry. Optimization of the experimental conditions and square wave parameters is discussed. For a 60 s deposition time, the detection limits restricted by the amount of cadmium and lead in the blank solution were  $1 \times 10^{-9}$  M and  $1 \times 10^{-10}$  M respectively. In comparison with the conventional mercury film electrode, the resistance to Triton X-100 interference was found to be superior with the Nafion film coating. The modified electrode was applied to trace metal determinations in real environmental samples.

**Key words:** Nafion-coated electrode; mercury film electrode; square wave anodic stripping voltammetry; cadmium and lead; flow analysis.

**Introduction**

The increasing release of heavy metals to the environment represents a serious problem that entails some unknown health risks for future generations [1]. Therefore it is mostly important from the analytical point of view to develop sensitive, selective, fast and economical methods for the quantitative determination of toxic metals in various matrices, even when present in trace amounts. Electroanalytical techniques have proved to be very useful for this purpose [2]. Stripping voltammetry using hydrodynamic electrodes [3] is widely recognized as a powerful electroanalytical method for trace metal measurements, especially when continuous on-line monitoring is required. Flow-through detectors such as

the wall-jet and the tube/channel electrodes are suitable, but the former offers more advantages owing to its higher flow rate dependence and lower dead volume [4].

Mercury film electrodes plated on glassy carbon are the most commonly employed for trace metal analysis using stripping voltammetry [5]. However, they are prone to fouling effects caused by adsorption of organic constituents of the sample matrix. These effects can be prevented by time-consuming sample pretreatment (e.g., mineralization) [6], that considerably lengthens the analytical procedure and introduces risks of contamination and losses; furthermore such extended pretreatments are not possible in many situations, namely in continuous flow applications. Chemical modification of electrode surfaces with permselective membrane coatings has received considerable attention [7-20] in order to improve electrode response, protecting its surface from adsorptive interferences. For this purpose, Nafion [7-15], cellulose acetate [10,16], other polymers [17,18] and dialysis membranes [19,20] have been employed in voltammetric sensors.

Nafion is a perfluorosulfonate cation-exchange resin that is chemically and thermally inert, nonelectroactive, hydrophilic, and insoluble in water [9]. Different preparation methods of Nafion-coated mercury film electrodes have been reported; the mercury film can be formed either before [21] or after [9] the polymer coating. Coating the glassy carbon with Nafion prior to mercury film plating has been found to be more advantageous in flow analysis, allowing one to perform the mercury deposition *in situ*. Nafion films on glassy carbon electrode surfaces can be easily recast from an alcoholic solution of the polymer by evaporation of the solvent. Subsequently, mercury is plated onto the electrode substrate through the film as described in previous work [9]. The resulting electrodes exhibit attractive permselective, ion-exchange, and antifouling properties that make them useful for voltammetric sensing. Anions are excluded from the electrode surface by the negatively-charged Nafion and the target cationic species are easily preconcentrated inside the Nafion film, leading to increased selectivity and sensitivity. In flow systems, there is another advantage to be taken into account: the mechanical stability of the mercury phase is improved, consequently, problems related with adhesion of the mercury film to the glassy carbon under convective conditions will be prevented [5,13]. Some authors have developed a different kind of Nafion coated mercury film electrodes by incorporating suitable chelating agents capable of binding only the metals to be determined [8].

Anodic stripping voltammetry (ASV) for the determination of trace metals at Nafion coated mercury film electrodes (NCMFE) has been reported using different potential modulations in the stripping step [13]. Although linear sweep voltammetry has been applied successfully, differential pulse and square wave voltammetry are preferred, since the confinement imposed by the film coating to the oxidized species produced after the application of each pulse leads to a very efficient replating process. Due to the faster repetition rates involved with square wave voltammetry increased sensitivity is obtained [13,18]. Moreover, the use of square wave rather than differential pulse voltammetry in the determination step should bring more advantages, allowing greater speed in analysis, yielding more reduced background currents and eliminating the need of oxygen removal [3].

In the present work the suitability of an *in situ* plated wall-jet NCMFE for square wave anodic stripping voltammetry (SWASV) of heavy metals in aqueous matrices is assessed and demonstrated. This study was carried out measuring traces of cadmium and lead in the presence of dissolved oxygen. Optimization of the experimental parameters is discussed. The performance of the NCMFE is investigated in aqueous solutions containing a nonionic surfactant (Triton X-100). Compared with a bare mercury film electrode (MFE) the NCMFE exhibited better sensitivity and improved resistance to interferences from the surfactant. Application to the determination of cadmium and lead in untreated water samples is described.

