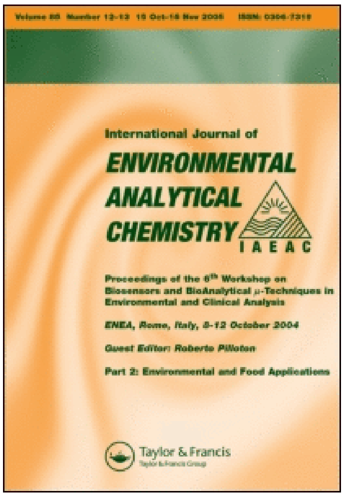

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POLYMER–MERCURY COATED SCREEN-PRINTED SENSORS FOR ELECTROCHEMICAL STRIPPING ANALYSIS OF HEAVY METALS

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In the perspective of in-field stripping analysis of heavy metals, the use and disposal of toxic mercury solutions (necessary to plate a mercury film on a carbon electrode surface) presents a problem. The aim of this work was the development of mercury coated screen-printed electrodes previously prepared in the lab and ready to use in-field. Thus some commercially available polymers like Nafion®, Eastman Kodak AQ29®, and Methocel® were investigated as mercury entrapping systems for electrochemical stripping analysis of heavy metals. Screen-printed disposable cells with a silver pseudo-reference electrode, a graphite counter electrode, and a graphite working electrode were used. To modify the sensor, the polymer solution was cast onto the carbon working electrode surface. Detection limits of 0.8 and 1 μg/L were obtained for lead and cadmium respectively. Since Methocel® based electrodes showed the best performance, they were used for the analysis of real samples. The results were compared with those obtained using a classical thin mercury film electrode and ICP spectroscopy.

All the experiments reported here were performed in un-deareated solutions as required for in-field analysis.

Keywords: Screen-printed electrodes; Heavy metals; Stripping analysis; Polymeric coatings; Methocel®

INTRODUCTION

Among the different analytical techniques to detect heavy metals, electrochemical stripping analysis is considered one of the most powerful techniques for in-field analysis of heavy metals [1].

Nevertheless, the use of conventional electrochemical cells and of classical bulky electrodes presents a problem for decentralised measurement, due to the large volume of solution needed. The use of disposable screen-printed electrodes (SPEs) is a great simplification in the design and operation of heavy metal determinations in accordance with the requirements of a decentralised assay, since they are miniaturised

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planar electrodes, and are used as a drop-on sensor. As reported in literature [1–10], for heavy metal analysis, mainly carbon working electrodes are used; generally, the procedure is to plate a thin mercury film (TMF) onto the carbon working SPE, coupling these sensors with highly sensitive electrochemical techniques such as potentiometric stripping analysis (PSA) or square wave anodic stripping voltammetry (SWASV). Lead, cadmium, copper and other heavy metals forming amalgam with mercury are thus detected at μg/L level in a few minutes [1–10].

The main concern related to the in-field application of these devices is the need to plate a mercury film and thus manage and dispose toxic mercury (II) solutions. In order to overcome these problems many approaches can be elaborated. For instance mercury-coated sensors, prepared beforehand in the lab and ready to use in-field, can be an interesting strategy.

Nowadays many different polymers, commercially available, are being widely used in electrochemical sensor and biosensor development since they are chemically inert, nonelectroactive, hydrophilic, some of them also insoluble in water, and thus very useful to protect the electrode surface fouling [16–19]. Moreover, since the coating is cast from a solution of the polymer, the sensor preparation becomes convenient and fast.

The aim of this study was to analyse the performance of different commercially available polymers as a mercury entrapping system for sensor modification in heavy metal analysis. Thus Nafion®, Eastman Kodak AQ29® (perfluorosulfonate polymers), and Methocel® (a cellulose derivative) were studied and their performance was compared.

Some examples of such coatings have already been reported in the literature. For instance to modify the electrode surface, Brainina *et al.* proposed soluble mercury compounds ($Hg(Ac)_2$) protected with Nafion® [11,12], among other modifications such as the use of organic insoluble mercury complexes. In these works disposable thick-film graphite electrodes were used as working electrodes and the mercury coatings were cast onto the surface of these electrodes. Faller *et al.* used these same modified thick film electrodes to detect tin (IV) [13]. The authors of the cited papers concluded that the well shaped peaks, the stable peak increments after standard additions and the satisfactory correlation between added and found concentrations of metal ions, during a long period of time, makes the electrodes promising for stripping voltammetry; moreover these modified electrodes contaminate the waste much less than the ordinary mercury film graphite electrodes [11–13]. In those works a conventional cell (classical reference and counter electrodes coupled with modified working electrodes) and differential pulse voltammetry (DPV) as the electroanalytical technique were used.