## Experimental

### Apparatus and Reagents

All voltammetric investigations were carried out using a computer controlled Autolab PGSTAT10 potentiostat (Eco Chemie, Utrecht, The Netherlands) equipped with GPES software.

The experiments were performed in a wall-jet flow cell described in earlier papers [4,22]. Potentials were controlled using a 3-electrode configuration comprising a wall-jet glassy carbon disc working electrode (3 mm diameter), an Ag/AgCl reference electrode (saturated KCl) and a Pt tube counter electrode also serving as solution outlet of the cell. The nozzle-electrode separation was 2.9 mm throughout to ensure wall-jet behaviour. Solutions were driven through the wall-jet cell by a LKB Bromma peristaltic pump.

All solutions were prepared from reagents of analytical grade without further purification and Millipore Milli-Q ultrapure water with conductivity values of less than  $0.1 \mu\text{S cm}^{-1}$ . Nitric acid (Merck) was used to make the supporting electrolyte solution. Pb(II) and Cd(II) solutions were prepared and diluted daily from 0.001 M lead acetate (Merck) and 0.001 M cadmium chloride (Merck) stock solutions. A stock solution of 0.01 M mercury(II) nitrate (BDH) in 0.01 M nitric acid for mercury plating was stored in a dark bottle. The Nafion coated electrode was prepared from Nafion in its solution form supplied by Aldrich (5% solution in a mixture of low weight aliphatic alcohols + 10% water), and *N,N*-dimethylformamide (DMF) purchased from Fluka. The commercial Nafion solution was previously diluted in 96% ethanol (Merck). Solutions of Triton X-100 (Fluka) were prepared by appropriate dilution in the supporting electrolyte.

#### Procedures

Prior to polymer coating the glassy carbon electrode was hand polished with a  $0.3 \mu\text{m}$  alumina slurry (Buehler), rinsed thoroughly with Milli-Q water and allowed to dry. The NCMFE was prepared by application of 1.5  $\mu\text{L}$  of a 0.25% (w/v) Nafion ethanolic solution, followed by 1  $\mu\text{L}$  DMF, to the glassy carbon electrode surface with a micropipette. Solutions were allowed to mix for a few seconds. The solvents were then evaporated in a warm air stream from an air gun held just a few millimeters above the electrode surface. Addition of DMF as a casting solvent as well as heating during the formation of the Nafion film were found to be advantageous to improve its mechanical properties [7]. The film appeared transparent and no cracks could be seen with the naked eye. This procedure was also followed using 0.1% and 0.5% (w/v) diluted Nafion solutions yielding coatings referred to as low and high thickness films, respectively [13,23]; the coating obtained using 0.25% diluted Nafion solution is referred to as medium thickness film. The Nafion-coated electrode was then placed in the wall-jet cell and the mercury film was formed *in situ* [24] from  $5 \times 10^{-5}$  M Hg(II) in 0.01 M  $\text{HNO}_3$ , at a fixed potential of  $-1.0$  V vs. Ag/AgCl. The bare MFE was prepared following the same procedure, apart from the Nafion coating.

Solutions were pumped to the wall-jet detector by the peristaltic pump at a flow rate of  $40 \text{ mm}^3 \text{ s}^{-1}$ . Flow rates were calibrated volumetrically each day.

The stripping voltammetric experiments were performed at the freshly coated electrode by the accumulation of metals, in potentiostatic conditions, at  $-1.0$  V vs. Ag/AgCl for 60 s,

followed by the application of a square wave potential scan in the positive direction, at  $200 \text{ mV s}^{-1}$  scan rate. The oxidation peak currents,  $I_p$ , were simultaneously recorded. After 3 hours working, the codeposited mercury film was electrochemically removed by holding the electrode potential at  $+0.3$  V for 60 s.

Experiments were conducted at room temperature of  $(25 \pm 1)^\circ\text{C}$  without solution deoxygenation.

#### Results and Discussion

SWASV of cadmium and lead was performed with codeposition of mercury at bare and Nafion coated glassy carbon wall-jet electrodes in 0.01 M nitric acid solution containing  $5 \times 10^{-5}$  M mercury(II) nitrate. In ASV the analytical procedure is greatly simplified by codepositing the mercury and the metals of interest [25,26]. The choice of nitric acid as the background electrolyte was due to two factors: firstly, to obviate any problems associated with sparingly soluble mercury salts in mercury film formation [27]; secondly, to facilitate the release of metals from matrices under analysis. Well shaped peaks were obtained at both electrodes with good reproducibility (see Figure 1).

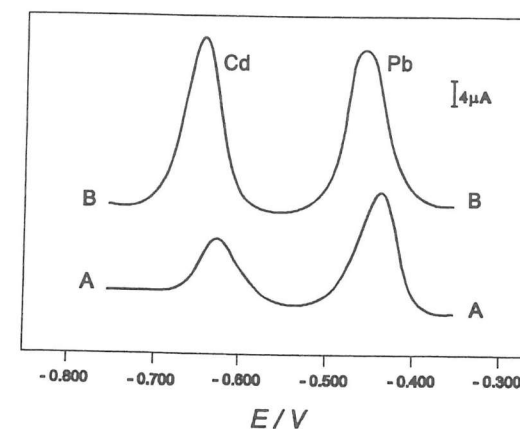


Figure 1. Square wave stripping voltammograms at a wall-jet (A) MFE and (B) NCMFE for SWASV of cadmium and lead in 0.01 M  $\text{HNO}_3/5.0 \times 10^{-5}$  M  $\text{Hg}(\text{NO}_3)_2$ ;  $[\text{Cd}^{\text{II}}] = 5 \times 10^{-7}$  M;  $[\text{Pb}^{\text{II}}] = 3 \times 10^{-8}$  M. Preconcentration: 60 s at  $-1.0$  V vs. Ag/AgCl. Flow rate:  $40 \text{ mm}^3 \text{ s}^{-1}$ ; square wave amplitude: 25 mV; frequency: 100 Hz;  $\Delta E_s$ : 2 mV.

A preliminary study was carried out to compare the responses of the MFE and the NCMFE with different film thicknesses to SWASV of cadmium and lead. The results obtained for the stripping peak parameters are summarised in Table I. The electrodes prepared with 0.1 % and 0.25 % Nafion (low and medium thickness NCMFEs, respectively) gave rise to higher cadmium and lead signals than in the case of measurements at the bare MFE, as a result of the cation exchange properties of the polymer. In contrast, at the high thickness NCMFE lower peak currents were recorded than those observed at the uncoated MFE. Despite the fact that no change was noticed at the correspondent peak potentials, this decrease in sensitivity was presumably due to the diffusional resistance associated with the thickest coating that hindered in some extent the transport of metal ions. This is also supported by the occurrence of some peak broadening (see Table 1). On the other hand, according to Hoyer *et al.* [13], the loss in sensitivity observed with the high thickness NCMFE may also be attributed to a partial opening of the polymer structure, leaving the mercury phase more exposed. This appears to be a plausible explanation, since a few macroscopic cracks could be visualized in the high thickness film. Nafion coatings shifted peak potentials which are more negative relative to those obtained at the uncoated electrode (Table I), suggesting that the polymer interacts with the stripping process. As previously pointed out [7] this observation may again be a reflex of the cation exchanging behaviour of the polymer, which favours the oxidized state of the test species. Thus, the medium thickness NCMFE was employed in all further experiments since it showed the best performance producing well-defined peaks with better sensitivity.

Table 1. Effect of Nafion film thickness on the stripping peaks of cadmium and lead. Experimental conditions as in Figure 1.

Electrode	Pb			Cd		
	$I_p / \mu A$	$E_p^a / mV$	$W_{1/2}^b / mV$	$I_p / \mu A$	$E_p^a / mV$	$W_{1/2}^b / mV$
MFE	8.57	-447	42	4.69	-637	55
Low thickness NCMFE	10.49	-475	41	7.33	-657	47
Medium thickness NCMFE	10.94	-475	41	9.51	-657	49
High thickness NCMFE	6.53	-475	54	1.98	-657	73

<sup>a</sup> Peak potentials are given to Ag/AgCl. <sup>b</sup>  $W_{1/2}$ : peak width at half maximum.