Also, Dalagin [14] and Maccà [15] reported the use of a Nafion®–mercury acetate membrane cast onto a glassy carbon electrode coupled with classical bulky reference and counter electrodes.

A completely screen-printed cell was used for this work, thus increasing the practicality of the proposed method for *in situ* analysis.

Moreover, in this study particular attention was devoted to analyse the behaviour of the different polymeric coatings in HCl, since it is a widely used reagent for electrochemical stripping measurements of heavy metals.

In this respect, Methocel®-based coatings showed better results, thus calibration curves of lead and cadmium were made and different real samples were tested.

EXPERIMENTAL

Reagents

Nafion® 5% solution in low aliphatic alcohol–water solution was obtained from Aldrich (Italy); Eastman-Kodak AQ29D® was obtained from Eastman-Kodak (USA); Methocel® 90HG was purchased from Fluka (Italy). Mercury acetate, mercury chloride, ethanol 96%, Suprapur grade hydrochloridric, nitric, acetic, perchloric acids were purchased from Merck (Italy). The water used for preparation of solutions was from a Milli-Q System (Millipore, Italy). Heavy metal stock solutions were prepared by diluting lead (II) and cadmium (II) standard solutions AAS grade (Fluka, Italy).

Electrodes

Screen-printed strips consist of the graphite working electrode (3 mm diameter), of the graphite counter electrode and of the silver pseudo-reference electrode. SPE preparation was reported elsewhere [20]. A scheme of the electrodes used was shown in Fig. 1.

1. SPE modified by Hg (II) and Methocel® HG90:
   The screen-printed carbon electrode was modified using a solution containing 100 mg of mercury acetate, 100 µL of acetic acid in 10 mL of H_2O (sol. A). To 1.5 mL of this solution, were added 3.5 mL of H_2O and 125 mg of Methocel® HG90. 5 µL of this solution was pipetted onto the surface of the working electrode, dried in the air at room temperature.
2. SPE modified by Hg (II) and Nafion®:
   To 1.5 mL of sol. A, prepared in 10 mL of ethanol 96%, were added 3.5 mL of Nafion®. 5 µL of this solution were pipetted onto the surface of the working electrode, dried in the air at room temperature.
3. SPE modified by Hg (II) and Kodak AQ29D®:
   To 1.5 mL of sol. A, prepared in 10 mL of ethanol 96%, were added 3.5 mL of Kodak AQ29D®. 5 µL of this solution were pipetted onto the surface of the working electrode, dried in the air at room temperature.
4. Mercury thin film SPE:
   The SPE was used as a substrate for a TMF, the mercury film was preplated from a stirred mercury (II) chloride solution, 100 ppm, in hydrochloric acid 0.1 M, by

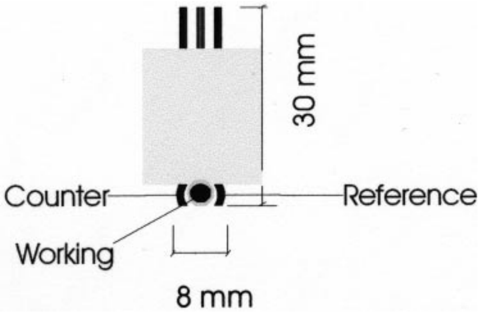

FIGURE 1 Scheme of the screen-printed strip; shape and dimension of the screen-printed electrochemical cell are reported.

holding the electrode at −1.1 V for 2 min. The potential was then switched to −0.2 V for a cleaning period of 2 min.

Electrochemical Analysis

All the experiments were carried out using an Autolab PSTAT 10 System (Ecochemie, Utrecht, Netherlands). Square wave (SW) voltammetry conditions were: conditioning potential −0.3 for 60 s, deposition potential −1.1 V for 120 s, equilibration time 30 s, SW amplitude 28 mV, step 3 mV, frequency 15 Hz. PSA conditions were: conditioning potential −0.3 for 60 s, deposition potential −1.1 V for 120 s, equilibration time 30 s, stripping current +1 μA.

Each mercury coated electrode is conditioned before using by applying −1.1 V for 300 s and then SW voltammetric or chronopotentiometric scans were carried out until low and stable background were obtained.

Sample Preparation and Analysis

To analyse wine and wastewater by stripping analysis, 0.5 mL of 1.2 M HCl were added to 4.5 mL of sample solution.

To mineralise the herbal samples, a nitric-perchloric digestion was used. The digestion was performed in a closed vessel. At 0.1 g of sample were added 3.2 mL of nitric acid and 0.8 mL of perchloric acid; everything was heated up at 200°C until having a white residual. The process was concluded adding 5 mL of supporting solution (0.1 M of HCI).

Metal content values by ICP were obtained from a private certified laboratory, where an ICP Spectrometer Optima 3000 SC (Perkin-Elmer) was used, after a microwave digestion of the samples.

RESULTS AND DISCUSSION

Mercury Coating Characterisation

Different commercial polymers were studied for the development of mercury coated sensors for in-field analysis of heavy metals: Nafion®, Eastman Kodak AQ29D®, Methocel®.

Each coating solution was prepared by mixing the same amount of mercury acetate in the polymer solution, in order to be independent of mercury concentration. The value of the ratio mercury–polymer solution used for these experiments was chosen in accordance with data reported in the literature [14], where an optimised value of 30% mercury–70%polymer solution (v/v) was given.

The response of each mercury coating was characterised in terms of sensitivity, peak resolution, reproducibility in HCl, a supporting electrolyte widely used in electrochemical analysis of heavy metals. These experiments were carried out using PSA with a stripping current of +1 μA.

In Fig. 2 calibration curves of lead in three different concentrations of HCl using Nafion®–mercury membrane were reported. Increasing the HCl concentration (in the

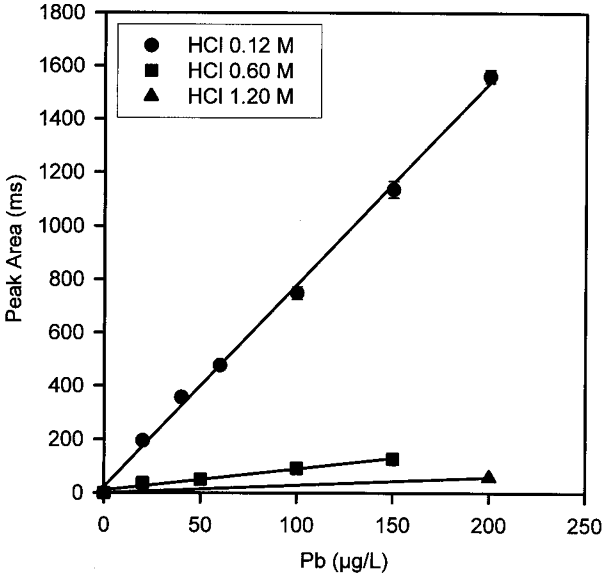

FIGURE 2 Nafion®–mercury coated SPE calibration plot for lead in 0.1, 0.6 and 1 M HCl concentration.

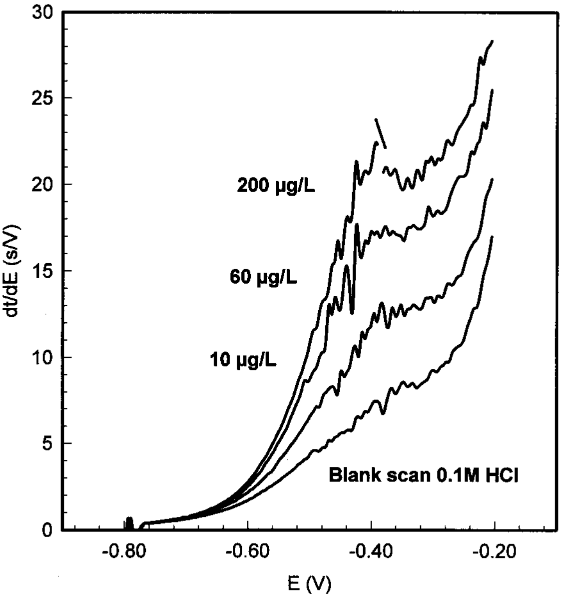

FIGURE 3 Potentiogram of Eastman-Kodak AQ 29D®–mercury coated SPE in HCl 0.1 M increasing the lead concentration.

range 0.1–1 M) the Nafion®–mercury membrane sensitivity towards lead decreased. In the case of the Eastman-Kodak®–mercury membrane, low sensitivity and poor resolution was observed in the HCl concentration range examined: the potentiograms of different concentrations of lead in HCl 0.1 M were reported in Fig. 3.