The solution flow rate through the wall-jet cell was then varied to investigate the influence of the transport properties of the Nafion film on the mass transfer process. Plots of the stripping peak current vs. flow rate for  $5 \times 10^{-9}$  M lead (Figure 2) at the NCMFE, as well as at the conventional MFE, show that the convective-diffusive mass transport of analyte was not affected by the Nafion coating. In a limited range of flow rates, there is good agreement between the theoretical predictions [4,28] and the experimental results for both electrodes. At  $45 \text{ mm}^3 \text{ s}^{-1}$ , peak current values start to deviate from linearity, until a plateau is reached. Very low flow rates ( $< 12 \text{ mm}^3 \text{ s}^{-1}$ ) were not employed, since the wall-jet hydrodynamics within an enclosed cell would not be followed [4]. A volume flow rate of  $40 \text{ mm}^3 \text{ s}^{-1}$  was adopted in all subsequent experiments.

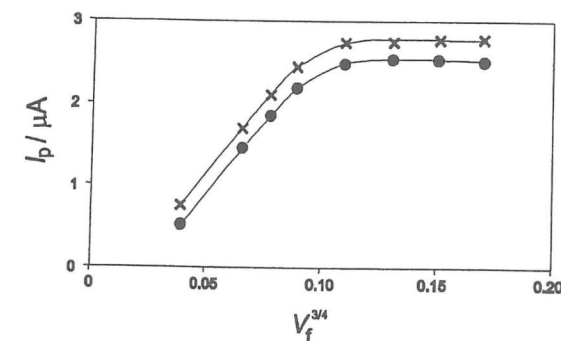


Figure 2. Effect of the volume flow rate on the SWASV peak currents of lead at (●) MFE and (×) NCMFE.  $V_f$  is measured in  $\text{cm}^3 \text{ s}^{-1}$ .  $[\text{Pb}^{II}] = 5 \times 10^{-9}$  M. Other conditions as in Figure 1.

With a view to optimizing the experimental conditions for the determination of cadmium and lead at the NCMFE by SWASV, an univariate method was performed with the deposition potential, the deposition time and square wave parameters as variables.

#### Dependence on the deposition time and potential

As shown in Figure 3a, sensitivity of the NCMFE is improved for cadmium and lead as the deposition potential becomes more negative, between  $-0.8$  and  $-1.0$  V. This behaviour is explained by the fact that more uniform mercury films are grown on glassy carbon substrates when the applied plating potential is as negative as  $-1.0$  V [27]. At less negative potential values, instead of a perfect coverage of the electrode surface, many small mercury droplets

will be formed; as a consequence the electrode sensitivity will decrease. Moreover, being positively charged, the reductive deposition of Cd(II) and Pb(II) will be favoured at more negative potentials. Although a range of optimum deposition potentials is available from  $-1.0$  to  $-1.2$  V (see Figure 3a), a preconcentration potential of  $-1.0$  V was chosen to prevent any disturbance due to hydrogen evolution that may take place at the electrode surface. At this potential value, the codeposition of mercury and cadmium and/or lead on the glassy carbon substrate during the deposition step is guaranteed.

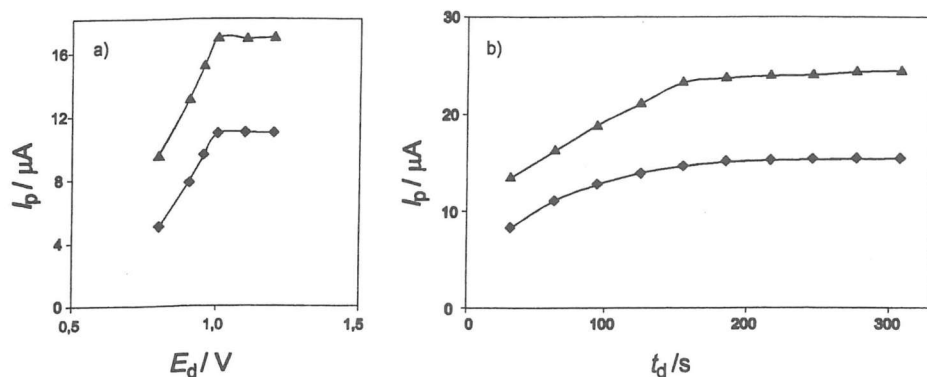


Figure 3. Variation of peak current for (◆)  $7 \times 10^{-7}$  M cadmium and (▲)  $5 \times 10^{-8}$  M lead with a) deposition potential and b) deposition time at the NCMFE. Other conditions as in Figure 1.

The influence of the preconcentration time on the square wave response for cadmium and lead is illustrated in Figure 3b. For  $5 \times 10^{-8}$  M lead(II) the peak current increases and starts to level off around 180 s, indicating that complete coverage of the mercury film is gradually being attained. For  $7 \times 10^{-7}$  M cadmium(II) the saturation region was reached around 130 s. A preconcentration time of 60 s was adopted to obtain well-defined peaks with good resolution in the simultaneous determination of cadmium and lead at the NCMFE.

#### Influence of square wave parameters

Square wave amplitude, frequency and staircase increment are interrelated and have a combined influence on the response of the NCMFE. To produce high sensitivity and fast scan rates, these parameters have to be optimized.

*Frequency:* A study of the variation of peak current with frequency shows that a linear dependence is observed below 140 Hz (see Figure 4). Above this value, ill-defined peaks and very high background currents are obtained. In order to achieve higher frequencies, the pulse width is shortened; as a result sensitivity decreases since the total measured current is markedly affected by the capacitive background current [29]. A frequency of 100 Hz was chosen so as to provide large and well-defined peaks and fast scan rates.

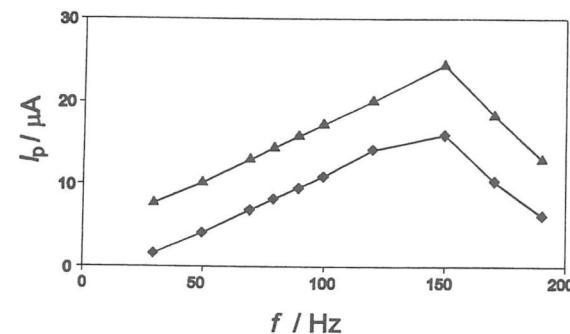


Figure 4. Frequency dependence of the SWASV response obtained for (◆)  $7 \times 10^{-7}$  M cadmium and (▲)  $5 \times 10^{-8}$  M lead with the NCMFE. Other conditions as in Figure 1.

*Amplitude:* The response for both cadmium and lead increases with square wave amplitude. However, larger values above 50 mV led to peak broadening offering little gain in sensitivity. Thus, our choice of 25 mV was the highest value consistent with adequate peak definition.

*Staircase Increment:* The staircase increment,  $\Delta E_s$ , was varied from 1 to 5 mV. No improvement was achieved for staircase increment above 3 mV; although peak currents were slightly increased, peak broadening occurred. The best value consistent with both adequate peak definition and evaluation was 2 mV. In combination with the selected frequency mentioned above, a scan rate of  $200 \text{ mV s}^{-1}$  was produced.

#### Reproducibility and Stability of the NCMFE

The assessment of both the reproducibility of the measurements and the stability of the NCMFE is very important for the reliability of the results. For this purpose, a test solution containing  $5 \times 10^{-8}$  M lead in  $5 \times 10^{-5}$  M Hg(II)/0.01 M HNO<sub>3</sub> was employed.

Using a freshly prepared Nafion coated electrode, reproducibility was tested in two ways. First, successive determinations were performed consecutively with 60 s preconcentration

time at  $-1.0$  V. Second, repeated determinations were carried out following the same procedure, but a potential of  $+0.3$  V was applied for 30 s between measurements to clean the mercury film. In both cases the results of eight successive cycles gave very small relative standard deviations of the peak currents ( $\sim \pm 0.1\%$ ). The inclusion of an additional step in the analytical method to renew the mercury film after each measurement was found unnecessary.

The stability of the response at the NCMFE and the bare MFE for lead was evaluated for 6 hours, at a continuous flow rate of  $40 \text{ mm}^3 \text{ s}^{-1}$ . Stripping peaks were recorded every 30 minutes, after 60 s codeposition of mercury and lead at  $-1.0$  V. Whereas the bare MFE gave decreased and distorted peaks after three hours operating, at the NCMFE well shaped and reproducible peaks were obtained for at least 5 hours. In fact, the lifetime of the mercury film electrode is shown to be lengthened by the Nafion coating, which mechanically improves its stability under the convective conditions inherent to the flow system [13].