Changes in the morphology and geometrical parameters of the polymeric microstructure, increasing the ionic strength, were observed and reported in literature [16,17] for perfluorosulfonate polymers; these changes could be an important contribution to the behaviour of the tested polymers towards stripping analysis in concentrated HCl solution.

As shown in Fig. 4(a), Methocel®–mercury coated electrodes can be used also in concentrated HCl solution since the signal suppression, when higher HCl concentration were

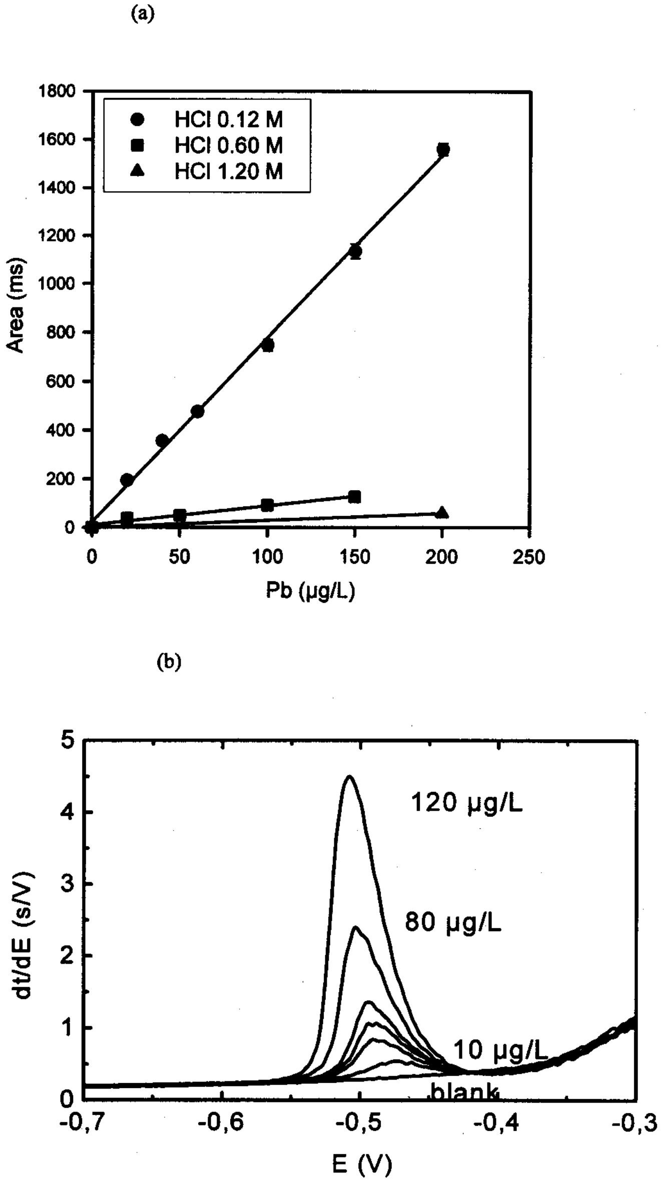

FIGURE 4 (a) Methocel®–mercury coated SPE calibration curves for lead in 0.1, 0.6 and 1 M HCl concentration; (b) potentiograms of Methocel®–mercury coated SPE in HCl 0.1 M increasing the lead concentration (10, 20, 30, 40, 80, 120μg/L).

used, was very low. In Fig. 4(b) are reported the potentiograms for the determination of lead in the concentration range of 0–50 µg/L; the supporting electrolyte was HCl 0.1 M.

Thus, since Methocel®-coatings can be used in a wide range of chloride concentrations, and because the use of this polymer has not been reported yet in the literature for stripping analysis, we decided to characterise these modified sensors and test their performance in more detail with standard solutions and real samples, making a comparison with classical mercury thin film electrodes, and moreover with ICP.