#### Calibration and Detection Limits

Under the optimized operating conditions selected above, the wall-jet NCMFE was calibrated by the standard addition method. Calibration plots of peak current vs. metal concentration were obtained after blank subtraction. Linearity was found up to  $1 \times 10^{-8}$  M cadmium and  $1 \times 10^{-9}$  M lead, when the ions were analysed separately and as a mixture containing equal amounts of both cadmium and lead. At concentrations higher than  $1.2 \times 10^{-6}$  M cadmium and  $1.0 \times 10^{-7}$  M lead, nonlinearity became evident reflecting saturation of the mercury film. The detection limit was taken as the concentration at which the signal equals three times the standard deviation of the background signal [30]. The blank signal was then investigated with fifteen blank solutions using 60 s preconcentration time. Detection limits of  $1 \times 10^{-9}$  M and  $1 \times 10^{-10}$  M were estimated for cadmium and lead, respectively.

#### Interferences

The direct determination of heavy metals in environmental matrices by stripping voltammetry at mercury electrodes is often complicated by the presence of surface active compounds [3]. The stripping peak currents are usually depressed or even suppressed, owing to the adsorption of such substances on the mercury surface. In the present study, Triton X-100 was used to simulate the effect of a typical non-ionic surfactant on the stripping response of both the MFE and the NCMFE for cadmium and lead. Our choice was based in the

experimental evidence [31] that Triton X-100 causes a very serious interference in SWASV at mercury film electrodes. Increasing concentrations of the surfactant ranging from 1 to  $100 \text{ mg L}^{-1}$  were tested. Plots of the normalised peak currents vs. Triton X-100 concentration (Figure 5) show gradual peak depression at both electrodes. However, the NCMFE was much less susceptible to this effect, since the antifouling properties of the polymer film greatly improve the analytical signal.

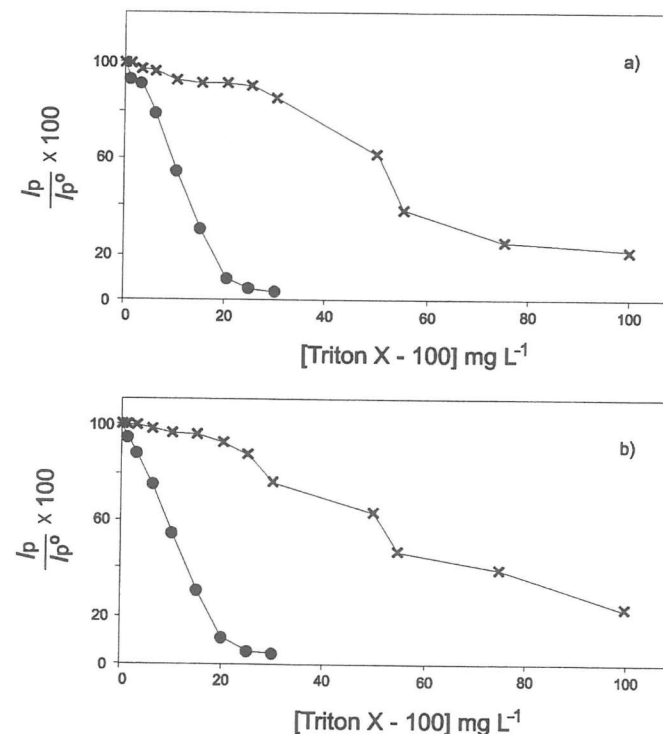


Figure 5. Effect of Triton X-100 on the stripping peaks of (a)  $5 \times 10^{-7}$  M cadmium and (b)  $5 \times 10^{-7}$  M lead at (●) the bare MFE and (×) the NCMFE.  $I_p^0$ : peak current in the absence of Triton X-100. Other conditions as in Figure 1.

At the bare MFE a drastic decrease in sensitivity was recorded up to  $20 \text{ mg L}^{-1}$  leading to peak suppression at  $30 \text{ mg L}^{-1}$ ; on the other hand, at the NCMFE surfactant concentrations up to  $30 \text{ mg L}^{-1}$  were reasonably tolerated yielding slight decreases in peak currents ( $\sim 15\%$  for cadmium and  $\sim 25\%$  for lead). Further additions of the surfactant resulted in more pronounced

signal depression. At the conventional MFE positive shifts in the peak potentials were also observed as an indication of loss of reversibility of the electrode reaction; this effect was unnoticed at the modified electrode. Although a remarkable improvement is attained with the Nafion coating, the interference can not be completely eliminated. This is probably due to partial blockage of the Nafion film pores owing to accumulation of the surfactant at the outer membrane surface, affecting mass transport [8, 13].