Analytical Performance of the Methocel®–Mercury Coating

Figure 5 shows a calibration curve of lead and cadmium in HCl 0.1 M, using SW voltammetry as electroanalytical technique. Good sensitivity and well-shaped peaks were observed with both analytes.

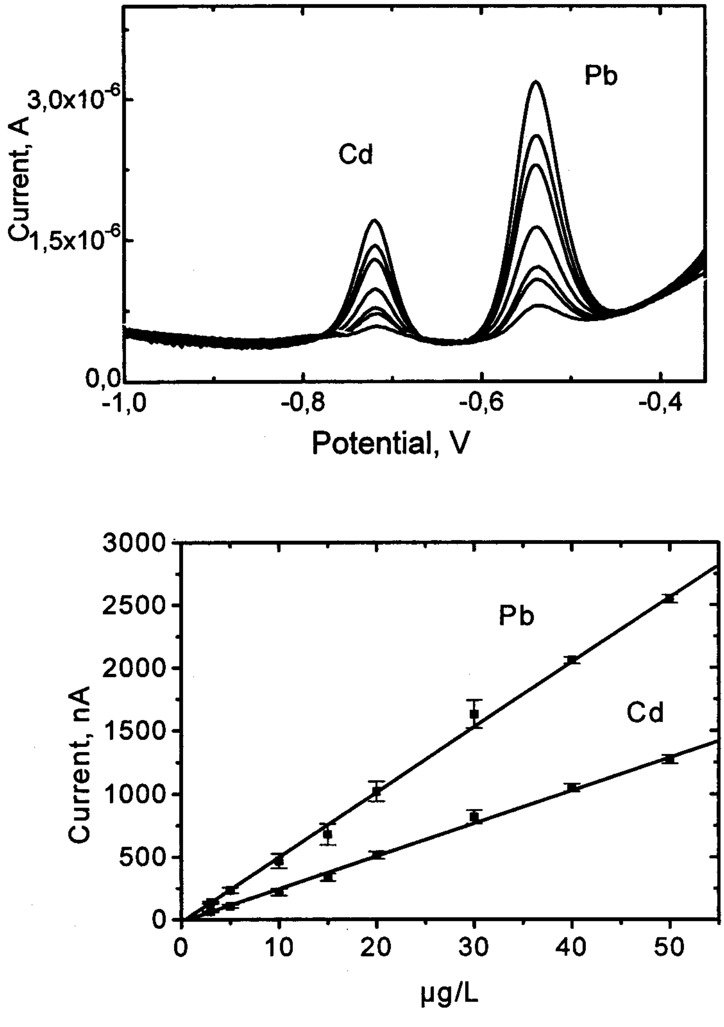

FIGURE 5 Calibration curves of lead and cadmium in HCl 0.1 M, using square wave anodic stripping voltammetry.

The detection limit, for 2 min of accumulation time with stirring, was 0.5 μg/L for lead in PSA. In SWASV the detection limits were 0.8 and 1 μg/L for lead and cadmium, respectively. The detection limit value was calculated as 3 times the noise measured at 10 μg/L of lead and cadmium.

The relative standard deviation (R.S.D.%) for 10 repetitions using the same strip was 2% (tested in 10 μg/L lead). The R.S.D. was 10% when different electrodes ($n = 6$) were tested.

As shown in Fig. 6, the response of a Methocel®-coated electrode was stable for at least 3 months, when stored in dark conditions at 4°C.

Real Sample Analysis

Figures 7 and 8 illustrated the suitability of the Methocel®–mercury coated SPEs for the determination of lead in food and environmental samples. In Fig. 7 were reported standard additions of lead in a wine sample. Three standard additions of 20, 40, 60 μg/L to the wine sample resulted in well-defined stripping peaks. The lead peak for the original sample can thus be quantified by means of the resulting standard addition plot. The resulting lead level in this sample correspond to 35 μg/L. Only a simple pre treatment (pH adjustment) of this sample was made.

In Table I was reported the analysis of wastewater samples. Some influent and effluent water samples of a wastewater treatment plant were analysed using the standard addition method. As reported in Fig. 8 the standard additions to the water samples resulted in well-shaped stripping peaks and quantification of the lead in the original samples was performed through the resulting standard addition plots. As in the case of wine analysis, water samples were just acidified by a concentrated aliquot of HCl to obtain a final concentration of 0.1 M HCl.

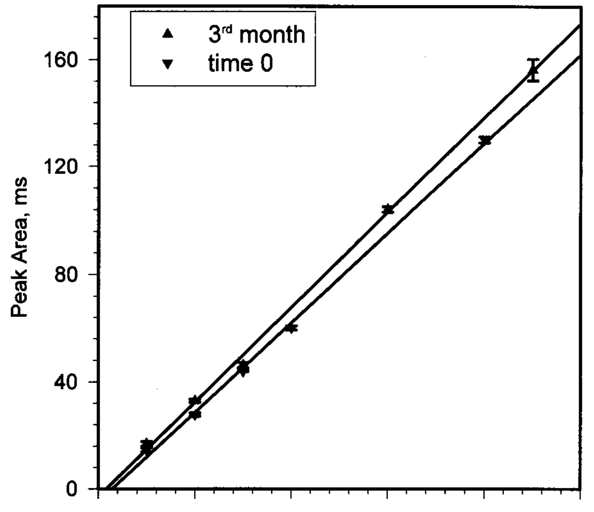

FIGURE 6 Stability of Methocel®–mercury coating: calibration curves for lead repeated after 3 months. PSA: + 1 μA. Deposition 120 s, −1 V *vs* Ag pseudo-reference.

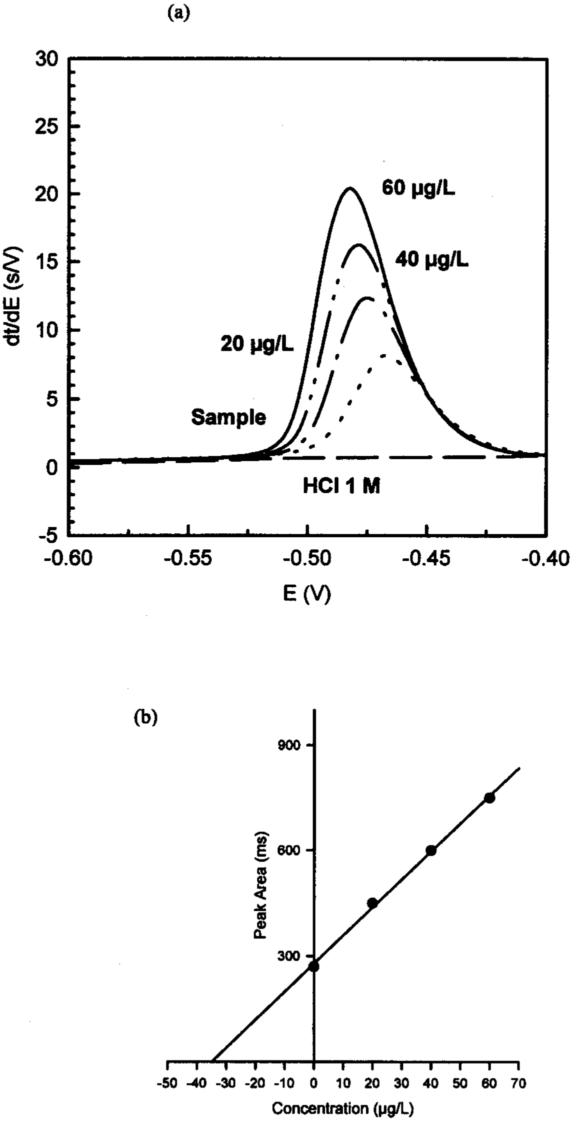

FIGURE 7 Standard additions of lead in a red wine sample (a) and corresponding standard addition plot (b).

In Table II were reported the results of the analysis of herbal samples. These samples were treated by wet digestion before stripping analysis. A good correlation between mercury thin film SPE and these modified sensors was obtained.

The samples of Tables I and II were also analysed by ICP after a microwave digestion. Only one analysis was carried out for spectroscopic analysis while the average of three repetitions was used for voltammetric analysis. The results obtained suited well with those obtained by stripping voltammetry, even if there are some discrepancies, probably due to the pre-treatment of the samples, that have to be investigated in more detail.