Using lead as test analyte, the stability of both the NCMFE and the MFE was tested by checking their behaviour in the presence of 10 mg L<sup>-1</sup> Triton X-100 during a long run of 10 successive determinations of 5x10<sup>-8</sup> M lead carried out over a total time of 5 h. A noticeable decrease in sensitivity was observed at the bare MFE (~22%); at the modified electrode the signal only decreased slightly (~2.2%) over the same period. The resulting relative standard deviations were ±46.7% and ±7.7, respectively. These results demonstrate that the Nafion coating forms a satisfactory protection for the transport of surfactants towards the mercury surface. Blank solutions (free of Triton X-100) were analysed at the beginning and at the end of this particular experiment to see if there was electrode surface deterioration. No change in the lead signal was observed.

Although it has been reported [10,34] that the anodic stripping determination of lead at Nafion coated electrodes is rather problematic in the presence of Triton X-100, it should be emphasized that in the experimental conditions presented here the interference can be largely minimized through the use of the NCMFE. The obtained results basically agree with data found previously by other authors at mercury film electrodes modified with cellulose acetate [16] and Nafion [13, 31-33].

The interfering effect of other metal species when using the NCMFE was also examined. Cr<sup>III</sup>, Mn<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> when present at 10<sup>4</sup>-fold more than the Pb<sup>II</sup> and Cd<sup>II</sup> concentrations were tolerated, but Cu<sup>II</sup> was found to interfere seriously leading to peak depression, although good peak resolution was still observed. At a 5-fold excess of Cu<sup>II</sup> over Cd<sup>II</sup> and Pb<sup>II</sup>, the cadmium peak height decreased by about 20% and that of lead by about 4%; for excesses lower than one-fold the lead signal was not affected.

#### Application

The analytical utility of the wall-jet NCMFE for real analysis was demonstrated by using it for the determination of cadmium and lead in rain water collected after passing along drainage

ditches from roads with high traffic density. Water samples collected from the river Jamor, near Lisbon, were also analysed. Prior to stripping voltammetric analysis, nitric acid and mercury(II) nitrate were added to the samples; filtration was then performed. All the samples had measurable amounts of lead but no detectable traces of cadmium were found in rain water. In the river water samples significant concentrations of cadmium were detected. The concentrations were evaluated using calibration plots. Confirmation of the values was obtained by atomic absorption spectrometry (AAS) with electrothermal atomization. As can be seen in Table 2, the values obtained using the NCMFE by SWASV are very close to those obtained by AAS.

Table 2. Analysis of Cd and Pb in rain water samples (S1 to S5) and in river water samples (S6 and S7)

	MFE* (nM)	NCMFE* (nM)	AAS (nM)
<i>Lead</i>			
S1	nd <sup>a</sup>	0.95±0.02	nd
S2	0.25±0.02	0.69±0.01	nd
S3	nd	1.3±0.1	2.0
S4	5.0±0.2	7.1±0.4	6.7
S5 <sup>b</sup>	30.0±2.2	48.2±4.3	50.0
S6	10.2±1.3	24.9±1.7	26.2
S7	7.8±0.5	16.9±2.4	19.1
<i>Cadmium</i>			
S6	12.1±1.0	19.3±2.0	21.0
S7	13.0±1.2	22.2±1.2	19.7

\*n = 5

<sup>a</sup>nd=not detected; <sup>b</sup>collected from a very high traffic density place.

#### Conclusions

This work shows that the wall-jet NCMFE plated *in situ* is an useful tool for flow measurements of heavy metals at trace levels by SWASV. It exhibited important advantages compared to the bare MFE, yielding higher sensitivity and a far superior resistance to organic interferences. The adopted Nafion coating has proved adequate, being thick enough to prevent adsorption of a surfactant but also thin enough to allow sufficient mass transfer of the analytes. Its applicability to the determination of cadmium and lead in rain water and water samples collected from a polluted river, near Lisbon, was demonstrated. The use of the wall-jet NCMFE appears to be very promising for routine flow analysis of trace metals in aqueous environmental matrices.

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