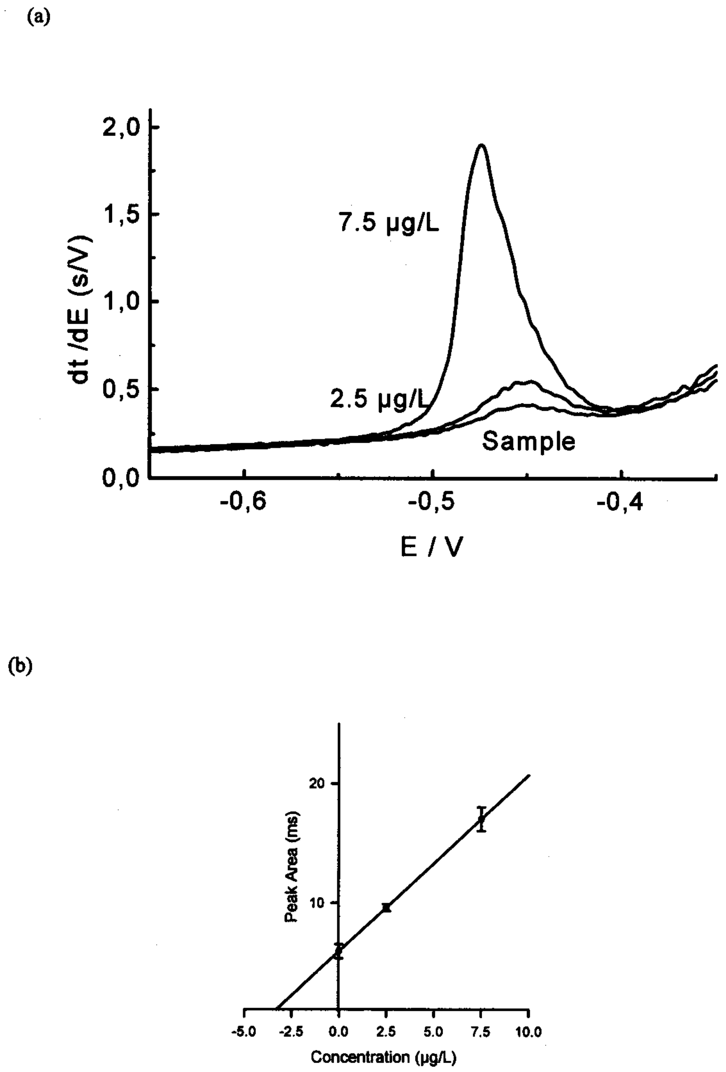

FIGURE 8 Standard additions of lead in a wastewater sample (a) and corresponding standard addition plot (b).

TABLE I Comparison of Methocel®–mercury electrode and ICP results testing wastewater samples. Influent and effluent water samples of a wastewater treatment were collected in three different days. For stripping analysis, the samples were acidified and analysed using the standard addition method

Samples	*Influent* (µg/L)		*Effluent* (µg/L)	
	Sensor	*ICP*	*Sensor*	*ICP*
1	4 ± 1	11	0	5
2	8 ± 2	18	5 ± 1	12
3	3 ± 1	6	2 ± 1	–

TABLE II Comparison of Methocel®–mercury electrode (MME), thin film mercury electrode (TFME) and ICP results testing herbal samples. For stripping analysis herbal samples were treated by wet digestion

	MTFE (mg/kg)		*MME* (mg/kg)		*ICP* (mg/kg)	
Samples	*Cd*	*Pb*	*Cd*	*Pb*	*Cd*	*Pb*
1	0.05	0.6 ± 0.1	0.1	0.5 ± 0.1	≤ 0.1	≤ 0.1
2	0.2 ± 0.1	0.4 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.15	0.9
3	0.8 ± 0.1	5.7 ± 0.2	0.7 ± 0.1	6.1 ± 1	0.35	5.8
4	1.5 ± 0.1	13 ± 2	1.7 ± 0.1	15 ± 2	1.3	19

CONCLUSION

In this work we demonstrated that Methocel®, a cellulose derivative, could be a very useful alternative in the construction of modified sensors for heavy metal detection. The performance of the Methocel®–mercury coated electrodes, in comparison with the other coatings examined in this work, can be very interesting especially when high concentration of HCl have to be used.

The use of mercury coatings, like the Methocel® one, eliminates the use of mercury solution during in-field experiments, since these coatings are pre-deposited on the electrode surface. Moreover, this kind of approach leads also to a decrease in the amount of mercury used in stripping analysis since few microlitres of solution are needed to cover the entire working surface instead of millilitres as in the classical plating step.

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